The structural characteristics of starches and their functional properties

Yael Isbeth Cornejo-Ramírez ☞, Oliviert Martínez-Cruz ☞, Carmen Lizette Del Toro-Sánchez ☞, Francisco Javier Wong-Corral ☞, Jesús Borboa-Flores ☞ and Francisco Javier Cinco-Moroyoqui ☞

Departamento de Investigación y Posgrado en Alimentos, Universidad de Sonora, Hermosillo, Sonora, México. C.P.

ABSTRACT
Starch is composed of amylose and amyllopectin and deposited as granules of different sizes and shapes with semi-crystalline and amorphous concentric layers that show the ‘maltese cross’. Starches from different sources show variable chemical composition as well as the structure of their components that are involved in thermal properties. Amylose, lipids, phosphorylated residues and long lateral chain amyllopectin interact among them avoiding water uptake. In contrast, high amyllopectin contents, especially with short lateral chains, allow hydration via hydrogen bonds to form gels with the tendency to retrogradation. Smaller starch granules have a larger superficial area, surface pores, and channels that enhance water uptake. High hydration increases the swelling, viscosity, and gelatinization ability of starch granules. The knowledge of those properties allows the selection of the most appropriate starch for a specific end use. This review discusses the relationship between the physicochemical composition of the starch and their rheological properties.

1. Introduction
Starch is the major polysaccharide in plants (Hoseney, 1994). Chemically is composed of two glucan polymers, amylose, and amyllopectin. These polymers are deposited in granules of different sizes, large A-, medium B- and small C-type, and shapes, as disk-like and spherical (Singh, Singh, Isono, & Noda, 2010). The starch granules are organized in semi-crystalline and amorphous concentric layers (Svihus, Uhlen, & Harstad, 2005).

Starches of different sources and also each type of starch show variation in their chemical composition (α-glucans, moisture, lipids, proteins and phosphorylated residues) and structure of their components (Tester, Karkalas, & Qi, 2004), which are related to the starch granules surface, hardness (Finnie, Jeannotte, Morris, Giroux, & Faubion, 2010) and crystallinity (Ao & Jane, 2007). Amylose influences the packing of amyllopectin into crystallites and the organization of the crystalline lamella within starch granules. This is important for properties related to water uptake as swelling and gelatinization (Copeland, Blazek, Salman, & Tang, 2009). Also, the variation of amylose content in starch with the same botanical source influences the granule size distribution, the molecular characteristics of amylose and amyllopectin (You & Izydorczyk, 2002) and the functional properties such as paste temperature and viscosity (Song & Jane, 2000). Another crucial factor that determines certain starch properties is amyllopectin chain length distribution (Copeland et al., 2009), which varies according to the botanical source (Singh et al., 2010). Low molecular weight amyllopectin with long branched chains facilitates the formation of amyllose-lipid helicoidal complex (Li, Jiang, Campbell, Blanco, & Jan, 2008). In addition, starches with higher amylose content are more exothermic and can form a more stable amyllose-lipid complex (Singh et al., 2010). This complex has an influence on the thermal properties and gel formation (Copeland et al., 2009).

The physical and chemical characteristics of the granule starches are involved in their properties and functionality. The knowledge of these allows the selection of starch with the necessary properties for a particular application and also, this knowledge is useful to select the starch source and the appropriate modification method to obtain the required functional characteristics for a specific end use. Enzymatic modification disintegrates fragile starch granules and causes
the emergence of numerous holes on the surface area, which reduces the ability to hold water, and decrease the viscosity; also, amylose is degraded into low molecular weight oligosaccharides, although these effects are reduced in starches with low amylose content and high swelling power (Uthumporn, Zaidul, & Karim, 2010). With an adequate selection of the starch source, the enzymatic modification produces highly branched amylopectin and amylose to obtain starches with low digestibility and high-water solubility desirable in the beverage industry (Lee et al., 2008). Chemical modification as acetylation allows better functional properties such as high solubility, water absorption, swelling power and lower gelatinization temperature than unmodified starches, which have wide applications mainly in the food industry (Han, Benmoussa, Gray, BeMiller, & Hamaker, 2005). In this regard, this chapter discusses the relationship between the physicochemical composition of the starch and their thermal properties related to the modification of starches (Kim & Huber, 2008) during cooking or in the industrial and chemical process in which they are involved.

2. Chemical and physical characteristics of starches

2.1. Chemical structure of the starches

Starch is the main storage polysaccharide of plants (Hoseney, 1994) and is fractionated into two types of polymers amylose and amylopectin. In general, normal starches contain around 20–30 % of amylose (Table 1) and 70–80 % of amylopectin (Svihus et al., 2005). For example, the amylose content in barley is 29.8 % (Song & Jane, 2000), wheat 21.5–26-6 (Yoo & Jane, 2002), sweet potato 22.6 %, cassava 19.8 %, arrowroot 20.8 %, yam 32.6 %, ginger 26.5 % (Peroni, Rocha, & Franco, 2006), maize 20.9 %, rice 29.1 %, potato 26.9 % (Stawski, 2008), and triticale 22.2–23.8 % (Cornejo-Ramírez et al., 2015). In contrast there are starches with high amylose content, such as high amylose barley 46.5–48 % (Song & Jane, 2000) and maize 62.8–85.6 % (Li et al., 2008), as well as waxy starches with negligible amounts of amylose, such as waxy barley 9.1 % (Song & Jane, 2000), waxy wheat < 0.2 % (Yoo & Jane, 2002) and waxy potato 3.4 % (Varatharajan, Hoover, Liu, & Seetharaman, 2010).

Amylose and amylopectin are glucans that differ in their structure and molecular weight (Figure 1). Amylose is a polymer of low molecular weight (1.03–4.89 x 10^5), which consists of linear chains bound by α-1,4 glycosides links and behaves essentially as a non-branched molecule. Amylopectin has a higher molecular weight (7.08–9.88 x 10^5) and its cluster-like structure implies a heavy branching (Mua & Jackson, 1997). In this regard, the amylopectin consists of highly branched chains formed by α-1,6 linked to linear glucans units, which form an organized structure by themselves (Smith & Martin, 1993).

Table 1. Apparent amylose content and amylopectin degree of polymerization (DP) of some starches.

| Starch      | Apparent amylose (%) | DP (A, B1, B2, B3, B4) |
|-------------|----------------------|------------------------|
| Barley      | 29.8                 | ≥37, 6–12 and 6–9      |
| Wheat       | 21.5–26-6            | ≥37, 25–36, 13–24, 6–12 and 6–9 |
| Rice        | 29.1                 | 51–69, 21–25, 7–18, 1–5 and 0.1–1.3 |
| Triticale   | 22.2–23.8            | 20–27, 12–18, 4–9 and 2–3 |

* Determined by measuring iodine affinities of defatted starches without correcting for amylopectin interference.

References: 1. Song & Jane, 2000; 2. Yoo & Jane, 2002; 3. Stawski, 2008; 4. Li et al., 2008; 5. Cornejo-Ramírez et al., 2016.

Figure 1. Schematic representation of a) a helical amylose and a possible structure of the amylopectin of b) complete and c) substituted triticales reported by Cornejo-Ramírez et al. (2016). d) Glucose unit of the structure of both polymers and e) the α-1,4 glycosides links of linear chains and α-1,6 links of the branches.

Figura 1. Representación esquemática de a) amilosa helicoidal y una posible estructura de amilopectina de triticales b) completo y c) sustituido reportados por Cornejo-Ramírez et al. (2016). d) Unidad de glucosa de la estructura de ambos polímeros y e) El enlace glucosídico α-1,4 de las cadenas lineales y α-1,6 del enlace de las ramificaciones.
Branched chains of amylopectin are known as large (A), long (B₁), mid-length (B₂), short (B₃) (Cao, Hu, & Wang, 2012; Cornejo-Ramírez et al., 2016), and B₄ chains (Lü, Guo, & Liang, 2008). The branch chain length may vary depending on the starch source (Table 1). The branches of amylopectin link each 20–25 glucose linear units (Smith & Martin, 1993), nevertheless, the length or degree of polymerization (DP) of the glucan chains varies according to the starch source, the action of the enzymes responsible for the synthesis of the starch granules due to genetic differences, and the environmental and nutritional conditions prevailing during the growth of the plants and seed formation (Cornejo-Ramírez et al., 2016).

The anomeric carbon of glucose molecules has the ability to act as an electron donor or proton receptor in reduction-oxidation metabolic reactions, which is known as the reducing end, whereas the opposite side carbon is known as the non-reducing end. The anomeric carbon linked to a molecule loses its reducing capacity. In starch the glucose reducing end is useful for amylose and amylopectin biosynthesis by the α-glycosides (α-1,4 and α-1,6) links, thus, both polymers have one reducing end.

2.2. Amylose and amylopectin packing into granules

The amylose and amylopectin that structurally form the starch are deposited in discrete granules in the amyloplasts in storage organs of plants. These granules are of different sizes and shapes (Figure 2). Granules can be of disk-like shape and spherical shape, as in the starch granules of the Triticeae family (wheat, barley, rye, and triticale) (Shannon & Garwood, 1984).

The starch granules are classified as A-, B- and C-type according to their dimensions (Singh et al., 2010). The types of granules, size, shape, and percentage vary depending on the starch source. Table 2 shows some examples of the starch granule distribution from different sources. In general, numerous reports in cereal grains report that the A- and B-type granules are present in greater proportion than the others (Ao & Jane, 2007). The A-type (>15 μm) starch granules of wheat grains are disk-like shape, whereas the B- (5–15 μm) and C- (<5 μm) type starch granules are spherical in shape (Singh et al., 2010). Wheat starch has the higher B-type granules (≤9.3 μm) proportion (20 %) than rye (10–15 %), which in turn has a higher percentage (85 %) of A-type granules (>62.5 μm) (Verwimp, Vandeputte, Marrant, & Delcour, 2004). Normal barley starches contain higher amounts (74.7 %) of A-type (≥8 μm) starch granules, followed by waxy and null barley starches (66.4 % and 43.9 %, respectively) and high amylose barley starches (19.4 %) (You & Izydorczyk, 2002).

Starch granules are made up of a very complex structure. The granules vary in their chemical composition (α-glucans, moisture, lipids, proteins and phosphorylated residues) and the structure of their components (Tester et al., 2004). The

![Figure 2](image-url). SEM images of starch granules of complete triticales (a, b and c for Beagle, Eronga and Fahad, respectively) and substituted triticales (d, e and f for Armadillo, Panda and Yoreme, respectively). Arrows show the pores on the surface of the starch granules. Scale bar = 40 μm. (Data from Cornejo-Ramírez et al., 2015.)

![Figura 2](image-url). Imágenes del Microscopio Electrónico de Barrido (SEM, por sus siglas en inglés) de gránulos de almidón de triticales completo (a, b y c de Beagle, Eronga y Fahad, respectivamente) y triticales sustituidos (d, e y f de Armadillo, Panda y Yoreme, respectivamente). Las flechas muestran los poros en la superficie de los gránulos de almidón. Escala = 40 μm. (Cornejo-Ramírez et al., 2015.)
### Table 2. Starch granule distribution of some starch sources.

| Starch source          | Size (μm) | A-type (%) | Size (μm) | B-type (%) | Size (μm) | C-type |
|------------------------|-----------|------------|-----------|------------|-----------|--------|
| Normal barley          | 8–26      | 74.7       | <8        | 25.3       | ND        | ND     |
| Waxy barley            | 8–26      | 66.4       | <8        | 33.6       | ND        | ND     |
| Zero amylose waxy barley | 8–26    | 43.9       | <8        | 56.1       | ND        | ND     |
| High amylose barley    | 8–26      | 19.4       | <8        | 80.6       | ND        | ND     |
| Rye                    | >62.5     | 85         | <9.3      | 10–15      | ND        | ND     |
| Wheat                  | >62.5     | 80         | ≤9.3      | 10         | ND        | ND     |
| Cassava                | >20       | 20         | 10.1–20   | 71.4       | 5–10      | 8.6    |
| Sweet potato           | >20       | 8.6        | 10.1–20   | 70.5       | 5–10      | 20.9   |
| Ginger                 | >20       | 10.7       | 10.1–20   | 82.7       | 5–10      | 6.6    |
| Yam                    | >35       | 67.2       | 15.1–35   | 67.2       | 5–15      | 19.3   |
| Arrowroot              | >30       | 6.8        | 20.1–30   | 50.5       | 5–20      | 42.7   |
| Barley, wheat and triticale | 10–35   | ND         | =2        | ND         | ND        | ND     |
| Wheat                  | 9.48–22.8 | 75         | 5.24–9.48 | 10         | ≤5.24     | 15     |
| Wheat                  | >15       | 51–73      | 5–15      | 14–37      | <5        | 10.5–15|
| Complete triticale     | 18–41     | 80         | 2–13      | 20         | ND        | ND     |
| Substituted triticale  | 8–38      | 75         | 0.5–6     | 25         | ND        | ND     |

ND = Not determined.

References: 1You & Izydorczyk, 2002; 2Verwimp et al., 2004; 3Peroni et al., 2006; 4Ao & Jane, 2007; 5Moita et al., 2008; 6Singh et al., 2010; 7Cornejo-Ramírez et al., 2015.

A-type granules have high amylose quantity (Shinde, Nelson, & Huber, 2003), lower crystallinity percentage and less lipid content than the B-type starch granules (Ao & Jane, 2007).

On the starch granule surface can be found polar lipids (75–89 % of the total lipids), mainly phospholipids, which probably remain of amyloplasts membrane, whereas the remaining part of lipids is non-polar lipids, generally triglycerides. The fatty acid composition of lipids in wheat starch is mainly composed of palmitic, linoleic and oleic acids (Konopka, Rotkiewicz, & Tánska, 2005). High lipid percentages of starch granules are associated with cold temperatures during the growing of the starch source (Matsoukas & Morrison, 1991). In cereals, the phosphorus is found mainly in phospholipids (Konopka et al., 2005), however in root and tubers the phosphorus is mainly found as phosphate monoester and its presence in lipids is low (less than 1 %) (Peroni et al., 2006). Also, on the starch surface can be observed the presence of channels and pores (Cai, Zhao, Huang, Chen, & Wei, 2014; Kim & Huber, 2008). Figure 2 shows the presence of pores on the surface of starch granules.

The starch granules possess multilevel structures from macro- to molecular scales. In the inner part of starch granules, α-1,4-glucans and some α-1,6-branches are placed parallel to each other allowing double helix formation. Structurally, branches are specifically placed forming the amorphous lamella, in contrast, a region made up exclusively of linear chains is known as crystalline lamella (O’Neill & Field, 2015). Figure 3 shows a schematic representation of the starch granules structure. A concentric threedimensional architecture from the hilum (corresponding to the core of grain), alternating amorphous and semicrystalline shells, growth rings that increase their surface area and become thinner to be added by a constant rate, crystalline and amorphous lamellae (periodicity), and macromolecular chains (Xie, Pollet, Halley, & Avérous, 2015).

In this regard, the amylose and amylopectin are orderly arranged into the starch granules in a radial order centered at the hilum and perpendicular to the granule surface. This arrangement of the polymers within the starch granules is known as ‘birefringence pattern’. The native starch granules are birefringent and showed a radial light as a cross on a dark background after their exposition at the polarized light, which is known as ‘maltese cross’ (Cai & Wei, 2013; Cai et al., 2014).

### 2.3. Characteristics and importance of the pores and channels of starch granules

The channels found in the starch granules are formed by the non-reducing ends of amylose and amylopectin that are oriented toward the center of the grain (Finnie et al., 2010; Kim & Huber, 2008). These pores connect the central cavity of the starch granules to its external environment (Huber & BeMiller, 1997) allowing certain molecules to enter the granule matrix (Finnie et al., 2010; Kim & Huber, 2008). This is important because the starch granules may have access to reagents (Huber & BeMiller, 1997), which is important for the chemical modification of starches (Kim & Huber, 2008).

The channels in the starch granules may be present from very early stages of granules development (Huber & BeMiller, 2000) and they can differ in size among the granules that form the starch. The A-type granules have channels relatively large, whereas the B-type granules have holes and channels less defined and predominantly large (Kim & Huber, 2008).

The characteristics of the surface and pores of starch granules from a diverse botanical source are different (Juszczak, Fortuna, & Wodnicka, 2002), showing some similarities to a lesser degree. On the starch surface and the central cavity can be found proteins and polar lipids (Han et al., 2005). Most channel structures in association with proteins in the A-type starch granules originate from the granule surface and are radially aligned toward the hilum with varied depths and dimensions. In this regard, the proteins associated to channels facilitate the transference of chemical reagents into the granule matrix. In addition, proteolytic enzymes can remove proteins, at least partially, to increase the access to the inner of the grain. In contrast, the B-type starch granules have few visible pores on their surfaces; despite this, there is an indirect evidence for voidlike inner channels blocked by protein (Kim & Huber, 2008).

Removal of the protein associated with channels facilitates hydration and swelling and enhances the access of reagents into the granule matrix; also, the size of the
channels is important in the access of reagents and to accommodate enzymes (Kim & Huber, 2008). The enzymatic attack is limited to specific areas of starch granules, but it is not restricted to their surfaces. Also, non-cereal starches are more resistant to enzymatic degradation than cereal starches (Uthumporn et al., 2010). These impact reaction patterns during chemical modification and is important in predicting the hydrolysis of starch granules for biofuel, among other applications (Kim & Huber, 2008).

2.3.1. Protein and lipids in the starch surface involved in starch texture
The compositional structure of starch surface plays a significant role in the hardness of endosperm (Finnie et al., 2010).
The presence of proteins called friabilins is directly related to the texture of the cereal grains (Li et al., 2006). These proteins have a molecular weight of about 15 kDa and are present in the soft endosperm (Greenwell & Schofield, 1986) in their two isomers, puroindoline-A (pin-a) and puroindoline-B (pin-b) (Finnie, Jeannotte, Morris, & Faubion, 2010; Martin et al., 2006). In hard endosperm these proteins are absent (Greenwell & Schofield, 1986). Similarly, when one puroindoline is mutated or absent can result in a hard texture phenotype. Thus, differences in the hardness of the endosperm depend on the strength of the interaction between the protein and starch granules (Giroux & Morris, 1997).

In the same way, the presence of polar and non-polar lipids present on the starch surface is inversely correlated with the hardness of the endosperm. The lipid content in starch can vary from 689–853 mg/100 g (Konopka et al., 2005). High lipid levels generally are usually associated with B-type granules and cold temperatures during the grain filling period (Gaines et al., 2000). Hard grains have a high percentage of large starch granules (A-type), whereas soft grains contain a high percentage of small (C-type) and medium size (B-type). Waxy starches exhibit an intermediate size distribution of starch granules (Moita, Lourenço, Bagulho, & Beirão-da-Costa, 2008). The hard wheat varieties have higher contents of oleic acid (Konopka et al., 2005). In contrast, soft wheat varieties exhibit a high contribution of linoleic acid. This fatty acid is more susceptible to oxidation on starch granules. This enables reactions in sulfur-rich proteins (Dubrell, Compont, & Marion, 1997) favoring the formation of lipid-protein structures on the starch surface (Konopka et al., 2005). Likewise, the tryptophan-rich loop puroindolines plays an important role in the protein-lipid interactions (Clifton, Green, & Frazier, 2007). Starch granules of soft endosperm containing a high amount of lipids and proteins of low molecular weight have higher hydrophobicity (Konopka et al., 2005), which facilitates the interaction among them resulting in a higher decreasing of water solubility of the starch granule.

The polar lipid content of the starch surface dramatically decreases when one of the puroindolines is null or if the pin-B mutates (Finnie et al., 2010). Pin-A is closely associated with phospholipids and galactolipids. Pin-B is freely associated with galactolipids and preferentially binds negatively charged phospholipids (Dubrell et al., 1997). Polar lipids are more related to puroindolines in their wild-type form. This implies that the mechanism of endosperm hardness is a structure that provides an anti-adhesion characteristic between the surface and storage proteins in the endosperm of the soft textured wheat kernels (Finnie et al., 2010).

2.4. Starch crystallinity

Different forms of crystalline polymorphism are present in the diverse starch sources. Cereal starches have an A-type diffraction pattern, while tuber and high amylose starches show a B-type pattern. Starches of legume, root and some fruits and stems have the C-type pattern (Sevenou, Hill, Farhat, & Mitchell, 2002; Wu & Sarko, 1978), and starches with amylose complexed by lipids and other compounds have the V-type pattern (Lebail, Buleon, Shiftan, & Marchessault, 2000). The A- and B-type crystalline structures are composed by parallel double helices in a hexagonal arrangement (Wu & Sarko, 1978), where twelve glucose residues are the main crystalline elements. The A-type crystallite structure has four water molecules forming a dense packing, while the B-type crystallite structure has 36 water molecules (Lebail et al., 2000). Structurally, the C-type structure is a mixture of the A- and B-type structures (Wu & Sarko, 1978). The V-type crystalline structure, in particular, is composed of singular helices (Lebail et al., 2000).

The crystallinity of starch granules is affected by several factors such as amylose content (Yoo & Jane, 2002), amyllopectin chain length (Shewry et al., 2009; Singh et al., 2010), lipid content, amylose-lipid complexes (Moita et al., 2008) and starch granule size (Ao & Jane, 2007). Amylose and amyllopectin in the starch granules form a semi-crystalline structure, consisting of crystalline lamella and amorphous lamella. The crystalline lamella consists of parallel glucan chains, ordered and closely packed, whereas the amorphous lamella consists predominantly of less ordered branching regions (Oates, 1997).

The amylose content affects the starch crystallinity. The lack of amylose does not affect the crystalline polymorphism, granule size, but increases the crystallinity degree (Yoo & Jane, 2002). Also, the double helices formed by the intertwining of amyllopectin outer chains has a crystalline arrangement and imparts semi-crystalline properties to starch (Shannon & Garwood, 1984). Amylopectins of longer chains form a more stable crystalline structure (Shewry et al., 2009). This is because amyllopectin molecules with short chains are unable to form stable double helix structures, making them easy to disrupt by heat at lower temperatures. In contrast, amyllopectin with medium and long chains forms a very strong crystalline network (Singh et al., 2010). High molecular weight amyllopectin in waxy starch influences the increased crystallinity degree, such as in the case of waxy wheat in comparison to normal wheat (Yoo & Jane, 2002). The crystallinity degree is also affected by the variation between diverse kinds of starch granules. That is because the amylose content is higher in the A-type starch granules than in the B-type granules, which produces lower percent of crystallinity in the A-type starch granules (Ao & Jane, 2007). In addition, industrial processes can affect the crystallinity degree as that the starch structure can be physically damaged. For instance, the milling process causes physical damage to the starch granules. In this process, the crystalline amyllopectin becomes amorphous amyllopectin with the formation of some low molecular weight fragments (Moita et al., 2008). A general example of the above is in the case of wheat. In wheat starches, the A-type crystalline structure predominates with an appreciable level of B-type crystallites in the big granules (Vermeylen, Goderis, Reinaers, & Delcour, 2005). The differences in behavior observed in softer wheats containing large amounts of lipids complexed with amylose are attributed to the magnitude of amylose-lipids complex or crystalline/amorphous structure. These characteristics affect the organization in the starch granule chains and the association between internal chains (Moita et al., 2008).

3. Diversity on the thermal properties for starch granules due to their differences in the structural characteristics

As described before, the starches for different botanical sources have similitude in levels of organization. The
starches are fractionated into two glucan polymers, linear amylose and cluster amylopectin, which are packing into starch granules of diverse sizes and shapes. The surface of the starch granules could have pores and channels and they may contain lipids and proteins. The starch granule morphology, the length, distribution, and proportion of each polymer affect the interaction between them and with other components, such as water, that interacts with the starch granules.

The ability of the starch granules to interact with water and hydrate at high temperatures is related to changes in the swelling power, viscosity and gelatinization capacity, which vary depending on the starch source. Those changes occur in cooking and industrial process where starch is used as the raw material and due to this, it is important to understand the effect of the structural characteristics of starches on the thermal changes that native starches undergo during the thermal processes.

3.1. Swelling power and viscosity of starch dispersions

The starch granule is a water-insoluble compound that can be hydrated at high temperatures. Thus, the starch granules hydrate and swell, followed by a thermal disordering of the crystal structures (Moita et al., 2008). Differences in the swelling power are due to the variation in structural organization and characteristics of the starch granules obtained from different botanical sources or crops (Singh et al., 2010). The double helices structure of amylose and lateral chains of amylopectin are stabilized by hydrogen bonds. When the starch granules are hydrated and submitted to high temperatures, the hydrogen bonds are broken and replaced with water. In this regard, the capacity of starch granules to hydrate and swell depends on the capacity of starch molecules to hold water via hydrogen bonding, influenced by the amylose content, lateral chains of amylopectin (Tang, Mitsunga, & Kawamura, 2004), the presence of phospholipids (Geera, Nelson, Souza, & Huber, 2006), the presence of holes and channels (Moita et al., 2008) and the presence of amylose (Singh et al., 2010).

The capacity to hydrate and swell allows changes in starch viscosity. The phospholipids in the starch granules may be in complex with the amylose, which, in normal starches, prevents water binding resulting in lower swelling power and low viscosity at high temperatures. In high amylose starches, the amylose-lipid complex and the low amylopectin content induce very low swelling power and low viscosity even at high temperatures. In contrast, the high amylopectin content is involved in higher swelling power and a higher viscosity at low temperatures (Song & Jane, 2000). Additionally, holes and channels inside the starch granules weaken their structures allowing the entrance of reagents and enzymes supporting starch modifications such as hydrolysis. Hydrolyzed starches could swell more than native starches, however, starches with few pores after hydrolysis results in a less disrupted structure (Uthumporn et al., 2010). Holes and channels also allow the entrance of water and ions as OH⁻ that disrupt the amorphous region that contains amylose chains, reducing in this way the restrictive effect of amylose and enhance therefore the hydration and swelling capacity of the starch granules (Nadiha, Fazilah, Bhat, & Karim, 2010). The smallest starch granules have the highest swelling power. However, the waxy starch granules have higher swelling power (Tang et al., 2004) that is positively correlated with their amylopectin content, particularly with amylopectin molecules with short chains, being repressed by the presence of amylose (Singh et al., 2010). The short chains of amylopectin can easily bind to water molecules via hydrogen bonds, while amylose, amylose-lipid complex and very long lateral amylopectin chains can interact between them via helical bounds not allowing the interaction with water molecules. In terms of size granules, B-type starch granules have low amylose content, high crystallinity percentage (Ao & Jane, 2007) and large radius of surface area per unit weight of starch allowing a more efficient hydration and swelling capacity than A-type starch granules. Figure 4a shows the results of apparent viscosity analyzed in a rapid visco-analyzer (RVA) of three kinds of starch wheats, soft with high volume of small granules (B- and C-type), hard with high volume of large granules (A-type) and waxy with medium size of starch granules. The small granules have a high capacity to hydrate and swell and the lipids can complex with amylose, however, the amylose content in small granules is low and their small size allows them to pack closely with more starch granules in the same unit weight than the bigger ones. Therefore, the small granules might completely hydrate and swell to reach high viscosity, contrary to the starch with granules of large volume. The granule size is not as important when there is a significant difference in chemical composition. The waxy starch is composed mainly of amylopectin, as it was mentioned before, which easily bind to water. In this regard, this kind of starch can hydrate and swell quickly reaching the highest pasting temperature in lesser time (Moita et al., 2008).

A gradual increase of swelling with hydration and temperature indicates weak interne associative forces maintaining the starch granule structure. In contrast, lower swelling power with light increase with temperature suggests resistance to swelling and strong forces maintaining the starch granule structure (Peroni et al., 2006). The swelling capacity of starch granules allows them to increase their viscosity and gel. In this regard, amylopectin with short lateral chains and small starch granule size advantage the hydration and swelling capacities.

Variations in the viscosity and paste properties could be measured using a rapid visco-analyzer. The pasting temperature indicates the temperature at which the viscosity begins to increase during the heating process (Singh et al., 2010). The peak viscosity represents the equilibrium point between the starch granule swelling and its rupture (Pongsawatmanit, Thanasukarn, & Ikeda, 2002). The pasting time is defined as the time required to increase the viscosity thirty Relative Viscosity Units (RVU) of the initial value (Geera et al., 2006). A mechanical shear stress occurs during a holding period at high temperature (95° C), which can lead to further disruption of starch granules and amylose leaching. Amylose lixiviation happens frequently in the direction of flow, contributing to shearing thinning or a breakdown in viscosity. Once the starch solution is cooling down after heating, the viscosity increases until reaching the final viscosity (Pongsawatmanit et al., 2002). The setback viscosity is the recovery of viscosity during the cooling of the heated starch suspension (Singh et al., 2010). Differences in paste properties in the starches are important for manufacturing of
commercial resistant starches (Shinde et al., 2003), among other uses.

The viscosity properties are related to the physicochemical characteristics of starches as described above and, also, are associated with the starch concentration in the solution (Figure 4b). A higher starch concentration in diluted solutions increases the connectivity between starch granules generating less filling space in the solutions. Although no changes occur during the swelling process, the starch granules need lower time and temperature to swell and increase the viscosity than solutions with very low starch concentration (Acosta-Osorio et al., 2011; Reddy & Bhotmange, 2014). The dependence of viscosity on time corresponding to the non-dimensional value, it is rather a structural parameter. This phenomenon could be measured through a flow curve, at which a starch solution is submitted to increasing shear rate with time (‘up’ curve) followed by decreasing shear rate with time (‘down’ curve) (Ptaszek, 2014).

During the starch pastes development from starch diluted solutions, it has been observed that at a low shear rate (up to 80/s) a shear thinning phenomenon happens, while a higher shear rates the viscosity increases. Besides, the starch structure also has an influence on the final effect after shear rate with time. Very low amylose concentration (1 %) results in shear thickening properties, in contrast, at higher amylose concentration (5 %) a shear thinning has been observed. This behavior is associated with an alteration in the helix arrangement of amylose molecules in the fluid within low shear rate, replaced by the rebuilding of the amylose structure within high shear rates. In contrast, amyllopectin does not form a structurally orderly fluid due to its branched structure, thus, low amyllopectin concentration (1–9 %) undergoes shear thinning, but at higher amyllopectin concentration (10 %) the viscosity increases as a function of shear rate. The amyllopectin coil begins to contract and hinder the interaction among them. At lower shear rates, the coils loosen and deform, however, during shear, the coils return to initial conformation. At higher shear rates, the large external forces stabilize the deformation of amyllopectin chains. Furthermore, the high molecular weight of starch the cause an increase in viscosity (Ptaszek, 2014), however, at very low starch concentration, the structure has higher influence in the viscosity (Guo, Lin, Fan, Zhang, & Wei, 2018; Ptaszek, 2014).

3.2. Physicochemical characteristics of starch related to its gelatinization capacity

The gelatinization process of the starch granules involves hydration and swelling at high temperatures followed by thermal disordering of the crystal structures (Moita et al., 2008) and the loss of the birefringence (Cai et al., 2014). The gelatinization process starts at the hilum of the granules. It is believed that this is because the central area of the granule around the hilum is the least organized region (Chen et al., 2010).

Figure 4 illustrates the changes in viscosity during the hydration and heating during time. Figure 5 shows the micro-morphologies of granules under polarized light at different temperatures. The figures do not correspond to the same starch samples. However, these figures are the representation of the changes that can occur at the starch granules during the gelatinization process. First, the starch granules in their native physicochemical characteristics have a clear peculiar hilum with many growth rings, namely, the amyllose and amyllopectin are orderly aligned in a radial order centered at the hilum and perpendicular to the granule surface, therefore, under the polarizing light, the starch granules show the ‘maltese cross’. With the time, hydration and heating of starch granules, the crystallinity starts to
disrupt from the hilum area accompanied by a partially swelling, initial loss of birefringence and slightly increases of viscosity; the disruption pattern is significantly affected by the hilum position in the starch granule (Figure 6) and the crystalline polymorphism; for eccentric hilum starches, the crystallinity disruption and swelling began on the proximal surface or on the distal surface of hilum. In contrast, for central hilum starches, the crystallinity disruption and swelling first occur from the central hilum or on the whole surface of the starch granule. As the temperature increases with the time, the changes increase, and there is more disruption of crystallinity and loss of birefringence, and the swelling increases from the hilum to the outer of the granules complemented with viscosity increases. With the time and higher increase of temperature, the crystallinity of the starch granules surface is disrupted (Cai & Wei, 2013; Cai et al., 2014; Moita et al., 2008). The time and temperatures needed for this process to occur depend on the physicochemical characteristics of the starch granules of each botanical source.

Differential scanning calorimetry (DSC) is used to measure the thermal behavior of starches during heating. Thermal transitions are defined in terms of onset (T₀), peak (Tₚ) and end set (Tₑ) transition temperature. The heat of transition or enthalpy (ΔH) is measured in joules per weight (g) of sample,
and it is calculated from peak areas of the thermogram resulting from the DSC evaluation (Moita et al., 2008). The gelatinization starts when the starch granules are unable to continue binding more water molecules, thus, the swelling is accompanied by partial rupture of granules and their loss of birefringence. The small amylose molecules leached from the starch granules and the remaining amylose and amylopectin are dispersed in the solution becoming a sol coupled with an increase in viscosity, reaching the peak viscosity. The $T_p$ is related to the beginning of the starch gelatinization and represents the melting of the weakest crystallites. Then, the viscosity is reduced (medium viscosity) due to the breaking of the starch granules by the effect of agitation. Under polarized light, the disrupted parts of the granules become of the same color as the background. The $T_p$ is reached with a complete loss of birefringence happens. As the temperature increase occurs, the formation of a network of swollen starch granules in the sol-to-gel transition starch dispersion starts to form. The viscosity of the starch granules reaches the maximum value. The $T_c$ is related to the final temperature needed to complete the gelatinization process (Cai & Wei, 2013; Cai et al., 2014; Moita et al., 2008). The $\Delta H$ is related to the changes during the melting of the crystallites and provides a measure of the degree of crystallinity or a damage in the starch structure before the gelatinization occurs. The amylose content, small granules, and damaged starch structure are inversely related to $\Delta H$ value (Ao & Jane, 2007; Moita et al., 2008; Stevenebo, Sälhlström, & Svilhus, 2006).

The viscoelastic properties also change during starch gelatinization and can be measured using a low deformation rheometer through the storage ($G'$) modulus that indicates elastic properties, loss modulus ($G''$) related to viscous properties, and loss tangent (tan $\delta$) parameters. During the initial heating, both moduli ($G'$ and $G''$) increased to a maximum. In the beginning, $G''$ is higher than $G'$, then, the $G'$ becomes higher than $G''$ suggesting a gel-like behavior. The crossover point of $G'$ and $G''$ moduli is related to $T_p$, and the maximum is associated to $T_c$. At the time with further heating, both moduli drop indicating the destruction of the gel. A decrease of tan $\delta$ is related to starch gelatinization (Kaur, Singh, Singh, & McCarthy, 2008; Sang, Bean, Seib, Pedersen, & Shi, 2008).

The starch gelatinization capacity and the time needed to achieve the gelatinized state depends on certain characteristic factors of the botanical source from which they come from, its amylose content, as well as the granules type that predominate in the starch (Bao, Sun, & Corke, 2002). For instance, the time to reach the gelatinization temperature of high amylose maize starch is lower than the normal and waxy maize, whereas the gelatinization time of high amylose barley starch, in contrast, is lower than the waxy starch but faster than normal barley (Koch & Jane, 2000). In the first situation, it is clear, that the quantity of amylose is inversely related to the gelatinization capacity, however, in the second circumstance, that relation is unclear. In the case of maize, the A- and B-type granules diameters are small, being the A-type granules bigger than 5 $\mu$m, whereas the B-type granules are smaller than 5 $\mu$m (Pan & Jane, 2000), thus, differences in size between A- and B-type maize starch granules are small, and the gelatinization is unaffected by the proportion of starch granules. In the case of normal barley, its starch contains a higher proportion of A-type granules (between 44–56% more) than that of the high amylose barley starch. In contrast, the high amylose barley starch contains a smaller proportion of A-type granules (between 11–19 % less) than the waxy barley starch (Asare et al., 2011). All those differences affect the gelatinization process. Additionally, the gelatinization process causes an increase in the starch viscosity, however, when the molecular weight is reduced to very small units as in the case of maize (2.41 x 10$^5$ g/mol), the heating does not affect the apparent viscosity of the milled grain. It is useful to obtain a high quantity of starch with low viscosity (Chen, Shen, & Yeh, 2010).

According to the above, bigger starch granules require more time to gel and reach higher gelatinization temperatures in contrast to smaller ones (Koch & Jane, 2000). That is because the smaller granules have more efficient hydration and swelling capacity than the bigger ones (Moita et al., 2008). Also, the initial temperature ($T_o$) for the gelatinization process is similar for the A- and B-type starch granules (Geera et al., 2006); however, the maximum gelatinization temperature is higher for small granules fractions, which is influenced by differences in the chain length distribution of amylopectin (Vermeylen et al., 2005). Starch granules with amylopectin molecules having small branched-length chains have a wider range of gelatinization temperature (Ao & Jane, 2007). In high-amylose starches, the amylose double helices require high temperatures and energy to disorder and therefore result in a high gelatinization temperature (Shi, Capitani, Trzasko, & Jeffcoat, 1998). The gelatinization time for different starches such as waxy barley, maize and potato starches is lower than their normal starch counterparts, in contrast, the gelatinization time for normal potato starch is higher than waxy maize, waxy barley and rice. That leads to conclude that the gelatinization time is lower for starches with higher amylopectin contents and shorter branches, however, there is not a definite correlation with the amylose-amylopectin ratio (Koch & Jane, 2000) as that the gelatinization time is only affected by the size of the starch granules. The milling process reduces the particle size damaging the starch granules causing an increase in gelatinization capacity and a decrease of gelatinization time. As a result, the starch granules that reach a smaller diameter show higher gelatinization capacity (Chen et al., 2010). However, when there is not much difference in granule size, the gelatinization process is unaffected by the proportion of starch granules. Hence, differences in the proportion of different size of starch granules in conjunction with amylose amount affect the gelatinization properties (Asare et al., 2011; Koch & Jane, 2000). In addition, pores and channels enhance the hydration, swelling and gelatinization capacity of starch granules (Nadigha et al., 2010).

Once the gelatinization is completed, the factors that most commonly affect the gel structure are the amylose quantity and the proportion of lateral amylopectin chains (Tang, Watanabe, & Mitsunaga, 2002). After cooling normal starch results in hard gels while low amylose starch results in soft gels (Sang et al., 2008). Gels formed by waxy barley starches are more stable in the center of the grain than in the surface area. By contrast, gels formed by normal barley starch are more stable in the surface layer of the grain (Tang et al., 2004). Lipids and other minor components have minor effects on the gel stability (Tang et al., 2002). The formation of stable gels is at disadvantage when the molecular weight
of the amylopectin is pretty small, and its branching chains are so long like amylose or are too short (Tang et al., 2004). Therefore, the characteristics and quantity of amylose and amylopectin in the starch influence the ability to form strong, cohesive and flexible gels. Mali, Karam, Pereira, and Grossmann (2004) found that the cassava starch showed the higher amylopectin content and its gels and films were less strong, more transparent and more flexible than those of corn and yam starches. This property of starches to forms gels, which is known as gelation power, can be useful for the industry. For example, the high gelatinization capacity that can be reached when the granule size is reduced during the milling process could be a useful method to make pre-gelatinized starch with ultrafine particles (Chen et al., 2010).

The amylopectin chain molecular profile affects the paste clarity. High clarity pastes are elaborated from starches containing amyloses of high molecular weight as they are more difficult to align and give a good interaction producing a translucent paste. In contrast, amylose with low molecular weight favors the molecular interaction between short chains contributing to a low percentage of transmittance (Mali et al., 2004). Another effect of amylose in the elaboration of pastes is the performance that presents the starch in the stress-relaxation process to which is submitted. Starch with a low amount of amylose has a viscoelastic-type gel behavior comparable to normal starch, whereas that of the waxy starch behave like a viscoelastic liquid without intermolecular bonds (Sang et al., 2008).

Finally, the gel structure can be destructed (Kaur et al., 2008) in the thermal process due to the ‘melting’ of the crystalline region, disentanglement of the amylopectin molecules in the swollen particles, or the loss of interaction between particles in the network (Hsu, Lu, & Huang, 2000).

3.3. Physicochemical characteristics of starch granules related to their retrogradation

The starch retrogradation occurs after gelatinization. This process consists in the recrystallization of the amylopectin of the gelatinized starch granules (Duran, Leon, Barber, & de Barber, 2001) passing from an amorphous or disordered initial state to a more crystalline and ordered state. All that is reflected in the tendency of starch pastes to thicken and become stiff gels (Aee, Hie, & Nishinari, 1998). The starch retrogradation is favored by affected by some characteristics of the starch and the process by which it is subjected. The amylose content and the amylose-lipid complex are two of the factors that limit starch retrogradation (Stevenenbo et al., 2006). Starches with higher amylose content and lower molecular weight undergo higher retrogradation (Mali et al., 2004). The starch granule size also affects the retrogradation being the larger ones the most stable. Therefore, the smaller starch granules are the easiest to retrograde (Tang et al., 2004). However, the starch granule has little influence on retrogradation when there is more variation in the granule characteristics. Thus, B-type starch granules with less amylose content, shorter branched chain amylopectin and higher quantity of lipids are more difficult to retrograde than A-type granules (Ao & Jane, 2007). The retrogradation properties of the small starch granules seem to disagree with the swelling power. To understand this is necessary to take in mind the starch granule characteristics, although it is difficult to find a universal law for all starches (Tang et al., 2004).

Barley grains with high amylose quantity have higher retrogradation level than normal and low amylose barley. This occurs even when high amylose grains show higher crystallinity and lower proportion of small starch granules (Stevenenbo et al., 2006). Another aspect that affects retrogradation is amylopectin. Starch formed by amylopectin with high content of short chains has higher retrogradation when is left stored for long time. Mali et al. (2004) noted that starch samples stored seven days underwent higher retrogradation than those stored for 24 h. Additionally, the handling process imposed on the grains can also affect the retrogradation. Both the cutting force and the local heat during milling can contribute to the retrogradation of the starch molecules (Chen et al., 2010).

3.4. Industrial applications of starch according to its physicochemical and functional properties

Some physicochemical properties of starches such as hydration at high temperatures, swelling, increasing viscosity and gelation capacity are important in industrial processes. In this regard, some examples are expressed to relate the structural characteristics and thermal properties for starches with their possible end uses.

Starches from different sources are used to manufacture bakery products, desserts, puddings, fillings for cakes, biscuits, candies, sweet gums, gum, etc. Also, they are used on an industrial scale in stationery, adhesives, bio-packages, glue, flocculants, hydrocolloids, gums, dextrins (Philippe, 1995), in the elaboration of starch nanocrystals (Angellier, Molina-Boisseau, Dole, & Dufresne, 2006), resistant starch (Topping & Clifton, 2011), as well as in the encapsulation of various food components, such as probiotics that increase the number of beneficial bacteria in the intestine (Fuentes-Saragoza et al., 2011). The ability to relate the starch structure within the suitable manufacturing process depends on the genetic knowledge, environmental factors that control the starch biosynthesis and the granule morphology, well as how the material is processed (Copeland et al., 2009).

Large and small starch granules from wheat and barley have different behavior in baking and brewing, respectively (MacGregor & Morgan, 1986). The rice starch properties have a significant effect in the eating and cooking quality of the rice (Bao et al., 2002). The highly branched glucans may have greatly desirable applications in the beverage industry for their high solubility in water (Lee et al., 2008). High amylose, normal and waxy barleys differ slightly in their amylopectin structure but show different responses to annealing. This is influenced by differences in the amylose/amylopectin ratio and agglomerated structure of the starch chains in the crystalline and amorphous regions of native starches (Waduge, Hoover, Vasanthan, Gao, & Li, 2006).

The starch can be chemically modified by acetylation, hydroxypropylation and cross-linking (Singh, Kaur, & McCarthy, 2007). Chemical modification involves the introduction of functional groups into the starch molecule, resulting in much altered physicochemical properties. Such modification of native starch granules strongly alters their gelatinization, pasting and retrogradation behavior (Choi & Kerr, 2003). Factors such as starch composition, heterogeneity of the granule population from an only source of starch and reaction conditions can affect the starch during chemical modification (Singh et al., 2007). Enzymatic modification can be used to obtain variations in amylose and
amylopectin. It is possible to obtain modified branched amylopectin, branched amylose, high branched cluster amylopectin and high branched amylose. The solubility of high branched cluster amylopectin is significantly increased as compared with the previous ones. Therefore, highly branched glucans may have greatly desirable applications in the beverage industry (Lee et al., 2008). The point on starch granules that could be attacked by enzymes or salts depends on the amylase and amylopectin organization in the cluster (Koch & Jane, 2000). Higher amounts of amylopectin make the starch to be less susceptible to enzymatic hydrolysis (Asare et al., 2011). Changes in the physicochemical, morphological, thermal and rheological properties of starch after modification can provide the advance to understand the efficiency of the starch modification in the industry (Singh et al., 2007). The growing demand for high-quality food products by consumers has allowed the development of innovative technologies and ingredients such as resistant starch. This is produced in almost all starchy food and has a long history as a food source for humans (Fuentes-Saragoza et al., 2011). This is due to its functional properties and potential benefits to health (Sajilata, Singhal, & Kulkarni, 2006). The nutritional value of resistant starch is related to the physiological effects similar to those of dietary fiber (Fuentes-Saragoza et al., 2011). Like functional fiber, fine particles and mild flavor make it possible to formulate several food products with better flavor than providing traditional fibers and greater acceptability by the consumers (Sajilata et al., 2006). Resistant starch includes the proportion of starch that resists digestion in human pancreatic amylase in the small intestine and thus reaches the colon (Fuentes-Saragoza et al., 2011). To elaborate resistant starch, native starch is subjected at high temperatures, enzymatic hydrolysis, and retrogradation (Gao, Li, Jian, & Liang, 2011). The development of resistant starch depends on amylose content (Li et al., 2008). High amylopectin content is favorable for its manufacturing (Gao et al., 2011). In addition, the crystal structure is more resistant to enzymatic hydrolysis, resulting in better resistant starch content (Li et al., 2008).

Resistant starch is ideal for use in ready to eat cereals, snacks, noodles, baked products and fried foods. In addition, permits for labeling are simple (Sajilata et al., 2006). Generally, some factors, such as particle size distribution, particle-particle interaction, the fraction of packed particles and continuous phase viscosity, can affect the rheological properties of starch, being the molecular weight a key factor (Chen et al., 2010). The amylopectin content affects the starch functional properties, although variations in the molecular structure of amylopectin create uncertainty in the prediction of the functional properties of amylose alone (Copeland et al., 2009). Furthermore, differences in functional properties may be caused by differences in gelatinization characteristics of both types of granule size (Sahlström, Bævre, & Brathen, 2003).

Formation of films with dilute starch solutions follows the order: helical formation, aggregation or gelation and retrogradation of the aggregates. The first step or process is impulse by the cooling and the last two through dehydration (Liu & Han, 2005). The ability of the starches to form films depends on amylose content (Mali et al., 2004) and the solid concentration. This is due to the amylose content that has a significant effect on the formation and aggregation of the double helix (Liu & Han, 2005). However, the final characteristics of the plasticizer films (Mali et al., 2004), such as solubility (Montaño-Leyva, Torres-Chávez, Ramírez-Wong, Plascencia-Jatomea, & Brown-Bojórquez, 2008), are strongly influenced by the interactions of amylopectin and plasticizers (Mali et al., 2004). Also, the starch granule structure and size influence the mechanical properties of the films. The starch granule type has a significant effect on the extensibility of the formed films (Montaño-Leyva et al., 2008). Molecular, physics and functional properties of starches extracted from different botanical sources, determine the different properties of films formed with these starches. The amylose content affects the opacity and strength of starch films and gels. The molecular profile of amylopectin influences the film properties (Mali et al., 2004). Films elaborated with amylose have a 4-fold dendrites pattern. Films of amylopectin show a biphasic structure in which the branching network is embedded in an amorphous background. Films elaborated with amylose/amylopectin (50/50) have a biphasic structure similar to amylopectin. The two phases are composed of molecular and supramolecular interactions among amylose and amylopectin through the helical formation and the packaging (Liu & Han, 2005). Understanding the relationship between molecular profiles and film properties is useful in selecting the starch source according to the application of the film (Mali et al., 2004). In addition, understanding the characteristics of film formation is important to produce starch films or coatings with desirable microstructures that determine their functionality (Liu & Han, 2005). Starches with amylopectin with a high degree of short chains favor the interactions and rearrangement of the chains. This contributes to the formation of starch films with compact, opaque and strong matrix (Mali et al., 2004).

The starch semicrystalline structure allows the production of nanoelements. Starch nanocrystals result from the breakdown of the amorphous domains of semicrystalline granules by acid hydrolysis. Starch nanoparticles are produced by the starch gelatinization (Le Corre, Bras, & Dufresne, 2010). One of the interests using starch nanocrystals is the possibility to adjust the thermoplastics starch properties and control their evolution over time (Angellier et al., 2006).

4. Conclusion
Starches of diverse sources differ in their chemical composition and in structural characteristics of their glucans and granules due to genetic, environmental and nutritional factors to which plants are exposed during their development. In the inner part of the starch granules amylose, lipids, phosphorylated residues, and long lateral chain amylopectin interact between them avoiding the water uptake. In contrast, a high percentage of amylopectin, especially that with short lateral chains, allow hydration via hydrogen bond more freely which produces gels susceptible to retrogradation when stored for a long time. Smaller starch granules have a bigger superficial area that allows fast hydration, however, surface pores and channels on the surface of starch granules enhance the water uptake. Thus, higher hydration rates increase the swelling, viscosity, and gelatinization capacity of starch granules. However, the set of chemical compounds found on the starch granule and their interactions are also involved in the thermal properties of starches.
Acknowledgments

Author Yaeel I. Cornejo-Ramírez acknowledges the Consejo Nacional de Ciencia y Tecnología (CONACyT, Mexico) for providing a doctoral fellowship.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by Consejo Nacional de Ciencia y Tecnología (CONACyT) of Mexico [grant number 270837].

ORCID

Yaeel I. Cornejo-Ramírez https://orcid.org/0000-0002-6865-0531
Oliver Martinez-Cruz https://orcid.org/0000-0002-3797-666X
Carmen Lizette Del Toro-Sánchez https://orcid.org/0000-0001-7029-7741
Francisco Javier Wong-Corral https://orcid.org/0000-0003-1647-8001
Jesús Borboa-Flores https://orcid.org/0000-0002-4539-7019
Francisco Javier Cinco-Moroyoqui https://orcid.org/0000-0001-8599-702X

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