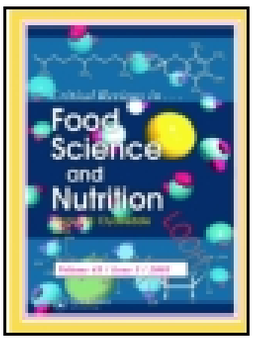

Critical Reviews in Food Science and Nutrition

ISSN: 1040-8398 (Print) 1549-7852 (Online) Journal homepage: http://www.tandfonline.com/loi/bfsn20

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To cite this article: Jinhu Tian, Yukiharu Ogawa, John Shi, Shiguo Chen, Huiling Zhang, Donghong Liu & Xingqian Ye (2018): The microstructure of starchy food modulates its digestibility, Critical Reviews in Food Science and Nutrition, DOI: 10.1080/10408398.2018.1484341

To link to this article: https://doi.org/10.1080/10408398.2018.1484341

Accepted author version posted online: 05 Jun 2018.

Publisher: Taylor & Francis

Journal: *Critical Reviews in Food Science and Nutrition*

DOI: https://doi.org/10.1080/10408398.2018.1484341

The microstructure of starchy food modulates its digestibility

Jinhu Tian[a,b], Yukiharu Ogawa[b], John Shi[c], Shiguo Chen[a], Huiling Zhang[d], Donghong Liu[a], Xingqian Ye[a,*]

[a]Zhejiang University, Department of Food Science and Nutrition, Hangzhou 310058, China

[b]Chiba University, Graduate School of Horticulture, 648, Matsudo, Matsudo 271-8510, Japan

[c]Agriculture and Agri-Food Canada, Guelph Food Research Center, Guelph, ON N1G 5C9, Canada

[d]Ningxia University, Department of Food Science, Yinchuan 750021, China.

*Corresponding author. Xingqian Ye; fax: +86(0571-88982151), E-mail: psu@zju.edu.cn

Abstract

Starch is the main carbohydrate in human nutrition and shows a range of desired food properties. It has been demonstrated that fast digestion of starchy food can induce many health issues (e.g., hyperglycaemia, diabetes, etc.); therefore, how to modulate its digestion is an interesting topic. Previous studies have revealed that the microstructure and digestibility of starchy food of different botanical origin or from multiple processes are quite different; modulating starch digestion by retaining or altering its microstructure may be effective. In the present review, the current knowledge of the relationship between microstructural changes to starchy food and its digestibility at molecular, cell and tissue, and food processing levels is summarized. New technologies focused on microstructure studies and ways to manipulate food microstructure to modulate starch digestibility are also reviewed. In particular, some insights focusing on the future study of microstructure and the digestibility of starchy food are also suggested.

Key words:

starch granules; microstructure; digestibility; modification; morphology

Introduction

Despite numerous studies have focused on the effect of microstructural changes to starch on its digestibility, starch digestion is not fully understood since most of our intake of starch is combined with other components such as proteins, lipids and

non-starch polysaccharides during protean processes (e.g. milling, extruding, frying, boiling, steaming, etc.), which affect the microstructure as well as the digestibility of starchy food significantly (Parada and Santos 2016). Thus, a better understanding of the microstructure of starchy food and its relationship with digestibility is demanded (Kaufmann and Palzer 2011). Here, current studies on the microstructure and digestibility of starchy food at different levels (molecular, cell and tissue, food processing) were reviewed, as well as the common technologies applied. In particular, ways to control the digestion of starchy food from the perspective of microstructural changes at different levels were also discussed. The review will be helpful for researchers to have a better understanding of the relationship between the microstructure and digestibility of starchy food and provide some new insights in this field.

Architecture and physiological effects of starchy food

Architecture of starch granules and starchy food

The architecture of starch granules has been reviewed by several authors (Parada and Aguilera 2011a; Wang and Copeland 2013). The architecture of a starch granule is described briefly in Figure 1; starch granules are considered to have an amorphous core of mostly amylose (in non-waxy starches) and disordered amylopectin, which is surrounded by a concentric pattern of alternating crystalline and amorphous growth rings (typically 120–400 nm in thickness, extending from the hilum towards the

surface of the granule). The concentric growth rings, which are made up of amylopectin and amylose, in turn, contain alternating crystalline and amorphous regions of higher and lower density, respectively. The high-density regions have a lamellar structure of alternating crystalline and amorphous layers with a repeat distance of 9–11 nm (this spacing does not seem to vary with the botanical source of the starch) (Wang and Copeland 2013). The crystalline layers are considered to be formed mainly by amylopectin chains packed into a crystalline lattice, whereas the amorphous layers contain amylopectin branching points and amylose in a disordered conformation. Long amylopectin chains are supposed to extend from crystalline regions into the amorphous region of the lamellae. In addition, amylose is located in the low-density layers of the growth rings, although amylose molecules are also considered to be interspersed between amylopectin in the crystalline layers, disrupting the crystal packing of amylopectin (Copeland et al. 2009). The semi-crystalline structure of raw starch decreases its susceptibility to enzymatic degradation; therefore, the rate and total quantity of sugar released are slower and smaller, respectively, than in processed starch (Chung, Lim, and Lim 2006).

Correlation between microstructure and digestibility of starchy food

Generally, the digestion of starchy food can be reduced by two approaches, hindering the enzyme molecules in contact with the substrate or reducing the activity of digestive enzymes (Blazek and Gilbert 2010). Considering that reducing the activity of digestive enzymes may be not an optimal choice, ways to hinder the enzyme

molecules in contact with the substrate has been fully studied. In particular, a number of studies have demonstrated that retaining or altering the microstructure of starchy food at different levels might be a good way to hinder the enzyme molecules in contact with the substrate (Parada and Aguilera 2011b). For instance, at the molecular level, starch digestion can be controlled by altering the degree of gelatinization and retrogradation as well as by modifying the structure of amylopectin, amylose–lipid complexes, etc. At the cell and tissue level, the cell wall structure can be retained as a physical barrier to enzymes, while at the food processing level, minimal processing can retain the raw, hard-to-digest part, and extensive processing (extrusion) can be used to obtain a dense structure of starchy food (Lehmann and Robin 2007; Wang and Copeland 2013).

Starchy food consumption and health issues

Starchy food, considered as food which has starch granules as its main components, is commonly consumed around the world. It is believed that starch contributes 50–70% of the energy in the human diet, providing a direct source of glucose, which is an essential substrate in the brain and red blood cells for generating metabolic energy, indicating its role as a food component essential to human health (Copeland et al. 2009). According to the effect of postprandial glycaemia, starchy foods are usually classified as having a high food (> 70), medium (55–70) or low (< 55) glycaemic index (GI) (Jenkins et al. 1981). Consumption of starchy food that is digested and absorbed rapidly (e.g. high GI food), will result in high postprandial blood glucose

levels, which over the long term are associated with increasing risks of obesity and diet-related diseases, including type 2 diabetes, cardiovascular disease and certain types of cancer (Fuentes-Zaragoza et al. 2011). Thus, how to modify the digestibility of starchy food and produce a more moderate glycaemic response in the human body is an attractive topic.

Current technologies for studying the microstructure and digestibility of starchy food

Analysis technologies involved at molecular level

As shown in Table 1, at molecular level, the most commonly used technologies are X-ray diffractometry, differential scanning calorimetry (DSC), gel-permeation chromatography (GPC), high-performance anion-exchange chromatography (HPAEC), nuclear magnetic resonance (NMR), attenuated total reflectance Fourier transform infrared (FTIR), and so on. X-ray diffractometry is applied to determine the crystalline structures of starch as well as its degree of crystallinity (Blazek and Gilbert 2011). Usually, the starch from cereals shows typical peaks at 15°, 20° and 23° (2θ) (You et al. 2014), and starch from tubers shows typical peaks at 5.5°, 17.1° and 22–24° (2θ) (Parada and Aguilera 2012), while lipid–amylose compounds show typical peaks at 13° and 20° (2θ) (Chanvrier et al. 2007). Additionally, with X-ray diffractometry, the relative crystallinity of starchy foods can also be calculated as the ratio of the crystalline peak area to the total diffraction area. The DSC method is

commonly applied to measure the energy changes in starch subjected to programmed heating or cooling, and its transition temperatures (onset, *To*; peak, *Tp*; conclusion, *Tc*); enthalpy change (*ΔH*) due to crystallite melting or formation of ordered structures can be derived from DSC thermograms (Wang et al. 2015). Usually, the *To*, *Tp* and *Tc* of starchy foods are exhibited between approximately 40 and 80 °C, and increases in *To*, *Tp*, *Tc* and *ΔH* are a reflection of more ordered crystallinity of starch. In particular, if lipid–amylose compounds are involved, another two small peaks at a higher temperature (> 100 °C) can also be observed, which indicates type I and type II starch–lipid complexes (Chang, He, and Huang 2013). However, DSC results also depend on the analysis conditions (e.g. excess water or other conditions will induce some phase transitions). In order to have a better understanding of the molecular structure of starchy food, other technologies are also applied simultaneously. For instance, GPC is applied to determine the weight distribution of starch molecules during digestion, AFM is applied to observe the molecular chains of amylose and amylopectin, NMR is applied to analyse the structural changes of starch during processing, and FTIR is applied to analyse the functional group shifts of starch reacted with other compounds (e.g. polyphenols, lipids, etc.).

Analysis technologies involved at cell and tissue level

The main purpose of analysis at cell and tissue level is observation of the morphology of starchy foods at micron level. Thus, scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM) are the most widely used technologies.

With SEM, an intuitive appreciation of the microstructural changes of starch granules during processing and digestion can be observed. Tian et al. (2016) observed SEM images of the microstructure of potato after cooling and reheating, and reported that the microstructures of potato after processing and those during *in vitro* digestion have quite different morphology. Similar results were also reported by Utrilla-Coello et al. (2013), who investigated the possibility of analysing the microstructure of retrograded starch (potato, maize and banana) quantitatively with SEM. Compared to SEM, CLSM is often used to observe the spatial structure of starch, protein and lipid during *in vitro* digestion, where the protein, lipid and starch can be identified by different colours after dyeing and laser excitation (Bordoloi, Singh, and Kaur 2012). With the CLSM technique, we can have a better understanding of how proteins, cell walls and other compounds impede the contact between digestive enzymes and starch. Tamura et al. (2016) stained digested rice with acridine orange and rhodamine and reported that cell walls and proteins on the surface of rice decreased rice digestibility significantly. In another study, Zou et al. (2015) also reported that the morphological differences of starch and protein components in cooked semolina, pasta and pasta powder can be revealed using CLSM.

Analysis technologies involved at the food processing level

At the food processing level, the Rapid Visco Analyzer is mostly applied to analyse the rheological parameters of starch or its mixtures (mixed with protein, polysaccharides or polyphenols). In particular, numerous studies have focused on the

relationship between the pasting characteristics of starch or its mixtures, and their digestibility. Bordoloi et al. (2012) reported that the viscosity values of starch (corn and potato) show a positive correlation with their *in vitro* digestibility in the presence of hydrocolloids. Similar results were also reported by Bai et al. (2017) and von Borries-Medrano et al. (2016). In addition to the Rapid Visco Analyzer, X-ray micro-CT (X-ray micro-computed tomography) is also attracting more and more attention for the analysis of food microstructure. With X-ray micro-CT, the geometric shapes of the inside parts of starchy food can be visualized directly, and it is much easier to design the microstructure of starchy food with a specific purpose (e.g. slowly digested food) (Renshaw et al. 2016).

Impact of molecular-level structure on the digestibility of starchy food

Molecular structures and constitution of amylose and amylopectin

Starch consists of amylose and amylopectin regardless of its botanical origins. Amylose is a linear and relatively short polymer of glucose units linked by α (1-4) bonds with an average molecular mass of 105–106 g/mol, whereas amylopectin is a branched and longer polymer, where glucose units are arranged linearly through α (1-4) bonds, with several branches emerging via α (1-6) bonds occurring every 24 to 30 glucose units, and has an average molecular mass between 107 and 109 g/mol (the chemical structures of amylose and amylopectin are shown in Figure 1 E and F) (Sajilata, Singhal, and Kulkarni 2006). Amylose is primarily a linear macromolecule

with less than 1% of long-chain branches forming predominately single-chain helices, usually densely packed and arranged tightly in the crystalline regions in starch granules; it is much harder to digest (Dona et al. 2010). On the contrary, amylopectin contains many short branches with a non-random distribution of branching points (4–5%) and seems to be loosely packed and arranged less tightly than amylose in the crystalline and non-crystalline regions in starch granules. Probably attributed to a much larger surface area per molecule than amylose, amylopectin is a preferable substrate for amylolytic attack and is much easier to digest (Dona et al. 2010; Parada and Aguilera 2011a).

Considering the structural difference between amylose and amylopectin, it might be easier to explain differences in starch digestibility by different amylose/amylopectin ratios. Generally, legume starch has lower *in vitro* and *in vivo* digestibility than starches from cereals or tubers. This may be partly because of its higher amylose content (legumes contain 30–40% amylose and 60–70% amylopectin in their starch granules, while most other food starches contain 25–30% amylose and 70–75% amylopectin) (Hoover and Zhou 2003). In addition to different botanical origins, amylose content is also different in different cultivars with the same botanical origins, and eventually affects starch digestibility. Hu et al. (2004) studied starch digestibility and the estimated glycaemic score of three types of rice (*indica*, *japonica* and hybrid rice) differing in amylose content (ranging from 0.7% to 26.8%) and reported that starch hydrolysis tends to be quicker and more complete for

low-amylose rice than for intermediate and high-amylose rice. In another study, Srikaeo and Sangkhiaw (2014) estimated the GI of rice noodles using *in vitro* and *in vivo* methods and reported that the GI value of rice noodles decreases as the content of amylose increases. Similarly, Xu et al. (2017) also observed that the higher amylose content and larger molecular size of oat starch might contribute to its lower digestion rate. In addition to amylose content, the fine structure of amylose and amylopectin also affects its digestibility; longer amylose branches, smaller ratios of long amylopectin and long amylose branches to short amylopectin branches also increase *in vitro* starch digestibility (Syahariza et al. 2013).

Molecular structures and digestibility of gelatinized starch

For most starchy food, regardless of the complexities during processing, starch granules suffer from heat at different temperatures in excess or limited water. During processing, starch granules swell and lose their crystallinity and molecular organization in a process commonly known as gelatinization. This phenomenon has been broadly defined as the 'collapse (disruption) of molecular orders (breaking of hydrogen bonds) within the starch granule manifested in irreversible changes in properties such as water uptake, granular swelling, unwinding of double helices, loss of birefringence, starch solubilisation and viscosity development' (Figure 2 IIa and IIb)(Goesaert et al. 2005). Basically, irreversible changes during gelatinization are attributed to destruction of the fine structure of amylose and amylopectin (e.g. the double helices are untwisted in amylose, and the branches become disordered in

amylopectin). *In vitro* studies have demonstrated that the rate of enzyme breakdown of gelatinized starch is much higher than that of native starch; when native wheat starches were incubated in the presence of high levels of alpha-amylase activity for 60 min, the starches degraded by only 10–15%, but after partial gelatinization, the rate of enzymatic degradation increased three-fold (Blazek and Copeland 2010).

Gelatinization occurs fully when starch granules are heated in excess water for enough time. However, in some methods of food processing, the heating time or water content is limited, and gelatinization might occur at different levels and then affect the digestibility. Contardo et al. (2016) reported that the lesser degree of starch gelatinization (28%) in vacuum-fried starch–gluten matrices results in lower *in vitro* digestibility than that of their atmospheric counterparts (which present 99% starch gelatinization). Similar results were also confirmed by Parada and Aguilera (2012); they focused on the relationship between the degree of gelatinization of potato starch and its glycaemic response *in vivo* and reported that the glycaemic responses of potato starch are positively associated with an increasing degree of gelatinization.

Molecular structures and digestibility of retrograded starch

With the expectation of extending shelf life, starchy food is stored at low temperature. Gelatinized starch will undergo retrogradation (or recrystallization), with the starch molecules re-associating into partially ordered structures that differ from those in native granules. This phenomenon leads to an undesirable mouth feeling. However,

attributed to its relatively ordered structure, retrograded starch is not recognized by enzymes and is less digestible than gelatinized starch (Parada and Aguilera 2011b). Tahvonen et al. (2006) studied the effects of cooling on the digestibility of boiled potatoes in an *in vivo* study; they found a lower GI in cold potatoes than in freshly-cooked potatoes and attributed their results to the formation of a crystal structure during cooling. Similar results were also reported by Tian et al. (2016) for the digestibility of cooked potato with an *in vitro* method; their results indicate that cooling and storage decrease the digestibility of potato significantly.

The retrogradation of starch depends on many factors such as amylose and amylopectin content, cooling time and temperature, etc. Amylose retrogrades over minutes to hours as the linear structure facilitates cross-linkages by means of hydrogen bonds (Figure 2 IIIa), whereas amylopectin retrogrades over hours to days, depending on the ability of the branched chains to form associations (Figure 2 IIIb). Thus, the lower digestibility of cooled and stored starchy food is mainly attributed to the content of retrograded amylose (Copeland et al. 2009; Parada and Aguilera 2011a). Different from being kept at low temperatures, temperature cycling during storage also decreases the enzyme digestibility of retrograded starch significantly (Wang et al. 2015; Zhang et al. 2011). Storage at cycled temperatures induces a greater amount of resistant starch and reduces GI more effectively than isothermal storage conditions (Park, Baik, and Lim 2009). Xie et al. (2014) investigated the effect of repeated retrogradation on structural characteristics and *in vitro* digestibility

of potato starch and found that the cycle times also affect retrogradation; the maximum slowly digestible starch yield (40.41%) was obtained by repeated retrogradation twice with a time interval of 48 h. They revealed that structural changes of waxy potato starch treated with different cycling times for repeated retrogradation significantly affect its digestibility.

Molecular structure and digestibility of modified starch

To alter the functional characteristics of starch during processing, physical, enzymatic or chemical methods are applied by the manufacturer; physical modifications include heat-moisture treatment, annealing treatment or extrusion, whereas etherization, esterification or cross-bonding are involved in chemical modifications, and debranching is involved in enzymatic modification. The detailed art and science behind modifying starch have been reviewed by Shah et al. (2016). Here we just discuss some typical modifications and their relationship to digestibility. Possibly, the introduction of different chemical groups into the starch structure changes the substrate and makes the starch less easily recognized by enzymes; modified starch is less digestible than native starch (Fuentes-Zaragoza et al. 2011). Hung, Chau and Phil (2016) compared the *in vitro* and *in vivo* digestibility of rice following heat-moisture and annealing treatments and found that those two physical modifications of rice resulted in significantly lower digestibility (*in vitro* and *in vivo*) than for native rice. They speculated that amylose–amylose, amylopectin–amylopectin and amylose–amylopectin chain interactions during heat-moisture or annealing treatment form an

inherent structure, reducing the accessibility of hydrolysing enzymes and being responsible for lower digestibility. A further study by Chen et al. (2015) also showed that higher moisture content during heat-moisture treatment is negatively correlated with starch digestion in wheat. As mentioned above, the branches, size, shape and surface of starch granules are closely associated with digestion. Thus, some enzymes can be applied to change the morphology of starch granules or debranch starch with the aim of reducing starch digestion. For instance, after debranching with pullulanase, autoclaved banana starch shows a lower *in vitro* hydrolysis rate than that of normal starch (González-Soto et al. 2004), while different digestion rates are obtained for gelatinized, retrograded starch by varying the enzyme dosage and reaction time (Han et al. 2006). In addition to physical and enzyme modification, chemical modification also has a positive or negative effect on starch digestion, and a number of studies have focused on this issue (Almanza-Benitez et al. 2015; Cai et al. 2014; Pornsuksomboon et al. 2016). However, the tendency to consume more 'natural foods' is increasing, and hence there is a need for greater understanding of how processing and nutritional performance are related to starch modification (Copeland et al. 2009).

Crystalline structures of starch from different botanical origins

A starch granule is composed of amylose and amylopectin, and differences in assembling those two molecules also affect its digestion. Three crystalline structures of starch have been identified as A, B and C types which contain differing proportions of amylopectin (type A > type C > type B); the detailed structural information has

been described by Jane, Wong and McPherson (1997) and Sajilata et al. (2006). The type A structure has amylopectin with chain lengths of 23 to 29 glucose units. Hydrogen bonding between the hydroxyl groups of the chains of amylopectin molecules results in the formation of an outer double helical structure. Between these micelles, linear chains of amylose moieties are packed by forming hydrogen bonds with outer linear chains of amylopectin (Figure 3). The type B structure consists of amylopectin with chain lengths of 30 to 44 glucose molecules with water interspersed (Figure 3) (Wu and Sarko 1978). The C-type structure is made up of amylopectin with chain lengths of 26 to 29 glucose molecules, a combination of types A and B. Generally, A-type crystalline structures are found in cereals and B-type in tubers and high-amylose starch, while the C-type is found in peas and beans (Fuentes-Zaragoza et al. 2010). Attributed to their arrangements in different types, the A, B and C types of starch granules also have different degrees of digestibility. Greater susceptibility of A-type crystallites to hydrolysis compared to B-type crystallites has been reported (Lehmann and Robin 2007), whereas the C-type is also much harder to hydrolyse than that with an A-type crystallinity pattern, possibly attributed to the higher amylose content (Srichuwong et al. 2005).

Starch–lipid complexes

Lipids can be observed in many native starch granules and starchy foods (e.g. maize, rice, beans). During molecular assembly and processing, lipids and starch granules form a starch–lipid complex, which has been demonstrated to reduce digestibility (De

Pilli et al. 2011). Compared with amylose, the lipid-binding capability of amylopectin is much weaker (the longer the amylopectin chains, the weaker the binding between amylopectin and lipid). Thus, starch–lipid complexes occur mostly as amylose–lipid complexes and can usually be found in high-amylose starch granules such as high-amylose maize (a schematic representation of a complex of amylose with monopalmitin is shown in Figure 4A). According to differences in molecular structure, amylose–lipid complexes can be divided into Form I and Form II. Form I appears to have a random distribution of aggregated helices, whereas Form II has a crystalline organization of amylose complexes. Form II requires higher temperatures and a longer time to form; the rate and extent of degradation by bacterial and pancreatic amylases has been assessed to decrease in the order: Form I > Form II (Copeland et al. 2009). In addition, the type of lipid is also an important factor in the formation of starch–lipid complexes and in starch digestibility. Lipids such as free fatty acids, monoglycerides and alcohols have been reported to form helical complexes with amylose (Fanta, Shogren, and Salch 1999; Tufvesson and Eliasson 2000). Ai, Hasjim and Jane (2013) studied the effects of lipids (corn oil, soy lecithin, palmitic acid, stearic acid, oleic acid and linoleic acid) on enzymatic hydrolysis and the physical properties of normal corn, tapioca, waxy corn and high-amylose corn starch, and stated that lipids of different structures have different effects on enzymatic hydrolysis rates, despite them all being able to decrease starch digestion significantly. In addition to the formation of starch–lipid complexes, lipids also reduce accessibility

to the enzyme α-amylose by surrounding the starch granules or enzymes or by changing the swelling capacity, increasing gelatinization temperature, reducing gel rigidity, retarding retrogradation and reducing the susceptibility to enzymatic hydrolysis (Ai et al. 2013; De Pilli et al. 2011). Hätönen et al. (2011) studied the digestion of a protein- and fat-modified mashed potato-based meal *in vivo* and stated that when the potatoes are combined with protein or fat, glycaemic and insulin responses are reduced significantly; similar results were also reported by Henry et al. (2005).

Starch–protein interactions

Early studies have demonstrated that starch–protein interaction in the starch matrix can reduce the rate of α-amylolysis in cereal and legume products, possibly attributed to gluing of the protein bodies into a matrix surrounding the starch granules that might act as a barrier to enzymes (Miao et al. 2015a; Singh, Dartois, and Kaur 2010). Jenkins et al. (1987) investigated the effects of starch–protein interaction in wheat and its effects on starch digestibility, reporting that the occurrence of starch–protein interaction in white flours might account for a decrease in *in vivo* glycaemic response as well as a reduction in *in vitro* digestibility. De la Hera, Rosell and Gomez (2014) stated that the removal of gluten from wheat flour induces a high GI in 11 kinds of gluten-free bread. In addition to acting as an enzyme barrier, protein also affects the properties of starch (gelatinization, retrogradation, etc.) which is then less digestible. Parada and Aguilera (2011b) investigated the microstructure, thermal properties and

starch digestibility of cooked dough made with potato starch and wheat gluten and reported higher enthalpy (ΔH) for starch as well as lower *in vitro* digestibility for mixtures of potato starch and wheat gluten.

Starch–polyphenol interaction

Polyphenol compounds have always been regarded as substances that reduce starch digestion by enzyme inhibition (Miao et al. 2015b). However, some researchers have reported that polyphenols also react with starch granules and alter their physicochemical properties (e.g. gelatinization, retrogradation) as well as their digestibility (Girard et al. 2016). Amoako and Awika (2016a) investigated the effect of tannins on starch swelling and gelatinization as well as its *in vitro* digestibility, and demonstrated that polymeric tannins, even at relatively low levels, interact with starch to alter its properties, and dramatically affect the starch digestibility profile. Another study, performed by Barros, Awika and Rooney (2012), indicated that it might be hydrophobic interactions between tannins that bind amylose to reduce starch digestion (Figure 4B).

In addition to tannins, other polyphenols also have effects on starch digestibility. Following investigation with X-ray powder diffraction and dynamic laser light scattering, Liu et al. (2011b) stated that an interaction might exist between green tea catechins and amylose, which facilitates the association of amylose molecules to form a special non-ordered structure and then affects the postprandial glycaemic response

in vivo. Similar results were also reported by Takahama, Yamauchi and Hirota (2013) and Camelo-Méndez et al. (2016), who reported that the addition of vignacyanidin and anthocyanins can promote a reaction with starches and inhibit starch–vignacyanidin/anthocyanin complex digestion by α-amylase. In another study, Takahama and Hirota (2018) reviewed the effect of flavonoids on the digestibility of starch. They speculated that, normally, the digestion of amylose can facilitate the diffusion of enzymes into starch granules and enhance the release of amylopectin fragments; the amylose and amylopectin fragments released can be digested rapidly by enzymes to form oligosaccharides. However, when there are flavonoids bound to those fragments, they might slow down the hydrolysis of both amylose and amylopectin in starch granules, suppressing the release of amylose and amylopectin fragments. The digestion of released amylose and amylopectin fragments is slow because of their binding to flavonoids.

Impact of cell and tissue level features on starchy food digestibility

Morphological characteristics of starch and its digestibility

Attributed to differences in botanical origin, cultivar, environment, maturity etc., starch granules occur in all sizes (from 1 μm to over 100 μm) and shapes (from spheres to rods). The morphology of starch granules from different plants, also considered an important factor in their digestion, is described in Figure 5. It has been reported that smaller granules have greater enzymatic susceptibility regardless of

botanical origin (Lehmann et al. 2007). The lesser susceptibility of large-granule starches to enzymatic hydrolysis has been suggested as being due to their smaller specific surface area, which might decrease the extent of enzyme binding and ultimately result in less hydrolysis than in small granules (Warren et al. 2011). Kaur et al. (2007) studied the enzymatic hydrolysis values for native potato starches of different sizes and reported that starch with a higher percentage of small granules has a higher hydrolysis rate than that of the large or medium-sized granules. In other research, Dhital, Shrestha and Gidley (2010a) studied the relationship between granule size and *in vitro* digestibility of maize and potato starches and reported that the *in vitro* digestibility of fractionated maize and potato starch granules is well fitted to an inverse square relationship between digestibility coefficient and granule size.

Surfaces of starch granules

The surfaces of starch granules also affect their digestibility; some small openings (pores) on the surfaces of maize, sorghum, millet and rice were reported by Fannon, Haruber and Bemiller (1992) (the surface of normal maize with pores is shown in Figure 5F). Considering the size and number of pores on the surface of starch granules, the pores might play a positive role in water diffusion and access of enzymes to the interior of granules during gelatinization and hydrolysis, respectively, and subsequently affect the digestion of starch granules (Pérez and Bertoft 2010). Zhang, Ao and Hamaker (2006) studied the digestion properties of native cereal starches and stated that in some native cereal starch granules, digestive enzymes enter

through pores extending to the surface of the granules and break down the structure from inside. In this case, the number and size of pores could be important factors in the digestion process. Compared with cereal starches, native or uncooked potato starch granules have a smooth surface with the absence of any pores or pits. Warren et al. (2011) stated that cereal starches are hydrolysed at a faster rate from the inside to the outer peripheral regions in an 'inside-out' pattern, whereas potato granules are hydrolysed more slowly by exo-corrosion, starting from the surface and moving towards the inside of granules, an 'outside-in' pattern.

Cell walls in starch digestion

At the multicellular level, cell walls, and multiple overlying layers of cells, may act as partial barriers to both digestive enzyme penetration into cells and carbohydrate diffusion out of cells, and influence the availability of starch that is embedded in them (Parada et al. 2011b). Starch granules in nature are located in the tissues of plants (e.g. in the chloroplasts of green leaves and in the amyloplasts of seeds, legumes and tubers) (Hernandez, Emaldi, and Tovar 2008; Tian et al., 2016) (Figure 5G). The starch is physically inaccessible to digestion (due to the presence of intact cell walls in grains, seeds or tubers limiting its interaction with digestive enzymes) (Wursch, Delvedovo, and Koellreutter 1986). Berg et al. (2012) studied the role of cotyledon cell structure during *in vitro* digestion of starch in navy beans and demonstrated that starch hydrolysis (%) increases significantly when the cotyledon cells in the cooked whole navy beans are disrupted using high-pressure treatment. Similar results were

also reported by Tian et al., (2018): thin and compact layers were observed on the surfaces of parboiled rice and were considered to be physical barriers that reduce the starch digestibility (Figure 5H).

In addition to acting as a physical barrier between starch granules and enzymes, the cell wall also affects the physicochemical properties of starch granules and, subsequently, their digestibility. When starch granules are embedded within the plant cell (typically in potatoes) or in a food matrix (cake mix, cookies, battered products, etc.), the amount of water available can be limiting either because the cells contain less water than needed for full gelatinization, or other components in the food matrix compete for water (Dhital et al. 2016). Edwards et al. (2015) investigated the role of cell walls from chickpeas in influencing the extent of starch gelatinization during hydrothermal processing and found that unlike isolated starch, some partially gelatinized birefringent starch is observed within intact chickpea cells. Similar results were also reported by Shin, Baik and Kim (2015); they studied the physicochemical properties of starches and parenchymal cells isolated from potatoes and reported different viscosity and thermodynamic properties as well as *in vitro* digestibility between pure potato starch and starch with parenchymal cells.

Microstructural changes during processing

Natural microstructure destroyed

Most of the native starch from cereals, tubers and legumes should be processed prior to consumption, such as by milling, parboiling, extruding, cooking, etc. This processing destroys the natural microstructure of the native starch granules as well as altering their size, which also affects starch digestibility significantly (Alsaffar 2011). Compared with the smooth surface structure and high resistance to enzyme hydrolysis of intact native starch granules, processing destroys the microstructure and breaks starch granules to increase their surface area as well as exposing the inner part of the starch granules, which makes them more susceptible to enzyme hydrolysis than native ones (Dhital, Shrestha and Gidley 2010b; Liu et al. 2011a). Li, Dhital and Hasjim (2014) reviewed the effects of grain milling on starch structure and flour/starch properties and concluded that the changes in starch structures caused by milling alter starch properties including gelatinization, pasting, swelling, solubility and digestibility. Rewthong et al. (2011) studied the effect of cooking, drying and pretreatment methods on the texture and starch digestibility of instant rice. They stated that after conventional boiling, rice exhibits a porous surface structure, while after preparation in an electric rice cooker, freeze-drying or cooling at 4 °C, the microstructure is significantly deformed, and starch digestibility is affected.

Similar to the correlation between the size of starch granules and their digestibility, the particle size of processed starchy food also affects its digestibility (Mahasukhonthachat, Sopade and Gidley 2010). At a larger level, food particle geometry might create structures that have an enormous impact on digestibility

through their influence on the surface area available for digestion (Monro, Mishra and Hardacre 2011). Tamura et al. (2016) studied the *in vitro* digestibility of cooked rice either intact or homogenized, and found that intact samples are less digestible than homogenized ones. Similarly, mashed potatoes showed a higher GI *in vivo* than normal cooked potatoes; a similar finding was also reported by Tahvonen et al. (2006). At a smaller level, the particle size of processed food also affects starch digestibility; in milled barley, the rate coefficients for digestion decrease with increasing size and can be well fitted to an inverse square relationship (Al-Rabadi, Gilbert, and Gidley 2009). Similar results were also reported by Tinus et al. (2012) and Mahasukhonthachat et al. (2010) in cowpea and sorghum, respectively, with different particle sizes.

Secondary microstructure established

With different processing aims, starchy foods with protean properties (e.g. crisp, soft, flexible, etc.) are produced. With the same starch equivalent, a more fluffy microstructure established during processing indicates greater specific volume and porosity, resulting in increased accessibility of amylases to starch granules, rendering starch more susceptible to hydrolysis. Lau et al. (2015) made a comparison of the starch digestibility of western baked bread and oriental steamed bread, and the results showed that the physical structure of those breads produced by different processing methods is a major factor causing their different digestibility *in vitro* and *in vivo*. On the contrary, some dense low-porosity structures are generated during processing

which then decrease starch digestibility significantly (Zhang, Dhital, and Gidley 2015). Casiraghi et al. (1993) reported that both parboiled and quick-cook parboiled rice are digested more slowly with a lower GI than polished rice, and they attributed this to modification of the surface making it accessible to enzymatic attack (e.g. cohesiveness, dense surface and different pore size distribution in parboiled rice). A typical starchy food with a dense porous structure is spaghetti, with different flour sources as well as extrusion and drying conditions; the surface of spaghetti has structures of different porosity, offering an optional way to retard starch digestion (Stuknytė et al. 2014).

Changes in microstructure and digestibility on addition of non-starch polysaccharides

Non-starch polysaccharides also play an important role in the microstructure of starchy food as well as its digestibility (Foschia et al. 2015). Dartois et al. (2010) studied the effects of adding guar gum on the rheological properties and microstructure as well as *in vitro* starch digestibility of native waxy and normal maize and concluded that guar gum acts by forming a barrier/layer around the granules(Kaur et al., 2008)(Figure 5I). This barrier not only restricts the transfer of enzymes to the granules but also changes the swelling pattern of starch granules during gelatinization, resulting in a different granule remnant size distribution, subsequently decreasing starch digestibility; similar results were also reported by Bordoloi et al. (2012). The microstructure of starch–guar gum extrudates was also investigated by von

Borries-Medrano et al. (2016); they stated that adding guar gum can result in the formation of air cells and expansion, and that a small amount of expansion might be due to a lesser degree of gelatinization. In another study, performed by Lightowler and Henry (2009), it was found that, compared with standard mashed potatoes, the addition of hydroxypropylmethyl cellulose decreases *in vivo* glycaemic responses significantly.

Summary

Ways to control starch digestion through microstructural changes

A number of methods to reduce starch digestion by altering or retaining the microstructure at molecular, cell and tissue, and food processing levels have been achieved (Singh et al. 2010). At the molecular level, common methods include decreasing gelatinization by limiting water or heating, debranching the amylopectin with chemicals or enzymes, promoting starch retrogradation by temperature cycling (Miao et al. 2010), forming starch–lipid or starch–protein complexes, etc. At the cell and tissue level, common methods include minimizing the effect of processing on the morphology, surface and size of starch granules and keeping cell walls intact, while at the food processing level, common methods include creating a dense surface by extrusion, retaining larger particle sizes by minimizing processing, forming a barrier/layer by adding some non-starch polysaccharides, etc. (Foschia et al. 2015).

The detailed ways to reduce starch digestion by microstructural changes are also listed in Table 1.

Future study suggestion

Current studies on the effect of the microstructure of starchy food on its digestibility from the perspective of molecular, cell and tissue, and food processing levels have been reviewed as well as the technologies and methods that modulate starch digestibility through microstructural modification. It is clear to state the importance of microstructure in the digestion of starchy food. However, the authors feel that more work should be performed to reveal the relationships between the microstructure of starchy food and its digestibility. Firstly, more advanced technologies (micro-CT, CLSM, etc.) should be combined to obtain further understanding of how the microstructure of starchy food modulates its digestion. Secondly, more information on mouth-simulated processing is needed since the mouth shapes the microstructure and mixes α-amylase in starchy food thoroughly by chewing. Thirdly, the relationship between starch and other compounds (proteins, lipids, polysaccharides, etc.) should be studied at least in a ternary system (starch–lipid–protein or others) to have a better understanding of the digestibility of complexes.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This work was supported by the National Postdoctoral Programme for Innovative Talents (208027) and the National Key Research and Development Programme (2016YFD0400805).

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Figure legends

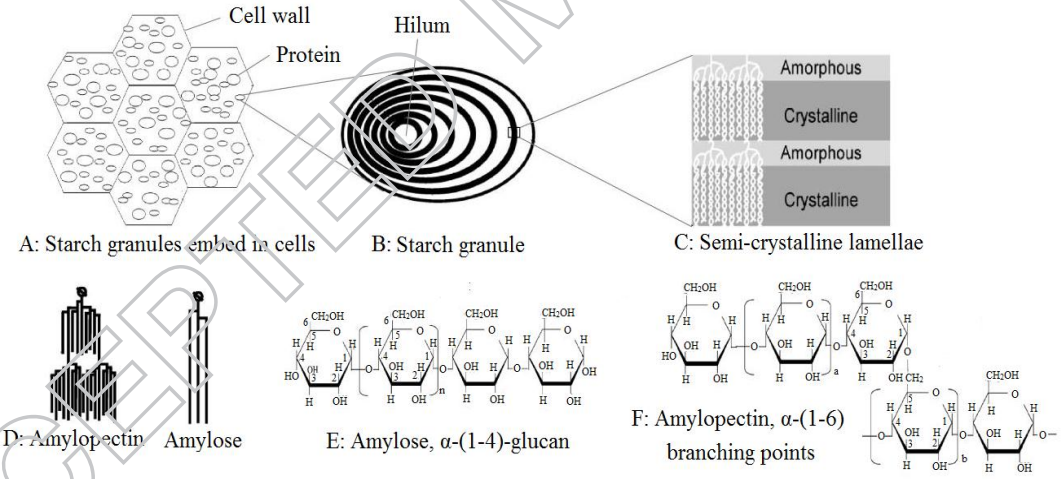

Figure 1 Architecture of starch structures, adapted and redrawn from Faraj, Vasanthan and Hoover (2004), Li, Dhital and Hasjim (2014) and Tester, Karkalas and Qi (2004).

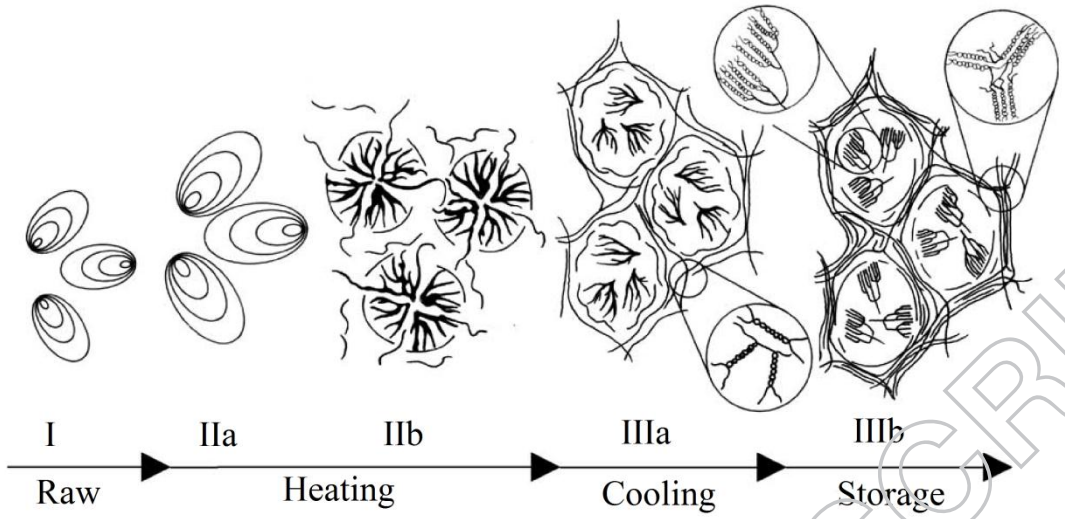

Figure 2 Schematic representations of changes that occur in a starch–water mixture during heating, cooling and storage. (I) Native starch granules; (II) gelatinization, associated with swelling [a] and amylose leaching and partial granule disruption [b], resulting in the formation of a starch paste; (III) retrogradation: formation of an amylose network (gelation/amylose retrogradation) during cooling of the starch paste [a] and formation of ordered or crystalline amylopectin molecules (amylopectin retrogradation) during storage [b]), adapted from Goesaert et al. (2005).

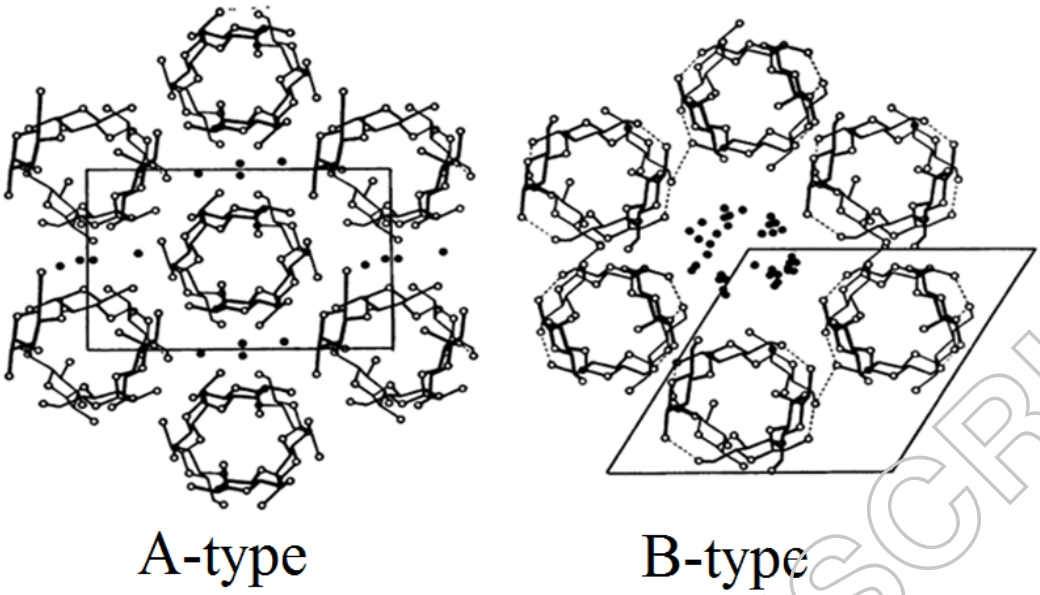

Figure 3 A- and B-type crystalline structures of different botanical origin, adapted from Wu and Sarko (1978).

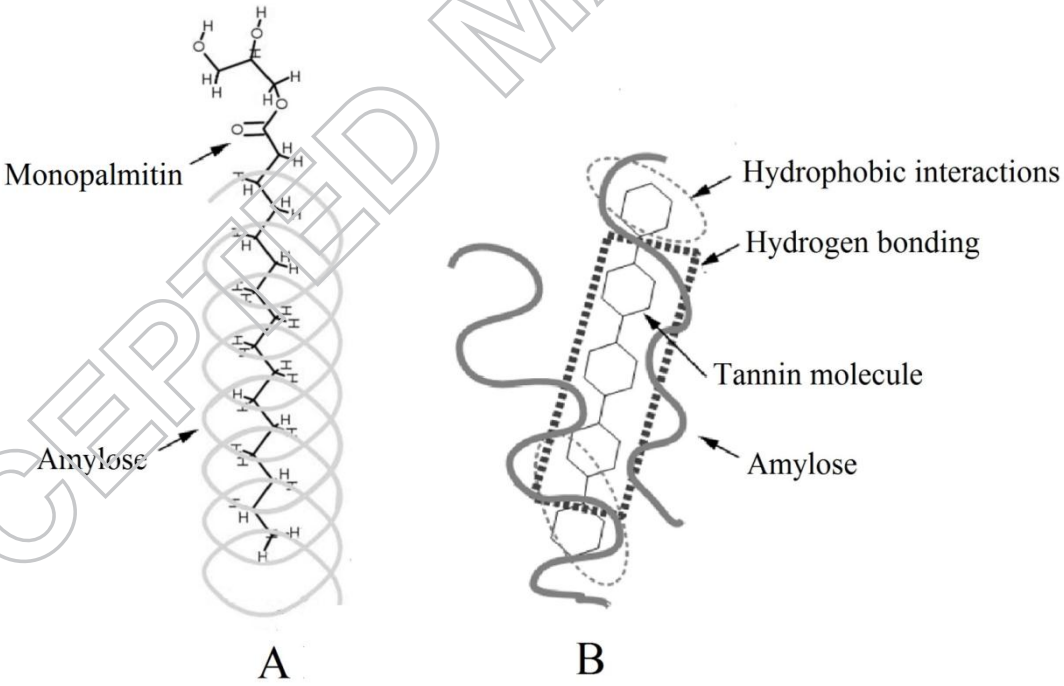

Figure 4 Structure of amylose with lipid and polyphenol (A: amylose–monopalmitin; B: amylose–tannin), adapted from Copeland et al. (2009) and Amoako and Awika (2016b).

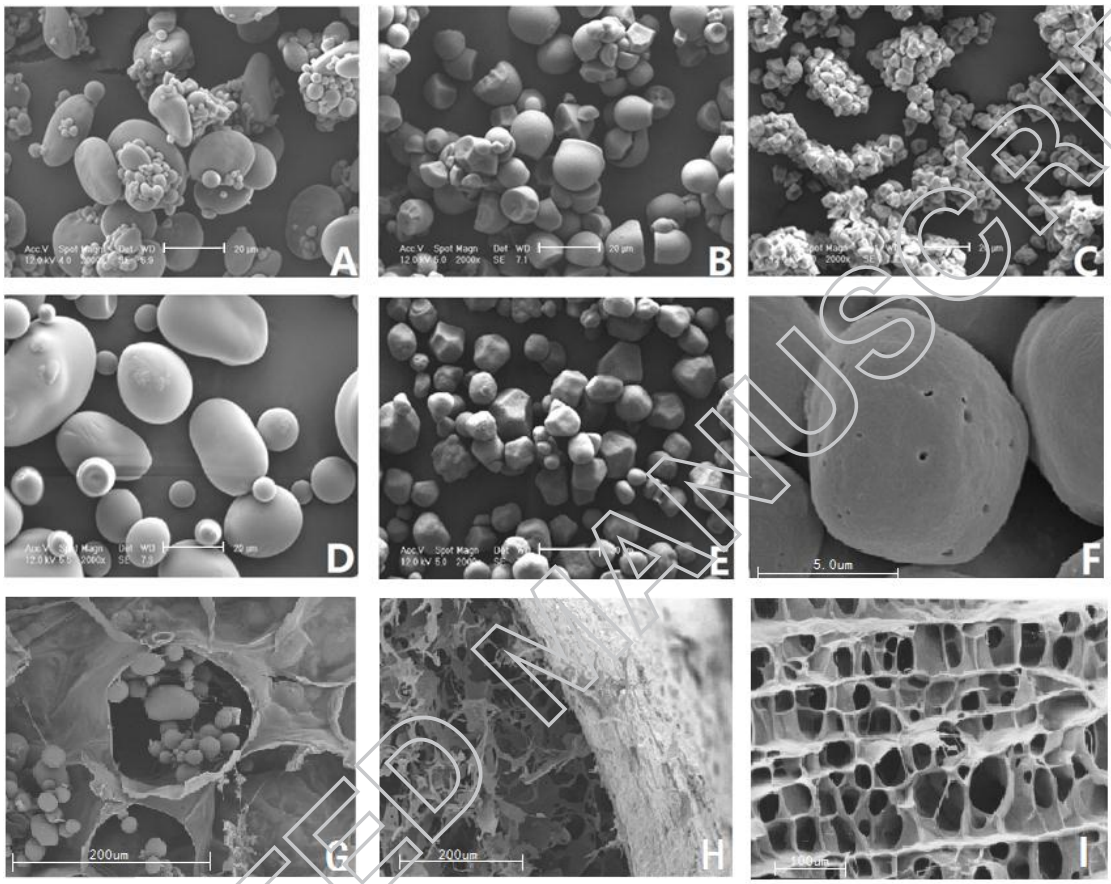

Figure 5 Morphology of starch granules of different botanical origin (A: wheat; B: tapioca; C: rice; D: waxy potato; E: normal maize; F: surface of normal maize), adapted from Blazek and Gilbert (2010), Chen and Zhang (2012), Tian et al., (2016), Tian et al., (2018), Kuar et al., (2008).

Table 1 Current technology on microstructure study and ways to reduce the starch digestion

Microstructure	Technology on microstructure study			Methods to reduce starch digestibility	
Structure level	Technology	Function	Reference	Technology	Reference
Molecular level	XRD	Crystal type and degree	Warren et al. (2016)	Gelatinization by limit water or temperature	Miao et al, (2010)
	DSC	Thermal Properties	Tian et al. (2016)	Retrogradation by temperature cycles	Parada & Aguilera, (2011a)
	GPC	Molecular weight distributions	Xu et al. (2017)	Starch-lipid	Ai et al. (2013)
	HPAEC	Amylopectin fractionation	Xu et al. (2017)	Starch-protein	Jenkins et al. (1987)
	AFM	Molecular networks	Tang & Copeland (2007)	Starch-phytochemical	Amoako & Awika, (2016)
	NMR	Quantify helices and amorphous conformational features	Warren et al. (2016)	Structure modification by chemicals	Cai et al, (2014)
	FTIR	Functional groups absorbance	Warren et al. (2016)	Debranching by enzymes	González-Soto et al, (2014)
	LCM-Raman	Characterize molecular order	Wang et al. (2017)		
Cell and tissues	SEM	Surfaces changes	Cieśla et al. (2015)	Alter granules size	Kaur et al. (2007)
	CLSM	Spatial	Tamura et	Retain the surface	Berg et al,

		position	al.(2016)	and cell wall	(2012)
Food level	RVA	Rheological characteristics	Bordoloi et al.(2012)	Minimal process	Li, Dhital & Hasjim, (2014)
	Micro-CT	3D structure	Renshaw et al.(2016)	Non-starch polysaccharide	Foschia et al, (2015)

Abbreviations: XRD: X-ray diffraction; DSC: Differential Scanning Calorimetry; GPC: Gel-permeation chromatography; HPAEC: High-performance anion-exchange chromatography; AFM: Atomic force microscopy; NMR: Nuclear magnetic resonance; FTIR: Fourier transform infrared; LCM-Raman: Laser confocal micro-Raman spectroscopy; SEM: Scanning electron microscope; CLSM: Laser scanning confocal microscope; RVA: Rapid viscosity analyzer; Micro-CT: Micro-computed tomography.