The European Journal of Plant Science and Biotechnology ***©2009 Global Science Books***

Buckwheat Starch: Structure and Characteristics – A Review

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ABSTRACT

Buckwheat, which contains high nutritional values of protein, dietary fiber, phenolic compounds and minerals, is a major pseudo-cereal for processing functional foods, especially the Japanese buckwheat noodles (soba noodles). In buckwheat flour, starch is a main component which plays an important role in the functional properties of end-use food products. Buckwheat starch granules were spherical, oval and polygonal in shape and granule size distribution ranged from 2 to 6 µm. The apparent amylose content of buckwheat starches varied from 21.1 to 27.4%, while the actual amylose content ranged from 16 to 18%. X-ray diffraction pattern of buckwheat starches was the typical A-type crystal with 38–51% crystallinity. The gelatinization temperatures of buckwheat starch were 57.8–64.3°C for onset (T_o), 63.7–70.8°C for peak (T_p) and 70.8–85.8°C for complete (T_c) temperatures, and ΔH values ranged from 2.14 to 15.0 J/g. Buckwheat amylopectin showed longer average chain length and larger amount of long chain than did the cereal amylopectins, while buckwheat amyloses were slightly larger than maize and rice amyloses, but similar to wheat and barley amyloses. The β-amylolysis limits of buckwheat amylopectins and amyloses were similar to those of the other cereals. The pasting characteristic studies showed that buckwheat starches had similar peak viscosity, higher hot and cool paste viscosities and higher resistance to shear thinning than did wheat starch. These characteristics of buckwheat starches are considered to contribute significantly to the texture and quality of buckwheat-based food products.

Keywords: amylose, amylopectin, soba noodle

CONTENTS

INTRODUCTION

Buckwheat (*Fagopyrum esculentum* Moench), a pseudo-cereal, is an alternative crop belonging to the *Polygonaceae* family and is usually grouped with cereals because of similarity in cultivation and utilization though it is not cereal grain. There are three major buckwheat species, common (*F. esculentum* Moench), tartary (*F. tataricum* Gaertner) and perennial (*F. cymosym* L.), in which the common buckwheat is the most commonly grown species (Marshall and Pomeranz 1982; Mazza and Oomah 2005). In addition, Japanese common buckwheat is classified into two groups according to harvest season (summer and autumn) (Yoshimoto *et al*. 2004). Buckwheat was originally cultivated in the southwest China and the Himalayan region (Ohnishi *et al*. 1998). Nowadays, buckwheat is grown as a traditional crop in China, Japan, Russia, Canada, USA, Australia, Central and Eastern Europe, etc. Buckwheat seed known as achene has a hard outer hull, which has a hard fibrous structure and surrounds the seed coat, endosperm and embryo tightly (**Fig. 1**). The embryo in a buckwheat seed is located in the center of the endosperm and the endosperm contains large amounts of protein, starch and vitamins. The protein of buckwheat consists of well-balanced amino acids with a high biological value (Pomeranz 1983) and is excel-

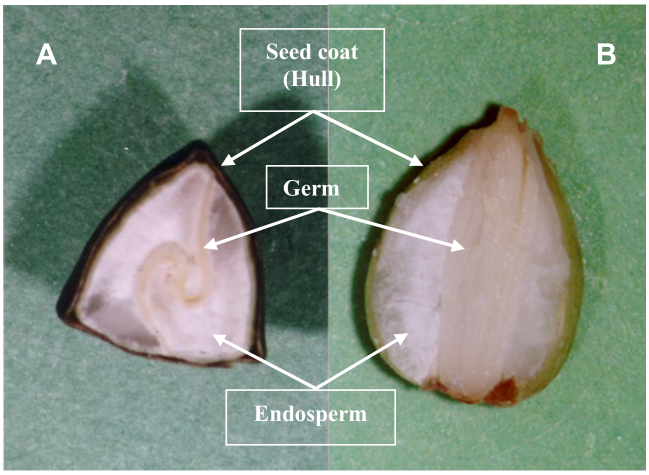

Fig. 1 Image of buckwheat grain. (**A**) Cross section; (**B**) Vertical section.

Received: 1 May, 2009. Accepted: 25 November, 2009.

Invited Mini-Review

lent supplement for cereal grains (Joshi and Rana 1995). In addition, buckwheat grains have been well known as a plant source of rutin, quercetin, kaempferol-3-rutinoside, and a trace quantity of a flavonol triglycoside (Holasova *et al.* 2002). Buckwheat flour containing mainly starchy central endosperm is obtained from the groats by roller-milling and sifting after removing its hull. In Eastern Europe, buckwheat is a basic food item in porridges and soups, while it is marketed primarily in pancake mixes, which may contain buckwheat flour mixed with wheat, maize, rice, or oat flour, plus a leavening agent in North America (Joshi and Rana 1995). In Japan, buckwheat is marketed primarily as flour for manufacturing a variety of noodles (soba) (Udesky 1988). Recently, buckwheat becomes a part of the renewed interest as an alternative crop for organic cultivation or as functionally healthy foods because of its low-calorie, high-fat content of unsaturated fatty acids, reasonable amino acid composition, high biological value of protein, potential anti-oxidative activity (Watanabe *et al.* 1997; Wijngaard and Arendt 2006; Hung *et al.* 2007; Hung and Morita 2008).

Starch is a major component of buckwheat endosperm, which plays an important role in appearance, structure and quality of food products. The studies on the molecular structure and physicochemical characteristics of starches isolated from both common and tartary buckwheats grown in different locations have been published (Li *et al.* 1997; Noda et al. 1998; Qian and Kuhn 1999; Yoshimoto *et al.* 2004; Inglett *et al.* 2009). However, it is necessary to summarize these results to make clear the general characteristics of buckwheat starches as well as the different ones among them. The aim of this article is to review the structure and physicochemical properties of buckwheat starches which have been investigated and published.

STRUCTURE OF BUCKWHEAT STARCH

Starch is the most important reserve polysaccharide and the most abundant constituent of many plants including cereal grains such as wheat, rice, corn and buckwheat, etc. It has some unique properties, which contributes to functionality of food products. The major components of starch are glucose polymers – amylose and amylopectin. Amylose is an essentially linear molecule, consisting of α-(1,4)-linked D-glucopyranosyl units with a degree of polymerization (DP) in the range 500–6000 glucose residues. It is now well recognized that a fraction of the amylose molecules is slightly branched by α-(1,6)-linkages (Hizukuri *et al.* 1981; Shibanuma *et al.* 1994). In contrast, amylopectin is a very large, highly branched chain molecule with a DP ranging from 3×10^5 to 3×10^6 glucose units and consists of α-(1,6)-linked D-glucopyranosyl units attached to α-(1,4)-bonds (Zobel 1988). The amylose/amylopectin ratio differs among starches, but typical levels of amylose and amylopectin are 25–28 and 72–75%, respectively. However, the starches of some mutant genotypes of maize, barley, rice and wheat, etc. contain either an increasing amylose content (*i.e.* high amylose or amylostarch with up to 70% amylose) or an increasing amylopectin content (*i.e.* waxy starch with 99–100% amylopectin) (Hung *et al.* 2006). In buckwheat, starch is also the major component of endosperms, followed by protein, dietary fiber, lipid and ash (Zheng *et al.* 1998; Steadman *et al.* 2001; Bonafaccia *et al.* 2003). Starch contents in buckwheat groats have been reported to be 54.5–55.8% for common buckwheat and slightly higher in tartary buckwheat (57.4%) (Steadman *et al.* 2001; Bonafaccia *et al.* 2003) (**Table 1**). Although Zheng *et al.* (1998) reported that the buckwheat groats contained 75% starch, this starch content might be resulted in the fancy flour after dehulling and removing its bran, as reported by Steadman *et al.* (2001) and Bonafaccia *et al.* (2003) (74.4–75.5 and 78.4%, respectively). As seen in **Table 1**, the amylose contents of common and tartary buckwheat starches are in a range of 21.3–26.5 and 22.7–25.7%, respectively (Li *et al.* 1997; Zheng *et al.* 1998; Qian and Kuhn 1999; Yoshimoto *et al.* 2004). These results are consistent with the data reported by Noda *et al.* (1998) who examined 17 kinds of common buckwheats and 10 kinds of tartary buckwheats and found these amylose contents were in a range of 21.1–27.4%. However, the apparent amylose content of buckwheat was also reported as high as 46.6% (Qian *et al.* 1998). This argument might be due to the different method used to determine amylose content in this study. The appearance of common buckwheat starch is shown in **Fig. 2**. The starch granules are spherical and polygonal shapes, which are the same as reported previously (Qian *et al.* 1998; Zheng *et al.* 1998; Qian and Kuhn 1999). Particle size distribution of buckwheat starch was a range of 2–14 μm (Qian *et al.* 1998; Zheng *et al.* 1998; Qian and Kuhn 1999), which were 1.6–2.4 times smaller than corn and wheat starch granules resulting in low starch recovery during wet extraction (Zheng *et al.* 1998).

Table 1 Starch composition in buckwheat groats.

Buckwheat varieties	Starch percentage (%)	Amylose content (%)	References
Common	54.5	n/a	Steadman *et al.* 2001
	55.8	n/a	Bonafaccia *et al.* 2003
	n/a	21.3-26.4	Qian and Kuhn 1999
	n/a	21.5-25.3	Li *et al.* 1997
	n/a	25.7-26.5	Yoshimoto *et al.* 2004
	75.0	21.3	Zheng *et al.* 1998
	n/a	46.6	Qian *et al.* 1998
	n/a	21.1-27.4	Noda *et al.* 1998
Tartary	57.4	n/a	Bonafaccia *et al.* 2003
	n/a	22.7-25.7	Li *et al.* 1997
	n/a	25.5	Yoshimoto *et al.* 2004;
	n/a	21.1-27.4	Noda *et al.* 1998

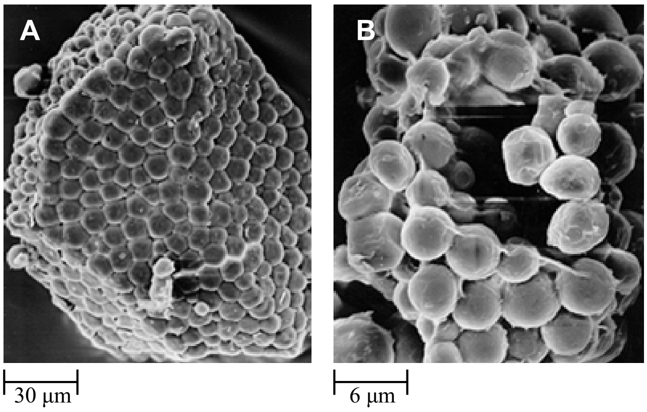

Fig. 2 Scanning electron microscope (SEM) of common buckwheat endosperm.

The amylopectin structure was known as a cluster model comprising by a single chain (C) per molecule which contains a sole reducing residue and either the unbranched outermost chains (A) or the branched inner chains (B) (Peat *et al.* 1956; French 1984) (**Fig. 3**). The B chains can be further divided in B1, B2 and B3 chains. The short (A and B1) chains form double helices, which are organized in discrete

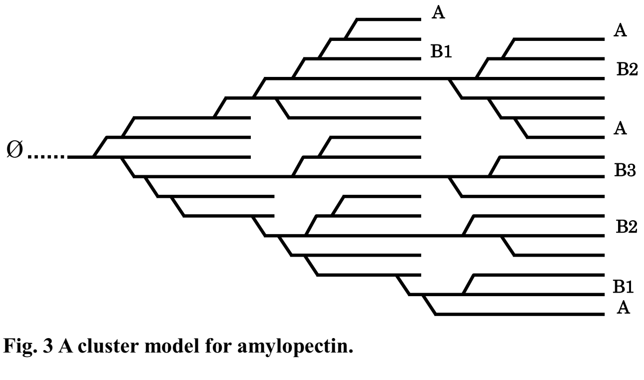

Fig. 3 A cluster model for amylopectin.

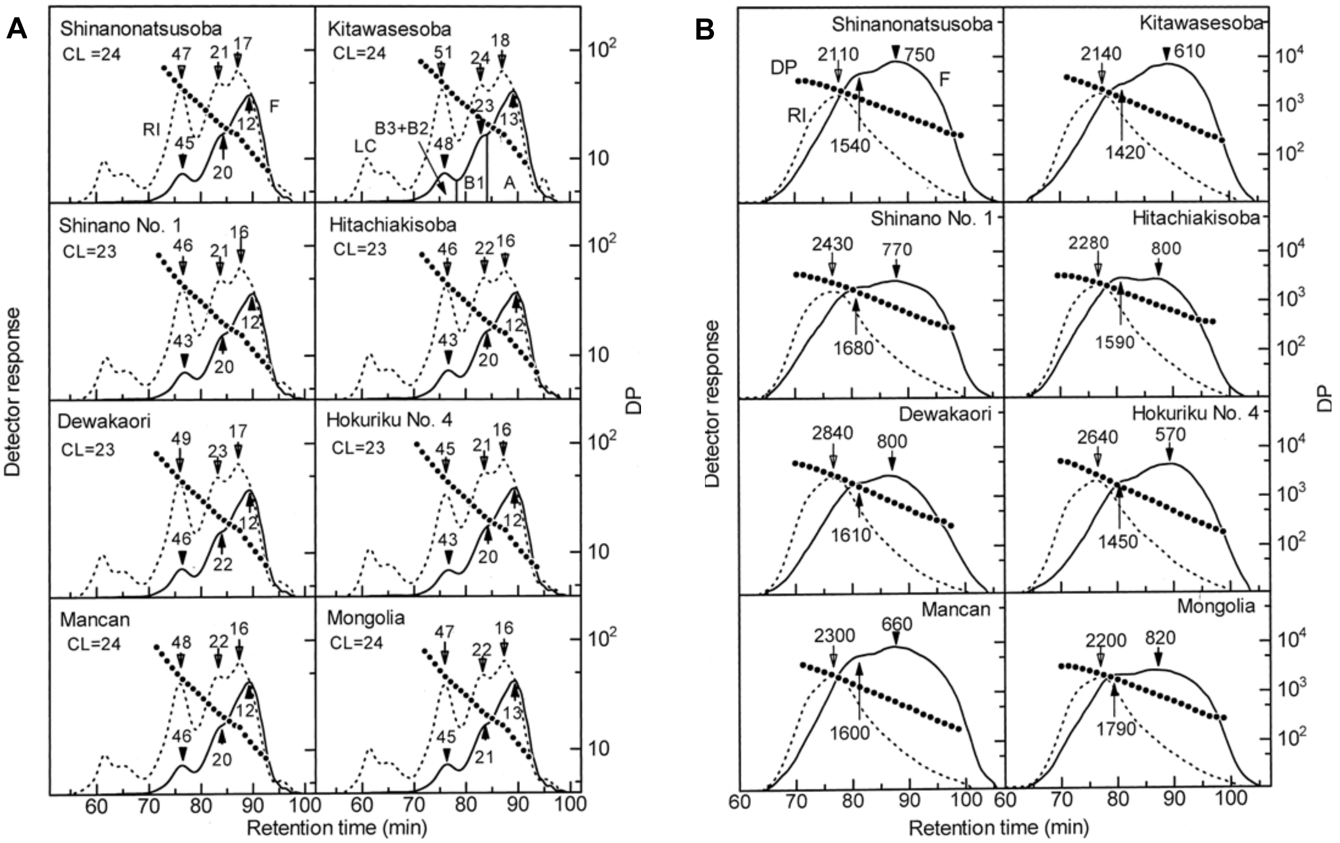

Fig. 4 Molar- and weight-based distributions of unit chains of buckwheat amylopectins (**A**) and amylose (**B**) by the fluorescent labeling/HPSEC: —, fluorescence response; - - - -, RI response; ●●●●, DP (arrows indicate DP values). Reprinted from **Yoshimoto Y, Egashira T, Hanashiro I, Ohinata H, Takase Y, Takeda Y** (2004) Molecular structure and some physicochemical properties of buckwheat starches. *Cereal Chemistry* **81**, 515-520, with kind permission of AACC International.

clusters, while the longer B2, B3 and B4 chains extend into 2, 3 or 4 clusters, respectively (Hizukuri 1986). The molar- and weight-based distributions of unit chains of buckwheat amylopectin are shown in **Fig. 4A** (Yoshimoto *et al.* 2004). The distributions were fractionated into LC (long chains), B2+B3, B1 and A chain fractions in order of elution (Hanashiro *et al.* 2002). The average chain length of buckwheat amylopectin was 23–24 as determined by three independent methods of rapid Smith-degradation, isoamylolysis and fluorescence labeling/HPSEC including 12–13% (by weight) of the long chains, 24–26% of B2+B3 chains, 24–25% of B1 chains and 36–38% of A chains (Yoshimoto *et al.* 2004). The molar ratio ((A1+B1)/(B2+B3)) regarding to the number of chains per cluster was 7.3–8.0 for buckwheat amylopectin, which was lower than wheat, rice and maize amylopectins (10.0–12.9) (Hanashiro *et al.* 2002; Yoshimoto *et al.* 2004). The distribution of short chains with DP < 60 examined by HPAEC showed a peak at DP 11 (Noda *et al.* 1998; Yoshimoto *et al.* 2002), which was similar to those of wheat (Shibanuma *et al.* 1996) and barley (Takeda *et al.* 1999; Yoshimoto *et al.* 2001, 2002), but lower than that of sweet potato (Noda *et al.* 1998). The amounts of buckwheat amylopectin at DP 6 and 7 were also lower than those of sweet potato amylopectin (Noda *et al.* 1998). The amylopectin structure was found to relate to the iodine-binding properties and DSC parameters. The large amount of LC of buckwheat amylopectin corresponded to the high amylopectin iodine affinity (Yoshomoto *et al.* 2002), while the amounts of shorter unit-chains of buckwheat amylopectin (DP 6–11) were negatively correlated with all DSC parameters (T_o, T_p and ΔH) but those of longer unit-chains (DP 13–17) were positively correlated (Noda *et al.* 1998).

The buckwheat amylose had DP_n of 1,020–1,380, which were slightly larger than maize (830–990) (Takeda *et al.* 1988; Takeda and Preiss 1993) and rice (920–1,110) (Takeda *et al.* 1986, 1989) amyloses, and in a range of wheat (830–1,570) (Shibanuma *et al.* 1994, 1996) and barley (810–1,570) (Takeda *et al.* 1999; Yoshimoto *et al.* 2000, 2001, 2002, 2004) amyloses. The average chain length of buckwheat amyloses were 280–380 with the average number of chains of 3.1–4.3 (Yoshimoto *et al.* 2004). The molar- and weight-based distributions of unit chains of buckwheat amylopectin are shown in **Fig. 4B** (Yoshimoto *et al.* 2004). The weight-based distributions of buckwheat amyloses showed a single peak. However, the molar fraction of branched amylose obtained as a percentage of fluorescent peak area of β-limit dextrin was in a range of 23–27%. This result also reveals that buckwheat amyloses also have minor amount of branched molecules (Yoshimoto *et al.* 2004).

PHYSICOCHEMICAL CHARACTERISTICS OF BUCKWHEAT STARCH

The X-ray diffraction pattern of the buckwheat starch shows a typical crystalline A-type (**Fig. 5** which is similar to other cereal starches such as wheat, rice, corn, etc (Zheng *et al.* 1998; Qian and Kuhn 1999). The crystallinity of buckwheat starches were a range of 38.31–51.31% (Qian and Kuhn 1999), which were higher than that of wheat (35.5%) (Morrison *et al.* 1994), but similar to that of rice (47–51%) (Qi *et al.* 2003), and corn (43%) (Cooke and Gidley 1992).

Starch, when heated in the presence of sufficient water, undergoes an order-disorder phase transition called gelatinization. The differential scanning calorimetry (DSC), which measures the gelatinization transition temperatures (T_o, onset temperature; T_p, peak temperature and T_c, completion temperature) and the enthalpy (ΔH) of gelatinization, is the most commonly used technique in studies of starch gelatinization. **Table 2** summarizes the thermal characteristics of common and tartary buckwheat starches. Qian and Kuhn (1999) reported that the gelatinization temperatures of common buckwheat starch are in a range of 58.6–62.1°C for T_o, 64.8–69.6 for T_p, 70.8–75.9 for T_c and 2.14–4.63 for ΔH. Other studies also reported similar results for T_o and T_p of

Table 2 Thermal characteristics of buckwheat starch determined by DSC[a].

Buckwheat arieties	**T_o (°C)**	**T_p (°C)**	**T_c (°C)**	**ΔH**	**References**
Common	58.6–62.1	64.8–69.6	70.8–75.9	2.14–4.63	Qian and Kuhn 1999
	62.7	69.0	80.9	12.7	Zheng *et al.* 1998
	57.8–62.4	66.3–68.8	77.3–79.2	9.1–10.0	Li *et al.* 1997
	59.5–64.1	63.7–68.4	82.5–85.8	14.5–15.0	Yoshimoto *et al.* 2004
Tartary	62.8–64.3	68.8–70.8	79.9–81.3	9.7–11.0	Li *et al.* 1997
	61.0	64.1	81.7	14.7	Yoshimoto *et al.* 2004

[a] T_o (°C), onset temperature; T_p (°C), peak temperature; T_c (°C), completion temperature and ΔH, the enthalpy of gelatinization.

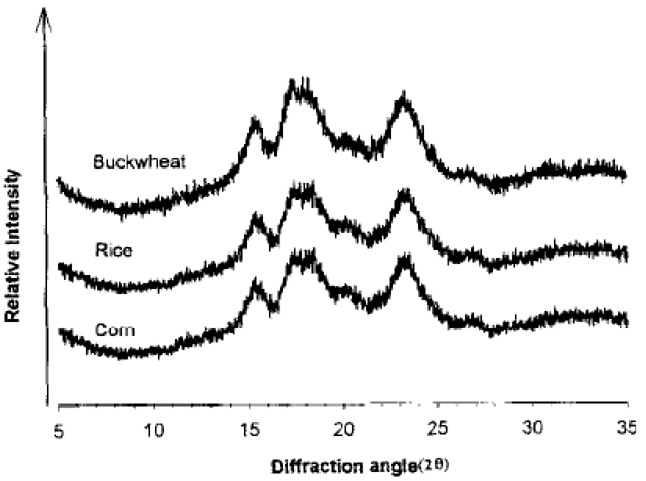

Fig. 5 X-ray diffractograms of buckwheat, rice and regular corn starches. Reprinted from **Zheng GH, Sosulski FW, Tyler RT** (1998) Wet-milling, composition and functional properties of starch and protein isolated from buckwheat groats. *Food Research International* **30**, 493-502, with kind permission of Elsevier Science Ltd.

common buckwheat starch but higher T_c (77.3–85.8°C) and ΔH (9.1–15.0) (Li *et al.* 1997; Zheng *et al.* 1998; Yoshimoto *et al.* 2004). The difference might be due to the different varieties and growing location of the examined buckwheats. The DSC data showed that the tartary buckwheat starch had higher T_o and T_p than did the common buckwheat starch, whereas the T_p and ΔH were similar (**Table 2**). The gelatinization temperatures of buckwheat starch was similar to those of corn starch or higher than those of wheat starch (Li *et al.* 1997) and barley starch (Yoshimoto *et al.* 2001) but lower than those of rice starch (Zheng *et al.* 1998) and sweet potato starch (Noda *et al.* 1998). In addition, the second transition, corresponding to the melting of amylose-lipid complexes, was also detected in buckwheat starch by DSC (Qian *et al.* 1998; Yoshomoto *et al.* 2001). The formation of amylose-lipid complexes could lead to the restriction of swelling power and solubility of starch (Qian *et al.* 1998).

The rapid viscosity analysis (RVA) curves of the common and tartary buckwheat starches are sown in **Fig. 6**. Although the angle and shape of the slope from initiation of viscosity increase to the peak viscosity were different between common and tartary buckwheat pasting curves, there were no systematic difference in peak and final viscosities between them (Li *et al.* 1997). Yoshimoto *et al.* (2004) also reported that there was no difference in pasting profile of starches from eight kinds of buckwheat cultivars. The buckwheat starches showed the pasting temperature at approximately 70°C, maximum viscosities in a range of 226–261 RVU, minimum viscosities in a range of 156–202 RVU, viscosity at 40°C in 336–404 RVU, breakdown in 37–98 RVU, and setback in 181–226 RVU (Yoshimoto *et al.* 2004). Both common and tartary buckwheat starches had higher peak and final viscosities than did wheat starch, whereas the time-to-peak viscosity of buckwheat starches was slightly lower than in wheat starch and there were effectively no differences in temperature at peak viscosity among all samples (Li *et al.* 1997). Buckwheat starches also had higher maximum viscosity, viscosity at 40°C, and setback than maize (Jideani *et al.* 1996) and barley (Yoshimoto *et al.* 2001) starches. These results suggested that buckwheat starches had higher granule swelling and gelling tendency than the cereal starches (Yoshimoto *et al.* 2004).

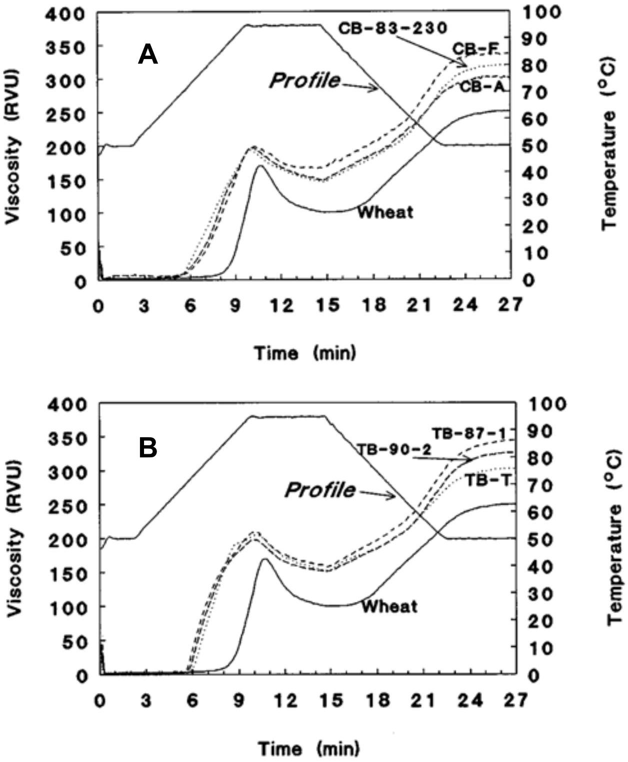

Fig. 6 Pasting curves of common buckwheat starches in water (**A**) and tartary buckwheat starches in water (**B**). Reprinted from **Li W, Lin R, Corke H** (1997) Physicochemical properties of common and tartary buckwheat starch. *Cereal Chemistry* **74**, 79-82, with kind permission of AACC International.

RESISTANT BUCKWHEAT STARCH

Resistant starch (RS) is defined *in vivo* as the sum of starch and products of starch degradation not absorbed in the human intestine (Englyst and Cummings 1990). There are four types of RS depending on the cause of resistance (Englyst *et al.* 1992; Annison and Topping 1994): RS_1, physically inaccessible starch; RS_2, native starch granules; RS_3, retrograded starch and RS_4, chemically modified starch. RS is considered to have beneficially physiological effects on human health (Topping and Clifton 2001). Buckwheat groats were found to have 33.5–37.8% of RS (Skrabanja and Kreft 1998; Skrabanja *et al.* 1998). However, the amount of buckwheat RS reduced to 7.5% after autoclaving treatment or to 8.5% after cooking. In contrast, the level of retrograded starch can be increased by either autoclaving or boiling from 1.0 to 4–7% (Skabanja and Kreft 1998; Skabanja *et al.* 1998, 2001). According to *in vivo* analysis, rats excreted ≈0% starch of native buckwheat groats, whereas 1.0–1.6% of starch from hydrothermally treated samples was excreted by Nb–rats (Skabanja *et al.* 1998). These results indicate that the buckwheat starch is a source of native resistant starch (RS_2) and it is possible to increase an amount of retrograded resistant starch (RS_3) in buckwheat groats or buckwheat-based food products by the physical treatments or during processing. The bread based from buckwheat groats flour supplementation contained 2.3–3.2% of RS (dmb) as compared to 0.8% RS of the white wheat bread (Skrabanja *et al*. 2001). As a result, the glycemic index (GI) of the bread with 50% of buckwheat groats flour supplementation reduced to 66 GI as compared to 100 GI of the white wheat bread (Skrabanja *et al*. 2001). Although the buckwheat starch has been known as a source of resistant starch, it is necessary to carry out further study on formation of resistant buckwheat starch related to its structure and to the ratio of amylose and amylopectin in buckwheat starch as well as producing conditions to increase its content in the buckwheat-based food products.

ROLE OF BUCKWHEAT STARCH IN FOOD PROCESSING

Starch properties and amylose/amylopectin ratio also have a great impact on the eating quality of noodle, especially on textural properties. High paste viscosity and breakdown, low gelatinization temperature and high swelling power of starch have been reported as desirable for textural properties of white salted noodles in Japan and Korea (Crossbie 1991; Panozzo and McCormick 1993; Endo *et al*. 1988), whereas the lower amylose contents were related to higher starch swelling properties and better white salted noodle qualities (Miura and Tanii 1994; Wang and Seib 1996; Noda *et al*. 2001). The buckwheat was widely used for noodle-making in Asian countries. In Japan, the noodle named "soba" was made from buckwheat and wheat flours with high nutritious quality (Udesky 1988). The soba noodles are prepared mainly from buckwheat flour, water and salt. The process of preparing soba noodle mainly consists of three steps, mixing of hydrated buckwheat flour, spreading of the dough, and cutting. Therefore, the mixing ingredients and the composition of buckwheat flour especially starch and protein are important to form the texture of soba noodle. Hung *et al*. (2007) studied on the noodle quality made from the polished graded buckwheat flours and reported that the inner fractions containing mostly endosperm starch showed higher peak viscosity than did the outer fraction containing higher amounts of protein, ash and dietary fiber and the noodles made from wheat flour substituted with 40% of the inner buckwheat flour were firmer and less elastic than those substituted with the outer buckwheat flour. Mariotti *et al*. (2008) also reported that the peculiar viscosity profile of the blends of dehulled buckwheat flour and wheat flour changed with increasing amount of dehulled buckwheat flour in the blend. The high increase of the viscosity of the blends during the heating phase suggested that buckwheat starch could play an important structuring action, mostly during the final step of the bread-making process, thus assuring a good consistency to the final product (Mariotti *et al*. 2008). The study on the effect of buckwheat flour fraction on dough quality showed that the dough made from inner-layer flour fractions exhibited significantly higher hardness and chewiness as compared with those made from outer-layer flour fraction (Ikeda and Kishida 1992). This finding suggested that the protein in buckwheat flour mainly associated with the texture of its dough. Maeda *et al*. (2004) reported that the substitution of buckwheat flour to wheat flour reduced the firmness of the baked cookie and lowered the values of cookie spread during baking. Thus, the presence of buckwheat flour had different effects on the quality of end-use products. Although buckwheat flour cannot be developed into a viscoelastic dough with good elasticity because of a lack of gluten-like proteins, the substitution of buckwheat flour for wheat flour did not worsen wheat dough rheology (Mariotti *et al*. 2008). As a result, the substitution of buckwheat flour for wheat flour in pasta processing did not significantly decrease the rheological properties of the pasta products from sensory test (Maeda *et al*. 2004). However, the presence of buckwheat starch made the noodle products firmer and less elastic (Hung *et al*. 2007). Regarding the buckwheat protein, a critical problem to our health is that buckwheat seeds contain proteins, which cause a hypersensitive reaction (allergy). Therefore, the proteins would limit the utilization of buckwheat as general food ingredients. By increasing in an amount of buckwheat starch to produce the buckwheat-based product, the healthy food products with increasing resistant starch and phenolic compounds and reducing allergenic proteins will be produced. However, it is still necessary to study more on the relationship between the physicochemical properties of buckwheat starch and the quality of the final product.

CONCLUSION

The molecular structure and physicochemical characteristics of buckwheat starches are summarized in this review. There are many differences in the structure and characteristics between the common and tartary buckwheat starches and between buckwheat and other cereal starches. In addition, the growing conditions and physical treatments prior to milling also affect the physicochemical properties of buckwheat starches. Both protein and starch present in buckwheat flour influenced in the textural properties and quality of the final products. By increasing in an amount of buckwheat starch in food processing, the healthy foods with eliminated allergen protein will be produced. However, more study on the relationship between the physicochemical characteristics of buckwheat starch and the end-use products should be carried out.

ACKNOWLEDGEMENT

The authors wish to thank Dr. David W. Hatcher, Head of Crop Section, Grain Research Laboratory, Canadian Grain Commission, 1404-303 Main Street, Winnipeg, Manitoba R3C 3G8, Canada, for his support and advice.

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