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Invited Review

Wheat starch production, structure, functionality and applications—a review

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Summary Starch is the main component of wheat having a number of food and industrial applications. Thousands of cultivars/varieties of different wheat types and species differing in starch functionality (thermal, retrogradation, pasting and nutritional properties) are grown throughout the world. These properties are related to starch composition, morphology and structure, which vary with genetics, agronomic and environmental conditions. Starches from soft wheat contain high amounts of surface lipids and proteins and exhibit lower paste viscosity, whereas that from hard cultivars contain high proportion of small granules and amylose content but lower gelatinization temperature and enthalpy. Waxy starches exhibit higher-percentage crystallinity, gelatinization temperatures, swelling power, paste viscosities and digestibility, but lower-setback viscosity, rate of retrogradation and levels of starch lipids and proteins than normal and high-amylose starches. Starches with high levels of lipids are less susceptible towards gelatinization, swelling and retrogradation and are good source of resistant starch, while that with high proportion of long amylopectin chains are more crystalline, gelatinize at high temperatures, increase paste viscosity, retrograde to a greater extent and decrease starch digestibility (high resistant and slowly digestible starch and low rapidly digestible starch).

Keywords Digestibility, functionality, gelatinization, morphology, retrogradation, starch, wheat.

Introduction

Wheat is one of the most grown, consumed and traded food grains of the world with a worldwide diversity of thousands of cultivars/varieties. It constitutes a major portion of diet of the world because of its agronomic adaptability, ease of storage, nutritional goodness and the ability of its flour to prepare a variety of palatable and satisfying foods. More than 713 million tonnes (MT) of wheat worth 85.94 billion dollars (BD) is grown throughout the world on approximately 218 million hectares of land (http://faostat3.fao.org/browse/rankings/countries_by_commodity/E). It is the fourth most important food commodity in terms of both production quantity (after sugar cane, maize and paddy) and value (after meat, milk and paddy). China, India, USA, Russia, France, Canada, Germany, Pakistan, Australia and Ukraine are the top ten wheat-producing countries (Fig. 1). Wheat is mainly utilized as food (67%); however, a significant portion is also used for feed, seed and industrial purposes (20%, 7% and 6%, respectively). The industrial uses of wheat include its wet milling for the production of starch and gluten (Maningat *et al*., 2009). European Union countries are the largest consumer of wheat (126.8 MT) followed by China (120.5 MT), India (81.6 MT), Russia (38.5 MT) and USA (32.3 MT).

Triticum aestivum (referred as bread wheat) is the most commonly grown species of wheat, accounting for 90–95% of total production. *T. durum* (durum wheat) is another commonly grown species contributing to ~40 MT in global wheat production. This wheat is preferred and used primarily for making pasta products (Sobota *et al*., 2015; Gélinas & McKinnon, 2016), hence, also referred as pasta wheat. Durum wheat has higher levels of proteins and yellow pigments (xanthophylls and carotenoids) than common wheat and also differs from the later in terms of gluten properties (Janković *et al*., 2015). Common wheat generally grows well under spring or winters, while durum wheat is well adapted to the hot and dry conditions

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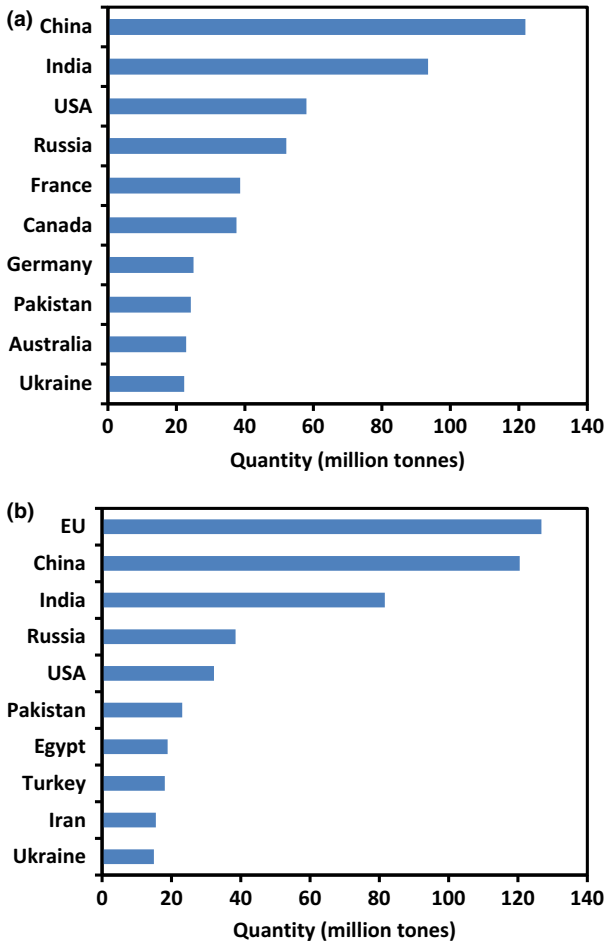

Figure 1 Top ten wheat producers (a) and consumers (b) of the world (source: a, www.faostat.fao.org/site/567/DesktopDefault.aspx?PageID = 567#anchor; b, www.earth-policy.org/datacenter/xls/book_fpep_ch1_13.xlsx). EU, European Union.

surrounding the Mediterranean Sea and similar climates in other regions (Shewry & Hey, 2015). Moreover, the popularity of durum wheat is increasing amongst farmers due to high yield and resistance to rusts and Karnal bunt (Kaur *et al*., 2016). *T. monococcum*, *T. dicoccum* and *T. spelta*, commonly referred as einkorn, emmer and spelt, respectively, are some ancient species differing from common and durum in being husked species, that is, lemma and palea form a husk that remains tightly attached to the grain. These species are grown as minor crops in Ethiopia, India, Italy, Turkey, France and Iran and used primarily for cultural reasons. However, interest in these species has recently increased because of the demand for speciality breads and beers as well as due to lower requirements of nitrogen fertilizers and crop protection chemicals (Gooding, 2009).

Starch is the main storage carbohydrate in wheat and comprises about 60–75% of grain and 70–80% of flour. It plays an important role in human nutrition as it contributes to >50% of caloric intake in Western world and up to 90% in developing countries (Wang *et al*., 2015a). However, the rate at which starch is digested and absorbed in human body varies depending upon composition and some starches that are digested slowly help in maintaining blood glucose levels and providing extended energy supply (Brennan *et al*., 2008; Woolnough *et al*., 2008). Starch is also an important industrial material. It is widely used in food, paper, textile, chemical and pharmaceutical industries as a thickener, stabilizer, adhesive, gelling agent, water-retaining agent and bulking agent. The estimated global starch production was approximately 84 MT in 2015. Maize was the major source of starch contributing to ~77% (64.6 MT) of total starch production (Fig. 2). Cassava was the second largest source of starch after maize and contributed to ~12% (10.2 MT) of the total production. Other important sources were wheat and potato, which accounted for ~7% (6.0 MT) and 4% (3.4 MT), respectively, of the total starch production (Waterschoot *et al*., 2015).

Wheat starch is produced as a coproduct in vital wheat gluten (VWG) industry. Estimated annual world wheat starch production was 2.36 MT in 1996, 4.24 MT in 2006, and 6.0 MT in 2015 (Maningat *et al*., 2009; Waterschoot *et al*., 2015). The increase in production was due to the expansion in capacity and improvements in the process of separation. European countries produced ~39% of the total starch from wheat. France, USA, Germany, Netherlands, Australia, UK, Belgium, Canada, Japan and China were top ten producers (Maningat *et al*., 2009). Commercial

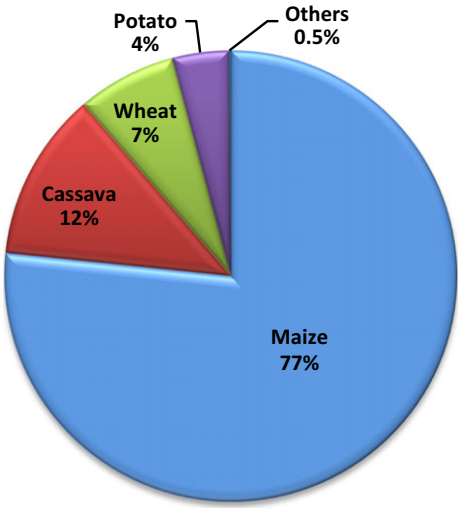

Figure 2 Commercial sources of starch.

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wheat starch contains ~98% carbohydrates (starch), 0.8–1.0% lipids, 0.2–0.5% proteins and 0.2–0.3% ash (moisture-free basis). Protein and lipid content in wheat starch have profound effects on functionality and utilization. In addition, starch composition also has effect on its utilization in gluten-free products for people suffering from coeliac disease which is considered as an important public health issue (Shevkani & Singh, 2014; Singh *et al*., 2015), and the starch with protein content of less than 0.23% has been observed to be gluten free (Skerritt & Hill, 1992).

The present review aims to provide an overview of the production, composition, structure, function, digestibility and application of diverse wheat starches and to highlight relationships amongst various starch properties.

Production

Wheat starch is produced by physical separation from nonstarch constituents. Various processes of wheat wet milling (*Halle fermentation*, *Alsatian*, *Longford-Slotter* and *Farmarco*) were developed for the production of starch. The basic steps in these processes were steeping, grinding and separation of grain components. The *Halle fermentation* process involved steeping of grains in water followed by crushing of softened grains, and fermentation of the mash. Fermentation degraded gluten and released starch that was separated by screening and refined by repeated dilution and decantation of the wash water and light solids that deposit above the settled starch (Knight & Olson, 1984). Other processes were nonfermentative processes. The *Alsatian* process involved steeping of wheat with repeated change of water followed by crushing and washing of mash through perforated trough fitted with rotating arms. Starch slurry and wash water were passed through the perforations and starch was subsequently refined. Up to 70% of total starch and 30–40% of total gluten proteins were recovered using the *Alsatian* process (Fellers, 1973). Chwalek & Olson (1979) patented wet-milling processes involving steeping of grains in 2000–4000 ppm sulphurous acid solution with agitation for 15 to 120 min, followed by screening and milling of the oversized particles. Similarly, in the *Longford-Slotter* process, wheat was steeped for about 24 h at 37 °C with 0.3–0.5% SO_2. The softened wheat was milled, and the mash obtained was sieved, tabled, centrifuged and refined to recover starch. This process yielded 55–60% of starch with a protein content of 0.2% (Knight & Olson, 1984; Kempf & Rohrmann, 1989). The *Farmarco* process involved tempering of grains to a moisture content of ~24% followed by milling and mixing with water to form a dilute homogeneous dispersion, which was centrifuged to separate gluten and starch (Rao & Shoup, 1978). The recovery and purity of the starch obtained using the wet-milling processes depended on steeping conditions (Yuan *et al*., 1998). The treatment with SO_2 gave the highest starch yield along with the lowest amount of proteins, whereas lactic acid steeping resulted in the lowest starch yield and the highest protein content in the starch (Yuan *et al*., 1998). Although wet-milling processes had advantages of low cost and absence of damaged starch, none of these processes achieved commercial success because of inferior quality of the products and high volume of effluents.

The main processes for commercial production of wheat starch are Martin or dough-washing, batter, *Alfa-Laval* or *Raisio*, hydrocyclone and high-pressure disintegration process. These processes consist primarily of mixing of refined flour with water followed by physical separation of starch granules and gluten aggregates in an aqueous system. The flour should contain high protein content (>11%) to facilitate rapid agglomeration of gluten proteins, but low damaged starch content, lipids, fibres and ash content, and no α-amylase activity. Therefore, main advantages of using flour instead of grain are efficient separation and high purity of starch obtained as most of fibres, lipids and minerals originally present in the grains are removed with bran and germ during the process of dry milling.

Martin or dough-washing process

The Martin or dough-washing process was originally developed in 1745 by Beccari and further proposed in Paris in 1835 by Martin. This was the most popular process for wheat starch and VWG production until 1970s (Mittleider *et al*., 1978). The basic steps involved in this process are mixing of flour and water to form a stiff dough, washing of the dough to separate gluten and starch, refining of starch and drying of the refined starch and gluten. A flow sheet of this process is shown in Figure S1. Wheat flour and water are mixed in a ratio of about 2:1 to form smooth, uniform and stiff dough. The flour from hard wheat requires more water to form dough than that from soft wheat. The dough is allowed to stand for approximately 30 min to ensure complete hydration and strengthening of gluten network. This is followed by washing of dough using ribbon blenders, rotating drums, twin-screw troughs or agitated vessels to obtain gluten strands and starch suspension (Knight & Olson, 1984). Starch suspension with approximately 10% solids is passed through a vibratory screen followed by a fine screen to recover gluten particles and fibres, respectively. Starch is then refined and dewatered using centrifuges and flash-dried to a moisture content of 8–11%. Approximately 75–85% of the starch present in flour is recovered as the prime starch (A-starch), while 5–10% is obtained as the second grade (B-starch) consisting of small granules, proteins, damaged granules and pentosans (Sayaslan, 2004).

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Batter process

The batter process was developed independently in 1944 by Shewfelt and Adams in Canada and Hilbert and coworkers in USA (Seib, 1994). This process involves mixing of flour with sufficient amount of warm water (50–55 °C) to form a smooth flowable batter at 40–45 °C. The amount of water required depends on the type of wheat and its protein, fibre and damaged starch content. The batter is allowed to rest for about 30 min and stirred vigorously with additional water to cause aggregation of gluten proteins. Gluten is washed and separated from starch by screening. Starch slurry is passed through a series of fine screens to remove fibres and centrifuges to obtain purified starch (Figure S2).

Alfa-Laval or *Raisio* process

The *Alfa-Laval* or *Raisio* process was founded in 1969 by Fellers and colleagues and commercialized in 1976 in Raisio, Finland. This process involves mixing of flour with sufficient quantity of water to form a flowable batter followed by shear mixing with additional water to form a homogeneous dispersion (30% solids) and centrifugation. The centrifugation is performed using a two-stage decanter centrifuge to separate the dispersion into starch and protein-rich fractions. The starch fraction is resuspended in water and refined (using a rotating conical fine screen) to get purified prime starch, while the protein-rich fraction is further processed to get second-grade starch and VWG (Figure S3). Prime-starch recovery is 75–80% with less than 0.3% protein content, while second-grade starch recovery ranges from 10% to 15% with 2–5% proteins (Sayaslan, 2004).

Hydrocyclone or dough-batter process

This process was developed in 1970 by the Koninklijke Schölten Honig Company, Holland (Zwitserloot, 1989). In this process, flour is mixed with water to form a dough which is then rested for 10–30 min and shear-dispersed with additional water to form a homogeneous dispersion of ~20–30% solid concentration. This dough-water dispersion is filtered to remove large particles and then pumped through a battery of hydrocyclones that separate prime starch from gluten. The starch slurry is fine-screened and again passed through hydrocyclones to wash starch and remove residual proteins (Figure S4). Low-cost compact equipments, wide range of operating conditions and low water usage (4–5 parts of water per part of flour) are main advantages of this process (Zwitserloot, 1989; Maningat & Bassi, 1999).

High-pressure disintegration process

High-pressure disintegration is the most advanced process for wheat starch production. This process was developed jointly by the Technical University of Berlin and Westfalia Separator, Germany. Originally, the process was developed and employed for potato and later for maize starch extraction (Zwitserloot, 1989; Sayaslan, 2004). However, at present, it is the most common process for the production of wheat starch (Maningat *et al*., 2009). This process involves rapid mixing of flour (1 part) with warm water (0.85–0.95 part) to form a smooth slurry (47% solids at 35 °C), which is then pumped through a high-pressure shear homogenizer. The high-pressure shearing frees starch granules from proteins and disperses these throughout the slurry. The dispersion is then diluted to approximately 30% solids and subjected to a decanter centrifuge, which separates it into three fractions, *viz*. the most dense fraction comprising of prime starch; medium density fraction containing gluten proteins and second-grade starch; and the least dense fraction consisting mainly of pentosans and other soluble solids (Figure S5). Low water usages and high yields of prime starch are main advantages of this process.

Structure and properties

Granule size distribution and morphology

Starch is synthesized as discrete granules of varying sizes in specialized bodies (amyloplasts). Different size and shapes of starch granules build up during the development of grain. Wheat starch exhibits a trimodal distribution of granules with the presence of large (A), intermediate (B) and small (C) granules (Fig. 3). A-granules ranged in size from 15 to 40 μm (average diameter 23–28 μm) and exhibited a disc-like lenticular shape, while B- and C-granules were roughly spherical or oval and irregular or cuboidal in shape and exhibited average size of 9–11 μm and 2–3 μm, respectively (Fig. 3). However, B- and C-granules were sometimes considered together as small B-granules (Bancel *et al*., 2010; Cao *et al*., 2015). The proportion of B-granules is of particular importance in commercial production of wheat starch because these granules owing to their smaller size are difficult to purify and recover than A-granules. The A- and B-granules differed according to the time of biosynthesis during grain filling. The biosynthesis of A-granules started 4 days after anthesis (DAA) with granule growth and development continuing over the next 20 days, while that of B-granules initiated 10–12 DAA with granule growth beginning 18–20 DAA (Wei *et al*., 2010; Yu *et al*., 2015a). Therefore, A-granules, possibly, got more time to grow, hence, were present in higher proportion (70–80% of starch by weight) but were much fewer in numbers (<10% of granules by number) than B-granules (<30% of starch by weight and ~90% of granules by number) (Lindeboom *et al*., 2004).

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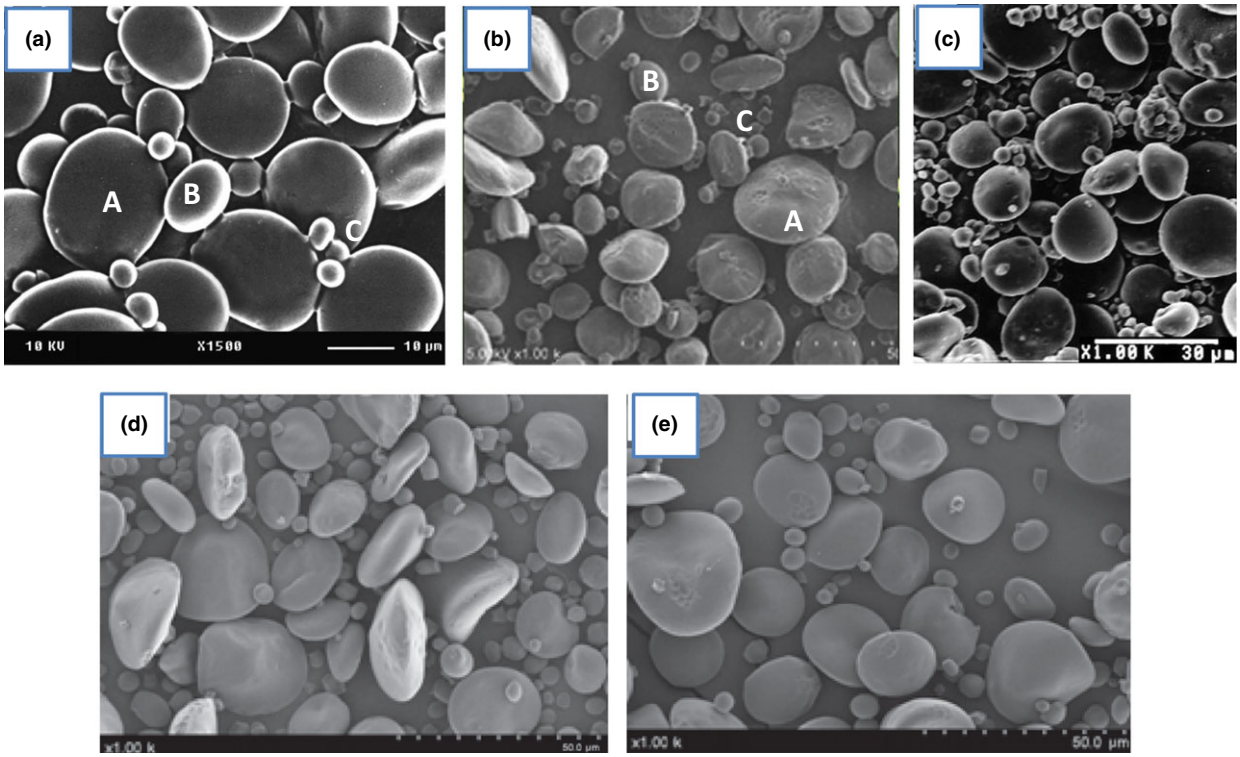

Figure 3 Scanning electron micrographs of starches from different wheat types: (a) normal, (b) waxy, (c) high-amylose, (d) hard and (e) soft wheat (source: a, Singh *et al*., 2010; b, Li *et al*., 2016a; c, Hung *et al*., 2008; d and e, Yu *et al*., 2015c).

Wide variation in granule size distribution exists amongst starches from different wheat type and cultivars/varieties (Table 1). The starches from hard wheat varieties were observed to contain higher proportion of B-granules and lower of A-granules than soft wheat (Li *et al*., 2008; Edwards *et al*., 2010; Singh *et al*., 2016). Normal and waxy starches contained both A- and B-granules; however, these differed in relative granule size distribution and morphology. The starch from normal wheat contained more B-granules (Zhang *et al*., 2013), while that from waxy cultivars/varieties showed more spherical disc-like granule morphology (Zhou *et al*., 2014). The A- and B-type granule fractions of waxy wheat starch exhibited slightly greater specific surface areas (0.9 and 2.8 $m^2\ g^{-1}$, respectively) as compared to the normal (0.8 and 2.3 $m^2\ g^{-1}$, respectively) counterparts (Kim & Huber, 2010). Environmental conditions and agronomic practices also

Table 1 Granule size distribution of starches from different wheat types and cultivars/varieties

Wheat	Type	Fraction	Distribution	A-granules (%)	B-granules (%)	C-granules (%)	Source
Common			Trimodal	71.36–79.10	12.13–19.70	7.61–9.40	Singh *et al.* (2008)
			Trimodal	45.6–73.2	14.0–37.0	10.5–17.5	Singh *et al.* (2010)
			Trimodal	63.7–68.9	20.2–22.3	10.8–14.9	Shevkani *et al.* (2011)
			Trimodal	71.36–79.10	12.13–19.70	7.61–9.40	Singh *et al.* (2009)
			Bimodal	57.6	42.4		Blazek & Copeland (2008)
	Hard		Bimodal	75.43	24.57		Li *et al.* (2013b)
	Soft		Bimodal	74.95	25.05		Li *et al.* (2013b)
	Hard	A-granules	Bimodal	92.32	7.68		Li *et al.* (2013b)
	Soft	A-granules	Bimodal	91.01	8.99		Li *et al.* (2013b)
	Hard	B-granules	Bimodal	13.29	86.71		Li *et al.* (2013b)
	Soft	B-granules	Bimodal	12.54	87.46		Li *et al.* (2013b)
Durum			Trimodal	69.9–85.4	9.4–20.1	4.7–10.0	Kaur *et al.* (2016)
Spelt			Trimodal	37.7–71.6	25.8–55.0	2.4–6.8	Wilson *et al.* (2008)

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affected granule size distribution of wheat starches. Low temperature during grain development extended grain-filling period, providing more time for the synthesis and development of B- and C-granules, leading to higher proportion of small granules, whereas higher temperatures accelerated grain development and caused early maturation, limiting the opportunity for the growth of small granules resulting in lower proportion of the same (Stone & Morell, 2009). Nitrogen and sulphur fertilization during grain filling increased the accumulation of both types of granules; however, the synthesis of B-granules was more sensitive to sulphur fertilization than A-granules (Li *et al*., 2013a). Further, water stress during grain filling decreased the proportion of B-granules (Singh *et al*., 2008; Yu *et al*., 2015a). Therefore, the variability in granule size distribution amongst different wheat types and cultivars/varieties could be attributed to the differences in genetic make-up as well as the activity of the enzymes relating to starch biosynthesis due to different climatic conditions and soil types during growth. Besides, the granule size distribution of wheat starch also varied with their locations within the grain. The starch present near the outer layers of the grain contained more small granules as compared to that present within the endosperm (Xie *et al*., 2008; Liu & Ng, 2015; Yu *et al*., 2015b). As the B-granules synthesized and grew at later stages than A-granules, the higher proportion of small granules in bran starch suggested delayed synthesis of granules near the grain periphery than within the inner core of the endosperm (Liu & Ng, 2015).

The surface of wheat starch granules is generally smooth; however, grooves or indentations are observed on some A-granules (Fig. 3). These grooves or indentations have been attributed to be the impressions from B-granules due to tight packing of starch granules within the endosperm. Pores and channels were also observed at surface of the starch granules from both normal wheat and waxy wheat (Fannon *et al*., 1992; Kim & Huber, 2008; Wang *et al*., 2013, 2015b), which were proposed to be the openings to granule interior (Fannon *et al*., 1992; Kim & Huber, 2008). A- and B-granules differed in terms of the presence of surface pores and channels. A-granules had large and fine channels at surface, while B-granules showed the presence of large, less-defined inner voids that penetrated to the surface (Kim & Huber, 2008).

Major and minor constituents

Amylose and amylopectin. Amylose and amylopectin are major constituents of wheat starch. Amylose is essentially a linear polymer of glucose with degree of polymerization (DP) and branching of 2000–5000 and 0.2–0.5%, respectively. Amylopectin, on the other hand, is highly branched polymer with DP and branching of approximately 10 000 and 5–6%, respectively. The synthesis of amylose and amylopectin in amyloplasts is initiated by adenosine-5′-diphosphate-glucose-pyrophosphorylase. Amylopectin synthesis is a complex process and involves the activity of a number of enzymes (starch synthases, branching and debranching enzymes), whereas that of amylose is largely brought about by granule-bound starch synthase (GBSS) enzyme also known as *waxy* or *wx* enzyme. The absence or nonfunctioning of this enzyme results in the synthesis of waxy starch composed essentially of amylopectin. Nakamura *et al*. (1995) first reported the production of waxy wheat (lacking GBSS and amylose) through traditional hybridization. In addition, the amylose content (AC) of cereal starches also depends on the levels of branching enzymes. Three isoforms of starch-branching enzymes (I, IIa and IIb) were observed in cereal starches (Rahman *et al*., 2007), and the reduced levels or activities of IIa and IIb enzymes resulted in the synthesis of high-amylose starches (Lafiandra *et al*., 2014). Normal wheat starch, generally, contains 25% amylose and 75% amylopectin. However, AC varying between 0% and 38% had been reported for starch from different wheat types and cultivars/varieties (Table 2). Meanwhile, wheat starch with AC as high as 74% has been developed through the reduction of starch-debranching enzymes (IIa and IIb) using RNA interference (Regina *et al*., 2006).

Starches from different wheat types and cultivars/varieties differ widely for AC (Table 2). Common wheat contained 18.2–28.8% amylose (Singh *et al*., 2010) against 17.5–28.4% for durum and 29.8–33.2% for spelt (Vansteelandt & Delcour, 1999; Wilson *et al*., 2008; Kaur *et al*., 2016). Singh *et al*. (2016) reported relatively higher AC for starch from hard wheat than that from soft cultivars. The varying activity of the enzymes involved in starch biosynthesis may be attributable for the variations in AC, although the variations in different studies may also be due to the employment of different starch extraction procedures and analytical methods. Varying environmental conditions and agronomic practices affected activities of starch biosynthesis enzymes, hence AC of starches. Li *et al*. (2013a) observed low AC for starch from wheat grown with nitrogen and sulphur fertilization. Starches from wheat exposed to water stress during grain development showed lower AC than that from wheat grown with sufficient watering (Singh *et al*., 2008; Yu *et al*., 2015a). Similarly, higher AC was observed in spring-sown wheat than winter-sown counterparts (Rosicka-Kaczmarek *et al*., 2016). The AC of wheat starch also varied amongst different granules and with their location within the grain. A-granules from both waxy and normal wheat starches contained comparatively more amylose than B-granules (Peng *et al*., 1999; Bertolini

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Table 2 Physicochemical properties of starches from different wheat types and cultivars/varieties

Wheat	Type	Fraction	Amylose (%)	Proteins (%)	Lipids (%)	Crystallinity (%)	Source
Common			25.3–26.8	0.44–0.63	0.33–0.42		Vansteelandt & Delcour (1999)
						10.9	Chakraborty *et al.* (2004)
			32.0			33.5	Ao & Jane (2007)
			25.6			27.7	Hung *et al.* (2007)
			25.72	0.35		14.70	Xie *et al.* (2008)
			26.8–34.7		0.38–0.78		Singh *et al.* (2008)
			18.2–28.8			28.2–36.5	Singh *et al.* (2010)
			27.4–37.2				Shevkani *et al.* (2011)
			27.1	0.46	0.59	32.7	Wang *et al.* (2014)
				0.28	0.31	21.16	Li *et al.* (2016a)
			22.6–27.0	0.24–0.27	0.55–0.61		Rosicka-Kaczmarek *et al.* (2016)
	Hard		22.25	0.25		33.74	Li *et al.* (2013b)
	Soft		23.79	0.33		32.78	Li *et al.* (2013b)
		A-granules	34.0			32.4	Ao & Jane (2007)
	Hard	A-granules	25.26	0.16		34.47	Li *et al.* (2013b)
	Soft	A-granules	25.30	0.18		34.82	Li *et al.* (2013b)
		A-granules	28.90	0.54	0.25	27.01	Tao *et al.* (2016)
		A-granules		0.23	0.30	34.46	Li *et al.* (2016a)
		B-granules	27.0			35.5	Ao & Jane (2007)
	Hard	B-granules	19.19	0.23		31.05	Li *et al.* (2013b)
	Soft	B-granules	21.58	0.28		30.98	Li *et al.* (2013b)
		B-granules	25.00	0.86	0.45	29.27	Tao *et al.* (2016)
		B-granules		0.30	0.28	31.33	Li *et al.* (2016a)
		Bran	27.61	0.15		16.40	Xie *et al.* (2008)
		Bran	24.63–25.87	0.27–0.36	0.35–0.45	21.06–21.75	Liu & Ng (2015)
		Endosperm	18.69–19.99	0.29–0.36	0.39–0.42	18.69–19.99	Liu & Ng (2015)
Durum			26.2–27.5	0.44–0.57	0.39–0.47		Vansteelandt & Delcour (1999)
			27.6–30.4				El-Khayat *et al.* (2003)
						10.1	Chakraborty *et al.* (2004)
Durum waxy						15.3	Chakraborty *et al.* (2004)
Waxy						14.4–15.0	Chakraborty *et al.* (2004)
			1.0			30.0	Hung *et al.* (2007)
			0.71–1.63	0.15–0.25	0.15–0.30	38.7–40.0	Wang *et al.* (2015b)
				0.16	0.32	24.67	Li *et al.* (2016a)
		A-granules		0.11	0.31	37.49	Li *et al.* (2016a)
		B-granules		0.13	0.30	36.71	Li *et al.* (2016a)
High-amylose			37.5			9.4	Hung *et al.* (2007)
			28.0–36.9				Hung *et al.* (2008)

et al., 2003; Ao & Jane, 2007; Kim & Huber, 2010; Tao *et al.*, 2016). Within the grain location, the starch present adjacent to the bran tissues contained more amylose than within the endosperm (Xie *et al.*, 2008; Liu & Ng, 2015).

Amylopectin structure is characterized by the length and distribution of branch chains. Wheat amylopectin exhibited a smooth polymodal distribution of branch chains with the peak maxima at DP 11-12 (Fig. 4). The chain length distribution of amylopectin varied amongst different wheat types and cultivars/varieties (Table 3). The proportion of most abundant amylopectin side chains of DP11 and that of short (DP 6-12), medium (DP 13-24) and long chains (DP > 24) ranged from 10.9% to 12.4%, 44.5% to 52.4%, 43.8% to 50.5% and 3.7% to 6.5%, respectively, amongst starches from different common wheat varieties (Singh *et al.*, 2010). Besides genetic background, the temperature during grain development also influenced amylopectin structure as the wheat cultivars grown at 15 °C showed greater proportion of amylopectin chains with DP 6-12 and lesser of DP 13-34 than the cultivars matured at 30 °C (Matsuki *et al.*, 2003). This was attributed to the decreased activity of heat-sensitive starch synthases and branching enzymes at temperatures above 25 °C. The ratio of long to short chains affected not only the shape of amylopectin molecules but also their packing in granule, hence the size of the granule. Amylopectin of A-granules consisted of more of long chains and lesser of short chains, while that of B-granules had more short chains and lesser long chains (Ao & Jane, 2007; Salman

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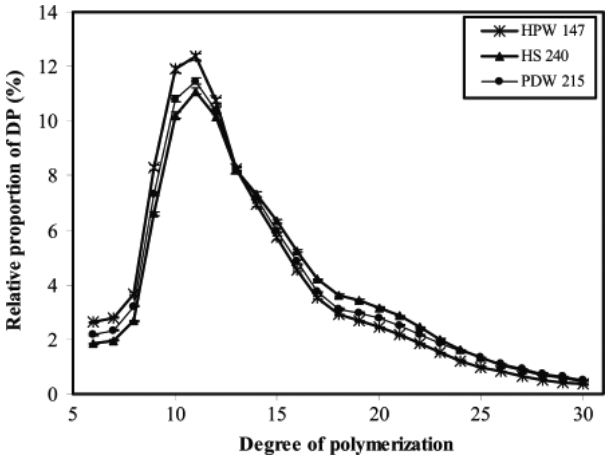

Figure 4 Amylopectin chain length distribution of starches from different common wheat varieties (source: Singh *et al*., 2010).

et al., 2009). Similarly, Kim & Huber (2010) and Yin *et al*. (2012) reported higher proportion of long amylopectin chains (DP > 33 and DP > 40, respectively) in A-granules than in B-granules. Liu & Ng (2015) also reported that wheat bran starch having higher proportion of B-granules contained amylopectin with more short chains than endosperm starch.

Starch-associated lipids and proteins. Lipids and proteins are minor constituents of wheat starch present at the surface and within the structure. Waxy starches had lower protein and lipid content than normal and high-amylose ones, while their contents differ slightly between common and durum wheat (Table 2). Lipids present at the surface of granules were essentially polar and composed mainly of triacylglycerides, free fatty acids (FFA), digalactosyldigylceride, monogalactosyldigylceride, phosphatidylcholine and lysophosphatidylcholine (Finnie *et al*., 2010; Pareyt *et al*., 2011; Rosicka-Kaczmarek *et al*., 2016). These were originated from lipid bilayer membrane surrounding the amyloplasts in which granules were synthesized and stored during grain development (Bechtel & Wilson, 2003). The internal lipids in wheat starch consisted of monoacyl lipids, FFA and lysophospholipids. About 90–95% of the internal lipids were lysophospholipids, which was comprised of lysophosphatidylcholine, lysophosphatidylethanolamine and lysophosphatidylglycerol. The exact origin of the internal lipids is not fully known; however, these were hypothesized to be the membrane lipids, which were rendered inactive by incorporation in granules (Perez *et al*., 2009). The amount of starch lipids varies with types, cultivars/varieties and even with granule size and location within grain (Table 2). Starches from soft wheat generally contained more lipids than that from hard cultivars/varieties (Pomeranz, 1988), and similarly B-granules contained more lipids than A-granules from the same genotype (Lindeboom *et al*., 2004; Kim & Huber, 2010; Tao *et al*., 2016).

Although lipids were present in small amounts (<1%), these markedly influenced functional properties

Table 3 Amylopectin chain length distribution (degree of polymerization, DP) of starches from different wheat types and cultivars/varieties.

Wheat	Fraction	DP 6-12 (%)	DP 13-24 (%)	DP 25-36 (%)	DP>36 (%)	Source
Common		22.4	46.1	14.4	[¶]17.1	Yoo & Jane (2002)
		26.7–32.6	[†]61.2–66.1		[‡]6.1–8.6	Matsuki *et al.* (2003)
		21.8–25.2	42.0–46.8	13.5–18.0	14.2–19.7	Ao & Jane (2007)
		44.9	48.7	5.7	0.7	Blazek & Copeland (2008)
		45	46.2	7.4	1.4	Blazek *et al.* (2009)
		39.2–42.6	47.6–48.5	8.2–8.6	1.6–4.5	Salman *et al.* (2009)
		41.1–49.1	47.3–52.3	[§]3.6–7.0		Singh *et al.* (2009)
		44.5–52.4	43.8–50.5	[§]3.7–6.5		Singh *et al.* (2010)
	A-granules	39.9–41.3	47.9–49.4	8.5–9.2	1.5–3	Salman *et al.* (2009)
	B-granules	42.7–43.3	46–47.2	7.5–8.5	1.6–2.8	Salman *et al.* (2009)
Waxy		21.5	45.0	14.8	[¶]18.7	Yoo & Jane (2002)
		43.6	46.9	7.9	1.6	Blazek *et al.* (2009)
		41.2-43.2	47.0–48.6	7.9–9.0	1.6–1.9	Blazek *et al.* (2009)
		40.2	49.3	8.7	1.9	Salman *et al.* (2009)
	A-granules	38	50.2	9.8	2.0	Salman *et al.* (2009)
	B-granules	39.3	50.3	8.6	1.9	Salman *et al.* (2009)
Durum		44.1	50.0	[§]5.9		Singh *et al.* (2009)

[†]DP 13-34.
[‡]DP ≥ 35.
[§]DP > 24.
[¶]DP ≥ 37.

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of starches because of their ability to form complex with starches during biosynthesis and heating of starch suspensions at gelatinization temperature or above. Amylose molecule occurs in helical form, the hydroxyl groups of glucose residue are present on the outer surface of the helix, while the internal space is hydrophobic. Therefore, the hydrophobic tail of monoacylglycerides enters the molecule and binds within the space (Carlson *et al*., 1979; Ottenhof & Farhat, 2004). This interaction inhibited the solubility and mobility of amylose molecules and hence influenced starch functionality (Putseys *et al*., 2010). Higher contents of monoacylglycerides in wheat starch favoured the formation of amylose–lipid complexes (AMLs). In addition to the internal lipids, the lipids present at the surface of the granules also contributed to the formation of AMLs (Rosicka-Kaczmarek *et al*., 2016). Starch lipids might also form complex with amylopectin, but amylose had greater complexing ability due to the linear structure and longer chain length than amylopectin which had relatively shorter chains and occurred in the form of double helices (Ottenhof & Farhat, 2004; Copeland *et al*., 2009).

The proteins present within granules (granule-bound proteins) comprised a number of polypeptides with molecular weight (MW) ranging from 60 to 149 kDa and corresponded mainly to the enzymes involved in starch biosynthesis. These proteins were categorized into five groups: (i) starch-branching enzymes of 140–145 kDa; (ii) starch synthases of 100–115 kDa; (iii) starch-branching enzymes of 87 kDa; (iv) starch synthase-I of 75–77 kDa; and (v) GBSS of 57–63 kDa (Gao & Chibbar, 2000; Peng *et al*., 2000). The polypeptides of MW from 60 to 120 kDa accounted to the majority of granule-bound proteins and their concentrations varied insignificantly between A- and B-granules (Ko *et al*., 2009); however, the polypeptides of 140 and 145 kDa were present in A-granules only, indicating their association with the biosynthesis of A-granules (Peng *et al*., 2000). In comparison, the surface proteins had MW < 30 kDa (Baldwin, 2001) and showed the presence of 14–15 kDa friabilin and 30 kDa salt-extractable protein (Pauly *et al*., 2012). Friabilin occurred in higher concentration at the surface of starch granules from soft wheat than hard wheat (Greenwell & Schofield, 1986) and was absent in durum (Bhave & Morris, 2008), suggesting that friabilin hindered adhesion between starch granules and protein matrix in the endosperm, leading to a softer endosperm. Friabilin level was related to the amounts of surface lipids in wheat starch as surface-bound polar lipids (glycol- and phospholipids) were essential for binding of friabilin to the surface of the granules (Greenblatt *et al*., 1995). A negative correlation between starch surface lipids and grain hardness has been reported (Konopka *et al*., 2005). The level of friabilin is primarily determined by genetic makeup of the grain. Friabilin was reported to be composed of membrane-bound proteins, puroindoline-A and B, which were gene products of alleles *Pina-D1a* and *Pinb-D1a*, respectively, and were located at Ha locus on the short arm of 5D chromosome (Morris, 2002). Hard wheat had specific mutations in either *Pina-D1* or *Pinb-D1* genes or might lack these genes (Morris, 2002; Nadolska-Orczyk *et al*., 2009). However, climatic conditions during growth also influenced the contents of the minor constituents as the starches from spring-sown wheat contained lower levels of surface proteins and lipids as compared to the counterpart winter-sown varieties (Rosicka-Kaczmarek *et al*., 2016).

Crystallinity

Wheat starch is semicrystalline with the degree of crystallinity varying from 9% for high-amylose starches to 40% for waxy starches (Table 2). The crystalline property arose from the hierarchical organization of amylopectin double helices within the granules, while amylose, less-ordered amylopectin and branch points connecting the double helices were responsible for the amorphous regions (Waterschoot *et al*., 2015). X-ray diffractometry (used widely to reveal the presence and characteristics of crystalline structure in different starches) revealed A-type pattern (typical of cereal starches) with strong crystalline peaks at ~15°, ~17°, ~18° and ~23° 2θ for different wheat starches. Additional peak at 2θ ~20° corresponding to the presence of AMLs (Zobel, 1988) was also observed (Fig. 5). Durum starches were reported to exhibit degree of crystallinity similar to the common ones (Chakraborty *et al*., 2004). However, the waxy starches were more crystalline than normal and high-amylose ones (Chakraborty *et al*., 2004; Hung *et al*., 2007; Salman *et al*., 2009; Wang *et al*., 2015b; Li *et al*., 2016a,b). In addition, the differences in crystallinity were also due to the varying proportion of long amylopectin chains. Higher proportion of amylopectin chain with DP > 13 formed strong crystalline structures within the granules compared to that with DP 6-12 (Singh *et al*., 2010). Amylopectin chains with DP at least 10 is necessary for the formation of double helices (Gidley & Bulpin, 1987); hence, the starches with higher proportion of long amylopectin chains exhibited higher degree of crystallinity and *vice versa*.

Gelatinization

The heating of starch with sufficient water above the critical temperature leads to an irreversible phase transition process known as gelatinization. Gelatinization is initiated by hydration and swelling of amorphous region followed by the disruption of molecular order (breaking of hydrogen bonds) leading to loss of

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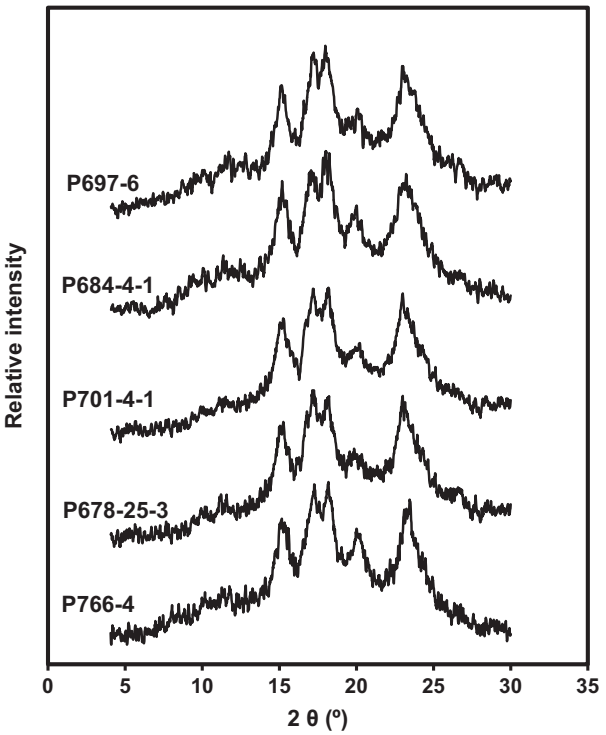

Figure 5 X-ray diffraction patterns of starches from different wheat lines (source: Shevkani *et al*., 2011).

crystalline structure (dissociation of amylopectin in crystalline regions), resulting in increased hydration and irreversible changes, *viz*. granular swelling and solubilization. Differential scanning calorimeter (DSC) is widely used to evaluate gelatinization properties of starches. It measures the heat absorbed by starches during gelatinization and provides useful information as transition temperatures and enthalpy. Transition temperatures indicate crystallite quality (the degree of crystalline perfection), while enthalpy reflects the amount of energy required for the dissociation of molecular (crystalline double helices) order (Singh *et al*., 2010).

Starches from different wheat types and cultivars/varieties differed for thermal properties (Table 4). High transition temperatures resulted from a higher degree of crystallinity providing structural stability, making the granule more resistant towards gelatinization. As amylopectin played a major role in crystallinity, the presence of higher amount of amylose lowered the melting point of crystallites and the energy for gelatinization (Flipse *et al*., 1996; Yuryev *et al*., 2004). In addition, the crystalline lamellae limited the hydration of amorphous regions (Tester *et al*., 2001); hence, amorphous regions were hydrated and subsequently swelled at higher temperatures in the presence of higher crystallinity. Therefore, waxy starches showed higher gelatinization temperatures than normal and high-amylose starches (Zhang *et al*., 2013; Blake *et al*., 2015; Li *et al*., 2016a,b). Similarly, soft wheat starches having lower AC showed higher transition temperatures and enthalpy than medium–hard and hard ones (Singh *et al*., 2016). As the amylopectin chain length distribution determined relative crystallinity of starches (previous section), it influenced their gelatinization behaviour too. Wheat starches with higher content of short amylopectin chains with DP < 12 showed lower transition temperatures and enthalpy than those with higher proportion of long chains (Singh *et al*., 2010). Additionally, starch lipids also influenced gelatinization behaviour of wheat starches. Higher levels of linoleic, palmitic, erucic and tricosanoic acids were attributed to lower susceptibility of starches towards gelatinization (Rosicka-Kaczmarek *et al*., 2016), while the removal of starch lipids decreased gelatinization temperatures and enthalpy (Li *et al*., 2016a).

Retrogradation

Retrogradation is a recrystallization process in which disaggregated amylose and amylopectin molecules in gelatinized starches re-associate during cooling and storage to form ordered structures. Retrogradation is a major determinant of starch functionality and can be desirable or undesirable in foods. It reduces the acceptability and shortens the shelf life of various foods; for example, starch retrogradation causes staling in breads, precipitation and separation defects in soups and sauces, and weeping/syneresis in gels/jellies. However, in some products (rice, dehydrated mashed potatoes and noodles), it is promoted to improve textural and sensory properties as increased firmness and reduced stickiness are desirable in such products. Additionally, retrogradation was also considered desirable in terms of the nutritional significance as retrograded starches were digested slowly and less completely than unretrograded starches, resulting in stable postprandial blood glucose levels (Singh *et al*., 2011).

Retrogradation in starches is commonly measured using DSC, texture analyser and dynamic rheometer. The DSC analysis is sensitive to chain ordering of the amylopectin fraction, while the mechanical tests are sensitive to chain entanglements with/without the formation of crystallites. DSC measures enthalpy (ΔH_{ret}) and transition temperatures for the melting of recrystallized starch. ΔH_{ret} is the amount of energy required for dissociation of the re-associated amylopectin; hence, it provides a quantitative measure of retrogradation; that is, higher ΔH_{ret} means higher retrogradation tendencies. Retrogradation properties of different wheat starch gels are presented in Table 5. The retrograded starches showed lower transition temperatures and ΔH_{ret} than native starches, indicating that the

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re-association of disaggregated amylopectin in stored starch gels occurred in a less-ordered manner than in the native granules.

Starch components responsible for retrogradation are amylose and amylopectin. During cooling and storage of starch gels, amylose molecules re-associate to form double helices, while the outer branches of amylopectin align themselves into partially ordered structures to form crystallites. Amylose enhanced the rate of retrogradation and was largely responsible for the increase in elasticity (due to the formation of amylose aggregates) during cooling and short-term storage of starch gels (Fig. 6). The accelerated retrogradation for high-amylose starch was attributed to low molecular weight amylose (Zhou *et al*., 2014). Amylopectin, on the other hand, re-associated slowly during storage. Therefore, waxy and normal starches showed slower and lesser retrogradation than high-amylose starches. However, despite similar AC, higher retrogradation was observed for waxy durum than waxy common starch, highlighting role of amylopectin structure on retrogradation tendencies (Chakraborty *et al*., 2004). Amylopectin recrystallization related positively to amylopectin chain length as the starches with higher proportion of short chains (DP 6-9) were less susceptible to retrogradation than that with higher proportion

Table 4 Thermal properties of starches from different wheat types and cultivars/varieties

Wheat	Type	Fraction	T_o (°C)	T_p (°C)	T_c (°C)	ΔH_{gel} (J g^{-1})	Starch water ratio	Heating rate (°C min^{-1})	Source
Common			53.6	56.6	59.7	2.8	2:5	4	Vermeylen *et al.* (2005)
			53.5–62.5	58.2–68.4	63.5–88.5	0.91–5.90	1:2	10	Ral *et al.* (2008)
			55.6–57.2	60.8–62.1	65.3–67.2	8.0–10.8	3:7	10	Singh *et al.* (2010)
			57.9–59.7	61.6–63.6	65.2–67.7	9.03–10.37	3:7	10	Shevkani *et al.* (2011)
			57.3	61.7	66.1	9.3		10	Wang *et al.* (2014)
			56.72	60.80	65.87	5.31	1:4	10	Li *et al.* (2016a)
			56.17–58.45	61.02–62.81	65.61–66.95	2.36–3.34	3:7	1	Rosicka-Kaczmarek *et al.* (2016)
	Hard		57.9–61.7	64.3–65.3		11.7–12.4	1:3	10	Ao & Jane (2007)
	Hard		56.40	60.84	66.72	5.85	1:4	10	Li *et al.* (2013b)
	Hard		60.0	65.9	75.9	4.6	1:4	10	Zhang *et al.* (2013)
	Soft		56.32	61.49	67.5	6.06	1:4	10	Li *et al.* (2013b)
		A-granules	61.2	64.3		11.7	1:3	10	Ao & Jane (2007)
		A-granules	57.0	64.5	75.4	15.9	1:2	10	Kim & Huber (2010)
		A-granules	55.26	60.49	66.54	10.31	1:2	10	Tao *et al.* (2016)
		B-granules	53.00	60.50	67.73	8.19	1:2	10	Tao *et al.* (2016)
		B-granules	57.9	64.7		12.1	1:3	10	Ao & Jane (2007)
		B-granules	54.7	66.6	79.5	13.3	1:2	10	Kim & Huber (2010)
		Bran	63.9	71.3	80.8	7.7	1:3	10	Yu *et al.* (2015b)
		Bran	57.73	63.68	–	11.88	3:7	10	Xie *et al.* (2008)
		Bran	56.0–57.2	61.6–62.9	74.6–75.7	10.3–11.3	3:7	5	Liu & Ng (2015)
		Endosperm	56.6–58.0	61.4–62.6	71.6–72.3	8.4–9.2	3:7	5	Liu & Ng (2015)
		Endosperm	63.7	67.6	72.8	6.9	1:3	10	Yu *et al.* (2015b)
Waxy			58.9	63.3	68.2	9.8	1:3	10	Hung *et al.* (2007)
			59.1	63.8	73.1	6.5	1:3	10	Zhang *et al.* (2013)
			60.0–61.3	64.1–65.9	69.7–72.2	13.9–15.1	1:3	10	Wang *et al.* (2015b)
		A-granules	57.0	64.5	75.4	15.9	1:2	10	Kim & Huber (2010)
		A-granules	60.65	63.87	70.69	8.57	1:4	10	Li *et al.* (2016a)
		B-granules	54.7	66.6	79.5	13.3	1:2	10	Kim & Huber (2010)
		B-granules	57.46	62.48	71.25	8.47	1:4	10	Li *et al.* (2016a)
High-amylose			47.2	51.8	56.8	1.7	1:3	10	Hung *et al.* (2007)
			55.6–57.5	60.8–62.6	67.3–69.0	5.3–6.5	1:3	10	Hung *et al.* (2008)
Durum			48.7–49.4	54.5–55.4	61.1–62.5	12.5–14.0	1:2	4	Vansteelandt & Delcour (1999)
			58.2–60.0	63.0–64.2	69.7–71.1	3.6–4.7	1:3	10	El-Khayat *et al.* (2003)
Spelt			53.6–58.0	62.1–65.6	70.2–75.7	8.2–13.2	1:4	10	Wilson *et al.* (2008)

T_o, T_p and T_c represent onset, peak and conclusion temperatures, respectively; ΔH_{gel} represents enthalpy of starch gelatinization.

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Table 5 Thermal properties (transition temperatures, enthalpy and percentage retrogradation) of retrograded starch gels from different wheat types and cultivars/varieties

Wheat	Fraction	T_or (°C)	T_pr (°C)	T_cr (°C)	ΔH_{ret} (J g^{-1})	Retrogradation (%)	Starch: water	Storage duration	Source
Common		38.7–40.6	49.1–51.2	57.2–61.0	3.0–4.3	24.8–35.9	1:3	1 week	Ao & Jane (2007)
		46.82	56.17		3.98		3:7	2 weeks	Xie *et al.* (2008)
		44.2–5.05	50.5–55.6	51.7–60.2	0.7–3.0		3:7	1 week	Singh *et al.* (2010)
		46.55–48.67	52.40–55.29		0.07–0.88		3:7	5 days	Shevkani *et al.* (2011)
	Bran	47.51	54.79		2.11		3:7	2 weeks	Xie *et al.* (2008)
	Bran	43.9–45.8	52.3–54.7	59.8–64.9	2.4–3.8	21.7–36.4	3:7	2 weeks	Liu & Ng (2015)
	Endosperm	45.8–46.0	54.0–56.4	61.1–64.2	2.2–3.1	33.2–37.4	3:7	2 weeks	Liu & Ng (2015)
Waxy		ND	ND	ND	ND		1:3	5 days	Wang *et al.* (2015b)

ND, not detected.

T_or, T_pr and T_cr represent onset, peak and conclusion transition temperatures, respectively; ΔH_{ret} represents enthalpy of retrograded starch gels.

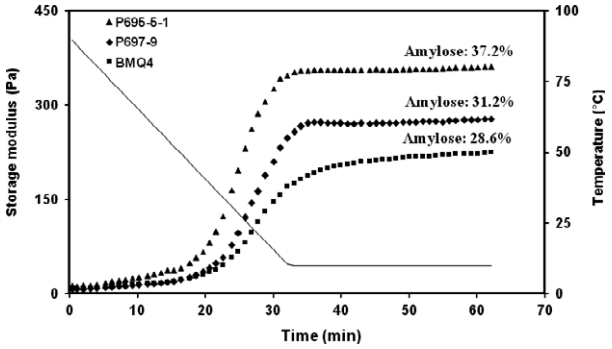

Figure 6 Changes in storage (elastic) modulus of cooked starch gels from 90 to 10 °C at a rate of 2.5°C min^{-1} and holding at 10 °C for 30 min from wheat starches varying in amylose content (source: Shevkani *et al.*, 2011).

of chains with DP 14-24 (Lin *et al.*, 2001; Biliaderis, 2009). Kohyama *et al.* (2004) also showed that retrogradation was more advanced with longer amylopectin chains. Similarly, Liu & Ng (2015) also reported lower retrogradation for bran starches having higher proportion of short amylopectin chains (DP 6-12). As a minimum DP of 10 was necessary for the formation of double helices (Gidley & Bulpin, 1987), the starches with long amylopectin chains had sufficient glucose units to form double helices during storage of gelatinized starches, hence showed higher rate of retrogradation.

Although lipids and proteins were present as minor constituents in starches, these played important roles in slowing down and retarding retrogradation. The removal of starch lipids and proteins increased retrogradation (Li *et al.*, 2016a,b) which suggested that the association of starch lipids and proteins with amylose and outer chains of amylopectin during gelatinization may have inhibited amylose aggregation and formation of double helices between amylose molecules and hindered amylopectin recrystallization during the storage of starch gels. The formation of AMLs has been reported to reduce solubility and mobility of amylose and prevent amylose helix formation (Putseys *et al.*, 2010).

Swelling power

When starch is heated with sufficient quantity of water, its helical structure is lost, exposing hydroxyl groups that bind with water through hydrogen bonds resulting in granular swelling. Starch characteristics that influence swelling power (SP) are AC, amylopectin structure, lipids and AMLs. Amylopectin contributed to SP, whereas amylose and AMLs retarded the same. Starches with high AC were better reinforced and more rigid and thus swelled less freely and *vice versa* (Tester & Morrison, 1990). It was also reported that swelling proceeded more rapidly after the exudation of amylose and AMLs are prevented from leaching out (Tester & Morrison, 1990). Therefore, common and durum starches with lower AC and AMLs exhibited higher SP (Grant *et al.*, 2001; Hung *et al.*, 2007; Singh *et al.*, 2010, 2016; Shevkani *et al.*, 2011). Furthermore, short amylopectin chains with DP 6-12 increased granular swelling, whereas long chains, on the contrary, resulted in the formation of stronger crystalline network leading to reduced swelling (Singh *et al.*, 2010). Although B-granules contained more lipids, these exhibited higher SP than A-granules due to lower AC and presence of amylopectin molecules with more short chains (Li *et al.*, 2013a,b). However, the unfractionated starches from both common and durum cultivars/varieties with higher proportion of large granules showed higher SP and *vice versa* (Shevkani *et al.*, 2011; Kaur *et al.*, 2016; Singh *et al.*, 2016).

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Pasting properties

Pasting refers to the changes occurring in the viscosity of starch suspension after gelatinization. Brabender Viscoamylograph, Rapid Visco-Analyzer and other rotational viscometers are used to measure the change in viscosity of starch suspensions under controlled heating, cooling and stirring conditions. During heating, the viscosity of starch suspension depends on granule swelling and polymer leaching, while amylose aggregation is a major factor influencing the viscosity of heated starch suspension upon cooling. A typical pasting profile of wheat starch is shown in Fig. 7. During heating above gelatinization temperature, the viscosity of starch suspension increased due to the swelling of granules. The temperature at which the viscosity of the suspension began to rise was referred as pasting temperature (PT). After reaching the maximum value, the viscosity started decreasing as the granules ruptured and starch components leached and dispersed in the aqueous phase because of continuous shearing at elevated temperatures. The maximum viscosity attained during heating (peak viscosity; PV), represented the point of maximum swelling of the starch granules, while the decrease in viscosity (breakdown viscosity; BV) was a measure of the resistance of swollen granules towards disintegration at high temperature. Shevkani *et al.* (2011) reported a positive correlation amongst SP, PV and BV, indicating that starches capable of swelling to a high degree were less resistant to disintegrate on cooking and hence exhibited greater breakdown in viscosity after reaching the maximum value. During cooling, the viscosity of starch pastes increased due to amylose re-association and gel network formation. The recovery in viscosity during cooling of starch paste is referred as setback viscosity (SV) and it measured retrogradation in starch pastes.

Pasting properties of starches from different wheat types and cultivars/varieties are presented in Table 6.

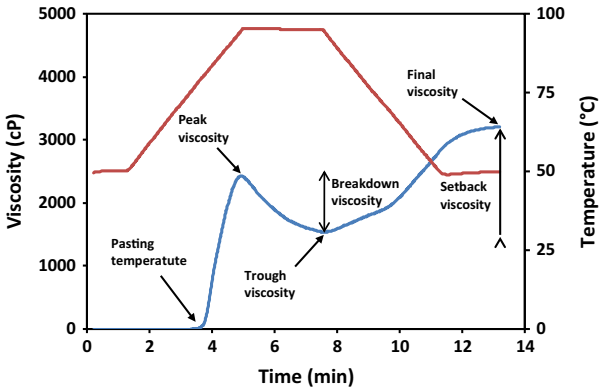

Figure 7 Typical pasting profile of wheat starch.

Amylose to amylopectin content, amylopectin structure, lipids and association of lipids with amylose were major factors influencing granular integrity, SP, amylose leaching and aggregation and consequently pasting properties of wheat starches. In general, amylose and AMLs were negatively related to PV. These increased PT and decreased PV by increasing granular rigidity and integrity (Shevkani *et al.*, 2011). Therefore, waxy starches showed higher PV and BV but lower PT than normal and high-amylose starches (Blazek & Copeland, 2008; Zhang *et al.*, 2013; Blake *et al.*, 2015; Li *et al.*, 2016a,b). Similarly, soft wheat starches with higher amounts of lipids showed lower PV than medium-hard and hard starches (Singh *et al.*, 2016), while the removal of lipids increased PV but decreased PT (Wang *et al.*, 2014; Li *et al.*, 2016a). A-granules, generally, contained more amylose, yet these showed higher paste viscosities than B-granules (Li *et al.*, 2016a,b). Liu & Ng (2015) also observed that bran starch with more B-granules was less viscous than endosperm starch. Similarly, common and durum starches with high proportion of A-granules exhibited higher paste viscosities as compared to that with more B- and C-granules (Singh *et al.*, 2010; Shevkani *et al.*, 2011; Kaur *et al.*, 2016). A-granules because of their large size exhibited loose packing ability and occupied relatively larger volume fraction in pastes than B- and C-granules, possibly for the reason A-granules contributed to high paste viscosities. In addition, the starches with higher proportion of long amylopectin chains (DP>36) showed higher paste viscosities, which was attributed to their ability to form intermolecular linkages with amylose in the gel structure (Blazek & Copeland, 2008). In addition to the starch structure and composition, the presence and content of damaged starch also influenced pasting properties of wheat starches. PV, FV, BV and SV decreased gradually with increased content of damaged starch as the damaged granules hydrated and swelled to a greater degree, hence resulted in more weakening and breakdown of the gelatinized granules as compared to the lesser damaged and intact granules (Barrera *et al.*, 2013).

Digestibility

The rate at which the starch present in food is digested and glucose is released plays an important role in human health by maintaining a proper blood glucose level and providing extended energy supply (Zhou *et al.*, 2014). Starches are classified into three types (rapidly digestible starch, RDS; slowly digestible starch, SDS; and resistant starch, RS) on the basis of their enzymatic digestibility (Englyst *et al.*, 1992). The RDS is hydrolyzed rapidly and completely in the small intestine and is associated with elevated and unstable blood glucose level. Therefore, long-term consumption of foods with high content of RDS may result in type

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Table 6 Swelling power and pasting properties of starches from different wheat types and cultivars/varieties

Wheat	Type	Fraction	SP (g g^{-1})	PT (°C)	PV	TV	BV	FV	SV	Viscosity units	Starch Suspension for pasting (%)	Source
Common					125–189	113–141	12–60	245–280		RVU	11	El-Khayat *et al.* (2003)
				91.0	93.5	62.5	31	158.5	96.0	RVU	8	Ao & Jane (2007)
				63.5–78.95	325.33–418.67	149.0–195.08	156.83–242.17	271.83–387.92	122.83–192.83	RVU	9	Ral *et al.* (2008)
			13.1–24.9	82.3–89.6	2264–3433	1932–2842	414–738	2624–4455	692–1817	cP	11.25	Singh *et al.* (2010)
				94.7	266.5	202.3	64.3	437.5	235.7	mPa.s	10	Zhang *et al.* (2013)
			8.36	85.28	2228	1826	402	2514		cP	7.4	Li *et al.* (2016a)
	Hard			70.9	4102	1400	2702	3276	1876	cP	7.4	Li *et al.* (2013b)
	Hard		12.3–13.6	87.2–89.7	1678–1921	1417–1668	252–369	1759–1975	381–526	mPa.s	8	Yu *et al.* (2015c)
	Soft			65.5	4983	1119	3864	3197	2078	cP	7.4	Li *et al.* (2013b)
	Soft		13.4–14.2	84.4–90.9	1635–1859	1310–1641	177–325	1836–2022	307–446	mPa.s	8	Yu *et al.* (2015c)
		A-granules		85.0	139.8	85.9	54	186.8	100.9	RVU	8	Ao & Jane (2007)
		A-granules	17.3		338.6	198.6	140	395.1	196.6	RVU	10.34	Kim & Huber (2010)
	Hard	A-granules		69.3	3981	1530	2451	3291	1761	cP	7.4	Li *et al.* (2013b)
	Soft	A-granules		54.4	4748	1504	3244	3206	1522	cP	7.4	Li *et al.* (2013b)
		A-granules	9.56	76.33	2889	2353	536	3496		cP	7.4	Li *et al.* (2016a)
		A-granules		87.3	3313	2609	704	3630	1021	cP	8	Tao *et al.* (2016)
		B-granules		92	97.6	78.8	18.8	155.3	76.57	RVU	8	Ao & Jane (2007)
		B-granules	24.1		215.8	171.2	44.6	282.7	111.5	RVU	10.34	Kim & Huber (2010)
	Hard	B-granules		75.1	2302	1005	1297	2895	1890	cP	7.4	Li *et al.* (2013b)
	Soft	B-granules		67.1	3385	803	2582	2008	1205	cP	7.4	Li *et al.* (2013b)
		B-granules	8.65	87.2	18.15	1458	357	2058		cP	7.4	Li *et al.* (2016a)
		B-granules		94.95	2197	1542	655	2493	951	cP	8	Tao *et al.* (2016)
		Bran			2312–2438		457–581	3147–3222	771–836	cP	8	Liu & Ng (2015)
		Endosperm			2523–3057		454–508	3509–4071	984–1015	cP	8	Liu & Ng (2015)
Waxy				73.6	505.6	336.8	169.6	444.2	108.4	mPa.s	10	Zhang *et al.* (2013)
		A-granules	27.3		455.6	114.2	341.5	180.1	65.9	RVU	10.34	Kim & Huber (2010)
		B-granules			227.5	77	150.5	110.1	33.2	RVU	10.34	Kim & Huber (2010)
Durum			7.5–12.4	66.8–85.1	1010–2910		721–1676	1070–4148	572–3459	cP	10	*Kaur *et al.* (2016)
High-amylose				87–88.5	30–240		0	100–670	220–450	BU	8	#Hung *et al.* (2008)
Spelt wheat				77.1–85.2	192.2–239.7	73.6–138.8	92.6–143.6	161.2–297.1		RVU	11	Wilson *et al.* (2008)

SP, swelling power; PV, peak viscosity; TV, trough viscosity; BD, breakdown; FV, final viscosity; SB, setback; PT, pasting temperature.
Pasting properties were determined using AntonPaar rheometer equipped with starch measuring cell (*) and Brabender Viscoamylograph (#).

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2 diabetes, obesity and coronary heart diseases. The SDS is the most desirable group because it is digested slowly and completely and has health benefits of stable blood glucose levels. In contrast to SDS and RDS, RS is resistant to enzymatic digestion. It is not digested in the small intestine by the digestive enzymes and, consequently, transferred to the large intestine where it performs physiological functions similar to dietary fibres. It functions as prebiotics and promotes the growth of probiotics in the human gut. It is fermented in the large intestine by colonic microflora, resulting in the production of gases (CO_2, CH_4 and H_2), organic acids and short-chain fatty acids (SCFAs) primarily butyrate, propionate and acetate. The SCFAs are the preferred respiratory fuel for the cells of colon lining (colonocytes) and further contribute to increased colonic blood flow, maintenance of low pH and prevention of abnormal colonic cell growth (Nugent, 2005). If not metabolized by colonocytes, the SCFAs are absorbed into the portal blood system and reach the liver, where these alter certain metabolic pathways involved in the metabolism of lipids (Bloemen *et al*., 2009). The SCFAs were also associated with the promotion of satiety and management of hyperlipidemia (Tapsell, 2004; Darzi *et al*., 2011). Therefore, starch digestibility influence not only gastric health and postprandial blood glucose levels but also the lipid metabolism.

The digestibility of starches from different wheat types and cultivars was related to their physicochemical, morphological and structural characteristics. Amylose to amylopectin ratio was one of the main factors affecting starch digestibility. Waxy starches were generally a source of RDS but high amylose of SDS and RS. The starches from high-amylose wheat were hydrolysed at a slower rate by exocorrosion or surface pitting, whereas those from waxy cultivars/varieties were digested at higher rates by internal corrosion (Salman *et al*., 2009; Zhou *et al*., 2014). Naguleswaran *et al*. (2014) isolated amylose and amylopectin from normal wheat starch and reported that the later was hydrolysed to a greater degree than the former. Therefore, more susceptibility of waxy starch to amylolysis may be attributed to more surface area per molecule of amylopectin. Besides amylose and amylopectin content, their structure also influenced the susceptibility of starches towards amylolysis. Longer amylose chains increased the rate of starch digestion (Zhou *et al*., 2014). The normal starches with short double helices were more susceptible to amylolysis and exhibited high content of RDS and SDS, whereas long amylopectin chains, contrarily, formed more stable helices, contributing to decreased starch digestibility (Lehmann & Robin, 2007). As enzymatic activity depends on the contact between enzyme and substrate, larger granules are supposed to digest at a slower rate than smaller ones because of relatively small contact area available for the enzymatic action. Meanwhile, separated B-granules digested to a greater degree than A-granules not only due to small size and large surface area but also because of lower content of amylose. Salman *et al*. (2009) reported that at the initial stages of enzymatic hydrolysis the rate of starch amylolysis depended primarily on the size and surface characteristics of granules (up to 4 h), while starch structure acts as the main determinant during the later stages of digestion. Starch digestibility also depended on pores and channels at the surface of starch granules. These facilitated the transfer of digestive enzymes or chemical reagents into the granule structure, although the effect was aided by granular swelling and removal of channel-associated proteins (Kim & Huber, 2008). Therefore, surface pores acted as the starting sites for enzymatic digestion of normal and waxy starches (Zhou *et al*., 2014).

Gelatinization increases digestibility, whereas retrogradation decreases the same. In general, starches in native granular form are hydrolysed at a slower rate than in gelatinized form. Native starches from both hard and soft wheat cultivars/varieties contained high levels of RS and SDS, whereas RDS was present in the highest proportion in gelatinized starches (Yu *et al*., 2015a). Gelatinization caused disruption of starch structure (unravelling of the glucan chains) and swelling, providing more space for enzymatic action, hence increased digestibility. However, the susceptibility of starch gels towards amylolysis was dependant on the extent of structural disruption during gelatinization (Wang & Copeland, 2013; Nhan & Copeland, 2015). Therefore, gelatinized waxy starches exhibited higher digestibility than normal and high-amylose starches (Zhou *et al*., 2014) likely due to more structural disruption in the absence of amylose and AMLs. Retrogradation caused recrystallization and made the starch gels more resistant towards amylolysis; hence, higher content of RS and lower of RDS were observed for the wheat starch gels stored for longer durations at 4 °C (Nhan & Copeland, 2015).

Although present in small quantities, minor constituents of wheat starch (lipids and proteins) could decrease starch digestibility by restricting the entry of digestive enzymes into starch structure and reducing the susceptibility of starches to gelatinize, while their removal with alkali treatment increased the same (decreased RS content and increased RDS and SDS levels) (Wang *et al*., 2014). Starch lipids were reported to decrease the rate and extent of amylolysis by blocking adsorption sites and influencing enzyme binding (Oates, 1997).

Applications

Food applications

Starch has a number of food applications. More than 60% of the total starch extracted is used for food and

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rest for nonfood purposes. Wheat starch has an edge over other starches owing to brighter appearance and blander flavour (Maningat *et al*., 2009). It is often used as an ingredient in several formulated foods to improve texture and mouth feel. It functions as tenderizer in cakes, doughnuts, cookies and cheese analogues. It is also incorporated to batters, ice creams, soups, gravies, etc., to provide adhesion, structure, moisture control and/or thickening. The incorporation of waxy wheat is desirable in bread making due to the retardation of staling and extension of shelf life. The breads prepared with waxy wheat (5–30% incorporation levels) had soft and tasty crumb and showed improved shelf life (Hayakawa *et al*., 2004). The waxy common and durum wheat flour incorporated (25%) to common flour also improved loaf expansion during baking and reduced loaf firmness of breads, attributing to the higher gelatinization temperatures and swelling ability of waxy starches that reduced overall water availability (Blake *et al*., 2015). Wheat starch is also used for the production of hydrolysis products such as syrups and sweeteners, which are widely used in beverages and confectionery industry (Cornell, 2004). It has also been used in yogurts or custards to provide thickening or gelling and in sausages and comminuted meats to improve water-binding properties. Wheat starch incorporation decreased cooking loss and firmness of low-fat sausages (Payne, 1993), but increased cohesiveness and chewiness and decreased syneresis in surimi gels (Kim & Lee, 1987). It also improved head retention in beer when used as adjunct (Mason, 2009). The starch from waxy wheat is preferred for applications where high water absorption, greater viscosities, low retrogradation rate and high digestibility are desired. On the other hand, high-amylose starches can be used for the enrichment of foods with nutritionally superior SDS and RS. In addition, the high-amylose starch also improve textural properties of noodles (Morita *et al*., 2003) and reduce oil uptake by fried foods (Cornell, 2004).

Nonfood applications

Nonfood applications of wheat starch include its use in paper, textile, chemical, fermentation, pharmaceutical and petrochemical industries and in the production of industrial alcohol. Starch is indispensably used in paper, glue and corrugated paperboard industries. In the pulp industry, it is employed as a flocculating agent to increase the rate of dewatering of pulp. Starch remained in the finished paper act as an internal sizing agent and increase paper strength. It is also used for coating on paper sheets to increase smoothness and improve printability and writing properties by filling up the pores. B-granules owing to smaller size were more suitable for paper coating (Wilhelm, 1993), while A-granules were effective protective (stilt) material in carbonless printing papers because of appropriate granule size and smooth surface (Nachtergaele & VanNuffel, 1989). Therefore, A-granules were found to be useful in the paper industry to replace relatively scarce and expensive arrowroot starch (Johnson *et al*., 1981). The application of wheat starch in corrugated paperboards and adhesives was advantageous over maize starch because of lower gelatinization temperature, resulting in the requirement of less quantity of caustic soda to reduce the gelatinization temperature (Knight & Olson, 1984). Starch is also used widely in textile industry to size and stiffen the clothes and to increase the mechanical strength of yarns. Wheat starch, owing to trimodal granule size distribution, produced a superior stiff finish: the smaller granules penetrated the fibres of the fabric, whereas the larger ones coated the exterior surface (Maningat *et al*., 2009). Starch also finds applications as filler and stabilizer in printing dyes. In the petrochemical industry, pregelatinized wheat starch was considered a suitable material to thicken the drilling fluids (Knight & Olson, 1984). Chemical industries utilize starch for production of biodegradable, nontoxic skin-friendly detergents, biodegradable plastics, surfactants and resins. Small B- and C-granules find applications in cosmetic products (*e.g*. face and talcum powders) because of their very small size that give smooth sensation when rubbed on skin (Mazza *et al*., 1992). Wheat starch is also used as binder in pet and fish feeds. Pregelatinized B-granules were utilized in calf feeding as milk replacer (Zwitserloot, 1989). Wheat starch also acted as a promising raw material to support *Saccharomyces cerevisiae* cell culture (Farmakis *et al*., 2007). Pharmaceutical industries use wheat starch as a tablet excipient and as an emulsifier, a stabilizer, a diluent, a disintegrant, a glidant or a binder in lotions, liquid medicines, creams, ointments and capsule shells (European Medicines Agency, 2014). Bone cements for providing immediate structural support have also been formulated with different starches. In addition, starch-based polymers, in the form of microsphere or hydrogels, have been found suitable for drug delivery.

Application in edible and/or biodegradable films

Recently, interests in development of biopolymer-based edible/biodegradable films have increased because of the demand for natural food ingredients and their potential to increase product shelf life and decrease environment pollution (Shevkani & Singh, 2015). Wheat starch can be an attractive choice for the preparation of edible and/or biodegradable films due to low cost, high availability, renewability and biodegradability. The utilization of starches in film formation depended on content and properties of amylose. The linear structure of amylose molecules provided greater opportunity for the formation of hydrogen bonds between the hydroxyl groups on the

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adjacent polymer chains, resulting in reduced affinity of the polymer for water and formation of opaque and less-brittle films (Lu *et al*., 2009). Wheat starch alone or in combination with whey proteins was evaluated for film-forming properties (Basiak *et al*., 2015). It was concluded that wheat starch-based films could be used in the food systems where edible films should disintegrate during cooking or mastication. In addition to edible films, the native granular starch was also utilized to increase biodegradability of conventional plastic films. Although the blending of wheat starch with low-density polyethylene also resulted in films with reduced tensile strength and flexibility, yet their strength was within the operational limits up to the incorporation level of 20% (Psomiadou *et al*., 1997). The granular wheat starch was also used as a filler material in biodegradable but costlier polymers (poly-beta-hydroxybutyrate-co-beta-hydroxyvalerate; PBHV) to decrease cost and increase the rate of biodegradation. The incorporation (up to 50%) increased the rate of biodegradation but decreased the tensile strength and flexibility of starch-PBHV films, yet the overall mechanical strength remained within the useful range (Ramsay *et al*., 1993).

Conclusion

Gelatinization, swelling, pasting, retrogradation and digestibility of starches from different wheat types and cultivars/varieties are influenced by a combination of different starch characteristics, *viz*. granule size distribution, AC, amylopectin structure, crystallinity and the contents of proteins and lipids, which in turn vary with genotypes, cultural practices and environmental conditions during growth. Wheat starches with high proportion of long amylopectin chains and high contents of amylose and lipids are good source of nutritionally superior SDS and RS having a number of health benefits such as improved cholesterol metabolism, effective management of obesity and reduced risk of type-2 diabetes and colon cancers. Hence, these are ideal for the development of dietetic foods. Waxy starches, on the other hand, are hydrolysed rapidly and more completely than normal and high-amylose starches; thus, these can be used for the development of starch-based sweeteners and industrial alcohol as in these products quantitative conversion of starch to sugar is desirable. Interactions of starch lipids with amylose has a profound impact on starch functionality and digestibility as AMLs reduce SP, paste viscosities, retrogradation tendencies and susceptibility of starch towards gelatinization and amylolysis. While much information is available on the characteristics of starches from different common and durum wheat cultivars/varieties, much less is available on ancient species of wheat, that is einkorn, emmer and spelt. The interest in these species has recently increased owing to agronomic advantages and demand of speciality foods; therefore, more studies are needed on the characterization and structure–function relationships of starches from these species.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Figure S1. Flow diagram of the Martin process employed for the production of wheat starch (adapted and modified from Sieb, 1994).

Figure S2. Flow diagram of the batter process employed for the production of wheat starch (adapted and modified from Sieb, 1994)

Figure S3. Flow diagram of the *Alfa-Laval* or *Raisio* process employed for the production of wheat starch (adapted and modified from Sieb, 1994)

Figure S4. Flow diagram of the hydrocyclone process employed for the production of wheat starch (adapted and modified from Sieb, 1994).

Figure S5. Flow diagram for the production of wheat starch using the High-pressure disintegration (adapted and modified from Sieb, 1994).

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