Physicochemical properties, modifications and applications of starches from different botanical sources

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Abstract

Present trends towards technologies and processes that increase the use of residues make starchy vegetal biomass an important alternative material in various applications due to starch's versatility, low cost and ease of use when its physicochemical properties are altered. Starch is increasingly used in many industrial applications and as a renewable energy resource. Starch can be modified to enhance its positive attributes and eliminate deficiencies in its native characteristics. In this article, the state of knowledge on conventional and unconventional starches and their properties, characteristics, modifications and applications are reviewed.

Keywords: starch modification; starch granules; paste properties; conventional starch; unconventional starch; starch biomass; food.

Practical Application: Use of unconventional starches and vegetal residues containing starch in industry.

1 Starch

Starch is the most abundant carbohydrate reserve in plants and is found in leaves, flowers, fruits, seeds, different types of stems and roots. Starch is used by plants as source of carbon and energy (Smith, 2001). The biochemical chain responsible for starch synthesis involves glucose molecules produced in plant cells by photosynthesis. Starch is formed in the chloroplasts of green leaves and amyloplasts, organelles responsible for the starch reserve synthesis of cereals and tubers (Smith, 2001; Tester et al., 2004). Starch production in the chloroplast is diurnal and performed rapidly by the plant. Conversely, starch reserves produced by amyloplasts are deposited over several days, or even weeks. Starch is stored and cyclically mobilized during seed germination, fruit maturation and the sprouting of tubers (Ellis et al., 1998). The main location of starch synthesis and storage in cereals is the endosperm. Major starch sources are cereals (40 to 90%), roots (30 to 70%), tubers (65 to 85%), legumes (25 to 50%) and some immature fruits like bananas or mangos, which contain approximately 70% of starch by dry weight (Santana & Meireles, 2014). The accumulation pattern of starch granules in each plant tissue, shape, size, structure and composition is unique to each botanical species (Smith, 2001).

Starch synthesized by plant cells is formed by two types of polymers: amylopectin and amylose. Amylopectin consists of linear chains of glucose units linked by α-1,4 glycosidic bonds and is highly branched at the α-1,6 positions by small glucose chains at intervals of 10 nm along the molecule's axis; it constitutes between 70 to 85% of common starch (Durrani & Donald, 1995). Amylose is essentially a linear chain of α-1,4 glucans with limited branching points at the α-1,6 positions and constitutes between 15-30% of common starch. Starch's structural units, amylose and amylopectin, are shown in Figure 1. The polymodal distribution

of α-glucans chains of different sizes and the grouping of branch points in the amylopectin molecule allow the formation of double helical chains. Amylose and amylopectin can be arranged in a semicrystalline structure forming a matrix of starch granules with alternating amorphous (amylose) and crystalline (amylopectin) material, which is known as the growth rings in superior plant starch (Jenkins et al., 1993).

Several types of starches are known as "waxy" starches due to the waxy appearance of the endosperm tissue from which they are derived; these tissues contain a minimal amount of amylose in their granule composition (<15%). Waxy starch requires high energy for gelatinization due to its high crystallinity (Hung et al., 2007). Other starches have a high content of amylose (>30%); these starches can also contain other polysaccharide molecules and exhibit a slight deformation in granule appearance.

Cereal starches contain lipid molecules in their structures in the form of phospholipids and free fatty acids; they are associated with the amylose fraction (Ellis et al., 1998; Tester et al., 2004). The presence of lipid complexes in starch granules is observed as a hydrophobic nucleus situated within helices formed by amylose chains. The lipid complexes vary between 0.15 to 0.55% of the amylose fraction in cereal starches (Tester et al., 2004). Lipids in starch granules, despite representing a small fraction, can significantly reduce the swelling capacity of the starch paste (Morrison & Azudin, 1987). Starch contains approximately 0.6% of protein associated with the molecule. The origins of protein and lipids on starch are situated on the granule surface. Lipids and proteins in starch granules can raise its functionality. In wheat for example, the associated protein in the starch granules receives a lot attention due to its association with grain
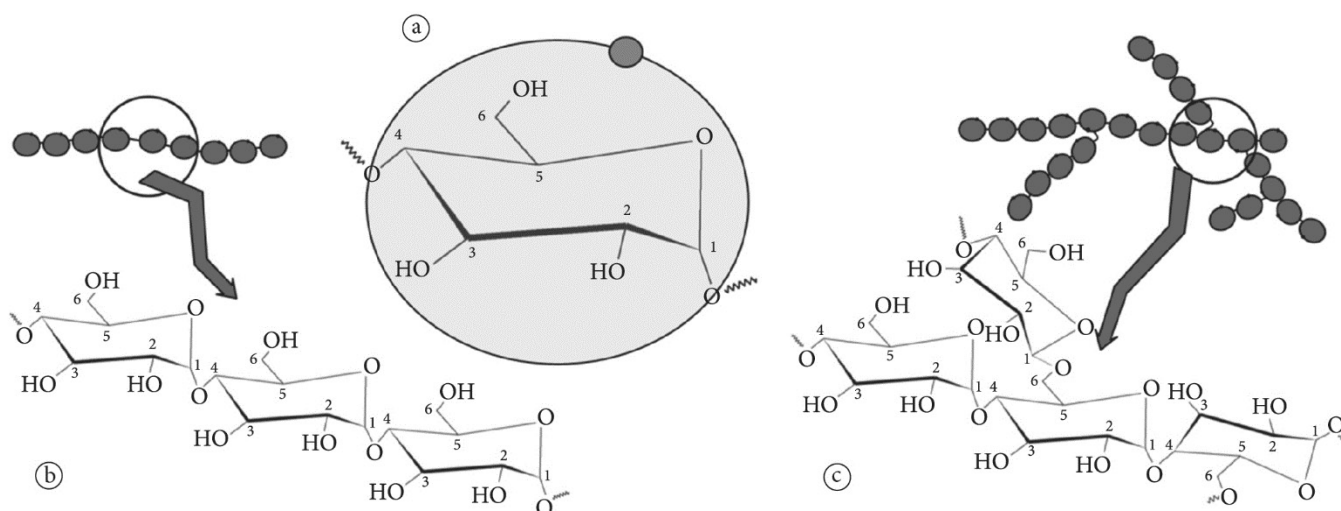
Figure 1. Basic structural design of (a) glucose units, (b) amylose and (c) amylopectin, along with the labeling of the atoms and torsion angles. Extension of the basic units to macromolecular structures was adapted from Pérez & Bertoft (2010).

hardness. Starch also contains a relatively small quantity (<0.4%) of minerals (calcium, magnesium, phosphorus, potassium and sodium). Among these, phosphorus is of primary importance and is present in starch in three main forms: monophosphate esters, phospholipids and inorganic phosphate.

The physical and chemical aspects of starch synthesis and the composition of amylose and amylopectin have been discussed in detail in other reviews by Smith (2001), Tester et al. (2004), Pérez & Bertoft (2010) and Conde-Petit et al. (2001).

2 Physicochemical properties of starch

The length of the α-glucan chains, amylose-amylopectin ratio and branching degree of amylopectin define the size, structure and particular utility of starch granules in each plant species. Other characteristics associated with the granule such as form, surface type and phosphate groups influence the starch's properties and uses (Smith, 2001).

2.1 Characteristics of starch granules: morphology, size, composition and crystallinity

Starch granules have microscopic sizes with diameters ranging from 0.1 to 200 μm, and its morphology varies between different shapes, such as oval, ellipsoidal, spherical, smooth, angular and lenticular, depending on the botanical source (Buléon et al., 1998; Hoover, 2001; Singh et al., 2003). Size distribution can be uni-, bi-, or polymodal. In amyloplasts, starch granules are present individually or in groups (Jane et al., 1994; Pérez & Bertoft, 2010). Common cereals such as wheat, barley and rye contain two types of starch granules: (i) A-type, lenticular shape and large size and (ii) B-type, spherical shape and small size (Tester et al., 2006; Vamadevan & Bertoft, 2015). The physicochemical properties of certain native starches are listed in Table 1. Starch granules are typically isolated before microscopic observation, and the isolation method is important because it can potentially affect the starch's original size (Gao et al., 2014; Lawal et al., 2011).

Granule morphology typically contains a central line known as the hilum or "Maltese cross". Each starch granule may contain one or more Maltese crosses, and this characteristic reduces the birefringence ability of the starch granule (Jiang et al., 2010).

The amount of amylose present in the granule significantly affects the physicochemical and functional properties of starch. The amylose content can vary within the same botanical variety because of differences in geographic origin and culture conditions (Gao et al., 2014). Researchers have highlighted the role of amylose in the initial resistance of granules to swelling and solubility, as swelling proceeds rapidly after leaching of amylose molecules. The capacity of amylose molecules of form lipid complexes prevents their leaching and consequently the swelling capacity (Singh et al., 2003). Amylose is anhydrous and can form excellent films, which are important characteristics for industrial applications. Films formed by amylose are very strong, colorless, odorless and tasteless (Campos et al., 2011).

Phosphorus is one of the non-carbohydrate components present in the starch granule and significantly affects its functional characteristics. Phosphorus is present as monoester phosphates or phospholipids in various types of starches. Monoester phosphates are associated with the amylopectin fraction by covalent bonds, increasing the clarity and viscosity of the paste, whereas the presence of phospholipids results in opaque and low viscosity pastes (Craig et al., 1989). The phospholipid content in starch granules is proportionally related to amylose. Phospholipids tend to form complexes with amylose and long branches of amylopectin, resulting in starch granules with limited solubility (Morrison et al., 1993; Singh et al., 2003). The nature of the phosphorus in starch granules has an important influence on the transmittance of the paste. Starches such as wheat and rice with high phospholipid contents produce pastes with low transmittance power compared to potato or corn starch pastes because the latter starches contain less phospholipids. Potato starch demonstrates high transmittance due to its phosphate monoester content (Singh et al., 2003).

Table 1. Morphology and composition of native starch granules from various sources.

Species	Variety/ Designation	Granule Shape	Diameter (μm)	Lipid (%w/w)	Protein (%w/w)	Phosphorus (%w/w)	Amylose (%w/w)	Degree of crystallinity/ Crystalline type
Wheat	Wild type	Spherical and lenticular (Singh et al., 2003)	< 30 (Singh et al., 2003) 22-36 (Jane et al., 1994)	0.08-0.12 (Buléon et al., 1998)	0.2-0.3 (Šubarić et al., 2012)	0.40 (Sang et al., 2007)	25.6±1.0 (Hung et al., 2007)	27.7±2.7/A (Hung et al., 2007)
	Waxy	A-type: Spherical or ellipsoidal (Zhang et al., 2013) B-type: Disc-shape and lenticular	A-type: >10 (Zhang et al., 2013)	0 (Morrison et al., 1984)			1.0±0.5 (Hung et al., 2007)	30.0±2.1/A (Hung et al., 2007)
	High amylose		B-type: < 10 (Zhang et al., 2013)				37.5±1.0 (Hung et al., 2007)	9.4±2.5/C (Hung et al., 2007)
Barley	Wild type	A-type: Disc-shape (Ellis et al., 1998) B-type: lenticular (Ellis et al., 1998)	A-type:10-25 (Ellis et al., 1998) B- type: 5 (Ellis et al., 1998)	0.7-1.2 (Morrison et al., 1984)	0.2-0.4 (Ellis et al., 1998)		19-22.1 (Ellis et al., 1998) 25.3-30.1 (Morrison et al., 1984)	
	Waxy		A-type:10-25 (Ellis et al., 1998) B- type: 5 (Ellis et al., 1998)	0.3-0.5 (Morrison et al., 1984)	0.06-0.15 (Ellis et al., 1998)		1.8-3.6 (Ellis et al., 1998) 2.1-8.3 (Morrison et al., 1984)	
	High amylose		A-type: 15-32 (Ellis et al., 1998) B-type :2-3 (Ellis et al., 1998)	1.0-1.7 (Morrison et al., 1984)			18.2-24.1 (Ellis et al., 1998) 38.4-44.1 (Morrison et al., 1984)	
Sorghum	Wild type	Polygonal, dented and round (Wankhede et al., 1989)	8-14,5 polygonal, 8-10 round (Wankhede et al., 1989)	0.8 (Emmambux & Taylor, 2013)	2.3 (Emmambux & Taylor, 2013)		23.7-27.6 (Boudries et al., 2009)	26-30/A (Boudries et al., 2009)
	Waxy	Larger than normal sorghum (Lawal et al., 2011)	5-25 (Sang et al., 2008)		< 0.3 (Sang et al., 2008)		3.5 (Sang et al., 2008) 0 (Sang et al., 2008)	
	Heterowaxy						14 (Sang et al., 2008)	
Rice	Wild type	Angular, polygonal (Hoover et al., 1996)	< 20 (Singh et al., 2003) 2-8 (Hoover et al., 1996; Patindol et al., 2015)	0.6-1.4 (Dhital et al., 2011)	0.1 (Hoover et al., 1996)	0.1 (Lim et al., 1994)	21-25 (Patindol et al., 2015)	
	Waxy						0-2 (Patindol et al., 2015)	
	High amylose						> 25 (Patindol et al., 2015)	
Corn	Wild type	Angular (Singh et al., 2003)	11.5± 0.3 (López et al., 2010)	0.6-0.8 (Dhital et al., 2011) 0.3-0.53 (Morrison et al., 1984)	0.4 (Dhital et al., 2011)	0.31-0.35 (Sang et al., 2007)	28.5 Nuwamanya et al., 2013) 23.86 ± 0.66 (López et al., 2010) 25.8-32.5 (Morrison et al., 1984)	19.2 ±1.4/A (López et al., 2010)
	Waxy			0.01-0.05 (Morrison et al., 1984)			1.4-2.7 (Morrison et al., 1984)	
	High amylose	Polygonal and Angular (Ellis et al., 1998)		0.38-0.67 (Morrison et al., 1984)		0.02 (Lim et al., 1994)	70 (Lim et al., 1994) 42.6-67.8 (Morrison et al., 1984)	

Lipid, protein and phosphorus contents are shown as % of total dry weight.

Table 1. Continued...

Species	Variety/ Designation	Granule Shape	Diameter (µm)	Lipid (%w/w)	Protein (%w/w)	Phosphorus (%w/w)	Amylose (%w/w)	Degree of crystallinity/ Crystalline type
Potato		Smooth-surfaced, oval and irregular (Singh et al., 2003)	< 110 (Singh et al., 2003)	0.1 (Dhital et al., 2011)	0.1 (Dhital et al., 2011)	0.6 (Dhital et al., 2011)	29.3±0.2 (Yuan et al., 2007)	45.9±0.6/B (Yuan et al., 2007)
Sweet Potato		Polygonal (Jane et al., 1994)	5-25 (Jane et al., 1994)				28.9±0.35 (Tan et al., 2006)	
Cassava		Flake-shape and irregular (Falade & Akingbala, 2010)	5-25 (Jane et al., 1994)	0.2 (Vasanthan & Hoover, 1992)	0.3 (Leelavathi et al., 1987)	0.01 (Lim et al., 1994)	23.7±0.1 (Yuan et al., 2007) 8-25 (Paes et al., 2008)	48±0.2/A (Yuan et al., 2007) 12-15/B (Paes et al., 2008)
Turmeric		Polygonal and Angular (Braga et al., 2006)	5-70 (Braga et al., 2006)		0.6±0.1 (Braga et al., 2006)		48±3 (Braga et al., 2006)	
Ginger		Polygonal and Angular (Braga et al., 2006)	5-40 (Braga et al., 2006)		0.53±0.01 (Braga et al., 2006)		34±2 (Braga et al., 2006)	
Dioscorea			3-22 (Yuan et al., 2007)				26.3±0.2 (Yuan et al., 2007)	48.5±0.3/C (Yuan et al., 2007)

Lipid, protein and phosphorus contents are shown as % of total dry weight.

Starch granules have very complex structures. The complexity is built around variations in their composition (α-glucans, moisture, lipids, proteins and phosphorylation), component structure and variation between amorphous and crystalline regions. Amylose associated with large branches of amylopectin molecules comprise the amorphous region of granules, and amylopectin molecules with short branches comprise the crystalline region; therefore, a higher proportion of amylopectin in starch granules results in greater crystallinity (Cheetham & Tao, 1998). There are three types of crystalline structures: A-type characteristics from cereal starches, B-type found in tubers and C-type present in legumes (Singh et al., 2003). Crystalline structures are based on the double helix formed by the amylopectin molecule. In A-type structures, the amylopectin branches are short (polymerization degree of 6-15) and linked by α-1,6 bonds. A-type is characteristic of amylopectin ramifications. In B-type, the glucose chains are more polymerized and can act as bases where the branches are A-type or form branched amylopectin molecules. B-type chains are subdivided into B1, B2, B3 and B4. B1 chains have a polymerization degree between 15 and 25, and B2 chains are typically between 40 and 50; B3 and B4 are the highest. C-type crystallinity is a combination of the A- and B-types and consists of amylopectin molecules with non-reduced ends (Cheetham & Tao, 1998).

2.2 Birefringence and glass transition temperature (Tg)

Birefringence is the ability to doubly refract polarized light. All starch granules in their native form exhibit birefringence that is proportional to their crystalline structure. Birefringence patterns in starch granules represent the radial arrangement of amylopectin molecules, and their chains form 90° angles with the reduced ends in the direction of the hilum or starch granule center. Weak birefringence patterns are indicative of disorganization of the crystalline region (BeMiller & Whistler, 2009). Loss of birefringence in starch granules is associated with deformation due to its modification (Liu et al., 1991).

T_g is an important parameter affecting the physical properties of polymers. Glass transition occurs similar to a thermodynamic second order transition, where the specific volume and enthalpy are functions of temperature (Biliaderis et al., 1999). T_g describes the induction temperature of the progressive transition from an amorphous state to a rubbery state as the material is heated, generally in the presence of a solvent or plasticizer when referring to polysaccharides (Tester & Debon, 2000). Because starch consists of an amorphous and a crystalline region, the exact T_g is detected with difficultly.

2.3 Swelling capacity and solubility of starch granules

One of the most important structural characteristics of starch is that it passes through several different stages from water absorption to granule disintegration. Water absorption and consequent swelling of the starch granule contribute to amylopectin-amylose phase separation and crystallinity loss, which in turn promotes the leaching of amylose to the inter-granular space (Conde-Petit et al., 2001). When starch molecules are heated in water excess, the semi-crystalline structure is broken, and water molecules associate by hydrogen bonding to hydroxyl groups exposed on the amylose and amylopectin molecules. This association causes swelling and increases granule size and solubility (Singh et al., 2003). The swelling capacity and solubility of starch illustrate the interactions of the polymeric chains comprising the amorphous and crystalline granule fractions (Zhang et al., 2005). The extent of this interaction is influenced by the amylose-amylopectin proportion and is characteristic of each molecule depending on the polymerization degree, length and grade of chain branching, molecular weight and molecular conformation (Hoover, 2001; Ratnayake et al., 2002). The swelling capacity of starch is directly associated with the amylopectin content because the amylose acts as a diluent and inhibitor of

swelling (Singh et al., 2003). Some species of starch that contain amylose-lipid complexes exhibit swelling capacity and solubility restrictions (Morrison et al., 1993).

The swelling stage of starch granules is the initial step of all other paste characteristics. Initially, granule swelling is reversible, increasing its volume up to 30% (Gryszkin et al., 2014). Water absorption and heating of the starch dispersion breaks the hydrogen bonds responsible for granule cohesion, partially solubilizing the starch (Hoover, 2001). Water penetrates the interior of the starch granule, hydrating the linear fragments of amylopectin (Xie et al., 2008). This process leads to irreversible swelling, increasing the granule size several fold and the paste viscosity. Paste viscosity is essentially the principal measure of the potential application of starch in industry (Gryszkin et al., 2014; Sarker et al., 2013).

2.4 Gelatinization and retrogradation properties of starch

Starch, when heated in the presence of excess water, undergoes a transition phase known as gelatinization, and there is a characteristic temperature interval for gelatinization corresponding to each starch species. Gelatinization occurs when water diffuses into the granule, which then swells substantially due to hydration of the amorphous phase causing loss of crystallinity and molecular order (Donovan, 1979; Jenkins et al., 1993; Jiménez et al., 2012). The gelatinization process starts at the hilum and quickly spreads throughout the periphery. Gelatinization occurs initially in the amorphous region, favored by the weak hydrogen bonds present in this area. The process then extends to the crystalline region. Amylose presence reduces the fusion point in the crystalline region and the amount of energy necessary to initiate gelatinization (Sasaki et al., 2000). The gelatinization process is represented by transition temperatures and gelatinization enthalpies in the paste, and these measures are characteristic for each species. High transition temperatures correspond to a high degree of crystallinity, high stability and resistance of the granule structure to gelatinization (Tester et al., 2004). Gelatinization of starch granules is associated with a loss of birefringence and crystalline order due to the breaking of the double helix in the crystalline region and the leaching of amylose (Donovan, 1979; Evans & Haisman, 1982). This transitions starch from a semi-crystalline form (relatively indigestible) to an amorphous form that is easily digestible (Tester & Debon, 2000). Similar to water, other solvents are also used to promote gelatinization. The principal consideration with solvents is their capacity to form hydrogen bonds with the molecules in the starch granules (i.e., liquid ammonia, formamide, formic acid, chloroacetic acid and dimethyl sulfoxide). The gelatinization process is affected by solvent type and starch/solvent proportions (Jiménez et al., 2012). Gelatinization is necessary for particular processes, e.g., textile and hydrolyzed starch industries. Gelatinization affects the rheological properties and viscosity of the paste, making the starch granule more accessible to enzymatic action. When starch granules swell and its components are in solution, the medium properties change from a simple starch granules suspension to a starch paste. Amylose and amylopectin form separate phases because of thermodynamic immiscibility. In food, starch is typically in combination with other polymeric ingredients, such

as proteins and other polysaccharides, forming different phases (Conde-Petit et al., 2001). Gelatinization of granules is caused by many processes or the manufacturing of products from raw materials based on starch, especially cereals. Gelatinization progress along the granule is determined by the physicochemical properties of the starch, the presence of other ingredients, the availability of water and process parameters applied (i.e., temperature, time and mechanical energy) (Schirmer et al., 2015).

The molecular interaction produced after gelatinization and cooling of the paste is known as retrogradation (Hoover, 2000). During retrogradation, amylose molecules associate with other glucose units to form a double helix, while amylopectin molecules re-crystallize through association of its small chains (Singh et al., 2003). After retrogradation, starch exhibits lower gelatinization and enthalpy compared to native starch because its crystalline structure has been weakened (Sasaki et al., 2000). Initially, the amylose content exercises a strong influence over the retrogradation process; a large amount of amylose is associated with a strong tendency for retrogradation. Amylopectin and intermediate materials influence the retrogradation process during storage under refrigeration; each polymer has a different recrystallization rate (BeMiller, 2011; Conde-Petit et al., 2001). Recrystallization of starch easily occurs at temperatures under 0 °C, but also occurs above 100 °C. Starch retrogradation is intensified by repeated freezing and thawing of paste (Leszczyñski, 2004). Some research has shown that paste components such as proteins influence the retrogradation properties of paste through emulsification. Proteins form complexes with starch that retards the retrogradation process during refrigerated storage (Wu et al., 2010). The presence of other components in addition to proteins and lipids, such as other carbohydrates, salts and polyphenols, significantly affects retrogradation (Fu et al., 2015). In general, retrogradation in starch pastes, as well as foods containing starch, is unfavorable in terms of food quality, causing syneresis of gels or hardness. Currently, retrograded starch is classified as a form of resistant starch (RS) (Zięba et al., 2011) and is used in industry for different purposes described in other sections of this review.

2.5 Rheological and thermal properties

Starch paste forms immediately after gelatinization, and starch granules are increasingly susceptible to disintegration by shearing because they are swollen. The paste obtained is a viscous mass consisting of one continuous phase of solubilized amylose and/or amylopectin and one discontinuous phase of the remaining starch granules (Ambigaipalan et al., 2011). Starch functionality is directly related to gelatinization and the properties of the paste. All of these properties affect the stability of products, consumer acceptance and production reliability (Šubarić et al., 2012). The characteristics of the native starch, the effects of the physical or chemical modifications of the granules, the process parameters and the botanical sources of the starch are all critical factors governing the behavior and characteristics of the starch paste. The transformation of starch during manufacturing depends on the temperature-time-mixture ratio and the modification ratio during processing (Conde-Petit et al., 2001).

Starch granules are insoluble in cold water due to the hydrogen bonds and crystallinity of the molecule. When starch is dispersed in hot water below its T_g, the starch granules swell and increase several times in size, breaking the molecules and consequently leaching amylose to form a three-dimensional network and increase the paste's viscosity (Sarker et al., 2013). Starch paste can contain un-swollen granules, partially swollen granules, aggregates of swollen starch granules, fragments and molecules of retrograded starch and starch that has dissolved or precipitated (BeMiller & Whistler, 2009).

The presence of relatively short chains of amylose and amylopectin adds opacity to starch suspensions and foods containing them. In products such as sources, dressings and puddings, this opacity is not a disadvantage; however, jellies and fruit fillings require starch suspensions with high clarity (Eliasson, 2004). Paste clarity is commonly determined by the percent transmittance from a dilute solution of starch (1% w/w) at a wavelength of 650 nm (Bello-Pérez & Paredes-López, 1996; Ulbrich et al., 2015). Products like potato starch have transmittances between 42 to 96% and are considered high clarity pastes, followed by cassava starch at 51-81%. Common cereals generally present transmittances of 13 to 62% (Craig et al., 1989; Nuwamanya et al., 2013). Low clarity in common cereals (non-waxy) is due to the presence of traces of swollen starch granules (Craig et al., 1989) and amylose-lipid complexes (Bello-Pérez & Paredes-López, 1996). Clarity in starch suspensions is modified during storage, decreasing due to amylose and/or amylopectin molecules (Jacobson et al., 1997; Waterschoot et al., 2015a).

Rheological properties describe the behavior of materials subjected to shearing forces and deformation, which are considered viscoelastic complexes. The basic feature of starch rheology is its viscosity. Other rheological characteristics involve texture, transparency or clarity, shear strength and the tendency for retrogradation. All of these features play important roles in the commercial applications of starch (BeMiller & Whistler, 2009; Berski et al., 2011). Rheological starch properties are studied through the behavior of viscosity curves, which are influenced by temperature, concentration and shear stress (Singh et al., 2003). "Paste properties" is the term used to describe the changes that occur in starch after gelatinization in excess water. Instruments like the Rapid Visco Analyzer (RVA) describe the viscosity parameter as functions of temperature and time. The RVA describes paste behavior in three periods: (i) a controlled heating period, increasing the temperature of the suspension from room temperature to a maximum that is generally determined at 95 °C; (ii) an isothermal period, maintaining the suspension at the maximum temperature for analysis; and (iii) a cooling period, decreasing the temperature to approximately 50 °C. Throughout the analysis, the suspension is subjected to shear forces. Suspensions typically exhibit a peak in viscosity that starts after gelatinization and increases as the granules swell, followed by a decrease in viscosity due to granule disintegration and polymer realignment. A "Breakdown" is defined by a difference between the viscosity peak and the minimum viscosity at the maximum analysis temperature. During the cooling period, amylose leaching forms a gel or three-dimensional network. Gel formation further increases the viscosity, called the "cold paste viscosity". The difference between the paste viscosity at

the end of the cooling period and the minimum viscosity at 95 °C is termed the "setback" (Saunders et al., 2011; Wang & Weller, 2006).

Starch gels are composed of amylose chains and intermediate materials dispersed in a starch suspension after granule disintegration in a three-dimensional network structure. The level and nature of the leached material and molecular interactions determine the viscoelastic properties. Methods used to describe the viscoelastic parameters of the paste include equipment such as a dynamic rheometer, an amylograph or a viscoamylograph (Schirmer et al., 2015). Several parameters describe the viscoelastic behavior of pastes: (G'), the measure of recovered or accumulated energy in each deformation cycle and an indicator of the elastic behavior of the paste; the dissipated energy (G"), the loss of energy in each deformation cycle that describes the viscosity behavior of the material; and the modulus or tangent (G"/G'), describing the material's behavior (high values (›1) indicate liquid-like behavior, and low values indicate solid-like (<1) behavior) (BeMiller & Whistler, 2009; Waterschoot et al., 2015b). Gel resistance is determined using a texture analyzer, in which parameters such as peak force [N] define the resistance of the three-dimensional network (Ulbrich et al., 2015).

The main factors affecting the rheological properties of starches are their source and the presence of other polymers (Sarker et al., 2013; Schirmer et al., 2015). Many polymers coexist with starch in aqueous mixtures and interact in different ways to produce several attributes influencing the stability, texture and quality of food products. Starch paste viscosity is associated with lipids, mainly phospholipids, that complex with amylose and hinder or reduce the granule's swelling capacity. Other effects associated with paste viscosity are decreased amylose solubility, increased formation time and limited gelling properties. Amylose-lipid complexes require high temperatures for dissociation (Singh et al., 2003). Rheology is widely recognized for its effect on the quality of food and its sensory characteristics. The rheological properties of starch determine its potential application as a thickener or gelling agent (Berski et al., 2011). Determining the thermal properties of starch involves terms such as the onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), difference between T_c and T_o, and enthalpy of fusion, all of which can be measured using equipment like a differential scanning calorimeter (DSC) (Kong et al., 2012) and depend on the starch concentration (Waterschoot et al., 2015b). During heating, T_o is the temperature at which the paste viscosity starts to increase; T_p is the maximum viscosity temperature; and T_c is the final temperature of the viscosity increment. (T_c-T_o) is a comparative measure, and an increase in this value indicates a high amount of granule modification in the amorphous and crystalline regions (Jenkins et al., 1993; Kong et al., 2012). Some researchers include retrogradation among the thermal properties of starch. This paste property typically begins 20 °C lower than its gelatinization temperature (T_{gel}), and retrogradation is proportional to the presence of amylopectin (Tan et al., 2006; Yuan et al., 1993). Variations in a starch's thermal properties after gelatinization and throughout refrigerated storage can be attributed to variations in the amylose/amylopectin ratio, the size and shape of the granule, and the presence or absence of lipids and proteins (Singh et al., 2003; Tan et al., 2006).

3 Starch modification

Starch is rarely consumed in its intact form and frequently used by industry in its native form. Most native starches are limited in their direct application because they are unstable with respect to changes in temperature, pH and shear forces. Native starches show a strong tendency for decomposition and retrogradation (Berski et al., 2011). Additionally, some starch granules are inert, insoluble in water at room temperature, highly resistant to enzymatic hydrolysis and consequently lacking in functional properties. Native starches are often modified to develop specific properties such as solubility, texture, adhesion and tolerance to the heating temperatures used in industrial processes (Singh et al., 2007; Sweedman et al., 2013).

Several methods have been developed to produce modified starches with a variety of characteristics and applications. All of these techniques alter the starch polymer, making it highly flexible and changing its physicochemical properties and structural attributes to increase its value for food and non-food industries (López et al., 2010). The starch modification industry is constantly evolving. Modifications of starch include physical, chemical and enzymatic methods (Yadav et al., 2013). Physical methods involve the use of heat and moisture, and chemical modifications introduce functional groups into the starch molecule using derivatization reactions (e.g., etherification, esterification, crosslinking) or involve breakdown reactions (e.g., hydrolysis and oxidation) (Singh et al., 2007; Wurzburg, 1986).

3.1 Physical modification of starch

Physical modifications of starch can improve its water solubility and reduce the size of the starch granules. Physical methods to treat the native granules include: different combinations of temperature, moisture, pressure, shear and irradiation. Physical modification of starch granules is simple, cheap and safe. These techniques do not require chemical or biological agents, and are therefore preferred when the product is intended for human consumption (Ashogbon & Akintayo, 2014). Table 2 gives examples of different research on the physical modification of starch.

Pre-gelatinized starch (PGS)

Pre-gelatinized starch (PGS) is starch that has undergone a cooking process until complete gelatinization and a simultaneous (or subsequent) drying process. Drying methods include drum drying, spray drying and extrusion. The main consequence of this treatment is the destruction of the granular structure, resulting in complete granular fragmentation, and the absence of birefringence properties. The principal properties of PGS are an increase in swelling capacity, solubility and cold water dispersion. PGS functionality depends on the cooking conditions, drying and the starch source (Ashogbon & Akintayo, 2014). Of the physically modified starches, PGS is primarily used as a thickener in many instantaneous products, such as baby food, soups and desserts, due to its ability to form pastes and dissolve in cold water. The use of PGS is preferred in sensible foods because it does not require heating to form a paste (Majzoobi et al., 2011).

Hydrothermal modification

This physical modification involves changes in the physical and chemical properties of the starch without destroying the granule structure (Zavareze & Dias, 2011). Physical modifications occur at temperatures above the T_g and below the T_{gel} of the starch granules (Tester & Debon, 2000). Essentially, hydrothermal modification can only occur when starch polymers transition from the amorphous region to the semicrystalline region. Starch in its native form exhibits amylopectin ramifications by forming a double helix chain, and this behavior imparts a crystalline structure to the starch molecule. Heat treatment involving temperatures between the T_g and melting temperature (T_m) may not alter the double helix conformation or degree of starch crystallinity; these conditions are present when starch pastes are drying. Physical modification of starch performance improves starch paste characteristics such as texture and plasticity by reducing T_g and consequently relaxing the hydrogen bonds and polymer-polymer interactions. The presence of water reduces the T_m (Conde-Petit et al., 2001). Hydrothermal modification is differentiated into annealing and hydrothermal treatments (Collado & Corke, 1999).

a) **Annealing (ANN)** is a physical treatment of starch granules in which the parameters of moisture, temperature and heating time determine the results obtained (Tester & Debon, 2000). The ANN process requires an excess of water (76% w/w) or an intermediate containing water (40% w/w) (Jacobs & Delcour, 1998). The objective of this treatment is to improve the molecular mobility. ANN is associated with a physical reorganization of the starch granule in the presence of water (Tester & Debon, 2000). Water is a suitable plasticizer for starch. Starch granule hydration causes a transition from a glassy to a static state, increasing the mobility of the amorphous regions to a crystalline state. These changes generate tangential and radial movements in the crystalline and amorphous regions, and physicochemical modifications increase chain interaction in the crystallinity region (Chen et al., 2014). The ANN process is associated with partial gelatinization of starch Tester & Debon (2000) state that the ANN term can only be used when the temperature of the process does not reach T_{gel} and therefore gelatinization does not occur. In ANN starch, the T_{gel} after modification is not less than the T_{gel} of the native starch. The ANN process has important industrial applications, imparting different characteristics to products due to an increase in starch granule size, thermal stability, T_{gel} and the availability of starch to digestion by enzymes such as α-amylase. However, there is no justification for its use in terms of energy and time because many cheaper chemical processes can modify starch properties rapidly and selectively, making them more competitive than ANN.

b) **Hydrothermal treatment (HMT).** This treatment includes a thermal application in the presence of a limited amount of water (typically less than 35% w/w) and a process time between 15 min to 16 h (Jacobs & Delcour, 1998). The effects of this treatment on the morphological and physicochemical

Table 2. Physical modification of starch.

Type of physical modification	Starch source	Parameters studied	Observed results	References
Pre-Gelatinization	Rice flour Rice starch	Temperature (100 °C) Time (20 min) Suspension[a] 35% (w/v) Storage (4 °C /7 days) Drying by lyophilization	The retrogradation process was delayed; rice flour was more susceptible to modification.	(Wu et al., 2010)
	Commercial wheat starch	Suspension[a] 10% (w/v) Drying by double drum: temperature (158 °C), pressure (5 bar)	Increased solubility and swelling capacity; viscosity initiated at 25°C[b].	(Majzoobi et al., 2011)
	Wheat starch	Suspension[a] 37% (w/v) Drying by drum: temperature (150 °C), pressure (5 bar)	Increased solubility, swelling capacity and viscosity[b].	(Li et al., 2014)
Hydrothermal modification				
Annealing	Water chestnuts (*Eleocharis dulcis*)	Temperature (65 °C) Time (24 h) Suspension[a] 35% (w/v)	Reduction of swelling capacity, solubility and viscosity[b].	(Yadav et al., 2013)
	Yam starch	Temperature (50 °C) Time (24 h) Suspension[a] 33% (w/v)	Reduction of granule density and swelling capacity[b].	(Falade & Ayetigbo, 2015)
	Polylactic acid (PLA) and commercial corn starch mixture	Suspension[a] 40% (w/v) Temperature (50, 60, 80, 100 and 120 °C)	Increase in crystallinity associated with the process temperature. Increased thermal stability and mechanical properties[b].	(Lv et al., 2015)
Hydrothermal Treatment (HTM)	Water chestnuts (*Eleocharis dulcis*)	Temperature (110 °C) Time (16 h) Suspension[a] 70, 75 and 80% (w/v)	Reduction of stability, solubility and viscosity of the starch paste[b].	(Yadav et al., 2013)
	Cassava (*Manihot esculenta* Crantz), Arrowroot (*Maranta arundinacea*), Sweet potato (*Ipomoea batata*)	Temperature (80, 100 and 120 °C) Time (6,10 and 14 h) Suspension[a] 50, 70 and 85% (w/v)	Reduction of paste clarity and swelling capacity of starches. Increase in solubility and stability[b].	(Jyothi et al., 2010)
	Potato Starch	Temperature (120 °C) Time (3 h) Suspension[a] 70, 75 and 80% (w/v) pH (5.6 and 6.5)	Reduction in swelling capacity of granules and amylose leaching. Acidity during treatment decreased the modification time and promoted acid hydrolysis in starch with lower levels of RS[b].	(Kim & Huber, 2013)
	Yellow sweet potato (*Ase jantan*) flour Purple sweet potato (*Ayamurasaki*) flour	Temperature (50 and 77 °C) Time (3 and 6 h) Suspension[a] 70% (w/v)	Increasing the operating temperature decreased the paste viscosity. HMT showed a reduced swelling capacity in the granules and amylose leaching[b].	(Putri et al., 2014)
	Rice Starch Rice flour	Temperature (100 °C) Time (16 h) Suspension[a] 70, 75 and 80% (w/v)	HMT primarily affected the paste properties of rice flour. The authors attributed these differences to presence of protein in the rice flour.	(Puncha-Arnon & Uttapap, 2013)
	Ginger and turmeric (Residues of supercritical fluid extraction-SFE)	Treatment assisted with high pressure using subcritical water and CO_2 Suspension[a] 33% (w/v) Pressure (150 bar) Time (11 min) Ginger: Temperature (200 °C) Turmeric: Temperatures (130, 150 and 180 °C)	Subcritical water was acidified by CO_2, producing hydrothermolysis. Modification of starch was monitored by sugar production (reducing and total reducing sugar).	(Moreschi et al., 2006)

[a]based on starch dry weight; [b]compared to native starch.

Table 2. Continued...

Type of physical modification	Starch source	Parameters studied	Observed results	References
Non-hydrothermal modification	Ginger (*Zingiber officinale* R.) Turmeric (*Curcuma longa* L.)	Treatment of SFE using CO_2 and a co-solvent. Ginger: Co-solvent (isopropyl alcohol, 1.5% v/v), temperature (35 °C), pressure (250 bar) Turmeric: Co-solvent (ethanol/isopropyl alcohol (1:1) mixture, 10% v/v), temperature (30 °C), pressure (300 bar).	SFE treatment did not alter granule morphology or amylose/amylopectin ratio. For ginger, the modification process reduced T_{gel} and the maximum viscosity. Turmeric starch showed the opposed behavior.	(Braga et al., 2006)
	Potato starch Wheat starch Corn starch Rice starch	Treatment using ultrasound Medium: Water and alcohol	Starches treated by ultrasound showed depolymerization of the granules. Modification of the paste properties[b]. Water was a better medium for starch modification.	(Sujka & Jamroz, 2013)
	Tapioca	Treatment with argon gas as a plasma Medium: Water Suspension[a] 40% (w/w)	During modification, two reactions occurred, crosslinking and depolymerization of the starch that may replace the chemical reactions.	(Wongsagonsup et al., 2014)

[a]based on starch dry weight; [b]compared to native starch.

properties of starch granules include important changes in crystalline structure, swelling capacity, gelatinization, paste properties and retrogradation (Hoover, 2010; Hormdok & Noomhorm, 2007; Jyothi et al., 2010). Structural and physicochemical changes generated by HMT are directly influenced by the botanical source of the starch granule with respect to its composition and organization of amylose and amylopectin. HMT is also used as a pre-treatment because of the structural modification into amorphous and crystalline regions on the granules. These alterations make the granule susceptible to chemical and enzymatic modifications and acid hydrolysis (Zavareze & Dias, 2011).

Non-thermal physical modification

Some processes in food production are applied to extend the life of a product using thermic treatments at boiling temperatures (or even higher) for seconds or minutes. Traditional treatments cause a loss of some vitamins and nutrients and alter their organoleptic properties. Non-thermal modification is an alternative to traditional processes that also eliminates pathogenic microorganisms and spores. Non-thermal techniques involve the use of high pressure, ultrasound, microwaves (Anderson & Guraya, 2006; Brașoveanu & Nemtanu, 2014; Hódsági et al., 2012; Mollekopf et al., 2011) and electric pulses. The high pressure technology in industry uses pressure from 400 to 900 MPa. High pressure generally restricts the swelling capacity and consequently decreases paste viscosity. Other technologies use pressure several times bellow atmospheric pressure (vacuum pressures); this technology uses gas in a plasma state and is the most recent technology used for starch granule modification (Deeyai et al., 2013; Wongsagonsup et al., 2014). Plasma is an ionized gas composed of several types of active ionic species: electrons, ions, excited atoms and protons (Bogaerts et al., 2002). For this treatment, the gases used include ethylene, hydrogen,

oxygen, ammonia, air, methane or argon in a plasma state. This treatment modifies the starch in different ways, including its hygroscopicity, degree of polymerization and oxidation (Wongsagonsup et al., 2014).

Modification of starch using microwaves involves several interacting mechanisms, such as irradiation, furnace dimensions and the characteristics of the starch. In the microwave irradiation process, the most important parameters are moisture and temperature, which influence the dielectric properties of the starch (Brașoveanu & Nemtanu, 2014). Starch modification by microwaves results from the rearrangement of starch molecules that generates changes in solubility, swelling capacity, rheological behavior, T_{gel} and enthalpies (Iida et al., 2008; Yu et al., 2013; Zuo et al., 2012). Depending on the starch source and moisture, modification by microwave also produces variations in morphology and crystallinity in the granule (Brașoveanu & Nemtanu, 2014).

The use of ultrasound is also considered a physical modification treatment. This treatment is applied to starches in suspension and starches that have undergone previous gelatinization (Iida et al., 2008; Yu et al., 2013; Zuo et al., 2012). Ultrasound primarily affects the amorphous region, while maintaining the granule's shape and size. The starch surface becomes porous, and properties such as the swelling capacity, solubility and viscosity of the paste are modified (Luo et al., 2008). Ultrasonic modification depends on the sound, frequency, temperature, process time and the starch suspension properties (i.e., concentration and botanical source of starch) (Zuo et al., 2009).

Other physical modification methods: grinding and extrusion

Large-scale extraction of starch from cereals such as wheat require grinding. Substantial granule damage occurs during grinding, and shear forces that compress the granule structure are generated. Damage to the starch granule is visible as cracks

in the starch surface. Grinding reduces the crystallinity of the amylopectin molecule and its double helix conformation severely. Fragmentation of the amylopectin molecule eliminates restrictions on the swelling capacity, thereby facilitating subsequent gelatinization. The easy gelatinization of the starch granules after grinding decreases parameters such as T_0 and enthalpies in the final starch product.

Extrusion is defined as a process at high temperatures and in short amounts of time (HTST), wherein starch granules are subjected to mechanical shearing forces in a relatively low moisture environment (Camire et al., 1990). Extrusion increases the T_{gel} of starch, changing the molecular extension and its associations, such as the amylose-lipid complex structure. The extrusion process also affects starch digestibility and can reduce the RS content (Martínez et al., 2014).

3.2 Chemical modification of starch

Chemical modification involves the introduction of functional groups on the starch molecule without affecting the morphology or size distribution of the granules. Chemical modifications generate significant changes in starch behavior, gelatinization capacity, retrogradation and paste properties (López et al., 2010). Food and non-food industries expand starch properties and improve them through chemical modifications. Table 3 shows examples of different chemical modifications of starch.

Cationic starch

Cationic starches are generally produced by reacting starch with compounds containing tertiary or quaternary ammonium, imino, amino, sulfuric or phosphate groups. Free hydroxyl ions present in the native starch molecule are commonly altered using cationic monomers such as 2,3-epoxypropyl trimethyl ammonium chloride (ETMAC) or 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CTA) in dry or wet processes. In dry cationic modification, in the absence of a liquid phase, the reactive is sprayed onto the dry starch during extrusion. The semi-dry method for cationization involves a mixture of starch and spray reagent prior to the thermal treatment. Wet cationization includes a homogeneous reaction with dimethyl sulfoxide (DMSO) or a heterogeneous reaction in alkaline solution. The physicochemical properties of the starch and granular structure are altered after the cationic process, particularly when the process involves a high degree of substitution. The cationic reaction reduces the paste temperature, increases the viscosity peak and results in various changes in starches from different sources. Among modified starches, cationic starch materials are preferred by the textile industry because the positive charge introduced in the molecular chains conform to the electrostatic bonds between the negative charges of the cellulose fibers (Hubbe, 2007). There are several applications for cationic starches (i.e., in water treatment as flocculants and as additives in textile products, paper and cosmetics), preferred for their low cost, excellent fit, biocompatibility and rapid degradation (Zhang, 2001).

Cross-linked starch

Crosslinking of a polymer occurs when linear or branched chains are covalently interconnected and is known as cross-linking or cross-ligation. The reagents used form ether or ester bonds with hydroxyl groups in the starch molecules (Singh et al., 2007). This modification increases the polymer's rigidity by forming a three-dimensional network. Crosslinking in starch increases the degree of polymerization and molecular mass; starch molecules lose water solubility and become soluble in organic solvents. Several agents are used to crosslink native starch: sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin (ECH) and phosphoryl chloride (POCl$_3$), among others (Woo & Seib, 2002).

Depending on the reagent used for crosslinking, the final product is classified in one of three types: i) monostarch phosphate produced by starch esterification with orthophosphoric acid, potassium or sodium orthophosphoric or STPP; ii) distarch phosphate produced when native starch reacts with STMP or POCl$_3$; or iii) phosphated distarch phosphate, resulting from combined treatments of monostarch and distarch phosphates (Gunaratne & Corke, 2007; Jyothi et al., 2006).

The source of starch granule, methods and parameters used for crosslinking modification has an important influence on the properties of the final product. Starch properties affected by crosslinking modification include the paste clarity and swelling capacity. Some authors suggest that both properties are linked, and a reduction in swelling is responsible for the decrease in paste clarity (Kaur et al., 2006; Koo et al., 2010). The degree of crosslinking also reduces the moisture, lipids and proteins associated with the native starch granule; these changes are produced by all of the aforementioned crosslinking agents in different proportions (Carmona-Garcia et al., 2009). In the food industry, cross-linked starch is associated with formulations of frozen products due to its stabilizing, thickening, clarity and retrogradation resistance properties of the pastes formed. Its uses also extend to other industries such as plastics (López et al., 2010).

Acetylated starch

Acetylation is a modification of polymeric starch molecules through the introduction of functional acetylated groups (CH$_3$CO) that react with free hydroxyl groups present in the branched chains of the starch polymer to produce a specific ester (Sweedman et al., 2013). Acetylation is the more common chemical modification method, resulting in native starch esterification using reactive reagents such as anhydrous acetic acid, vinyl acetate or OSA in the presence of an alkaline catalyst (NaOH, KOH, Ca(OH)$_2$, Na$_2$CO$_3$) (Wang & Wang, 2002). Starch modified with OSA is an effective emulsifier used in the food, pharmaceutical and cosmetic industries; in this modification, OSA adds hydrophobic chains to the hydrophilic structure of starch (Chen et al., 2014). The introduction of acetyl groups reduces the resistance of bonds between the starch molecules. Acetylated starch increases the swelling capacity and solubility compared to native starch (Berski et al., 2011). The presence of hydrogen bonds in acetylated starch is restricted due to electrostatic repulsion forces on the starch molecule (Lawal &

Table 3. Chemical modifications of starch.

Type of chemical modification	Starch source	Parameters studied	Observed results	References
Cationization	Waxy maize starch	Esterification reaction. Chemical reactive: 2,3-epoxypropil trimethyl ammonium chloride (EDMAC). pH (9.0)	Reduction in starch granule size and fragmentation. Esterification reaction is produced on the granule surface[a].	(Liu et al., 2015)
	Commercial potato starch	Halogenation and amination reactions. Chemicals reactive to halogenation: Epichlorohydrin and hydrochloric acid. Temperature (100 °C) Time (1 h) Amination agents: putrescine, histamine, cadaverine and tyramine. Temperature (60, 80 and 100 °C) Time (4, 8 and 12 h)	Researchers studied the effects of amine groups in cationization reactions. Due to sensible amine structures, lower temperatures gave better results.	(Anthony & Sims, 2013)
Crosslinking	Oat starch	Chemical reactive: Sodium tripolyphosphate (STPP) and sodium phosphate (STMP)	Reduction in the amylose content due to alkaline conditions; increase in the swelling capacity of starch granules; viscosity increase at high temperatures; and rapid development of viscosity at cooling temperatures[a].	(Berski et al., 2011)
	Commercial starches from wheat, corn, oat, rice, banana and potato.	Starch suspension (≈33%, w/w) Chemical reactive: mixture of STMP:STPP (99:1) Temperature (25-70 °C) pH (10.5 -12.3) Time (5-24 h)	RS production was ≤ 100% in all studied materials. RS produced was less water-soluble at 95 °C and increased the T_{gel} and enthalpies of starch paste[a].	(Woo & Seib, 2002)
	Commercial corn and wheat starch	Starch suspension (50 g / 70 ml of water) 12% mixture of STMP:STPP (99:1) 10% sodium sulfate. Temperature (38-70 °C) pH (10-12) Time (3 h)	Researchers studied the application of parameters such as temperature and pH to produce RS. At higher pH, the RS production was increased for both starches.	(Kahraman et al., 2015)
Acetylation	Commercial potato starch	Pretreatment: gelatinization and retrogradation Chemical reactive: anhydrous acetic acid.	Increased resistance to enzymatic action over retrograded starch.	(Zięba et al., 2011)
	Commercial potato starch	Pretreatment: enzymatic hydrolysis and extrusion Chemical reactive: anhydrous acetic acid. Catalyst: sodium hydroxide.	Increase in solubility and decrease in swelling capacity caused by both pretreatments[a]. Acetylation effects were directly dependent on the pretreatment.	(Kapelko et al., 2013)
	Commercial corn starch	Hydrothermal pretreatment: Suspension[a] 65% (w/v) Temperature (48, 52, 57, 60 and 62 °C) Time (3 h) Chemical reactive: Octenyl succinic anhydride (OSA). Catalyst: Sodium hydroxide.	Pretreatment increased the swelling capacity of granules and the peak of viscosity. Decrease in paste temperature[a].	(Chen et al., 2014)
	Oat starch	Chemical reactive: anhydrous acetic acid Catalyst: Sodium hydroxide.	Reduction in amylose content, temperature of the paste and viscosity at high temperature. Rapid development of viscosity upon cooling[a].	(Berski et al., 2011)
	Commercial corn starch	Chemical modification Chemical reactive: OSA. Catalyst: Sodium hydroxide. Temperature (35 °C) Time (2 h)	Improved performance of starch for textile applications. Reduction in surface tension, impregnation, wetting and diffusion of starch in textile fibers[a].	(Zhang et al., 2014)

[a]when compared with native starch.

Table 3. Continued...

Type of chemical modification	Starch source	Parameters studied	Observed results	References
Acid hydrolysis	Wheat (30% starch) Potato (25% starch) Peas (38% starch)	Acid solutions: chlorhydric acid and sulfuric acid (0.36 and 0.72 N). Starch suspension: 40% (w/w, dry basis). Temperature (40 °C) Time (4 and 24 h)	Hydrolysis reduced granule size and paste viscosity. The amylopectin depolymerization increased the quantity of linear chains similar to amylose, favoring gel formation and its strength.	(Ulbrich et al., 2014)
	Sorghum (*Sorghum bicolor*)	Acid solution: chlorhydric acid (0.1 N). Starch suspension: 40% (w/w, dry basis). Temperature (50 °C) Time (1.5 h).	Granule surface was highly porous, reducing its swelling capacity[a].	(Ali & Hasnain, 2014)
	Amaranth starch	Acid solution: chlorhydric acid (0.5 N). Starch suspension: 66% (w/w, dry basis). Temperature (35 °C) Time (0-72 h).	Reduction in size and molecular mass of granules. Increase in solubility, and reduction in gel formation[a].	(Kong et al., 2012)
	Commercial wheat starch (87.5% starch, dry basis) Commercial potato starch (84.9% starch, dry basis) Commercial pea starch (89.3% starch, dry basis)	Acid solutions: chlorhydric acid and sulfuric acid (0.36 and 0.72 N). Starch suspension: 2.5% (w/w, dry basis). Temperature (21 °C) Time (4 and 24 h).	Modification of starch by acid hydrolysis was different for each source. Amylopectin depolymerization increased the quantity of linear chains similar to amylose, favoring gel formation and its strength.	(Ulbrich et al., 2015)
	Yam starch	Acid solution: chlorhydric acid (6%, w/v). Starch suspension: 1/2 (w/v, dry basis). Temperature (27 °C) Time (192 h). Neutralization with sodium hydroxide (10%, w/v)	Increase in granule density. Breakdown or fragmentation of granules. Increase in swelling capacity[a].	(Falade & Ayetigbo, 2015)
Oxidation	Sorghum (*Sorghum bicolor*)	Starch suspension: 35% (w/w, dry basis). Chemical reactive: sodium hypochlorite. Catalyst: Sodium hydroxide. pH (9.5) Time (10 min)	Decrease in swelling capacity and viscosity of the paste[a].	(Ali & Hasnain, 2014)
	Commercial potato starch	Comparison between microwave use and conventional oxidation. Chemical reactive: hydrogen peroxide. Catalyst: sodium tungstate ($Na_2WO_4 \cdot 2H_2O$)	Decrease in the viscoelastic properties of the paste due to oxidation. Microwave uses are not significantly difference from the conventional method.	(Ptaszek et al., 2013)
	Oat Starch	Chemical reactive: sodium hypochlorite.	Apparent increase in linear molecules due to amylopectin depolymerization. Reduction in viscosity at high temperature and faster development of viscosity upon cooling[a].	(Berski et al., 2011)
Dual modifications	Sorghum (*Sorghum bicolor*)	Chemical modifications: oxidation and acetylation.	Increase in paste clarity[a].	(Ali & Hasnain, 2014)
	Commercial corn starch	Chemical modifications: oxidation and alkali treatment. Chemical reactive for oxidation: sodium hypochlorite. Alkaline reactive: sodium hydroxide.	Combined treatments generated several damages to the surfaces of the starch granules, making them more susceptible to enzymatic hydrolysis.	(Spier et al., 2013)
	Wheat starch	Chemical reactive: mixtures of i) succinic acid and acetic anhydride and ii) Azelaic acid and acetic anhydride	Decreased T_{gel} and retrogradation tendency. Increase in paste stability during storage.	(Šubarić et al., 2012)
	Potato Potato peel (industrial residue)	Application of ultrasound and microwave. Medium of dispersion: i) neutral water, ii) acidified water (sulfuric acid, 3 M) and iii) alkaline water (sodium hydroxide, 1 M)	Starch depolymerization was quantified by reducing sugar production. Ultrasound method in acidified water showed the highest degree of depolymerization.	(Hernoux et al., 2013)

[a]when compared with native starch.

Adebowale, 2005). In acetylated starch, hydroxyl groups and anhydrous glucose have been converted to acetylated groups (Huang et al., 2010). Acetylated starch with a low degree of substitution (0.01-0.2) has several applications in conforming films, adherents, thickeners, stabilizers, texturizers and encapsulation agents (Elomaa et al., 2004). Bello-Pérez et al. (2000) studied the acetylation process in banana starches. Acetylation modified the starch granule, decreasing the retrogradation tendency and increasing the solubility and swelling capacity of banana starch considerably compared to native starch. Acetylated banana starch also increased the paste viscosity.

Other methods of chemical modification

The oldest chemical modification technique is acid modification. Products of acid modification have several applications and uses in the food, paper, textile and pharmaceutical industries (Hoover, 2000). Acid modification methods involve the application of acidic solutions (commonly HCl and H_2SO_4) to form a concentrated paste (35–40% of solids) at a temperature below T_g for a specific duration depending on the desired viscosity or conversion degree (Amaya-Llano et al., 2008; Thirathumthavorn & Charoenrein, 2005). The mechanism of acid modification is also known as acid hydrolysis (Amaya-Llano et al., 2008). Hydrolysis is produced randomly, breaking the α-1,4 and α-1,6 links and shortening the polymeric chains. Acid hydrolysis of starch develops in two stages: an early stage in which hydrolysis preferentially attacks the amorphous regions of granules at a high reaction rate and a subsequent stage in which hydrolysis occurs in the crystalline region at a slower rate (Wang & Wang, 2001). The hydrolysis rate and starch modification are in proportion to the amylose:amylopectin ratio, as well as to the size and conformation of granules (Hoover, 2000). After acid hydrolysis, the molecular mass of the starch granules decreases, and its crystallinity increases (Zuo et al., 2014). Singh & Ali (2000) studied the influence of various acids used in starch modification (HCl, HNO_3, H_2SO_4, H_3PO_4); the starch sources were wheat, corn, peas, tapioca and potato. These authors concluded that H_3PO_4 produced a lower hydrolysis rate, whereas HCl and HNO_3 resulted in a higher reduction in molecular mass and consequently a higher hydrolysis rate. Acid hydrolysis reduces the amylose content in starch granules, and this reflects an increase in paste temperature and gelatinization enthalpies (Lawal, 2004). The use of dilute acid solutions for starch modification improves gel consistency and reduces paste viscosity due to depolymerization of the starch granule (Pérez & Bertoft, 2010; Ulbrich et al., 2015).

Another important process for starch modification is oxidation, a process in which functional groups such as carboxyl and carbonyl groups are introduced in the starch molecule and depolymerize the molecule (Kuakpetoon & Wang, 2001). During oxidation, it is important to maintain the appropriate parameters, such as temperature and pH. The reactive oxidants used include hydrogen peroxide, per-acetic acid, potassium permanganate, sodium hypochlorite, chromic acid and nitrogen dioxide (Sánchez-Rivera et al., 2005; Sandhu et al., 2008; Wang & Wang, 2003). In recent years, starch modified by oxidation has had great use in the food industry to form adherent surfaces and coatings (Lawal et al., 2005).

Dual modifications

Dual modifications include chemical modifications and different types of modifications combined. Dual modifications have been used in industry to optimize modified starch functionality (Ashogbon & Akintayo, 2014). This new approach involves the combination of chemical and physical agents (e.g., acetylation assisted by microwave, phosphorylation assisted by high pressures). Specifically, dual chemical modifications involve two processes of chemical modification (e.g., acetylation/oxidation, crosslinking/acetylation, crosslinking/hydroxypropylation) (Adebowale & Lawal, 2002; Carmona-Garcia et al., 2009; Huang et al., 2010). Starches modified by two chemical methods, such as emulsifiers, agglutinants and thickeners, are commonly used in the food industry and are included as adsorbents of heavy metals in the non-food industry (Ashogbon & Akintayo, 2014).

4 Resistant starch (RS)

Starch is quantitatively the major source of energy in the human diet. Starch digestibility is attributed to the interaction of several factors, including the vegetal source, granule size, amylose/amylopectin ratio, degree of molecular association between components, degree of crystallinity, amylose chain length and presence of amylose-lipid complexes on starch granules (Cummings & Englyst, 1995). Lipids are fatty acids specifically interacting with amylose to form complexes and reduce starch digestibility because their presence decreases enzymatic hydrolysis by amylase (Taylor et al., 2015).

Until recently, starch was considered completely digested after cooking. This concept has been challenged by observations that some of starch crosses the colon, where it is subject to bacterial fermentations. Today, this indigestible starch is recognized as part of the dietary fiber fraction of food (Conde-Petit et al., 2001). Most polysaccharides of interest for nutrition (e.g., starch, dextrin, glycogen and cellulose) are unions of glucose units, differing only in the type of linkage. As a group, polysaccharides may contain monosaccharides in addition to glucose, either alone or combined.

Starch digestion begins in the mouth, with α-amylase enzymes present in saliva. Enzyme activity is partially preserved until reaching the stomach. However, most starch is digested in the small intestine by enzymes from the pancreas. Degradation products of amylose are maltose and maltotriose, whereas amylopectin degradation produces dextrins and oligomers formed by α-1,6 linkages. Until the end of the intestine is reached, all of these polymers are degraded to glucose by enzymes such as α-glycosidase and oligo-α-1,6-glucosidase. Glucose absorption is followed by an immediate increase in glucoses levels in blood (Perera et al., 2010).

Factors that affect starch digestibility include the structural characteristics of the starch (i.e., the amylose:amylopectin ratio, degree of gelatinization, retrogradation and formation of amylose complexes), the structural characteristics of the food and the presence of other components such as soluble dietary fiber (Conde-Petit et al., 2001). RS is defined as the sum of starch or the sum of starch degradation products that are not absorbed by the small intestine in healthy individuals (Champ et al., 2003).

RS is divided into five types that have been substantially affected by the transformation process (Homayouni et al., 2014). The first group (RS I) is the product of treatments in which starch is physically inaccessible and the breakdown of the granular structure does not occur (Hasjim & Jane, 2009). The second group, RS II, consists of gelatinized starch (i.e., the starch has lost its crystalline conformation and is composed primarily of amylose); this type is very common in most starchy foods (Fuentes-Zaragoza et al., 2011). On the other hand, RS III is formed during starch retrogradation, which occurs after manufacturing in the presence of water, cooling and storage (Sanz et al., 2009; Yao et al., 2009). Chemical modifications to produce gelling and emulsification agents result in RS IV. Starch containing amylose-lipid complexes and requiring high temperatures of gelatinization are recognized as RS V, which is water insoluble (Cummings & Englyst, 1995; Jiang et al., 2010).

The RS is undigested starch that reaches the end of the digestive system, where it is the substrate of fecal microflora. Fermentation products from the RS are short chain fatty acids with different physiological and probiotic effects (Conde-Petit et al., 2001). The scientific interest in RS has increased significantly in recent decades because of its capacity to produce high levels of butyrate throughout the colon (Fuentes-Zaragoza et al., 2011). Butyrate is the most important energy source for colonocytes and has demonstrated beneficial effects on metabolism and cell growth; it also inhibits a variety of factors that propagate the initiation, progression and growth of colon tumors (Champ et al., 2003). The RS associated with small chains of fructooligosaccharides act synergistically in the digestive system to cause a prebiotic effect that benefits human health (Fuentes-Zaragoza et al., 2011).

5 Unconventional starches

The overall starch market is continually expanding, and the current demand is covered by four conventional sources: wheat, corn, potato and cassava. There are significant differences in the starch properties of these conventional groups in addition to the differences in their amylose-amylopectin ratios and the characteristics of these molecules. Non-amylosic components such proteins, lipids and phosphate groups are also important differences in the characteristics of conventional and unconventional starches.

Emmambux & Taylor (2013) studied the starch properties of cereals, legumes and tubers grown in Africa. The starch granules of certain cereals and beans possessed the common characteristics of small size, slightly porous surfaces and special paste properties, making them an interesting alternative for industry. These properties suggest treatments involving shearing operations or mimetic agents of fats because of their organoleptic characteristics and texture (D'Silva et al., 2011; Wokadala et al., 2012). Starch from beans (*Vigna unguiculata*) had a very high degree of retrogradation, which makes it suitable for incorporation into gluten-free pastes because this feature helps to maintain the texture of the product.

Zhang et al. (2005) studied the production, physicochemical properties and digestibility of banana starch. Pulp in immature bananas contains between 70-80% starch (dry basis); this amount is comparable to starch in the endosperm of corn grains and potato pulp. Banana starch is resistant to digestive enzymes (Faisant et al., 1995), which makes its use viable and competitive in a market of low-carb food consumption and products with reduced calories.

Almeida et al. (2013) studied the use of unconventional starches and commercial starches in the manufacturing of English cake and compared their behavior in this product. Unconventional starches incorporated into this formulation increased the sensory quality of the product. Starch from beans, followed by Peruvian carrots, yielded better results compared to commercial starch in terms of the technological quality of the paste during beating. Starch present in chickpeas and beans showed similar characteristics to that of commercial starch in terms of sensory properties, texture and moisture.

Today, chemical modifications of starch remain necessary. The industry requires these chemical processes to meet the demand of consumers favoring natural products. A simple way to impact starch properties is by mixing different types of native and/or physically modified starch (Sandhu et al., 2010; Waterschoot et al., 2015b). The use of these mixtures, as well as enabling improvements in the starch properties and pastes, also provides economic advantages when the replacement starch source is cheaper than the conventional source. However, there are limited studies on the physicochemical properties and functionality of starch mixtures (Waterschoot et al., 2015b) and the use of unconventional starches.

Currently, unconventional starches are often ignored or wasted during the isolation or separation of bioactive compounds from raw materials such as seeds and legumes (Braga et al., 2006; Yuan et al., 2007). These starches are subjected to unit operations that often involve thermal or hydrothermal treatments, causing alterations in the structural characteristics of the starch and physical modifications and improving the physicochemical properties and characteristics of the paste conformation. Additionally, raw materials from the extraction processes remain in the extraction residues including the starch fraction and a small fraction of bioactive compounds, which increase the technological and nutritive value (Braga et al., 2006; Santana & Meireles, 2014). Starches present in legumes, rhizomes, herbs and seeds are considered unconventional and may be used as ingredients in the same manner as starches from cereals and tuber due to their similar physicochemical and functional properties. These properties are improved by modification treatments and may be used to develop new processes and consequently new products (Santana & Meireles, 2014).

6 Starch applications in the food industry

The biological function of starch in plants is as a reserve of carbon and energy. As food, starch is the most abundant and important digestible polysaccharide. The starches in food are commonly derived from grains or seeds (wheat, corn, rice, and barley), tubers (potato) and roots (cassava) (Buléon et al., 1998; Waterschoot et al., 2015a). Starch provides 70 - 80% of the calories consumed by humans worldwide.

As food, starch functions as a structural agent because of the modifications introduced during manufacturing. Starch is used in the food industry mainly as a modifier of texture, viscosity, adhesion, moisture retention, gel formation and films (Waterschoot et al., 2015a).

An important utilization of starch in the food industry is in baking flour. Among the bakery products, cakes and breads are the most important due to their high consumption. In the formulations of the baking industry, starch is one of the components responsible for the structure and properties of the final products. Other industrial processes include starch in small quantities as a food additive or a thickening and gelling agent.

Starch is often used in granular form and is thus is included in the confectionery industry as a molding powder for the various forms of sweets, which can be reused many times. Starch is also used in the preparation of diverse types of pasta in the preparation of noodles and those intended for extrusion and in the formulation of instant foods and fried foods.

In the food industry, edible films are barriers that prevent moisture transfer, gas exchange, oxidation and the movement of solutes, while maintaining their organoleptic properties (Dhall, 2013). During manufacturing, films are incorporated as plasticizers, flavors, colors, sweeteners, antioxidants and antimicrobials. Edible films have received much attention due to their advantages over synthetic films. Edible films are produced from renewable materials; they can be consumed together with coated food and otherwise do not contribute to pollution because their degradation is faster than synthetic films. Their main disadvantage lies in their mechanical and permeable properties (Bourtoom, 2008). The basic materials used to produce edible films are cellulose, starch, gums and chitosan; the linear configuration of polymers can produce films with flexible, transparent and oil resistant properties. For these reasons, amylose is the most important fraction in starch granules. Typically, the starch granule is composed of 25% amylose and 75% amylopectin. Edible films require starches with a high amylose content ($\geq$ 70%). The amylopectin molecule cannot adequately form films; the branched structure imparts poor mechanical properties to the film, reducing its tensile strength and elongation (Bourtoom, 2008; Dhall, 2013).

Polysaccharides are typically hygroscopic and therefore are poor barriers to moisture and gas exchange. The use of plasticizers in the film composition improves the barrier against moisture exchange and restricts microbial activity. The starch used in edible film preparation is incorporated to partially or completely replace the plastic polymers. Native starch does not produce films with adequate mechanical properties and requires pretreatment, the use of a plasticizer, mixture with other materials, genetic or chemical modification, or a combination of these treatments. Among the plasticizers, for hydrophilic polymers, such as starch, are glycerol and other low-molecular weight polyhydroxy-compounds, polyether, and urea. Processes such as extrusion adjust the parameters of temperature and mechanical energy over the starch paste, making it a thermoplastic material that is also suitable for the production of edible films (Dhall, 2013).

7 Starch destined for non-food applications

New processing techniques and the current demands of biodegradable and renewable resources have highlighted the versatility of starch and introduced it to new markets. Furthermore, starch is a chemical feedstock for conversion into numerous products with considerable value (Ellis et al., 1998).

In the pharmaceutical industry, starch is used as an excipient, a type of bonding agent to active drugs. Because of its content of amylose, starch is capable of forming an inclusion complex with many food ingredients, such as essential oils, fatty acids and flavoring ingredients. It therefore acts as an encapsulant and increases the shelf life of products.

Plastics obtained from oil are being replaced by natural polymers; starch is known for its ability to form films in food packaging applications (Jiménez et al., 2012). Edible and biodegradable starch films can be obtained from native starch or its components amylose or amylopectin by two main techniques: a wet method that includes a starch suspension and posterior drying or a dry method that involves a thermoplastic process (Paes et al., 2008). Modified starches can also be used in film production (Bourtoom, 2008; Campos et al., 2011; Dhall, 2013; López et al., 2010)

For new industrial applications of starch, especially in plastic polymer production, the hygroscopicity of starch is a disadvantage because the main feature of plastics films is their hydrophobic property. Starch granule size, its form and associated molecules influence film production. Wheat starch is typically associated with a significant amount of protein, which may result in a Maillard reaction and cause bleaching; therefore, this type of starch is not used in to manufacture biodegradable plastics films (Ellis et al., 1998).

In the textile industry, starch films are also used during textile production as fiber coatings. Native starch forms rigid and brittle films due to its cyclic structure. Brittle films are not advantageous because they reduce protection, increase friction and thus damage the thread. The polarity of native starch minimizes the adhesion of synthetic fibers, affecting the tensile strength and abrasion. Starch is commonly modified to improve the physical properties, emulsifying ability and film formation (Zhang et al., 2014).

Many industrial processes use starch after partial or complete destruction of its structure. When this occurs, the properties of its components and the relationships between them increase their importance. Differences between the amount and type of lipids originally present in the native starch may cause two starches with the same amylose-amylopectin ratio to have different physical properties, such as viscosity (Ellis et al., 1998).

Starch solutions are viscous, and the ability of starch to change the viscosity of other solutions and pastes is well known and exploited in the food industry. This property is also used in the oil drilling industry, where starch is used to adjust the viscosity of the mud used during drilling operations. Highly viscous starch solutions are desirable for industrial processes involving starch pastes for mechanical manipulation, such as the paper, corrugated and textile industries (Ellis et al., 1998).

Several studies have concluded that is possible to produce a new generation of detergents in which the surfactants and bleaching components are derived entirely from starch. An estimated 50 to 60% of chemical products in formulations for powder detergents and 65 to 75% of liquid detergent formulations could be substituted with products derived from starch.

High viscosity is important in the adhesive field. Most native starches do not maintain a stable viscosity when transformed to pastes and or subjected to high shear velocity or longer heating periods. However, chemically modified starch behaves properly under these conditions (Ellis et al., 1998).

The production of biodegradable plastics is still young when compared to the petrochemical plastic industry. Starch will play an important role in its growth in container production and in the form of biodegradable materials that conform to suitable matrices because it is a relatively inexpensive material compared to other polymers (Bourtoom, 2008; Dhall, 2013).

In recent years, starch has been studied for the production of nanoelements as nanocrystals that result from the breakdown of the amorphous region in semicrystalline starch granules by acid hydrolysis or for the production of nanoparticles from gelatinized starch (Le Corre et al., 2010). These nano compounds have unique properties due to their nano size compared to conventional size materials. Nanoparticles can be used as fill material in filtration and form effective barriers in flexible packaging (Bondeson et al., 2006).

8 Conclusions, perspectives and future trends

Starch has a major role in the food industry not only in for its nutritional value, but also for its broad technological functionality. The amylose and amylopectin polymers, lipids, proteins and phosphorus present in granules have significant effects on the physicochemical properties and functionality of starch.

Starch is rarely consumed in its native form; this form is also not commonly used in industry because native starches have restricted solubility in water, which limits industrial applications. Several methods have been developed for the production of modified starch, with a variety of features and applications.

Modification processes can greatly improve the characteristics of native starch by altering its physicochemical properties and structural attributes and increasing its technological value. Starch characteristics depend on the modification used and are necessary for its use in industry; they include cold water solubility, viscosity and swelling capacity after cooking, retrogradation tendency, loss of structural order after gelatinization and consequent syneresis of systems conformed by starch. The industry of starch modification is constantly evolving. Starch is a highly flexible polymer, and there are several ways to modify its structure and obtain a functional product with adequate properties for specific industrial applications, increasing its added value.

Physical modification of starch can enhance its water solubility and reduce the size of the starch granules. Physical methods for the treatment of native granules include combinations of temperature and moisture, pressure, shear and irradiation. Physical

modification is simple, inexpensive and safe. These modification techniques are preferred because they do not require chemical or biological agents that may be harmful to health.

Physical modifications of starch consist of three categories. i) PGS is produced by cooking until complete gelatinization with subsequent drying, which destroys the granular structure and increases the swelling capacity, solubility, viscosity and dispersion capacity in cold water. ii) Hydrothermal modifications do not destroy the granular structure and occur at temperatures above T_g and below T_{gel} of the granule (these parameters are different for each botanical source) in the presence of water. Two processes for the latter modification were considered: ANN, which requires water in intermediate quantities or excess (40-76%, w/w), and HTM, which uses a restricted water content in a dispersion medium ($\leq$ 35%, w/w). Hydrothermal modifications reduce starch solubility, swelling capacity and amylose leaching and increase the crystallinity and T_{gel} of the starch granules. In starch pastes, modifications reduce the viscosity and increase the stability. iii) Physical non-thermal modifications are preserve the quality of nutrients that may be contained in the starch paste and are susceptible to heat. The use of high pressure reduces the swelling capacity and viscosity of starch; vacuum pressures have the opposite effect, increasing the swelling capacity and reducing the degree of polymerization. Microwaves modify the dielectric properties of starch and its morphology and crystallinity, and ultrasound modifies the swelling capacity of granules and pastes. Industrial processes such as grinding and extrusion also physically modify starch granules.

Chemical modification of starch involves the introduction of functional groups to the starch molecule without affecting the morphology or granule size distribution. Cationization modifies the dielectric properties of granules depending on their substitution degree, reducing the paste temperature and increasing its viscosity. Crosslinking of polymeric chains increases the degree of polymerization in starch granules, modifying its solubility in organic solvents and reducing its swelling capacity. Acetylation results in the esterification of starch, increasing its swelling capacity and solubility. Other chemical modifications, such as acid hydrolysis and oxidation, reduce the degree of polymerization of starch and the paste viscosity.

Not all starch is digestible, and the indigestible portion is part of the fraction of dietetic fiber or RS. Chemical modifications such as crosslinking are used to increase the amount of RS, and these starches are included in paper and textile processes.

The starch industry is in constant expansion, and modification processes increase its versatility. When starch is physically or chemically modified, it can be adapted for different purposes in food and/or non-food industries. Applications of starch modifications (physical or chemical) can increase the use of unconventional starches and vegetal residues containing starch in industry. Depending on cost and accessibility, the use of conventional starch can be replaced in whole or in part by unconventional starches in industrial processes when appropriate. Determining the required characteristics of starch for each process is necessary to select the best modification method according to the application requirements, market trends, availability, structural characteristics and cost.

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Acronyms: Glass transition temperature (T_g), Resistant Starch (RS), Rapid Visco Analyzer (RVA), Onset temperature (T_o), Peak temperature (T_p), Conclusion temperature (T_c), Differential Scanning Calorimeter (DSC), Gelatinization temperature (T_{gel}), Supercritical fluid extraction (SFE), Pre-gelatinized starch (PGS), Melting temperature (T_m), Annealing (ANN), 2,3-epoxypropil trimethyl ammonium chloride (EDMAC), Sodium tripolyphosphate (STPP), Sodium phosphate (STMP), Octenyl succinic anhydride (OSA), 2,3-epoxypropyl trimethyl ammonium chloride (ETMAC), 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CTA), Dimethyl sulfoxide (DMSO), Sodium trimetaphosphate (STMP), Sodium tripolyphosphate (STPP), Epichlorohydrin (ECH), Phosphoryl chloride ($POCl_3$).

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