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Physicochemical properties of hydroxypropylated and cross-linked starches from A-type and B-type wheat starch granules

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Abstract

The large (A-type) and small (B-type) wheat starch granules were characterized and used for hydroxypropylation and cross-linking. The A-type granules contained higher amylose content and exhibited lower gelatinization temperature and higher transition enthalpy as compared with the B-type granules. Hydroxypropylated starches (HS) and hydroxypropylated and cross-linked starches (HCS) from the A-type granules were more hydroxypropylated than were those from the B-type granules. Moreover, HS and HCS of A-type granules had higher swelling power and resulted in greater paste consistency and clarity than HS and HCS of B-type granules. Hydroxypropylation of starches increased swelling power, paste consistency and clarity. In contrast, cross-linking of the HS inhibited granule swelling and reduced paste viscosity and clarity. Both the HS and HCS decreased the gelatinization temperature but improved freeze–thaw stability as compared with the native starches.

Keywords: Modified starch; Hydroxypropylation; Cross-linking; Wheat starch granule

1. Introduction

Wheat endosperm has a bimodal granule-size distribution with significant differences in chemical composition and functional properties such as amylose and lipid contents and gelatinization characteristics between two granule types (Peng, Gao, Abdel-Aal, Hucl, & Chibbar, 1999; Soulaka & Morrison, 1985). Those differences are believed to affect starch modification such as chemical reactivity and subpopulation, distinguished by substitution level. In cross-linking, the small granules were consistently derivatized to a greater degree than the large granules (Bertolini, Souza, Nelson, & Huber, 2003). Fortuna, Juszczak, and Palasinski (2001) found that smaller corn starch granules were more phosphorylated than larger granules of the same sample, whereas the larger wheat starch granules incorporated more phosphorous than did the smaller granules when reaction with sodium trimetaphosphate (STMP), a slow-reacting reagent. However, there are no substantial differences in molar substitution and reactivity with propylene oxide between large and small granules within a starch type for all three levels of substitution (Bertolini et al., 2003; Stapley & BeMiller, 2003). The differences in relative reactivities were also observed among cultivar native starches (native, partial waxy and waxy starches). Cross-linked waxy starches, which consist predominantly of amylopectin, generally proved to be more reactive and produced higher paste stability, and resistance to cooking shear, temperature, and low pH as compared with native and partial waxy starches (Bertolini et al., 2003; Whistler & BeMiller, 1997). Thus, the heterogeneity of modification, which results from common starch modifications, is undesirable.

Although the previous studies have been reported on the effects of granule sizes on the reactivity of hydroxypropylated and cross-linked starches (HCS) (Bertolini et al., 2003; Fortuna et al., 2001; Stapley & BeMiller, 2003), no studies reported on effects of granule sizes on physicochemical properties of modified starches. In this study, the A- and

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B-type wheat starch granules were characterized and the physicochemical properties of HS and HCS modified from the A- and B-type starch granules are investigated.

2. Materials and methods

2.1. Materials

A- and B-type starch granules of wheat were obtained from Tajima Food Industrial Co., Ltd (Hyogo, Japan). The size distributions of A- and B-type granules were reported around 12–20 and 2–8 μm, respectively. Propylene oxide was obtained from Wako Pure Chemical Industries Ltd (Osaka, Japan), STMP from Sigma Chemical Co. (USA) and sodium tripolyphosphate (STPP) from Nacalai Tesque, Inc. (Kyoto, Japan).

2.2. Methods

2.2.1. Scanning electron microscope (SEM)

The A- and B-type starch granules were observed using SEM. The starches were suspended in 95% ethanol for a few minutes and sprinkled on a double-sided adhesive tape mounted on aluminum stub, coated with Pt/Pd and photographed using a SEM apparatus (Hitachi model S-800, Tokyo, Japan) at an accelerating potential of 10 kV.

2.2.2. Iodine absorption spectra and amylose content

Iodine absorption spectra were measured according to the method of Takeda, Takeda, and Hizukuri (1983) with a slight modification. The starch (10 mg, db) was suspended in 0.2 ml of 99% ethanol and 1 ml of distilled water, followed by heating at 100 °C for 5 min. After cooling to room temperature, 0.5 ml of 1 M NaOH was added and the suspension was completely dissolved by heating in a boiling water bath for 10 min with shaking. Then the slurry was adjusted to pH 6.5 with 1 M HCl and diluted to 10 ml with distilled water. An aliquot (0.4 ml) of the solution was added to 0.4 ml of 0.2% iodine solution and made up to 10 ml with distilled water. The mixture was kept at room temperature for 1–2 h. Then an absorbance curve was measured between 450 and 800 nm with a spectrophotometer (UV-160A, Shimadzu, Osaka, Japan). Blue value of iodine–starch complex at 680 nm was measured according to the procedure of Takeda et al. (1983). Amylose content was measured based on the approved method 61-03 (AACC, 1995) with a slight modification. A calibration curve was established using a mixture of amylose and amylopectin fractionated from high-amylose wheat starch according to the method of Klucinec and Thompson (1998). Amylose content was calculated by the equation: $\mathrm{AM}\ (\%) = 110.78 \times \mathrm{BV} - 24.481$, $R^2 = 0.9995$, in which BV is blue value of starches measured at 620 nm.

2.2.3. X-ray diffraction

X-ray diffraction analysis was performed using an X-ray diffractometer (Rigaku Co., Ltd, Rint-2000 type, Tokyo, Japan) operated at 40 kV and 80 mA. Diffractograms were obtained from 4° 2θ to 40° 2θ with a scanning speed of 8°/min and scanning step of 0.02°.

2.2.4. Hydroxypropylation of wheat starch

Hydroxypropylation of wheat starches was performed according to the method of Zheng, Han, and Bhatty (1999) with a slight modification. Starch was modified in the presence of 1% sodium hydroxide and 10% sodium sulfate as follows. Starch (100 g, db) was suspended in distilled water (150 ml) containing 1 g of NaOH and 10 g of Na_2SO_4 in a 500-ml round-bottomed flask. After adjusting to pH 11.5 with 0.1 M NaOH and replacing the air with nitrogen gas, 10 g of propylene oxide was added to the mixture. The flask was capped and kept in a 40 °C water bath with continuous shaking. After 24 h, the slurry was adjusted to pH 6.0–6.5 with 1 M HCl and the hydroxypropylated starch (HS) was isolated by centrifuging ($3000 \times g$, 10 min), washed with water (4×500 ml) and air-dried overnight.

2.2.5. Cross-linking of wheat starch

The HS was cross-linked using a mixture (99:1, w/w) of STMP and STPP based on the methods of Woo and Seib (2002). After hydroxypropylation, STMP (11.9 g, sb) and STPP (0.12 g, sb) were added directly to the slurry and then the slurry was held in a 40 °C water bath for 3 h with continuous stirring. The HCS were recovered in the same manner as for the HS.

2.2.6. Determination of hydroxypropyl group

The hydroxypropyl group in modified starches was determined according to the procedure as described by Joint FAO/WHO Expert Committee on Food Additives (2001). Sample (50–100 mg) was weighed into a 100-ml volumetric flask and 25 ml of 0.5 M sulfuric acid was added. Native starch was prepared in the same manner. The flasks were placed in a boiling water bath and heated until the solution became clear. The samples were cooled and the contents were diluted to 100 ml with distilled water. One milliliter of the solution was pipetted into 25-ml graduated test tubes with glass stoppers, and the tubes were immersed in cold water and then 8 ml of concentrated sulfuric acid was added dropwise to each tube. The solution was mixed well and the tubes were placed in a boiling water bath for exactly 3 min. The tubes were immediately transferred to an ice bath until the solution was chilled. An aliquot (0.6 ml) of ninhydrin reagent was added, carefully allowing the reagent to run down the walls of the test tubes. The tubes were immediately shaken well and placed in a 25 °C water bath for 100 min. The volume in each tube was adjusted to 25 ml with concentrated sulfuric acid and mixed by inverting the tubes several times. Portions of the solutions were immediately transferred to 1-cm cells, and after exactly

5 min, absorbance was measured at 590 nm, using the starch blank as a reference. A calibration curve was prepared with an aliquot (1 ml) of standard aqueous solutions, containing 10, 20, 30, 40 and 50 μg of propylene glycol per ml. Hydroxypropyl groups (%) were calculated by an equation: Hydroxypropyl groups $(\%)=(C\times 0.7763\times 10\times F)/W$, where C is amount of propylene glycol in the sample solution read from the calibration curve (μg/ml); F is dilution factor and W is weight of sample (mg).

2.2.7. Differential scanning calorimetry (DSC)

Thermal characteristics of native and modified starches were determined using a differential scanning calorimeter (DSC-60, Shimadzu Co., Kyoto, Japan). Sample (3.0 ± 0.1 mg) was weighed directly in an aluminum vessel and then 10 μl of distilled water was added. The vessel was sealed and kept at room temperature for more than 30 min for equilibration. Then the sample-containing vessel was heated from 30 to 100 min at a rate of 10 °C/min. An empty vessel was used as a reference. The initial, peak and completion temperatures and transition enthalpy were recorded and automatically calculated using a TA-60WS program (Shimadzu Co., Kyoto, Japan).

2.2.8. Paste clarity

The paste clarity of native and modified starch was determined according to the method of Reddy and Seib (1999). Stach (0.05 g, db) was suspended in distilled water (5 ml) in a glass-stoppered tube and heated at 95 °C for 30 min with shaking every 5 min. After cooling, clarity of starch was measured on a spectrophotometer (Shimadzu model UV-160A) at 650 nm against a water blank.

2.2.9. Swelling power

The swelling power of native and modified starches was measured according to the method of Sasaki and Matsuki (1998) with a slight modification. The starches (0.16 g, db) were weighed directly into glass tubes with coated screw caps and then 5 ml of distilled water was added. The tubes were placed in a shaking water bath and heated at 40, 50, 60, 70 or 80 °C for 30 min, the heated samples were cooled quickly to room temperature by a cold water bath and then centrifuged at $3000\times g$ for 15 min. The supernatant was removed carefully and the swelling power was determined as weight of the sediment by an equation: Swelling power $(\mathrm{g/g})=(W_2-W_1)/W$, where W_2 is weight of tube after supernatant was removed (g); W_1 is weight of dry tube (g) and W is weight of db starch (g).

2.2.10. Brabender amylograph

Pasting properties of native and modified starch suspensions (8%, w/v, db) were tested using an amylograph (Brabender, Germany). The starch slurries were heated from 30 to 93 °C at the rate of 1.5 °C/min. After keeping at 95 °C for 15 min, the starch pastes were cooled to 30 °C at the same rate of 1.5 °C/min and also kept at this temperature for 15 min. The amylograms of the pastes were recorded.

2.2.11. Gel stability

Net syneresis of the pastes from native and modified starches during freeze–thaw treatment was determined as follows. The pastes after heating and cooling in the amylograph were used for determination of gel stability (net syneresis) according to the method of Zheng and Sosulski (1998). The pastes (60 g/sample) were kept in 100-ml bottles sealed with screw caps and stored at −18 °C (freezer) for 96 h (4 freeze–thaw cycles). Net syneresis was determined by a difference between the total water separation of expelled and absorbed water and free water. The free water was separated by centrifugation from fresh paste. The expelled water was the amount of water released from the paste after freeze–thaw treatment, and it was removed by decantation and weighed. The absorbed water was the water removed by centrifugation after removal of the expelled water.

2.2.12. Statistical analysis

All tests were performed at least in duplicate. Analysis of variance (ANOVA) was performed using the Duncan's multiple-range test to compare treatment means (Steel & Torrie, 1960). Significance was defined at $P<0.05$.

3. Results and discussion

3.1. Scanning electron microscope

The shapes and sizes of the A- and B-type wheat starch granules are shown in Fig. 1. The results showed that the A- and B-type starch granules were oval to round in shape and 12–20 and 2–8 μm in size, respectively. The surface appearances of the A- and B-type granules were smooth and no evidence of cracks, suggesting the low level of starch damage during fractionation.

3.2. Iodine absorption spectra and amylose content

$\lambda_{\max}$, BV at 680 nm and amylose content of the A- and B-type wheat starch granules are shown in Table 1. The A-type granules had higher blue value and amylose content than did the B-type granules, as previously reported (Peng et al., 1999; Soulaka & Morrison, 1985). Thus, there are the differences not only in size but also in structure between the A- and B-type granules of wheat, which might result in different properties of chemically modified starches.

3.3. X-ray diffraction

The X-ray diffraction patterns of the A- and B-type wheat starch granules are shown in Fig. 2. The major peaks at around d-spacings 5.8, 5.2, 4.8, 4.4 and 3.8 Å of both A- and

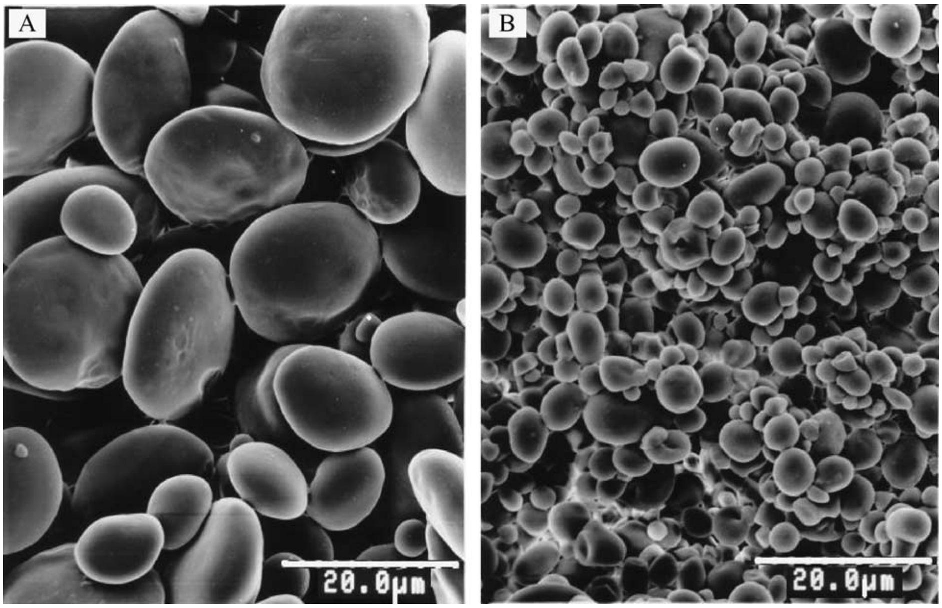

Fig. 1. Scanning electron microscope of the A- (A) and B-type (B) wheat starch granules.

B-type granules indicate the characteristics of A-type crystal as classified by Zobel (1988). Additionally, the intensity peak at 4.4 Å d-spacings shows that the amount of amylose-lipid complex in the B-type granules was larger than that in the A-type granules though it had lower amylose content.

3.4. Hydroxypropyl group

Hydroxypropyl groups in modified starches are shown in Table 2. The amount of hydroxypropyl groups in the modified starches from the A-type granules was significantly larger than those from the B-type granules under the same condition of chemical modification. The results are the same as for both HS and HCS, which indicate that the A-type granules reacted with propylene oxide more easily than did the B-type granules. This finding is different from some previous studies (Bertolini et al., 2003; Stapley & BeMiller, 2003). The difference might be caused by different methods for modification. In this study, the A- and B-type granules were modified separately, whereas the previous studies fractionated the A- and B-type starch granules after modification. In addition, the results are also affected by the different reaction conditions such as differences in reagents, pH, temperature and shaking condition, etc.

3.5. Differential scanning colorimetry

Gelatinization characteristics of native and modified starches are shown in Table 2. The onset temperatures of the A- and B-type granules were similar, whereas the peak and completion temperatures of the A-type granules were significantly lower than those of the B-type granules. These results agreed with the conclusions of previous studies (Eliasson & Karlsson, 1983; Peng et al., 1999; Soulaka & Morrison, 1985), whereas Seib (1994) reported that the A-type granules started gelatinization at a higher onset temperature but had lower peak and completion temperatures as compared with the B-type granules. In addition, Ghiasi, Hoseney, and Varriano-Marston (1982) reported that both A- and B-type granules had similar gelatinization temperature regimes.

In this study, transition enthalpy of the A-type granules was considerably higher than that of the B-type granules. This result is consistent with some previous studies (Eliasson & Karlsson, 1983; Klucinec & Thompson, 1998; Peng et al., 1999; Soulaka & Morrison, 1985). However, other studies reported that the transition enthalpies of the A-type granules were either similar (Ghiasi et al., 1982; Stevens & Elton, 1971) or lower (Wootton & Bamunuarachchi, 1979) as compared to that of the B-type granules. These differences were caused by imprecise measurement of the transition enthalpy of the A- and B-type granules as explained by Soulaka and Morrison (1985).

The HS and HCS from A- and B-type wheat starch granules exhibited significantly lower gelatinization temperatures than did the native starches. The transition enthalpies of the modified starches were also lower than those of the native starches. These results were probably due

Table 1
Absorbance of starch–iodine complex and amylose content of the A- and B-type wheat starch granules

Type of granule	λ_{max} (nm)	Blue value (at 680 nm)	Amylose content (%)
A-type	607.5 ± 2.0	0.374 ± 0.012	30.0 ± 0.5
B-type	602.0 ± 1.0	0.316 ± 0.006	23.0 ± 1.5

Values are means ± standard deviation of six separate measurements.

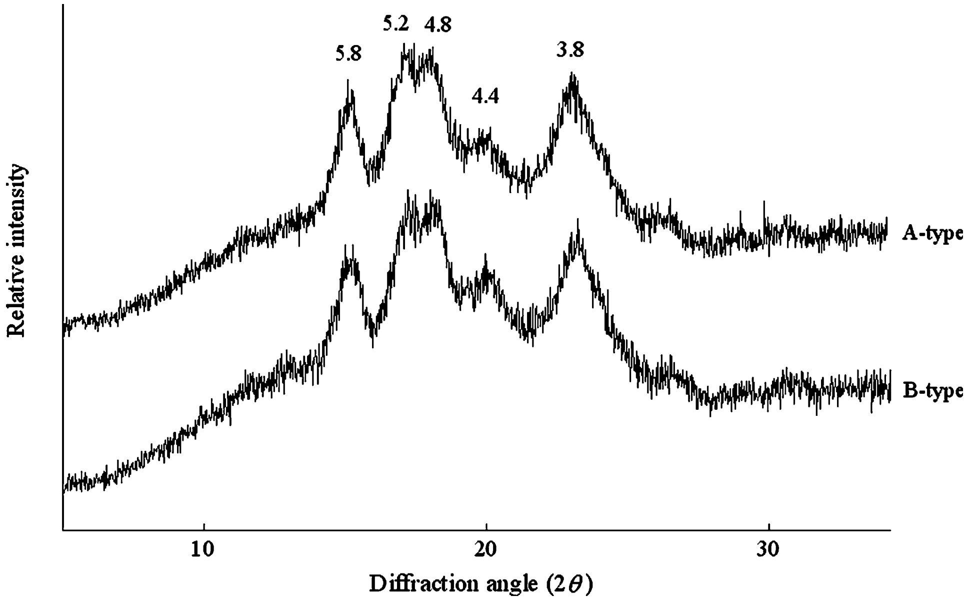

Fig. 2. X-ray diffraction patterns of the A- and B-type wheat starch granules.

to the fact that substitution occurred primarily in the amorphous region (Biliaderis, 1982; Hood & Mercier, 1978). Therefore, substitution promoted swelling in that region and disrupted the crystalline phase, resulting in melting at a lower temperature as compared with the native starches (Reddy & Seib, 2000). The gelatinization temperatures and enthalpies of the HS and HCS from A- and B-type granules were not significantly different. However, these results were partly affected by a slight gelatinization of starches during modification, which occurred as a translucent layer atop the residue in centrifugal separation. This layer was separated by hand after drying.

3.6. Paste clarity

The clarity of paste prepared from the A-type granules was significantly higher than that from the B-type granules (Table 2). This result indicates that the paste of A-type granules had less swollen granule remnants than that of the B-type granules after gelatinization. The pastes of HS and HCS from the A-type granules were clearer than those from B-type granules. The higher clarity of the HS and HCS pastes from A-type granules was caused by higher amounts of hydroxypropyl groups in these starches, which resulted in less reflection of light than did those from B-type granules. The paste clarity of HS prepared from both A- and B-type granules improved, whereas that of HCS decreased as compared with the native starches as previously reported (Rutenberg & Solarek, 1984; Tuschhoff, 1986; Woo & Seib, 1997).

3.7. Swelling power

Swelling powers of A- and B-type granules of the native and modified starches are shown in Fig. 3. At a low temperature, the swelling power of A-type granules was less than that of the B-type granules. However, increase in the heating temperature to more than 50 °C led to the fact that the swelling power of the A-type granules was higher than that of the B-type granules. Hence, the A-type starch

Table 2
Properties of native and modified starches from the A- and B-type wheat starch granules

Sample	Type of granule	Hydroxypropyl group (%, wt)	Transition temperature (°C)			Enthalpy (J/g)	Paste clarity (% T_{650})
			Onset	Peak	Completion		
NS	A-type	nd	55.6b	60.5c	64.2c	6.2c	16.1c
	B-type	nd	55.8b	61.6d	66.9d	4.7b	7.9b
HS	A-type	4.7b	46.3a	51.9b	53.9a	2.2a	38.8e
	B-type	3.8a	45.8a	51.1ab	55.6b	2.2a	29.4d
HCS	A-type	4.6b	46.4a	50.7a	55.9b	2.4a	6.9b
	B-type	3.9a	45.0a	50.4a	56.2b	2.1a	3.9a

NS, native starches; HS, hydroxypropylated starches; HCS, hydroxypropylated and cross-linked starches. The same letters in the same column are not significantly different, $n=3$.

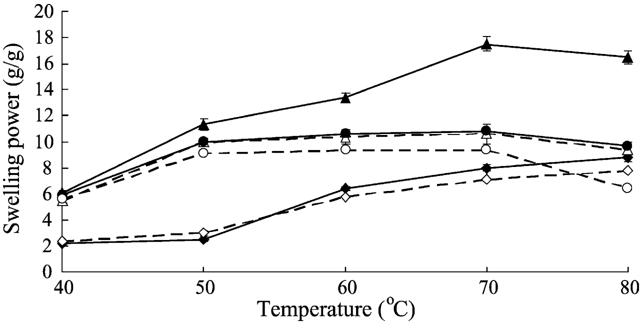

Fig. 3. Swelling power of native and modified starches from the A- and B-type wheat starch granules. Abbreviations are the same as in Table 2. —◆—, NS-A-type granules; - - -◇- - -, NS-B-type granules; —▲—, HS-A-type granules; - - -△- - -, HS-B-type granules; —●—, HCS-A-type granules; - - -○- - -, HCS-B-type granules.

granules absorbed more water at high temperature than the B-type granules. The differences in the swelling power are partly affected by hydrocarbon chains of internal lipids, which suppress hydration of amorphous regions in starch granules (Tester & Morrison, 1990). Therefore, the B-type granules which contained larger amount of amylose-lipid complex swelled less than that of the A-type granules.

The swelling powers of HS and HCS from A-type granules were significantly greater than those from the B-type granules. This result is due to the presence of higher hydroxyl groups in the A-type granules than those in the B-type granules. The swelling powers of HS increased greatly than those of the native starches. After cross-linking with 10% of STMP/STPP, the swelling powers of HCS decreased significantly as compared to those of HS. In addition, the swelling powers of HS and HCS decreased at more than 70 °C because of disintegration and solubility of these starches in water at a high temperature.

3.8. Brabender amylograph

Amylograph data showed no difference in the pasting and peak temperatures of the A- and B-type granules, while the A-type granules had slightly higher peak, breakdown and final viscosities than did the B-type granules (Fig. 4).

The HS had significantly lower pasting and peak temperatures than did the native starches, whereas the peak and final viscosities of the HS was significantly higher than those of the native starches. In addition, the hot paste of the HS had significantly higher breakdown than did the native starches. After cross-linking with 10% STMP/STPP, the HCS had higher pasting and peak temperatures, lower peak and breakdown viscosities of hot paste than did the HS. Thus, the cross-linking of the HS stabilized viscosity of starch paste. The HS and HCS showed higher setback viscosities than the native starches because re-association degree of molecules in the modified starches was higher than that of the native starches.

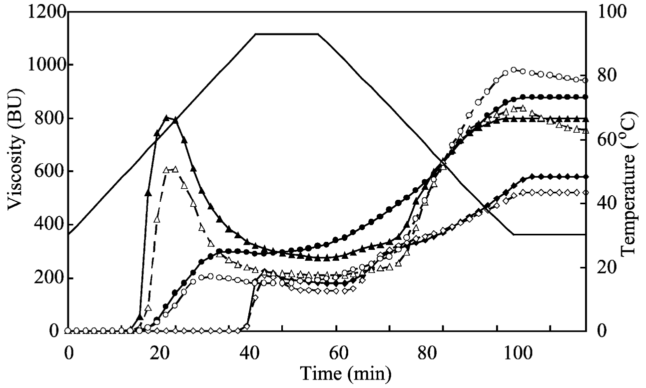

Fig. 4. Amylograph of native and modified starches from the A- and B-type wheat starch granules. Abbreviations are the same as in Table 2. —◆—, NS-A-type granules; - - -◇- - -, NS-B-type granules; —▲—, HS-A-type granules; - - -△- - -, HS-B-type granules; —●—, HCS-A-type granules; - - -○- - -, HCS-B-type granules.

The peak and breakdown viscosities of the HS from A-type granules were significantly higher than those from the B-type granules. Likewise, the HCS from A-type granules had moderately higher peak and breakdown viscosities than that from B-type granules. In particular, the peak viscosity of the B-type granules after hydroxypropylation and cross-linking with 10% STMP/STPP was similar to the native starch. In addition, the peak temperature of the HCS from A-type granules was higher than that from B-type granules.

3.9. Gel stability

Net syneresis data of the pastes (8% solids) prepared from the native and modified starches are shown in Table 3. There were no significant differences in free water of fresh pastes prepared from the A- and B-type granules, whereas the paste prepared from the B-type granules was more tolerant to freeze–thaw than that from the A-type granules. Net syneresis of the paste prepared from the B-type granules was significantly lower than that from the A-type granules during 4 freeze–thaw cycles. Water-bonding ability of starch is largely dependent on the degree of granule swelling

Table 3
Net syneresis of native and modified starches from the A- and B-type wheat starch granules during 96 h of freeze storage

Sample	Type of granule	Free water (%)	Net syneresis (%)			
			24 h	48 h	72 h	96 h
NS	A-type	2.8a	46.3d	52.2d	58.9d	59.4c
	B-type	4.0ab	43.8c	46.7c	50.2c	51.7b
HS	A-type	4.7b	2.8a	3.4ab	3.7ab	3.7a
	B-type	4.3b	4.2b	4.5b	4.5b	5.1a
HCS	A-type	2.7a	2.4a	2.4a	2.5a	3.6a
	B-type	3.8ab	3.9b	3.9ab	4.0ab	4.8a

NS, native starches; HS, hydroxypropylated starches; HCS, hydroxypropylated and cross-linked starches. The same letters in the same column are not significantly different, $n=4$.

and molecule dispersion during cooking (Zheng et al., 1999). In this study, the A-type granules, which have high welling power, showed little resistance to freeze–thaw as compared with the B-type granules.

Hydroxypropylation greatly improved freeze–thaw stability of the starch pastes. Net syneresis of the pastes prepared from the HS was significantly lower than those of the native starches. There is a high tolerance to freeze–thaw because of the hydrophilic nature of the hydroxypropyl group, which prevents the water in the starch paste from separation. However, the amounts of free water separated from the fresh paste of the HS were larger than those of the native starches. The net syneresis of the pastes prepared from the HCS was not significantly different from that of the HS, while the amount of free water separated from the fresh paste was smaller. These results indicate that the cross-linking of the HS improved separated water stability of the fresh pastes.

The free water and net syneresis of the pastes prepared from HS and HCS of the A- and B-type granules did not differ. Hence, the A-type granules after modification showed improved gel stability.

4. Conclusion

The physicochemical properties of native and modified starches from the A-type wheat starch granules were significantly different from those of the B-type granules. The A-type granules had the higher amylose content and transition enthalpy and lower gelatinization temperature than did the B-type granules. The HS and HCS from the A-type granules were more hydroxypropylated resulting in higher swelling power and paste consistency and more clarity than those from the B-type granules. The starches modified by hydroxypropylation and cross-linking had the lower gelatinization temperature and more tolerance to freeze–thaw, higher swelling power and paste consistency than the native starches.

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