

Understanding the Physicochemical and Functional Properties of Wheat Starch in Various Foods

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ABSTRACT

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This report highlights the structure and myriad properties of wheat starch in various food systems. Granule shape, size, and color, plus the proportion of A- and B-granules, amylose content, and molecular structure largely determine its functionality in food. The role of wheat starch is portrayed in three categories of flour-based foods that differ in water content. Wheat starch influences the appearance, cooking characteristics,

eating quality, and texture of pasta and noodles, and its role is more than a filler in yeast-leavened bread products. Recent developments in the properties and applications of commercially important wheat pyrodextrins and RS4-type resistant wheat starches are reported, along with their use to produce fiber-fortified foods. Gluten-free foods are also discussed.

Wheat (*Triticum aestivum* L.) is unique because of the properties of two principal macromolecular components, protein (gluten) and starch. Wheat gluten is responsible for the dough-forming ability of wheat flour to make bread, which is unmatched by any other proteins of plant, animal, or microbial origin (Gianibelli et al 2001; Wrigley et al 2006). Wheat starch and the other *Triticeae* starches contain two, and possibly three, distinct populations of granules that differ in shape, dimension, composition, and properties (Evers 1971, 1973; Meredith 1981; Morrison 1989; Bechtel et al 1990; Seib 1994; Maningat and Seib 1997; Peng et al 1999; Bechtel and Wilson 2003; Wilson et al 2006; Maningat et al 2009; Kim and Huber 2010b). The so-called A-granules and B-granules from wheat and other *Triticeae* starches (barley, rye, triticale) are not exhibited in other botanical sources of starch. Recent developments on physicochemical and functional properties of wheat starch are reported and, where appropriate, compared with other botanical sources of starch. These properties are examined as they relate to the performance of wheat starch in flour-based foods and other selected food products. The ratios of A-granules to B-granules and amylose to amylopectin plus granular, structural, and molecular characteristics of wheat starch dictate the overall properties and behavior of wheat starch in foods.

Structure of Wheat Starch

Wheat starch is essentially a pure carbohydrate, but minor components consisting of proteins, lipids, ash, and dietary fiber exist in the exterior and interior of the granules (Maningat and Seib 1997; Maningat et al 2009). More than 150 surface-associated proteins consisting primarily of histones, purothionins, and glutenins were identified from commercially available wheat starches (Kasarda et al 2008). Friabilin proteins that predominate on the surface of soft wheat starch granules (Greenwell and Schofield 1986) are composed of two isomers (puroindoline-A and puroindoline-B) that function as molecular markers for wheat endosperm hardness (Morris et al 1994; Morris 2002). The prominent protein located in the granule interior is granule-bound starch

synthase I. Other embedded proteins with enzyme activities are soluble starch synthase, starch branching enzyme, and two polypeptides that may have starch synthase activities (Rahman et al 1995; Gao and Chibbar 2000).

The lipids consist of 0.7–1.4% that is interior-bound (Morrison 1989) and some surface-bound glycolipids and phospholipids at 38.8–476.5 nmol/g (Finnie et al 2010). Lipids inside the granules consist of 89–94% lysophospholipids of 70% lysophosphatidylcholine, 20% lysophosphatidylethanolamine, and 10% lysophosphatidylglycerol (Morrison 1989). In agreement with preceding results, Finnie et al (2009) demonstrated that bound lipids extracted from the interior of the granules are predominantly lysophosphatidylcholine followed by lysophosphatidylethanolamine, digalactosyldiglyceride, and lysophosphatidylglycerol and lesser amounts of other phospholipids and glycolipids. In samples of near-isogenic wheat lines, surface-bound glycolipids are primarily digalactosyldiglyceride and monogalactosyldiglyceride and the majority of phospholipids consist of phosphatidylcholine and lysophosphatidylcholine (Finnie et al 2010). In a separate study (Finnie et al 2009), a hard red winter cultivar had essentially no extractable free lipids on its starch surface whereas a soft white spring wheat cultivar contained free lipids amounting to 0.01–0.42 mol% of total polar lipids (free + bound). A majority of polar lipids bound on the starch surface of both hard and soft wheats consists of digalactosyldiglyceride and monogalactosyldiglyceride, with moderate amounts of phosphatidylcholine and lysophosphatidylcholine and lesser amounts of other glycolipids and phospholipids (Finnie et al 2009).

At the macromolecular level, starch from common wheat contains a mixture of amylose-to-amylopectin at a weight ratio of $\approx 1:3$ (Maningat et al 2009). Wheat amylose is a glucan with $>99\%$ α -1,4-linkages, with a number-average degree of polymerization (DP_n) of $\approx 1,000$ (Hizukuri et al 2006). The size of amylose molecules in wheat, as well as in the endosperm of other cereals, is one-fifth to one-half that in tapioca and potato starches. Approximately 20% of the weight of wheat amylose is likely complexed with lysophospholipids (90% pure), whereas $\approx 20\%$ of corn amylose is complexed with a 3:2 (w/w) mixture of free fatty acids and lysophospholipids (Seib 1994). Those monoacyl lipid complexes with amylose are predominantly amorphous (Chanvrier et al 2007; Lopez-Rubio et al 2008). Root and tuber starches contain negligible amounts of lipids. A large percentage of the amylose in wheat and corn starches can be leached from swollen granules at 0.5–

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1.5% solids in water at 95°C (Shi et al 1991). However, the extent of leaching decreases at 4.5% solids, which is near the critical concentration of 5–8% starch solids where the swollen granules occupy the entire volume of a cooked paste.

Whereas amylose molecules are largely responsible for the gelling and film-forming properties of cooked starch, amylopectin molecules are associated with the crystallinity, gelatinization, and swelling of starch. Wheat amylopectin comprises thousands of α -1,6-linked unit chains, where each unit chain contains an average of 20–21 α -1,4-linked D-glucose units. The weight-average molecular weight of wheat amylopectin was $260\text{--}524 \times 10^6$ da in HP-SEC (Yoo and Jane 2002; Chung et al 2008). But recent work indicates that HP-SEC underestimates the size of amylopectin due to shearing of that polysaccharide (Cave et al 2009).

After debranching of wheat amylopectin and chromatographic separation of the unit chains, a tetramodal distribution of chains is observed with a periodicity of ≈ 12 glucose units (Hizukuri 1986). The shortest chains are called A-chains with DP 6–12; next are B₁ chains with DP 13–24, then B₂ chains at DP 25–36, and finally B₄ and longer chains at DP > 37. Extra-long chains of DP $\approx 1,000$ occur in wheat and corn amylopectins, but not in their waxy counterparts nor in potato starch (Yoo and Jane 2002; Maningat et al 2009). On a molar basis, the ratio of (A+B₁ chains)/(B₂ + B₃ chains) is a measure of the proportion of chains in one cluster to those in two or more clusters. Wheat amylopectin shows the highest ratio (12.3–12.9) compared with amylopectin from corn (10.0), rice (10.1–10.8) and potato (5.4–6.4). The preponderance of short chains in wheat amylopectin is likely related to the low crystallinity, low gelatinization temperature, and rapid viscosity development of wheat starch (Maningat et al 2009).

According to the “cluster model” of Hizukuri, the A and B₁ chains, which dominate the distribution, occur as parallel strands in amylopectin and are believed to wind into left-handed double helices (Hizukuri 1986). In wheat starch, ≈ 10 double helices hydrogen-bond together along with a low percent of water molecules to form crystals of 7–10 nm (Maningat et al 2009). The B₂, B₃, and B₄ chains in amylopectin are thought to transverse two, three, and four clusters in amylopectin molecules, respectively.

Independent measurements indicate that the level of double helices and relative crystallinity in starch are equal and that normal wheat starch contains $\approx 25\%$ of both, which is below that of potato (44%), rice (37%), and waxy maize (46%) starch (Lopez-Rubio et al 2008). The crystals in wheat starch display the A-type X-ray diffraction pattern, which is common to native starches with short unit chains in amylopectin, and different from the B-type pattern of root, tuber, and high-amylose starches.

The α -1,6-branch points in amylopectin are clustered between crystalline lamellae. The branched region of amylopectin plus the amylose molecules constitute the amorphous phase of starch granules. The amorphous phase of a fully hydrated native starch granule is accessible to water-soluble reagents with a cut-off molecular weight of $\approx 1,000$ da (Brown and French 1977).

Waxy and High-Amylose Wheat Starch

The granule-bound starch synthase I, also called the waxy protein, is encoded at the *Wx* locus and catalyzes the synthesis of amylose in wheat endosperm (Graybosch 1998; Chibbar and Chakraborty 2005; Lafandra et al 2010). Hexaploid wheat carries three homologous *Wx* loci: *Wx-A1*, *Wx-B1*, and *Wx-D1* (Kiribuchi-Otobe et al 2004). Depending on whether these loci alleles are active or inactive, there can be eight possible combinations (Nishio et al 2009) consisting of one normal (wild-type), six partial waxy (reduced amylose), and one perfect waxy (amylose-free). Nearly isogenic lines of the eight types of wheat have been produced and assayed for amylose by blue color of the amylose-iodine complex. Wheat lines with single, double, and triple nulls of the waxy proteins produced starch whose amylose was reduced by 2–3, 6–9, and 22 percentage points, respectively. The wild-type

wheat contains 25% amylose (Maningat et al 2009). As expected, waxy wheat starch displays higher crystallinity than the wild-type, and much lower lipid content (Hung et al 2007; Chibbar and Chakraborty 2005).

Natural or intentional mutations in starch-synthesizing enzymes alter amylose content in wheat. A triple-mutant hexaploid wheat, deficient in starch synthase IIa, contains 4–8% more amylose than the wild-type. However, mutations in the branching enzymes for amylopectin give much higher amylose in wheat. By transgenesis, both starch-branching enzymes IIa and IIb were suppressed, resulting in wheat starch containing >70% amylose (Rahman et al 2007). More recently, high-amylose durum wheat (>70% amylose) was developed by silencing starch-branching enzyme IIa with RNA interference (Sestili et al, *in press*).

Wheat Starch Granules

Wheat starch possesses a bimodal granule-size distribution consisting of large lenticular-shaped granules (also called A-granules) representing $\approx 75\%$ by weight (or $\approx 5\%$ by number) and small round granules (also called B-granules) representing $\approx 25\%$ by weight (or $\approx 95\%$ by number) (Morrison 1989; Seib 1994; Peng et al 1999; Ao and Jane 2007; Maningat et al 2009; Kim and Huber 2010b). The existence of a third distinct type of granule called C-type ($\approx 5 \mu\text{m}$) was described earlier by Bechtel et al (1990) and more recently by Bechtel and Wilson (2003). Image analysis gives the typical size of A-granules at 29–34 μm and B-granules at 8–10 μm , whereas laser-diffraction analysis gives 17–20 μm and 4–5 μm , respectively (Wilson et al 2006). The dual distribution of granule sizes is shared by the other *Triticeae* starches from barley, rye, and triticale but not by other cereal, root, tuber, or legume starches. The lenticular or disk shape of A-granules from *Triticeae* starches is unique compared with other botanical sources, except in lesser known starches from ginger, shoti, and diffenbachia (Jane et al 1994).

Although most granules have generally a smooth surface appearance when viewed by SEM, some nano-sized globular structures or protrusions are visible when examined by atomic force microscopy. These surface protrusions are believed to be part of “blocklet” structures of amylopectin observed inside the granules. Potato starch contains protrusions of 10–50 nm to 50–300 nm in diameter, while tapioca starch possesses 56–144 nm structures (Juszczak et al 2003a). Other researchers (Hatta et al 2003) discovered larger structures in potato granules measuring $\approx 1,000$ nm in width and raised nodules measuring <300 nm or 50 nm. Regularly spaced structures or nodules measuring 20–50 nm were reported on wheat starch (Baldwin et al 1997) but other researchers (Juszczak et al 2003b) observed larger (<200 nm) protruding structures. According to Ayoub et al (2006), rice starch exhibits globular structures (70 nm) with inner particles of 30 nm, which corresponds to an individual single cluster as reported by Ohtani et al (2000). The surface of corn starch granules has numerous fine particles with diameter of 20–40 nm (Sujka and Jamroz 2009) but the internal structure contains blocks of 400–500 nm in size that span the growth rings (Baker et al 2001).

Beside the protrusions on granules of wheat starch, their surface contains polar lipids that may originate from the membrane of the amyloplast in which the granule was synthesized. Polar lipid composition consisted principally of digalactosyldiglyceride, monogalactosyldiglyceride, phosphatidylcholine, lysophosphatidylcholine and minor amounts of other glycolipids and phospholipids (Finnie et al 2009, 2010). Wheat starch from a soft-textured kernel of a hexaploid wheat contains more polar lipids on its granules than starch from a hard wheat, perhaps because during desiccation of the kernels the membrane in the soft wheat was not degraded. The polar lipids on soft wheat starch associate with the puroindoline-A and -B proteins in the endosperm due to their common hydrophobic character and to their difference in charge (Greenblatt et al 1995; Feiz et al 2009). On the other hand, the

hard-wheat starch granules, being deficient in surface lipids, bond strongly with the gluten matrix proteins rather than puroindolines. Puroindoline-A is missing in hard hexaploid wheats, and puroindoline-B is mutated. The close association between starch granules and matrix proteins in wheat endosperm accounts for kernel hardness. Plant pigments occur in low concentrations in wheat endosperm, so when isolated, wheat starch appears bright white. Applications like donut sugars or Japanese fish cake (“kama-boko”) benefit by the bright white color of wheat starch (Maningat and Seib 1997; Maningat et al 2009).

Surface pores are visible on the A- and B-granules from wheat when examined by SEM (Fannon et al 1992a,b, 1993; Kim and Huber 2008). Those pores are openings to serpentine-like channels that apparently penetrate radially into the hilum. Channels in A-granules are clustered around the equatorial groove region (Fannon et al 1992a,b, 1993; Gallant et al 1997), but finer channels that occur as less-defined voids can be visualized in B-granules (Kim and Huber 2008). These channels are partially filled with protein. By comparison, images of depressions 1- μ m wide suggest the possible existence of surface pores in potato starch granules when examined by atomic force microscopy (Juszczak et al 2003a). Pores with oval to slit-like shapes are observed in tapioca starch.

Large and small wheat starch granules differ in composition, properties, and reactivities. A-granules contain more amylose but less lipid than B-granules (Maningat et al 2009). For example, Ao and Jane (2007) reported A-granules contain 30.9% absolute (corrected for iodine affinity of amylopectin) amylose, whereas B-granules contain 25.5% absolute amylose. Maningat et al (2009) summarized the compositional differences of the two granule types that reflect the differential properties observed by various researchers (Kim and Huber 2010a,b; Park et al 2004, 2005).

The amylopectin in B-granules contains a larger proportion of short chains than in the A-granules, which may explain the increased level and density of crystals in the B-granules (Ao and Jane 2007). However, Kim and Huber (2010b) observed that A-granules from waxy and normal soft wheat starches possess

greater relative crystallinity than the corresponding B-granules, which is in agreement with the results of several workers (Ando et al 2002; Chiotelli and Le Meste 2002, Vermeulen et al 2005). By comparison, no difference in relative crystallinity was observed for the two granule types by Salman et al (2009).

A-granules had higher reactivity with acetic anhydride and with propylene oxide compared with B-granules (Van Hung and Morita 2005a,b). Stapley and BeMiller (2003) found contrasting results where A-granules were less reactive to propylene oxide than B-granules. By comparison, similar reactivities to propylene oxide or a propylene oxide analog were displayed by A- and B-granules from waxy and normal wheat starches (Bertolini et al 2003; Kim and Huber 2010a). Using phosphorus oxychloride as the modifying reagent, B-granules from normal, partial waxy, and waxy wheat starches exhibited higher reactivity than the corresponding A-granules (Bertolini et al 2003).

Model of Food Containing Wheat Starch

Starch in wheat-based foods makes a major contribution to eating quality and texture (Takahashi et al 1993; Maningat and Seib 1997; Maningat et al 2009). Several researchers found wheat starch viscosity increased with increasing heating rate (Doublier 1987; Ellis et al 1989; Deffenbaugh and Walker 1989; Yun and Quail 1999). Maningat and Seib (1997) confirmed those results in the Rapid Visco-Analyser using three size fractions of wheat starch, 7.5–10.0% starch solids, and a heating rate of 1.5–12.0°C/min. Jacobs et al (1996) postulated that the viscosity was enhanced either because swollen wheat starch granules had a shorter shearing time at faster heating rates or there is a concomitant increase in both granular swelling and leaching of solubles with accelerated heating (Ellis et al 1989). In a mixture of hot water with a low percent of starch (soup, sauce, or gravy), the hot mixture forms a composite structure of swollen granules suspended in a dilute solution of amylose (Fig. 1). The swollen granules are tiny gel particles and frictional collisions generate viscosity that increase on cooling because the swollen granules stiffen. Because the starch concentration is low, the concentration of leached amy-

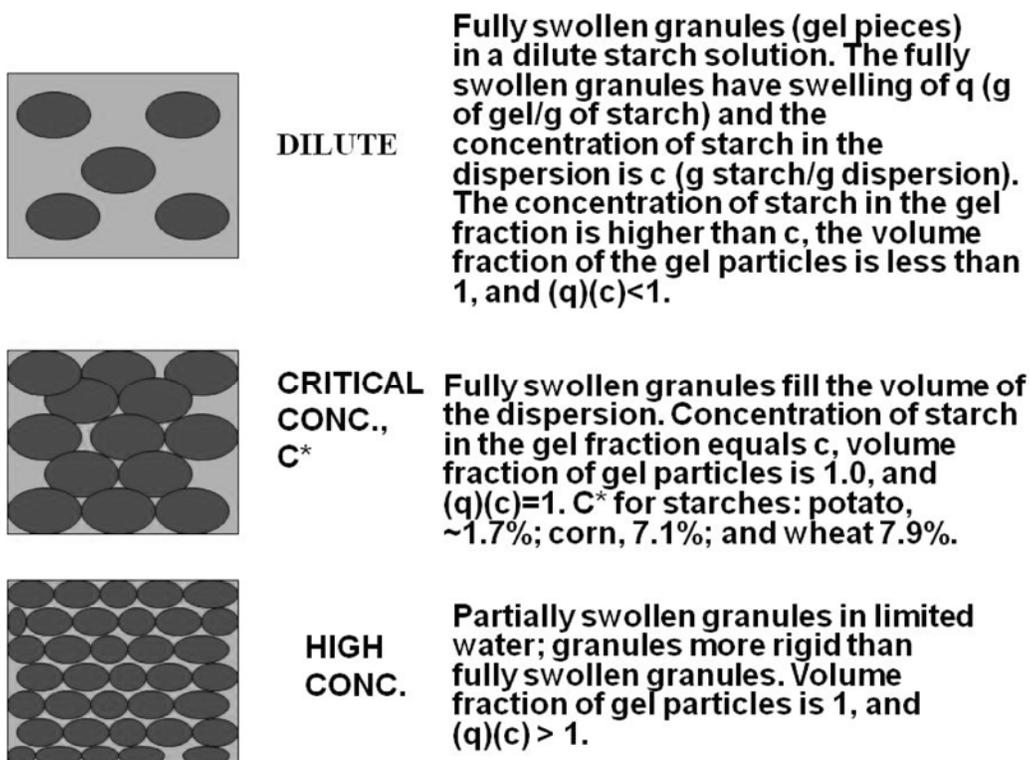


Fig. 1. Composite structure of wheat starch granules heated in water (Ring 1985; Steeneken 1989).

lose also is low. Leached amylose from the wheat starch, with an average DP < 1,000 and at a concentration <1% in water, generally precipitates or forms a discontinuous gel on cooling, so the leached amylose contributes minimally to the viscosity of a wheat starch paste.

When the concentration of wheat starch in hot water is increased from several percent up to ≈8%, the volume of the swollen granules occupies all the space of the mixture (Fig. 1). In other words, the volume fraction occupied by the swollen granules equals 1.0. The concentration of starch where fully swollen granules occupy all available space is the critical concentration (C^*) (Steeneken 1989). A model aqueous system for a pudding or starch-based filling might contain ≈6% wheat starch, which is a concentration somewhat below C^* . At 6%, wheat starch granules would be fully swollen in hot water and the granules would release much of their amylose. The amylose in the continuous phase gels upon cooling and now >1%, entraps swollen granules. The composite gel structure comprises swollen granules (gel pieces) dispersed in a continuous amylose gel. The strength of the macroscopic gel is dependent on amylose concentration and stiffness of the dispersed granules, plus any attractive forces between the granules and the continuous phase. Starch gels appear opaque due to phase separation of the double-helical amylose molecules.

When the concentration of wheat starch in the hot aqueous mixture exceeds critical concentration (C^*), the granules do not swell fully in the limited amounts of hot water and they exude only a small fraction of their amylose. Partially swollen granules are stiffer than fully swollen granules and their stiffness becomes more important than the volume fraction of the granules in generating consistency and gel strength. This phenomenon is called the crossover effect (Ring 1985; Steeneken 1989). The wheat starch granules do not gelatinize and swell at ≤100°C unless the moisture content is >30% on a wet basis. Some ingredients in foods, sugars and sodium chloride, etc., compete with starch for water in a formula and inhibit granule swelling. Not all wheat starch consumed in foods is swollen granules. Dry wheat starch is used in powdered sugar coatings and as a dusting powder in confectioneries and bakery foods. Also, many dry baked foods contain ungelatinized wheat starch granules, which are considered slowly digestible starch.

High-Moisture Foods Containing Wheat Starch

Among the common food starches (Table I), wheat starch gelatinizes at 5–10°C below the other four starches. The low gelatinization temperature of wheat starch can be attributed to the large proportion of A and B₁ chains in amylopectin. Such a low gelatinization temperature results in rapid cooking in microwaveable soups, sauces, and gravies. However, wheat starch generally exhibits a lower paste viscosity compared with other commercial starches (Ral et al 2008), which may be related to lower swelling power, lower molecular weight of amylopectin, or higher phospholipid content (Melvin 1979; Takeda et al 1987; Shi et al 1991; Shi and Seib 1989). Amylopectin is the macromolecular component in wheat starch responsible for generating viscosity as evidenced by the highly negative correlation ($r = -0.85$, $P = 0.004$)

between Rapid Visco-Analyser peak viscosity and total amylose content (Zeng et al 1997).

Instant waxy wheat flour (Limagrain Cereales Ingredients, France) and heat-treated normal wheat flour (Siemer Milling, Teutopolis, IL) are marketed as thickeners in foods with “natural” labeling. The heat-moisture treatment likely denatures (polymerizes) gluten and reorganizes molecules inside the starch granules. Both changes inhibit swelling of starch, which avoids the formation of “stringy” pastes caused by the entanglement of highly swollen granules. Doubly modified wheat starch, which is cross-linked and acetylated or hydroxypropylated, is used as a thickener in foods. Pastes of the modified wheat starch produce a nonsticky (melt-in-your-mouth) texture with rapid release of flavor. Waxy wheat starch and its modified forms, which possess excellent thickening and cold-temperature stability (Reddy and Seib 2000), are not available commercially at present, principally because of difficulties in the isolation of waxy wheat starch (Guan et al 2009).

Intermediate-Moisture Foods

Pasta is made by extrusion compacting of particles of moistened durum semolina at ≈40°C to form a dense deaerated structure. During cooking of pasta, the tightly bound protein and starch inhibit water movement into the interior of a pasta strand. This leads to rapid gelatinization and swelling of starch granules at the surface of a strand and a gradient of less and less gelatinization and swelling toward the core (Brennan 2008). The reported low glycemic effect of pasta (Jenkins et al 1983) appears to be related to the compacted, protein-encased state of wheat starch in pasta. A low glycemic index of 32–47 was reported for macaroni or spaghetti compared with a glycemic index of 69 for whole meal bread, even though both foods are rich in available carbohydrates (Foster-Powell et al 2002; Brennan 2008). It is important to note that durum wheat starch tends to have a lower swelling power and solubility than hard and soft wheat starches, probably because of increased levels of amylose and lysophospholipids (Seib 1994).

Oriental noodles fall into two broad classes based on ingredients or color. White salted noodles are made from a low-protein wheat flour, water, and table salt; yellow alkaline noodles are made from a medium- to high-protein wheat flour, water, and sodium and potassium carbonates (Miskelly 1996; Nagao 1996). Approximately 95% of the dry weight of nonfried oriental noodles is wheat starch, so the swelling properties of wheat flour, especially one of low protein content, modulate the eating texture of cooked noodles. A high-swelling, partial-waxy wheat flour is preferred for white salted noodles and a low-swelling nonwaxy wheat flour is desired for yellow alkaline noodles.

A working model of starch in cooked wheat noodles has been proposed to explain the cooking characteristics and appearance and texture of cooked noodles (Ross et al 1997; Zhao and Seib 2005). For example, during cooking of salted noodles, which are made from high-swelling, low-protein wheat flours, the surface region of a strand is exposed to excess boiling water. Below the surface, hot water is limited, liquid shear forces are absent, and salt concentration increases. Cooked salt noodles from high-swelling flours have a smooth, clean, and shiny surface and they display a soft and cohesive eating texture, reduced cooking loss, and an increased cooked noodle yield. Favorable noodle smoothness and appearance appears to result from swollen wheat starch granules filling in cracks and crevices at the surface of a strand. Meanwhile in the interior of the strand, amylose exuded from the swollen starch gels upon cooling, and the amylose gel surrounds the swollen granules and gluten matrix. Extra swollen granules with increased water content, plus a low level of matrix protein, produce a soft bite in the cooked salted noodle, while the starch gel creates the cohesive texture. Paradoxically, low-swelling wheat starch contains more total amylose than high-swelling wheat starch, but low-swelling wheat starch releases less amylose on cooking than high-swelling wheat starch (Seib 2000).

TABLE I
Differential Scanning Calorimetry Results^a
for Common Starches of Commerce (Seib 1994)

Starch	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Wheat	52	59	65	10.1
Corn	65	71	77	13.9
Rice	70	76	82	13.0
Potato	62	66	72	17.6
Tapioca	62	70	73	12.9

^a T_o , T_p , and T_c , represent onset, peak, and conclusion temperatures of gelatinization, respectively; ΔH , enthalpy.

Prepared from wheat flours with moderate- to high-protein contents, the interior of cooked alkaline noodles contains low-swelling wheat starch that is restricted further in swelling by the carbonate salts in the formula (Moss et al 1986). The increased level of protein and low swelling of the granules results in the cooked noodle strand possessing a hard, elastic, and chewy texture that can approach the al dente texture of spaghetti.

In breadmaking, wheat gluten has the unique ability to form wheat flour into a dough that exhibits the rheological properties required for production of yeast-leavened bread (Gianibelli et al 2001). While the function of gluten in breadmaking is well known, the function of wheat starch is also important, and contrary to common belief, its role is more than just a filler. Wheat starch supplies additional sugar for fermentation through amylase action on the damaged starch in bread flour. Mechanically damaged wheat starch contains water-soluble amylopectin, which contrasts with mechanically damaged corn starch containing both amylose and amylopectin (Glennie et al 1987). Malted cereals are added to bread dough to provide α -amylase, which along with endogenous β -amylase in flour, converts the damaged starch to fermentable sugars.

During mixing of bread dough, wheat starch provides a surface suitable for a strong union with the gluten adhesive and dilutes the gluten to a consistency desirable for dough processing (Hoseney et al 1971; Hoseney 1994). High-molecular weight glutenin and, to a lesser extent, low-molecular weight glutenin were reported to be preferentially adsorbed on the surface of wheat starch granules (Eliasson and Tjerneld 1990). Bread dough is considered a foam structure consisting of gas cells dispersed in a protein-starch matrix containing $\approx 45\%$ moisture content.

When white bread dough is baked at an oven temperature of $\approx 210^\circ\text{C}$, the gas cells in the dough expand to increase loaf volume, enzymes and yeast are inactivated, starch and proteins undergo changes, and a crust and crumb are formed. The starch granules in the bread dough gelatinize over a temperature range of $50\text{--}100^\circ\text{C}$ as determined by differential scanning calorimetry (Lagrain et al 2008). The gelatinization of starch in bread dough is $\approx 25^\circ$ higher than the gelatinization temperature of wheat starch in excess water. That rise is attributed to the limited water in the dough and the presence of salt, sugar, and hydrated gluten. When the granules in dough gelatinize, they become flexible and elongate as the gas cell walls expand, but the granules do not disintegrate. As the granules swell, they also exude amylose that pools in the center of swollen granules, between granules, and at the starch-gluten interface (Hug-Iten et al 1999). Starting at $\approx 50^\circ\text{C}$, the gluten phase undergoes denaturation and polymerization and much of the water that hydrated the gluten is released and absorbed by the swelling starch granules. Toward the end of starch gelatinization at $\approx 83^\circ\text{C}$, the polymerization of glutenin together with the pasting of the starch appear to cause strain hardening of the gas cell walls and they rupture to form a gas-continuous crumb structure. Baking is continued until the center of the loaf reaches 100°C . Upon cooling, the crumb structure in the fresh bread is set further by the gelling and crystallization of the pooled amylose and the stiffening of the swollen granules.

Storage of bread over a period of time causes undesirable textural changes and loss of flavor. In bread staling, the "glassy" textured crust becomes "leathery" as moisture migrates from crumb to crust. Meanwhile, the "rubbery" crumb of fresh bread also changes with time (not due to moisture loss) and becomes firmer and less resilient (elastic recovery of compressed crumb). Glycerides and certain surfactants can "shorten" bread texture and increase softness. In recent years, maltogenic α -amylase, usually of intermediate thermal stability at $\approx 45\text{--}75^\circ\text{C}$, may be added to bread dough to inhibit firming of stored bread. Research on the mechanism of α -amylase action in bread has improved our understanding of the role of wheat starch in bread. During baking, maltogenic α -amylase depolymerizes the outer chains of amylopectin

in the swollen starch granules and also depolymerizes the amylose-rich phase. Enzymolysis, however, ceases during the storage of bread near room temperature. Endo-acting, thermally stable α -amylase also inhibits firming of bread crumb. But in contrast to the exo-acting α -amylase, the endo-acting enzyme fails to retain the resilience of the crumb (Hug-Iten et al 2003; Goesaert et al 2009). In addition, the endo-acting α -amylase gave bread with a more open crumb grain compared with the control (Lagrain et al 2008).

The antifirming effect of thermally stable α -amylase has been explained by 1) cleavage of starch networks, 2) formation of maltodextrins that act as a plasticizer, or that interfere with formation of starch-starch interactions or starch-gluten interactions, and 3) prevention of retrogradation (recrystallization) of amylopectin, which concomitantly prevents removal of some of the water that plasticizes the amorphous biopolymers in the crumb. Recrystallization of amylopectin in control bread gives the B-polymorphic crystal form of starch. Those crystals contain $\approx 25\%$ water that is immobile.

With less mobile water, the bread crumb in control bread becomes firmer and less resilient (Goesaert et al 2009). An exo-acting α -amylase prevents recrystallization of amylopectin and thereby prevents the immobilization of a portion of crumb moisture. The net result is retardation of crumb firming and preservation of resilience. On the other hand, an endo-acting α -amylase randomly cleaves starch networks in bread crumb, which does not prevent the partially hydrolyzed amylopectin from recrystallizing. The net result is a softer crumb due to random cleavage of starch chains, but loss of resilience due to crystallization of amylopectin and the immobilization of some of the crumb moisture.

Another explanation has been proposed for the mechanism of action of maltogenic α -amylase in bread crumb (Hug-Iten et al 2003). The antifirming effect again originates with the predominant hydrolysis of the outer chains of amylopectin and the lack of retrogradation of the amylopectin in the swollen granules. However, the antifirming is attributed to the lack of stiffening of the swollen granules as amylopectin retrogrades with time. The partial hydrolysis of the amylose phase by the heat-stable maltogenic α -amylase increases crystallization of amylose during cooling of a baked loaf. As a result, the crumb firmness of the fresh bread is elevated somewhat over control bread, but more importantly the increased crystallization of amylose is proposed to preserve resilience in the crumb. Hug-Iten et al (2003) emphasized that the effectiveness of enzymes to prevent firming of bread crumb cannot be predicted always by DSC or X-ray measurements because firming is caused by structure on a scale of millimeters as opposed to nanometers, which affect DSC and X-ray data.

The classic report of Hoseney et al (1971) established a unique functionality of wheat starch in bread systems that can be matched only by the genetically related *Triticeae* starches. Granule size, amylose content, starch modification, and resistant starch provide additional considerations in determining the performance of wheat starch in flour-based products such as bread and noodles as well as in other foods.

Bread yield can be increased by incorporating 1.5–2.0% of a pregelatinized hydroxypropylated wheat starch or a cross-linked and hydroxypropylated wheat starch (Miller et al 2008). Bread made from reconstituted flour with 30% small granules and 70% large granules had the highest crumb grain score, with a high fineness value and elongation ratio (Park et al 2005). Crumb grain score has a positive linear correlation with the size of A-granules ($r = 0.65$, $P < 0.05$) and a polynomial relationship ($R^2 = 0.45$, $P < 0.05$) between crumb grain score and weight percentage of B-granules (Park et al 2004). The best crumb grain score was for flour with a weight percentage of B-granules of 19.8–22.5%.

Wheat dough absorption is increased in waxy versus normal flours (Guan et al 2009). With decreasing amylose content in a blend of waxy wheat starch and normal wheat starch in white pan

bread, bread loaves exhibited increased volume and “openness” in crumb structure (Lee et al 2001). Bread with 10% waxy wheat starch had softer crumb. The presence of waxy wheat starch tended to cause the retention of more moisture in the crumb after storage for seven days at 4°C. Partial waxy wheat flour produced bread of larger loaf volume and softer bread crumb than did the hard red spring wheat flour at comparable protein content (Baik et al 2003). Bread baked from double-null partial waxy wheat flours displayed a slower firming rate during storage than bread from hard red spring wheat flour.

Partial waxy wheat and wild-type flours have comparable hearth breadbaking performance. While waxy wheat flour shows loaf volume potential comparable to wild-type and partial waxy wheat flour, it gives a more open crumb structure and poor overall appearance (Sahlstrom et al 2006). Tortilla height and opacity were adversely affected by partial waxy wheat flour due to decreased amounts of amylose (Waniska et al 2002).

Improvement of cake volume, softness, and shelf life by addition of modified wheat starch was observed by Karaoglu et al (2001). Nishio et al (2009) found amylose content of wheat was strongly correlated with sugar snap cookie diameter ($r = 0.69$, $P < 0.001$). Waxy soft wheat lines displayed higher alkaline water-retention capacity compared with single-null and double-null lines (Kim et al 2003).

Low-Moisture Foods

Varying degrees of granular swelling of wheat starch in different baked products are depicted in the work of Hosenev et al (1977). A-granules and B-granules undergo little transformation during baking of low-moisture products such as pie crusts or sugar cookies, but they are swollen and deformed in bread and cake.

Cookie formulas, in general, are high in fat (shortening) and sugar, which undergo melting and dissolution, respectively, upon baking of cookie dough (Hosenev 1994). The combination of elevated amounts of fat and sugar and low levels of water restrict the gelatinization and partial swelling (puckering) of the granules (Bowler et al 1980). Baked sugar cookies contain starch granules that are essentially in their native, ungelatinized state.

Extrusion-cooked products from starchy materials are normally subjected to high temperature and 15–50% moisture levels together with mechanical energy input that depends on extruder configuration. After melting of starch crystallites, compaction of the mass, and die expansion, the granular features of starch are lost in the low-moisture extrudate product. Analysis of wheat starch extru-

date shows not only disruption and fragmentation of the granules but also molecular degradation and amylose-lipid complexation (Colonna et al 1984; Diosady et al 1985).

Gluten-Free Foods

Ingestion of wheat-based food products can cause a certain form of malady that elicits hypersensitivity reactions. This inflammatory disorder, called celiac disease, is characterized by inflammation of the small intestines that can lead to malabsorption of nutrients (Wieser and Koehler 2008). If left untreated, damage to the small intestinal villi results, which can increase the risk for developing anemia, edema, osteoporosis, infertility, T-cell lymphoma, cancer, short stature, neurological problems, and other autoimmune disorders (Engleson and Atwell 2008; Wieser and Koehler 2008). Approximately 1 in 133 of the U.S. population and 1 in 266 of the population worldwide are afflicted by celiac disease (Omary et al 2009).

Medical nutrition therapy is the only accepted treatment for people suffering from gluten intolerance or celiac disease (Kupper 2005). It includes a life-long avoidance in the diet of the offending storage (gluten) proteins from wheat, rye, barley, triticale, durum, spelt, kamut, emmer, and einkorn (Taylor 2009). Thus, a gluten-free diet is considered a safe and an effective treatment for this disease. Choices for formulating gluten-free food products include the use of flours and starches from corn, rice, potato, tapioca, sorghum, buckwheat, or beans, gums/hydrocolloids such as guar gum, xanthan gum, inulin, or cellulose derivatives, and proteins from corn, soy, eggs, or milk (Arendt and Renzetti 2009; Mezaize et al 2009). While the preceding ingredients do not constitute a comprehensive list, many other ingredients qualify to make gluten-free food products (Engleson et al 2008). The use of gluten-free ingredients does not normally guarantee desirable appearance and eating qualities that are normally exhibited by wheat-flour based foods. Given the absence of wheat gluten in the formula, it is worthwhile examining the possible role of *Triteceae* starches in gluten-free foods. Wheat starch, in particular, has the potential for improving the appearance, taste, texture, mouthfeel and shelf life as surmised from its unique functional property in the fractionation and reconstitution study conducted by Hosenev et al (1971).

Commercial wheat starch and its modified versions in the United States typically contain <10 ppm of gluten, which is the minimum detection level for gluten content when assayed by Ridascreen (R-Biopharm) ELISA method (Table II). Because the Codex standard is “not exceeding 20 ppm gluten in foods” (Codex Alimentarius Commission 2008), wheat starch can be a suitable ingredient in gluten-free foods, although additionally it has to comply with allergen labeling regulations if used in the U.S. market as established in the Food Allergen Labeling and Consumer Protection Act that took effect in 2006. The data in Table II also suggest that current manufacturing practices for wheat starch separation and modification can be controlled for efficient removal of contaminating gluten in wheat starch. As wet-processing methods differ among wheat starch or wheat gluten manufacturers around the world (Maningat et al 2009), the key to consistently attain <20 ppm of residual gluten in wheat starch will involve a combination of improved and efficient process control and accurate gluten assay.

Studies in Europe support the application of wheat starch in gluten-free foods as exemplified in the work of Peraaho et al (2003), who reported that dietary response to a wheat starch-based gluten-free diet was as good as that for a natural gluten-free diet in patients with newly detected celiac disease. Foods containing wheat starch have been successfully incorporated into the diets of celiac patients as described by Kaukinen et al (1999) and Lohiniemi et al (2000). Furthermore, a review by Kupper (2005) reported research indicating no differences in patients choosing a strict wheat-starch-containing, gluten-free diet versus a naturally gluten-free diet.

TABLE II
Level of Gluten Protein in Modified Wheat Starches^a

Wheat Starch Sample	Gluten, ppm
Acetylated distarch adipate	BLD
Acetylated distarch adipate (pregelatinized)	BLD
Acetylated distarch phosphate	BLD
Acid-modified	BLD
Aluminum starch 1-octenyl succinate	BLD
Distarch phosphate	BLD
Hydroxypropylated	13
Hydroxypropyl distarch phosphate (MS)	BLD
Hydroxypropyl distarch phosphate (M/HS)	BLD
Native (unmodified)	BLD
Oxidized (low level)	BLD
Oxidized (medium level)	BLD
Oxidized (medium level, pregelatinized)	BLD
Oxidized and hydroxypropylated	BLD
Phosphated distarch phosphate	BLD
Phosphated distarch phosphate (gelatinized)	BLD

^a BLD, below lower limit of detection of 10 ppm of gluten using Ridascreen (R-Biopharm) ELISA Method. MS, medium substitution. M/HS, Medium/high substitution.

Amylase-Resistant Wheat Starch

Undoubtedly, one of the most important events that highlights the uniqueness and versatility of modified wheat starch is in fiber fortification of foods (Woo et al 2009). The commercial development of two RS4-type resistant wheat starches (75–85% total dietary fiber, minimum, db, by AOAC Method 991.43), which are sources of insoluble fiber, and two wheat dextrins (70% and 82–88% total dietary fiber, db, by AOAC Method 2001.03), which are sources of soluble fibers, effectively improved the nutritional status and competitive performance of wheat starch in the food industry (MGP Ingredients, Roquette, France; and National Starch Food Innovation). These four products compete with approximately 21 other resistant starches or resistant carbohydrates in the market. In general, resistant starches and carbohydrates are allowed in foods at levels that impart the desired technical effect, meet good manufacturing practices (GMP), and also comply with FDA nutrient labeling claims of “good source” or “excellent source” of fiber. An additional function is calorie reduction, which results from fiber fortification and partial or complete substitution of fats or sugars in the food and beverage formulas. Recently, “double fiber” breads fortified with resistant starches and carbohydrates and conventional fibers are being manufactured by large wholesale bakeries and can be found in most grocery stores and major supermarkets.

The two wheat dextrins mentioned above are partially hydrolyzed starch obtained by heating in the presence of food-grade acid (Anonymous 2009). The number-average molecular weight (M_n) and weight-average molecular weights (M_w) are 2,600 and 5,000 da, respectively, when analyzed by HP-SEC. They dissolve easily in water with a clear appearance, very low viscosity, and essentially undetected odor, flavor, or sweetness. In addition to contributing fiber, wheat dextrins add body and mouthfeel to foods and beverages when they replace fat and sugar. Labeling declarations in food packages include “Wheat Dextrin”, “Dextrin” or “Resistant Dextrin” with optional descriptors in parenthesis, (soluble fiber) or (soluble dietary fiber).

The technology for producing RS4-type resistant wheat starch was patented in 1999 and commercialization was started in 2003 during the height of popularity of low-carbohydrate food products (Seib and Woo 1999; Maningat et al 2005, 2008). This product was prepared by cross-linking and substitution reactions with sodium trimetaphosphate and sodium tripolyphosphate to yield a swelling-resistant phosphated distarch phosphate derivative (Seib and Woo 1999; Woo and Seib 2002). Structural studies by ^{31}P nuclear magnetic resonance spectroscopy indicated the presence of distarch monophosphates (cross-linked) and monostarch monophosphates (substitution) in a 1:1 molar ratio (Sang et al 2007). DSC demonstrated an elevation of ≈ 4 , 8, and 11°C of T_o , T_p , and T_c , respectively, for resistant wheat starch over that of native (unmodified) wheat starch (Woo and Seib 2002). When heated in excess water at 95°C , resistant wheat starch displays restricted swelling, maintains granular structure and exudes little or minimal amounts of glucans out of the granules (Shin et al 2003). Soaking in aqueous sodium hydroxide solution at pH 12 and 40°C for 4 hr changed the content of total dietary fiber and resistant starch only very slightly (Sang et al 2009).

When formulated in consumer packaged goods, RS4-type resistant wheat starch is labeled as “Modified Wheat Starch”. The cook-up version of resistant wheat starch with 85% minimum total dietary fiber (db) can be converted into a pregelatinized version by hydrothermal treatment to yield a sister product with 75% minimum total dietary fiber (db). This latter product has a dual function of fiber booster as well as fat replacer (Woo et al 2009).

RS4-type resistant wheat starch has several advantages over other resistant starches as well as conventional dietary fibers (Woo et al 2009). It has one of the highest levels of total dietary fiber (85% minimum, db) versus other resistant starches, which implies cost savings for end-users. It is white in color, which makes it a

source of invisible fiber that does not detract from the appearance of some bakery products, for example, white bread or cakes. It has a fine particle size that provides smooth (nongritty) texture in food products versus the coarse granulation and gritty particles of cereal brans.

Resistant wheat starch possesses low water-holding-capacity (0.7 g water/g of starch) near room temperature and absorbs about the same amount of water as wheat flour (0.8 g water/g of flour), requiring little or no formulation changes with respect to water absorption, mixing time, and baking time of dough products (Woo et al 2009). It is highly compatible with flour-based foods such as bakery products, pasta, and noodles because the wheat starch in the flour has the same size, shape, and surface characteristics as the resistant wheat starch (Maningat et al 2005, 2008; Yeo and Seib 2009).

From health and wellness perspectives, resistant wheat starch reduces glycemic and insulin response, which has potential to help healthy individuals and those with type 2 diabetes manage blood glucose levels (Haub 2009; Al-Tamimi et al 2010; Haub et al 2010). It promotes gastrointestinal health through its prebiotic effect by selectively increasing the microbial communities of *Bifidobacterium adolescentis* in the large intestine (Walter 2009).

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