

Partial Characterization of Buckwheat (*Fagopyrum esculentum*) Starch

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ABSTRACT

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Laboratory-isolated buckwheat (*Fagopyrum esculentum*) starch was compared to commercial corn and wheat starches. Buckwheat starch granules (2.9–9.3 μm) were round and polygonal with some holes and pits on the surface. Buckwheat starch had higher amylose content, water-binding capacity, and peak viscosity, and it had lower intrinsic viscosity when compared with corn and wheat starches. Buckwheat starch also showed restricted swelling power at 85–95°C and lower solubility in water at 55–95°C and was more susceptible to acid and enzymatic attack. Gelatinization temperatures, determined by differential scanning calorimetry, were 61.1–80.1°C for buckwheat starch compared to 64.7–79.2°C and 57.1–73.5°C for corn and wheat starches, respectively. A second endotherm observed at 84.5°C was an amylose-lipid complex attributed to the internal lipids in buck-

wheat starch, as evidenced by selective extraction. The retrogradation of buckwheat, corn, and wheat starch gels was examined after storage at 25, 4, and –12°C for 1–15 days. In general, buckwheat starch retrogradation was slower than that of corn and wheat starch, but it increased as storage time increased, as did that of the other starch pastes. When the values of the three storage temperatures were averaged for each storage period analyzed, buckwheat starch gels showed a lower percentage of retrogradation than did corn and wheat starch gels. Buckwheat starch also had a lower percentage of water syneresis when stored at 4°C for 3–10 days and had better stability to syneresis after three freeze-thaw cycles at –12 and 25°C.

Buckwheat (*Fagopyrum esculentum* Mönch) is a dicotyledonous plant of cool climates adapted to high elevation and a short growing season (Lorenz and Dilsaver 1982). Buckwheat has a triangular fruit 4–9 mm long, with a solid or mottled gray to dark brown hull (Pomeranz and Sachs 1972). Dehulled buckwheat kernels resemble other cereal kernels in general chemical composition and structure, with a nonstarchy aleurone layer and starchy endosperm (Javornik 1986). Buckwheat grain forms an important part of the diet in Eastern Europe (Taira 1974), is praised as a functional food in Asia (He 1987), and is marketed as an ingredient of pancake mixes in the United States (Mazza 1986).

The range of starch content in buckwheat groats is 37–70% (db), depending on the species (Javornik 1986). Buckwheat starch granule size is 1.0–11.4 μm (Kim et al 1977, Soral-Smietana et al 1984). According to Alekseeva et al (1979), starch from nine buckwheat cultivars had different swelling power patterns. Hurusawa and Kobayashi (1963) found that the pasting points of buckwheat starches from different locations and harvest times were 64.3–67.7°C at 8% concentration. Buckwheat starch defatted with 85% hot methanol showed lower viscosity amylograph pasting patterns.

Hurusawa and Miyashita (1964a,b; 1965; 1966) reported that starches from summer-harvested buckwheat had lower intrinsic viscosity and Brabender peak viscosity than did starches from autumn-harvested grain in Japan. Lorenz and Dilsaver (1982) studied the physicochemical properties and functional characteristics of untreated, defatted, and enzyme-inactivated buckwheat starch. They found that the X-ray diffraction pattern, swelling power and solubility, water-binding capacity, gelatinization temperature, and amylograph pasting pattern were similar to those of other cereal starches.

Initial and final gelatinization temperatures of buckwheat starch were 60 and 76°C, respectively (Lorenz and Dilsaver 1982). Soral-Smietana et al (1984) studied the effects of toasting and steam-processing on buckwheat starch chemical composition and properties in commercial Polish and Brazilian buckwheat. They showed

that hydrothermal treatment increased the initial temperature of gelatinization, swelling power, and solubility. The properties of buckwheat starch in food systems need to be explored further to enhance its use as a food ingredient and to improve its marketability. The objective of this study was to determine some rheological and thermal properties, acid hydrolysis, enzyme digestibility, and the retrogradation and freeze-thaw stability of buckwheat starch as compared to commercial wheat and corn starches.

MATERIALS AND METHODS

Materials

Light buckwheat flour was donated by Minn-Dak Growers (Grand Forks, ND). Native wheat starch was obtained from Midwest Grain Products (Atchison, KS) and corn starch was obtained from American Maize Products (Hammond, IN).

Isolation of Starch

Buckwheat flour (300 g) was steeped in 0.2% NaOH (1:6, w/v) in a 45°C water bath for 90 min. The flour was blended for 1 min at high speed in a Waring Blendor, screened through U.S. no. 450 sieve (32 μm), and centrifuged at 3,000 \times g for 15 min. The supernatant was discarded and the top yellow protein layer was removed. The white starch layer was resuspended in distilled water and centrifuged, and the yellow protein layer was removed again. This procedure was repeated until the yellow layer was no longer visible. The sedimented starch was resuspended in distilled water, adjusted to pH 6.5–7.0 with dilute HCl, and centrifuged. The starch was washed with distilled water three times and air-dried.

Proximate Analysis

Moisture, ash, protein, and crude fat contents were determined by Approved Methods 44-15A, 08-01, 46-13, and 30-25, respectively (AACC 1995).

Starch Lipids

Buckwheat starch surface lipids were extracted with hexane using a Soxhlet extractor for 16 hr. The residue was extracted at ambient temperature for 4 hr each with chloroform and methanol (2:1, v/v) and methanol and water (4:1, v/v) at a 35:1 (v/w) solvent-to-starch ratio. Buckwheat starch internal lipids were removed using the method of Morrison (1981) at 90–100°C with *n*-propanol and water (3:1, v/v) at a 20:1 (v/w) solvent-to-starch ratio. The extraction was repeated three times (twice for 2 hr and once for 1 hr). Lipid-extracted starches were air-dried.

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Damaged Starch

Damaged starch was tested using a Megazyme starch damage assay kit (Warriewood, Sydney, Australia) based on the procedure of Gibson et al (1992).

Water-Binding Capacity

Water-binding capacity was measured using the method of Medcalf and Gilles (1965).

Amylose Content

Amylose content of defatted starch samples was estimated by the method of Jarvis and Walker (1993). After the suspension was heated at 100°C for 1 hr, a sonicator (15 min, 25°C) was used to improve the solubility of starches.

Intrinsic Viscosity

Intrinsic viscosities of the starches were determined according to the method of Leach (1963). Flow times of the starch, diluted to four different concentrations (0.125, 0.167, 0.25, and 0.5%), were measured at 25°C and used to calculate intrinsic viscosity. A Ubbelohde viscometer (Cannon-Fenske, State College, PA) with a capillary size of 75 was used. A viscosity bath (Temp-Trol, Precision Scientific, Chicago, IL) was used along with an automatic viscosity timer (Wescan Instrument, Santa Clara, CA).

Swelling Power and Solubility

The swelling power and solubility of starch were analyzed using the procedure of Leach et al (1959). The temperatures used were 55, 65, 75, 85, and 95°C.

Acid Hydrolysis

Acid hydrolysis of starch was performed with 2.2*N* HCl (1:40, w/v) at 35°C. The starch slurries were shaken by hand daily to resuspend the granules. After intervals of 1, 2, 3, 4, 8, 12, 16, 20, and 24 days, the reaction mixtures were neutralized and centrifuged at 3,000 × *g* for 15 min. An aliquot of the supernatant was assayed for total carbohydrate (Dubois et al 1956). The extent of hydrolysis was determined by expressing the solubilized carbohydrate as a percentage of the initial starch (Hoover et al 1991).

Enzymatic Digestibility

Enzymatic digestibility studies on native starch samples were performed according to the method of Hoover et al (1991), using porcine pancreatic α -amylase (type IA) crystallized twice (A6255) (Sigma Chemical Co. St. Louis, MO). Digestion took place in a constant temperature water bath at 37°C. Gentle stirring was administered before α -amylase addition.

Pasting Properties

The pasting properties of the starch samples were evaluated using a Rapid Visco Analyzer (RVA-3C, Newport Scientific, Sydney, Australia) as described by Walker et al (1988). Starch (2.5 g, db) was suspended in deionized water and adjusted to a total weight of 28 g. The sample was equilibrated at 30°C for 2 min, heated for 8 min to 95°C, and cooled for 8 min to 50°C.

Thermal Properties

Thermal properties of starches were analyzed using differential scanning calorimetry (DSC) (Perkin Elmer DSC7, Norwalk, CT) equipped with a TAC 7 instrument controller and DEC computer. Native buckwheat, wheat, and corn starches, and defatted buckwheat starch were weighed (3.5 mg, db) directly into DSC aluminum pans, and deionized water was added (1:2.28, w/v). The sealed pans were allowed to equilibrate overnight and scanned the next day at 10°C/min from 30 to 120°C. An empty sealed pan was used as a reference. The thermal transition of starch was recorded as onset (T_o), peak (T_p), and conclusion or end (T_e) temperature. The range of gelatinization temperature (T_i) was calculated as $2(T_p - T_o)$ according to Krueger et al (1987). Enthalpy of gelatinization (ΔH) was calculated as J/g.

Retrogradation

The percent of retrogradation of starch samples was investigated using DSC as described by Zhang and Jackson (1992). Starch samples (1:2.28 starch-to-water ratio, w/v) were gelatinized in the calorimeter and stored for 1, 5, 10, and 15 days at 25, 4, and -12°C, respectively. After each storage period, the samples were equilibrated at room temperature (25°C) for \approx 2 hr before being scanned at 20–100°C at 10°C/min. The extent of retrogradation was determined by expressing the enthalpy of gelatinization (ΔH) of the retrograded gel as a percentage of initial gelatinization (Paton 1987). Defatted buckwheat starch samples were stored at 4°C for 1, 5, 10, and 15 days.

Degree of Syneresis and Freeze-Thaw Stability

The degree of syneresis of buckwheat, wheat, and corn starch suspensions (6%, w/v) was based on the methods described by Hoover et al (1991) and Yanez et al (1991). Starch paste (30 g) was poured into a 50-mL polypropylene centrifuge tube. The tubes were stored for 3, 7, and 10 days at 25, 4, and -12°C. At the end of each storage time, the tubes were centrifuged at 1,500 × *g* for 10 min, and the weight of the water expelled from the gels was recorded. The degree of syneresis of the starch pastes was expressed as a percentage of the total weight of the gel sample.

To measure freeze-thaw stability, 6% (w/v) starch pastes were frozen at -12°C for 24 hr, thawed at room temperature for 6 hr, and refrozen at -12°C. Three freeze-thaw cycles were performed. The amount of water separated from the starch pastes for each cycle was weighed after centrifugation (1,500 × *g* for 15 min). The freeze-thaw stability of the starch pastes was expressed as a percentage of the total weight of the gel sample (Yanez et al 1991).

Statistical Analysis

A randomized complete block design with factorial arrangement was used for the starch retrogradation study. Analysis of variance (ANOVA) and Duncan's multiple range test were conducted using the SAS program for physicochemical, thermal, and retrogradation properties analyses (SAS Institute, Cary, NC).

RESULTS AND DISCUSSION

Chemical Properties

The proximate composition and starch damage of buckwheat starch as compared to that of commercial corn and wheat starches are shown in Table I. Buckwheat starch had comparable protein and ash, higher crude fat, and lower starch damage than did corn and wheat starches. Soral-Smietana et al (1984) reported that protein, fat, and ash content of starch from Brazilian buckwheat was 0.31, 0.45, and 0.56%, respectively. Lorenz and Dilsaver (1982) reported that protein and fat content of buckwheat starch was 0.75 and 0.96%, respectively. Doublier (1987) analyzed the protein and fat of commercial corn and wheat starches and found that both starches had 0.3% protein and 0.8% fat content (db). The

TABLE I
Composition (% db) and Starch Damage (%) of Buckwheat, Corn, and Wheat Starches

Starch	Protein ^a	Crude Fat	Ash	Damage
Buckwheat	0.16a ^b	0.41a	0.10b	3.14c
Corn	0.18a	0.27c	0.09c	8.86a
Wheat	0.16a	0.32b	0.13a	7.31b

^a N × 6.25 for corn and buckwheat starch, N × 5.70 for wheat starch protein.

^b Values followed by the same letter in the same column are significantly different ($\alpha = 0.05$) using Duncan's multiple range test ($P > 0.0001$).

protein, fat, and ash content of buckwheat, corn, and wheat starches reported in the present study were lower than in other reports. The different buckwheat varieties and starch isolation methods used may be, in part, the cause of the differences in the composition of the buckwheat starch. Concomitantly, different milling and starch isolation methods may also account for the lower starch damage of the buckwheat starch compared to that of the corn and wheat starches.

Microscopy of Starch Granules

A comparison of the size and shape of buckwheat, wheat, and corn starch granules is shown in Table II. Buckwheat starch granules were 1.6–2.4 times smaller than corn and wheat starch granules. The general appearance and size of buckwheat starch resembles the small corn starch granules. The buckwheat starch granule surface appeared smooth, with some surface pores that may have been caused by enzyme attack. The granule characteristics of buckwheat, wheat, and corn agree with previous reports (Lorenz and Dilsaver 1982, Hosney 1994).

Physical Properties

Water-binding capacity at 25°C, apparent amylose content, and intrinsic viscosity of buckwheat, corn, and wheat starches are given in Table III. Buckwheat starch had a higher water-binding capacity than did wheat and corn starch. It has been suggested that starch water-binding capacity reflects the water absorption of the starch granule and the degree of association of the molecules within the starch granule (Leach et al 1959, Medcalf and Gilles 1965). When starch granules are dispersed in water, the water molecules form a hydrated layer with the hydrophilic hydroxyl groups. The higher water-binding capacity obtained for buckwheat starch may be explained, in part, by the smaller size of its granules and, thus, more surface area than corn and wheat starch granules. Differences in molecular packing of starch granules could also contribute to the water-binding capacity values obtained.

The apparent amylose content of the starches (measured in the presence of lipids) was postulated as a positive proportional relationship between amylose and lipid content (Morrison 1981, 1988). Buckwheat starch had a 1.6–2.0 times more apparent amylose than did corn and wheat starches (Table III). Accordingly, the crude fat content of buckwheat starch was 1.3–1.5 times higher than of wheat and corn starches. The apparent amylose content of buckwheat starch reported in this study agreed with the values reported by Soral-Smietana et al (1984). The apparent amy-

lose content of corn and wheat starches was in the range of the amylose content reported previously (Medcalf and Gilles 1965, Tester and Morrison 1990). Morrison (1988) reported a low lipid content in the low-amylose corn starches, while high-amylose corn starches have a higher lipid content than the corresponding normal corn starches. He indicated that amylose and lipid contents are closely linked, heritable characteristics in normal and single- and double-mutant lines of corn.

The intrinsic viscosity of starch expresses the internal friction or resistance needed to displace high-polymeric molecules in solution without any intermolecular interaction (Leach 1963, Tian et al 1991). The intrinsic viscosity of buckwheat starch was 1.4–2.1 times lower than that of corn and wheat starches. These data suggest a smaller molecular size and lower degree of polymerization (Daniels and Alberty 1961) for buckwheat starch as compared to corn and wheat starch.

TABLE II
Granule Size^a (μm) of Buckwheat, Corn, and Wheat Starches

Starch	Length		Shape
	Mean	Range	
Buckwheat	5.8	2.9–9.3	Round, polygonal
Corn	9.5	3.6–17.1	Polyhedral
		2.9–9.8	Round
Wheat	13.8	2.1–31.4	Lenticular
		2.1–12.8	Round

^a Measured on 15 randomly selected starch granules from scanning electron microscopy.

TABLE III
Water-Binding Capacity (WBC) at 25°C, Apparent Amylose, and Intrinsic Viscosity of Buckwheat, Corn and Wheat Starches

Starch	WBC (%)	Apparent Amylose (%)	Intrinsic Viscosity (η)
Buckwheat	109.9a ^a	46.6a	0.80c
Corn	97.0b	28.6b	1.13b
Wheat	87.5c	27.5c	1.72a

^a Values followed by the same letter in the same column are significantly different ($\alpha = 0.05$) using Duncan's multiple range test ($P > 0.0001$), $n = 2$.

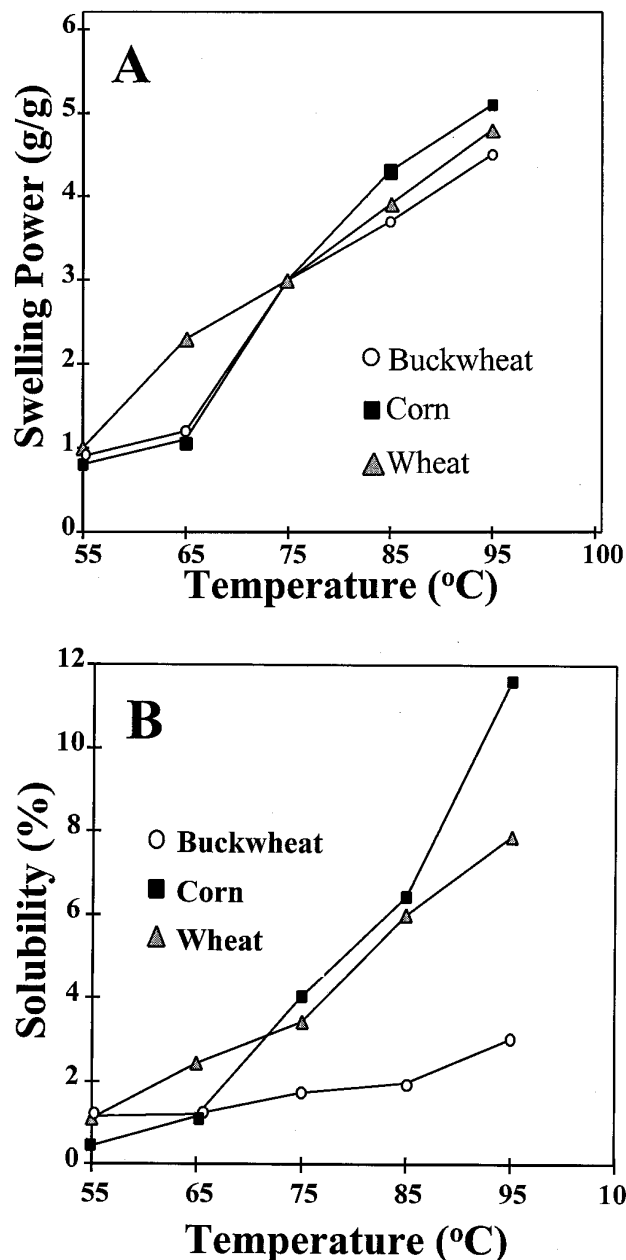


Fig. 1. Swelling power (A) and solubility (B) of buckwheat, corn, and wheat starches.

Swelling Power and Solubility

Swelling power and solubility of the three starches are shown in Fig. 1a and b. Solubility increased as the temperature increased. A similar swelling power pattern was observed, except for the value of wheat starch at 65°C. Buckwheat starch showed lower swelling power at >75°C than did the wheat and corn starches (Fig. 1a). The buckwheat solubility pattern (Fig. 1b) differed from that of corn and wheat, with an almost flat line except for a slight increase in solubility at 95°C. This suggested a limited amount of amylose leaching from the starch granule, in contrast to higher solubility values for corn and wheat starches. The buckwheat starch swelling power results reported here were higher than those reported by Lorenz and Dilsaver (1982) over the same temperature range. The swelling power and solubility of the corn and wheat starches were lower than those reported by Lorenz (1979). The differences observed may be partially explained by different varieties and preparation of the starches.

Starch swelling power is attributed to the strength and character of the micellar network within the starch granule. A strongly bonded micellar structure of the starch granule may render it relatively resistant to swelling (Stone and Lorenz 1984). As the temperature increased, the starch vibrated more vigorously, breaking intermolecular bonds and allowing hydrogen-bonding sites to engage more water molecules (Whistler and Daniel 1985). The leaching mobility of small polysaccharide molecules would increase due to internal pressure if the micellar network within the starch granule was weak. Stone and Lorenz (1984) reported that amaranth starch containing 100% amylopectin had higher swelling power than amaranth with 5% amylose. They suggested that amylose reinforced the internal network within the granule and restricted swelling.

Doublier (1987) also reported that legume starches containing 1.3 times more amylose content than corn and wheat starches have shown restrictive swelling properties. The presence of an amylose-lipid complex could be another factor that inhibits starch swelling and solubilization (Doublier 1987, Tester and Morrison 1990). The amylose-lipid complex acts as a mobilization barrier for the amylose monomers and prevents the amylose from leaching from the starch granules (Eliasson et al 1981). Buckwheat starch had higher crude fat content (Table I) and apparent amylose content (Table III) than corn and wheat starches, which may favor the for-

mation of the amylose-lipid complex and thus restrict swelling and solubility.

Acid Hydrolysis and Enzymatic Digestibility

Figure 2 shows the degree of hydrolysis with 2.2N HCl at 30°C for 24 days. The three starches showed similar hydrolysis patterns. Biliaderis et al (1981) reported that legume starch showed a fast hydrolysis of the amorphous region and a slow degradation of the crystalline region. Buckwheat, corn, and wheat starches showed a lag time for days 1–3, then a faster hydrolysis rate was observed for days 3–12. During this time, the amorphous regions of the buckwheat, corn, and wheat starch granules were most likely attacked as suggested by Biliaderis et al (1981). After 12 days, buckwheat, corn, and wheat starches showed 84.6, 65.3, and 79.7% hydrolysis, respectively. These results suggested that the buckwheat starch granule might have a larger amorphous region (and be more susceptible to acid hydrolysis) than corn and wheat starches.

The digestibility of native buckwheat, corn, and wheat starches with porcine pancreatic α -amylase is shown in Fig. 3. Starch hydrolysis of buckwheat was significantly higher than for corn and wheat starches ($P < 0.05$). After 9 hr of digestion, buckwheat starch was hydrolyzed at 77%, compared to 62.9 and 71.2% for corn and wheat starches, respectively. The higher digestibility of buckwheat starch may be influenced by its smaller starch granule particle size and higher amylose content (Tables II and III). Starch with higher amylose content may form more amorphous regions that are easily attacked by α -amylase.

Franco et al (1992) suggested that the percentage of enzymatic hydrolysis of starch increased with decreasing starch granule size, thereby providing more surface area accessible to the hydrolytic enzyme. Fannon et al (1992) proposed that starch pores would be the site of the initial enzyme attack. Dreher et al (1984) reported that normal corn, sorghum, and millet starch granules showed random circular pits on their surfaces that were susceptible to enzymatic digestion. Wheat, barley, rye, and triticale starch granules were susceptible to hydrolysis along the equatorial grooves (Dreher et al 1984). Starches with surface pores showed more susceptibility to enzymatic activity than starches with equatorial grooves (Evers and McDermott 1970, Evers et al 1971, Dronzek et al 1972, Hood and Liboff 1983). The amylose-lipid complex in

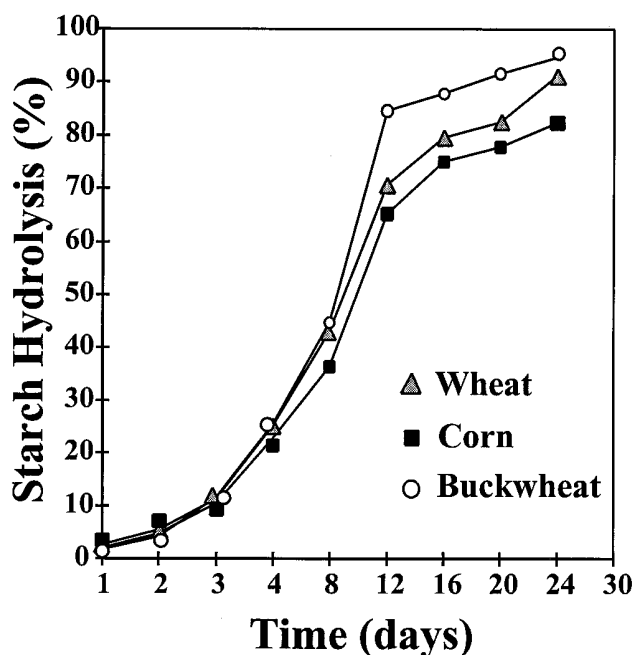


Fig. 2. Hydrolysis (%) of buckwheat, corn, and wheat starches in 2.2M hydrochloric acid at 30°C.

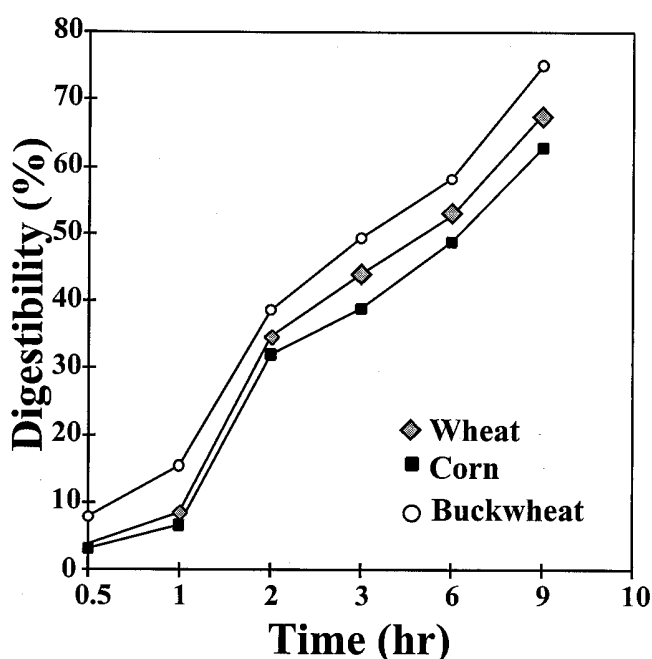


Fig. 3. Enzymatic digestibility of buckwheat, corn, and wheat starches with porcine pancreatic α -amylase at 37°C.

potato starch appeared to be resistant to α -amylase attack (Larsson and Miezi 1979). This was believed to be due to the V-helix of the amylose-lipid complex retarding the enzymatic attack (Holm et al 1983). One factor reported to affect the increased resistance of enzymatic hydrolysis is the increase in chain length of saturated monoglyceride in the amylose-lipid complex (Eliasson and Krog 1985).

Pasting Properties

The pasting properties of buckwheat starch (6% w/v) were compared with those of commercial corn and wheat starches (Table IV) using a Rapid Visco-Analyzer (RVA). Buckwheat starch exhibited a significantly higher peak viscosity, trough, and final viscosity than did corn and wheat starches ($P < 0.05$). This was due, in part, to the higher amylose content and water-binding capacity of buckwheat starch (Table III). The leached amylose molecules and swollen starch granules have been reported to contribute to starch pasting properties (Rasper 1982). Final viscosity indicates a gelling tendency of starch paste cooled at 50°C (Miles et al 1985b). The forces within the buckwheat starch gel were stronger than those within the corn and wheat starch gels (Stone and Lorenz 1984). The difference in peak minus trough viscosity (R) was an indication of the stability of the starch paste to shear (Stone and Lorenz 1984). The order of stability of starch gels against mechanical shear was wheat > corn > buckwheat ($P < 0.05$).

Thermal Properties

The DSC thermal properties of the starch samples are shown in Fig. 4 and Table V. The peak temperature (68.4°C) of buckwheat starch was lower than that of corn starch (69.9°C) and higher than that of wheat starch (61.2°C). The T_e and T_r of buckwheat starch were significantly higher than those for corn and wheat starches. The ΔH (10.0 J/g) of buckwheat and wheat starches was the same, but was significantly lower than corn starch (11.3 J/g). The T_r of buckwheat starch agreed with the results of Stone and Lorenz (1984). The T_p and ΔH of the wheat and corn starches were comparable to the values reported by Kugimiya et al (1980). Wang and White (1994) reported a commercial corn starch with a T_p of 71.5°C and a ΔH of 12.8 J/g. Uriyapongson and Rayas-Duarte (1994) reported T_p of 67.6 and 62.2°C and ΔH of 9.2 and 5.0 J/g for commercial corn and wheat starches, respectively. These differences could be due to variations in the source and milling methods of the various starches. A second melting thermal transition peak

was observed at $\approx 84.5^\circ\text{C}$ for buckwheat starch, which was lower than that of corn (98.4°C) and wheat (98.9°C) starches (Fig. 4). The T_p of the second endotherm for corn (96°C) and wheat (97°C) starch was comparable to the value reported by Kugimiya et al (1980).

The T_r and ΔH of the second endotherm were lower than the first gelatinization endotherm for buckwheat starch. This phenomenon was similar to reports for corn and wheat starches by (Kugimiya et al 1980, Wang and White 1994). The second melting transition in other starches is generally accepted to be caused by starch-lipid complexes (Kugimiya et al 1980, Larsson 1980, Maningat and Juliano 1980, Ohashi et al 1980, Biliaderis et al 1986, Paton 1987). Saturated lipid or free fatty acids formed amylose-lipid complexes in corn and wheat starches (Kugimiya et al 1980). Morrison et al (1978) suggested that lysophospholipids can form complexes with amylose that are similar to fatty acid-amylose complexes. Some authors reported that starch-lipid complex was formed mainly with amylose in native starch (Morrison and Coventry 1985, Morrison 1988, Morrison et al 1993). Other authors suggested that the starch-lipid complex may occur during gelatinization of starches with natural lipids (Kugimiya et al 1980, Kugimiya and Donovan 1981) or when lipids are added to defatted or lipids-free starch (Biliaderis and Krog 1985, Biliaderis et al 1986).

Godet et al (1995) reported that the melting temperature of amylose-lipid complexes increased as the amylose chain length increased. They also found that ΔH was increased as fatty acid chain length increased and decreased as the degree of polymeriza-

TABLE IV
Starch Paste Viscosity Analysis (RVU)^a of Buckwheat, Corn, and Wheat Starches

Starch	Peak	Trough	Final	Breakdown ^b
Buckwheat	148.0a ^c	100.0a	264.0a	48a
Corn	113.5b	73.5b	138.5b	40b
Wheat	74.0c	43.0c	10.5c	31c

^a Measured on the Rapid Visco Analyser (Newport Scientific, Narrabeen, Australia) as Rapid Visco Analyser units (RVU).

^b Breakdown = peak minus trough viscosities.

^c Values followed by the same letter in the same column are significantly different ($\alpha = 0.05$) using Duncan's multiple range test ($P > 0.0001$), $n = 2$.

TABLE V
Thermal Properties^a of Buckwheat, Commercial Corn, and Wheat Starches Analyzed by Differential Scanning Calorimetry

Starch	First Endotherm					Second Endotherm				
	T_o	T_p	T_c	T_r	ΔH (J/g)	T_o	T_p	T_c	T_r	ΔH (J/g)
Buckwheat	61.1b ^b	68.4b	80.8a	14.6a	10.0b	70.8b	84.6	99.7c	30.2a	2.0a
Corn	64.7a	69.9a	79.2b	10.4b	11.3a	92.2a	98.9a	106.4a	15.0b	0.63c
Wheat	57.1c	61.2c	73.5c	8.3c	10.0b	92.7a	98.4a	103.7b	10.6c	1.2b

^a Temperatures (°C) T_o , T_p , T_c , and T_r = onset, peak, completion, and range. Range calculated as $2(T_p - T_o)$. ΔH = Gelatinization enthalpy.

^b Values followed by the same letter in the same column are significantly different ($\alpha = 0.05$) using Duncan's multiple range test ($P > 0.0001$), $n = 3$.

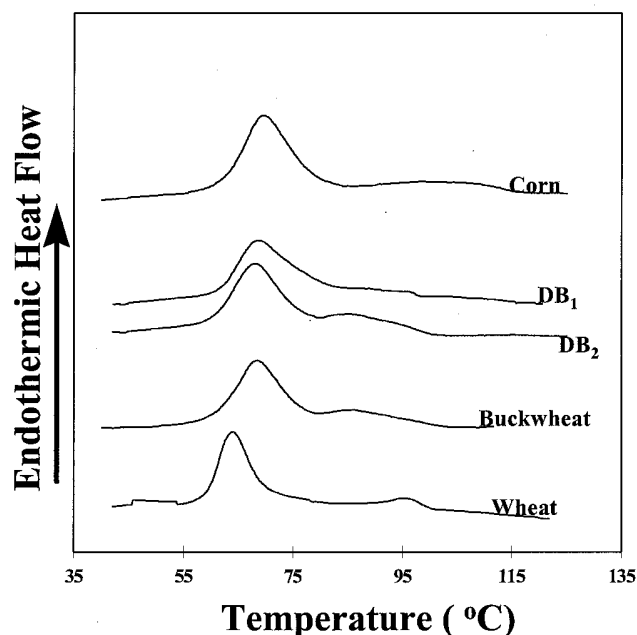


Fig. 4. Differential scanning calorimetry thermograms of starches heated with 2.3 parts of water (v/w) at a heating rate of 10°C/min. DB1 and DB2 Buckwheat starch defatted with water-saturated butanol at 90–100°C (internal lipids) or defatted with chloroform and methanol solvent and methanol and water solvent at room temperature (surface lipids), respectively.

TABLE VI
Effect of Defatting Treatment on Thermal Properties^a
in Buckwheat Starch

Starch	T_o	T_p	T_c	T_r	ΔH (J/g)
Gelatinization					
Native	61.3a ^b	68.4a	80.8a	14.2a	10.0a
Defatted 1 ^c	60.7b	67.9b	77.8b	14.2a	10.0a
Defatted 2 ^d	60.0c	67.4c	77.5b	14.8b	10.0a
Amylose-lipid complex					
Native	79.5a	84.5a	93.9a	10.0a	1.7a
Defatted 1	79.5a	84.3a	93.3a	9.6a	0.8a
Defatted 2	nd ^e	nd	nd	nd	nd

^a Temperatures ($^{\circ}\text{C}$) T_o , T_p , T_c , and T_r = onset, peak, completion, and range. Range calculated as $2(T_p - T_o)$. ΔH = Gelatinization enthalpy.

^b Values followed by the same letter in the same column are significantly different ($\alpha = 0.05$) using Duncan's multiple range test ($P > 0.0001$), $n = 3$.

^c Defatted with chloroform and methanol solvent and methanol and water solvent at room temperature (surface lipids).

^d Defatted with water-saturated butanol at 90–100 $^{\circ}\text{C}$ (internal lipids).

^e Not detected.

tion in amylose increased. Buckwheat starch amylose and lipid association may differ from the commercial corn and wheat starches in degree of polymerization, fatty acid composition, and chain length. The effect of different defatting treatments on thermal properties of buckwheat starch (Fig. 4, Table VI) showed a reduction in T_o and T_p when compared to native starch. The T_o (60.7 $^{\circ}\text{C}$) and T_p (67.9 $^{\circ}\text{C}$) of surface-lipids defatted buckwheat starch were lower than those of native buckwheat starch.

Surface lipids of starch granules could act partially as a diffusion barrier (Eliasson et al 1981) and alter the distribution of water between starch granules and the surrounding matrix (Eliasson and Krog 1985). After the removal of internal lipids with *n*-propanol and water, the T_o (60.0 $^{\circ}\text{C}$) and T_p (67.4 $^{\circ}\text{C}$) were lower than both native and surface-lipids defatted buckwheat starches. To remove the internal lipids, the starch granules were heated (90–100 $^{\circ}\text{C}$) in *n*-propanol and water for 6 hr. As expected, the treated buckwheat starch did not show a second transition endotherm when analyzed with the DSC (Fig. 4). The ΔH of native and internal- and surface-lipid defatted buckwheat starches remained unchanged (10.0 J/g). Also, the thermal properties of the amylose-lipid complex were not altered by removing only surface lipids, as compared to native buckwheat starch.

Retrogradation

Retrogradation percentage of buckwheat, corn and wheat starch pastes stored at 25, 4, and -12°C for 1, 5, 10, and 15 days are shown in Fig. 5. The retrogradation percentage of buckwheat starch paste was significantly ($P > 0.05$) lower than that of corn and wheat starch stored at 25 and -12°C for 1–15 days. At 4 $^{\circ}\text{C}$, the retrogradation of buckwheat starch paste was significantly lower than that of corn and wheat starch pastes for 10 storage days. However, after 15 days storage at 4 $^{\circ}\text{C}$, the retrogradation of buckwheat paste was not significantly different from the other starch pastes. The analysis was done on the average values of retrogradation, and the interactions of storage temperature and time by type of starch were significant ($\alpha = 0.05$). Because the interaction terms were significant, we cannot comment on the main effects.

The effect of storage temperature on buckwheat starch retrogradation was lower than for corn and wheat starches (4 $^{\circ}\text{C}$ > -12°C > 25 $^{\circ}\text{C}$, respectively). The retrogradation (%) increased as the storage time increased for all three starch pastes. Overall, buckwheat starch exhibited lower retrogradation percentages for each storage period than did corn and wheat starches for the three storage temperatures studied (25, 4, and -12°C). These results agree with previous reports. The maximum rate of recrystallization of wheat starch has been reported at 4 $^{\circ}\text{C}$ and is suggested to be its optimum nucleation temperature (Slade and Lavine 1986).

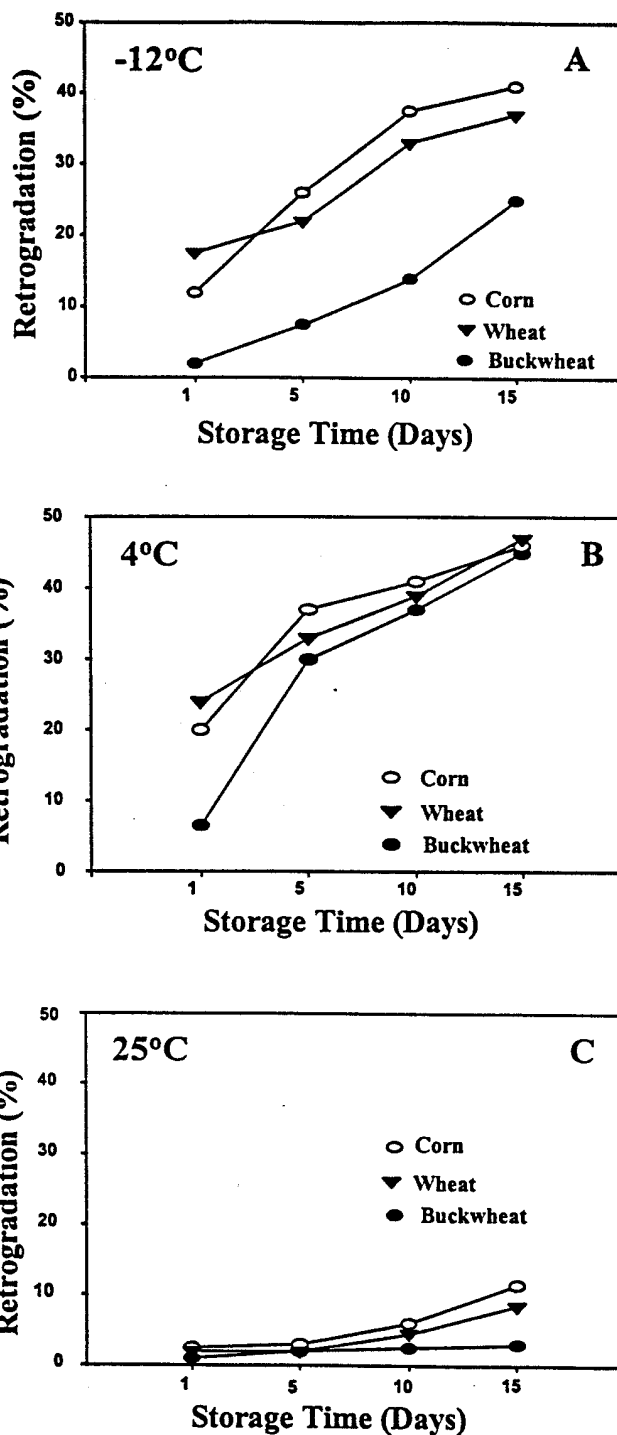


Fig. 5. Percent retrogradation as a function of storage time of 44% starch gels at -12°C (A), 4 $^{\circ}\text{C}$ (B), and 25 $^{\circ}\text{C}$ (C).

Retrogradation has been reported to involve both fast crystallization of amylose and slow recrystallization of amylopectin (Slade and Levine 1986). The amylose-lipid complexes may restrict the recrystallization of amylose domains (Paton 1987). The starch retrogradation was reported to be controlled by the nonequilibrium recrystallization behavior of amylopectin (Slade and Levine 1986). The early stages of starch retrogradation were dominated by the chain-folded lamellar microcrystalline junction zones of amylose ($\text{DP} \approx 15\text{--}50$) and the later stages by amylopectin branched chain ($\text{DP} > 12\text{--}16$) (Miles et al 1985a, Slade and Levine 1986, Shi and Seib 1992).

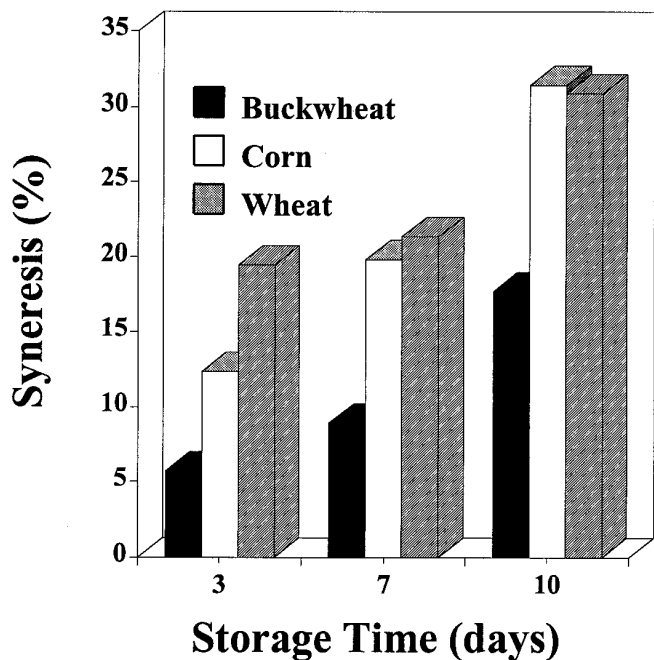


Fig. 6. Syneresis of buckwheat, corn, and wheat starch gels stored at 4°C.

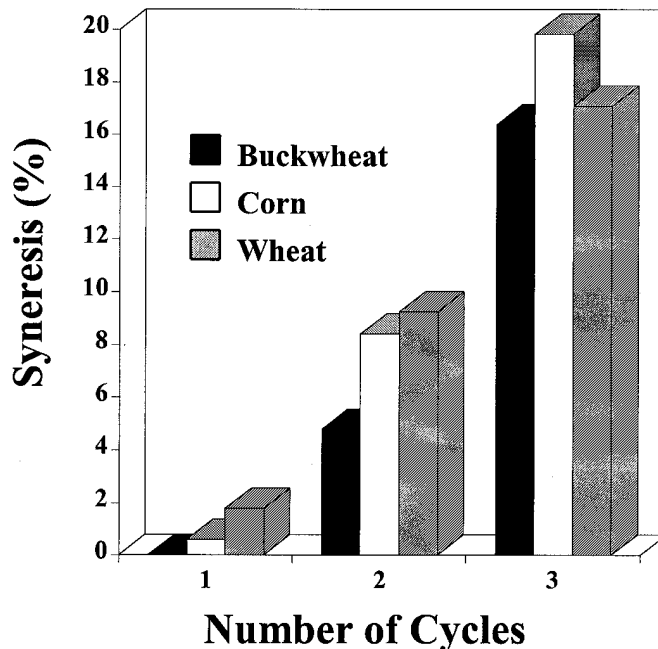


Fig. 7. Syneresis of buckwheat, corn, and wheat starch gels stored at -12°C subjected to three freeze-thaw cycles.

Degree of Syneresis and Freeze-Thaw Stability

The percentage of syneresis of the buckwheat, commercial corn, and wheat starch gels (6%, w/v) stored at 4°C for 3, 7, and 10 days is shown in Fig. 6. The buckwheat starch gel exhibited less syneresis than corn and wheat starch gels ($P < 0.05$). For all starch gels, syneresis increased as storage time increased. Syneresis has been primarily attributed to amylose molecules aggregating through increased intra- and intermolecular hydrogen bonding (Dreher et al 1983). Hoover et al (1991) reported more syneresis in lima bean starch gels (*Phaseolus lunatus*) than in corn and potato starch gels stored at 4°C for 3, 7, and 10 days. They suggested that the extent of syneresis could be attributed to the combination of amylose content, degree of association between starch components, length of outer branches of amylopectin, and degree of polymerization of the amylose and amylopectin. Syneresis of buckwheat starch when compared to commercial corn and wheat starch gels stored at -12°C and subjected to three consecutive freeze-thaw cycles is shown in Fig. 7. During the three freeze-thaw cycles, the buckwheat starch gel showed significantly lower syneresis than did corn and wheat starch gels ($P < 0.05$). Buckwheat starch showed better freeze-thaw stability than did commercial corn and wheat starches for the same storage conditions. Factors contributing to more stable buckwheat gels include higher lipid content, suggested lower molecular weight (lower intrinsic viscosity), and higher water-binding capacity. It appears that high amylose content alone does not explain the higher stability of the buckwheat gels. The water released from the three starch gels increased as the number of freeze-thaw cycles increased (Fig. 7). Storage temperature <4°C has been reported to inhibit nucleation and retard recrystallization (Slade and Levine 1986). However, during freezing and thawing, a fast nucleation could have occurred in a previously nucleated matrix after thawing, as speculated by Slade and Levine (1986).

Wu and Seib (1990) reported that waxy barley and tapioca starches were stable to freeze-thaw cycles due to their relatively shorter amylopectin branched chains ($DP \cong 12-13$), which were less prone to recrystallization than those of waxy maize ($DP \cong 15$). White et al (1989) used DSC to determine the amount of energy required to break down the recrystallized starch as a method to evaluate freeze-thaw stability of starch gels. They found that corn (27% amylose) and waxy corn (<1% amylose) starch displayed

nearly the same freeze-thaw stability. Tapioca and rice had about the same amylose content, but the rice starch gel showed nearly twice the enthalpy value of tapioca starch (White et al 1989).

CONCLUSIONS

Buckwheat starch differs from corn and wheat starches. It may have a relatively smaller molecular size and degree of polymerization, as suggested by its lower intrinsic viscosity. Buckwheat starch showed significantly lower swelling power at 85–95°C, lower solubility at 55–95°C, and higher amylose content than corn and wheat starches. These results suggest that the strength of the micellar network within the amylose region and the amylose-lipid complex in buckwheat starch might govern its swelling and solubility. The T_p of buckwheat starch was lower than that of corn starch but higher than that of wheat starch. An amylose-lipid complex was observed at 84.5°C (T_p) which may involve internal lipids.

The susceptibility of buckwheat starch to acid and α -amylase hydrolysis suggested a larger amorphous region in the buckwheat starch granule than in corn and wheat starches. Buckwheat starch had a lower retrogradation percentage when compared to corn and wheat starches over 1–15 days of storage at 25 and -12°C. It also showed a lower retrogradation percentage than did corn and wheat starches at 4°C for 10 days. But no difference of retrogradation (%) was detected among the three starches after 15 days of storage at 4°C. Buckwheat starch gel showed a lower degree of syneresis at 4°C storage for 10 days and a higher syneresis stability than did corn and wheat starch gels after three consecutive freeze-thaw cycles at -12°C and 25°C.

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