Adil Gani
Bilal Ahmad Ashwar *Editors*

Food biopolymers: Structural, functional and nutraceutical properties

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Part I

Starch: Structure, Functions, Bioactivity and Applications

Starch: An Overview

Khalid Gul, Nisar Ahmad Mir, Basharat Yousuf, Farhana Mehraj Allai, and Savita Sharma

Introduction

Starch is one of the most abundant biopolymers and serves as energy reserve in many plants including cereals, tubers, roots, fruits and seeds. Starch, the second largest biomass on earth, is a natural, abundant, cheap, available, renewable, and biodegradable polymer (Doi et al. 2002; Chandanasree et al. 2016; Le Corre et al. 2010). It is the primary source of stored energy in cereal grains. Although the amount of starch contained in grains varies, it is generally between 60 and 75% of the weight of the grain and provides 70–80% of the calories consumed by humans worldwide.

Commercial starches are obtained from cereal grains, particularly from corn, wheat, and rice, and from tubers and roots, particularly potato, sweet potato, and tapioca (cassava). Starch obtained from corn, potatoes, cassava, and wheat in the

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native and modified form accounts for 99% of the world production. The importance of starch, both biologically and technologically, is well known, as is its central role in the human diet. Starches have an enormous number of food uses, including adhesive, binding, clouding, dusting, film forming, foam strengthening, anti-staling, gelling, glazing, moisture retaining, stabilizing, texturizing, and thickening applications. The demand of starch has increased enormously in recent years as starch is being widely used in production of ethanol and biodegradable plastics (Wani et al. 2012) apart from being used in food processing industries (Gul et al. 2014). Native starches when cooked can easily retrograde and there is a gelling tendency of pastes besides easily undergoing syneresis. Therefore, starches are modified primarily to overcome the shortcomings of native starches and increase their usefulness for industrial applications. To meet specific requirements or demands, different modification methods such as physical, chemical, and enzymatic have been used to enhance or inhibit their inherent properties or to endow specific properties of starch.

Starch Chemistry

Starch is organized in discrete particles called granules whose size, shape, morphology, composition, and supramolecular structure depend on the botanical source (Fig. 1). Depending on the origin of starch, the granules can vary in shape, size, structure and chemical composition (Smith 2001). Starch granules are relatively dense and insoluble and hydrate only slightly in cold water. They can be dispersed in water, producing low-viscous slurries that can be easily mixed and pumped. Starch granules occur in all shapes and sizes (spheres, ellipsoids, polygons, platelets, irregular tubules). Their dimensions range from 0.1 to over 200 µm, depending

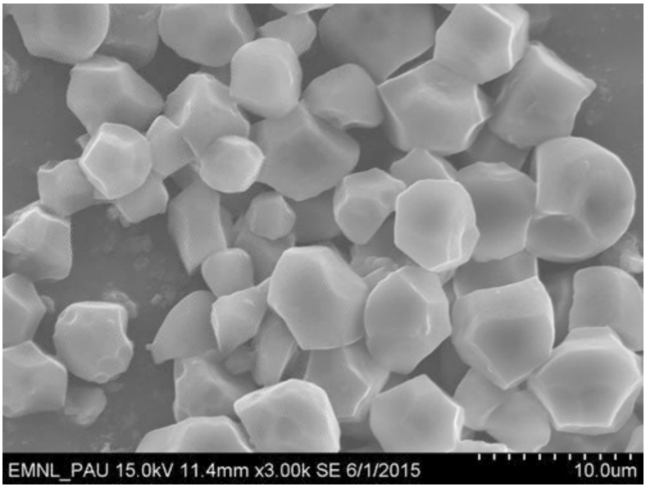

Fig. 1 Scanning electron micrograph of rice starch granules

on the botanical source. Differences in external granule morphology are generally sufficient to provide unambiguous characterization of the botanical source, via optical microscopy.

Regardless of the botanical source, starch is a polymer of the six-carbon sugar D-glucose, often referred to as the "building block" of starch. Starch granules are partially crystalline particles composed mainly of two homopolymers of glucopyranose with different structures: amylose, which is composed of units of D-glucose linked through α–D–(1–4) linkages and amylopectin,the branching polymer of starch, composed of α–D–(1–4)-linked glucose segments containing glucose units in α–D (1–6) branches (Fig. 2).

Although amylose and amylopectin are both composed of D-glucopyranose molecules, dissimilarities between these two polymers result in major differences in functional properties. Some important characteristics of amylose and amylopectin are presented in Table 1.

Amylose is a linear polymer, although evidence has suggested some branches in its structure. Amylose can also be present as a hydrophobic helix, allowing the formation of a complex with free fatty acids, fatty acid components of glycerides, some alcohols, and iodine (Thomas and Atwell 2005). Amylopectin is larger than amylose and their chains are classified as small chains, with an average degree of polymerization (DP) of about 15, and large chains, in which the DP is larger than 45. This unique configuration ordered in the packing arrangement contributes to the crystalline nature of the starch granule. The crystallinity reflects the organization of amylopectin molecules within the starch granules, whereas amylose makes up most of the amorphous materials that are randomly distributed among the amylopectin clusters (Blanshard 1987). Native starch granules observed microscopically under plane-polarized light exhibit the characteristic polarization of "Maltese Cross", which is due to birefringence properties of the crystalline portion of the granule (Fig. 3).

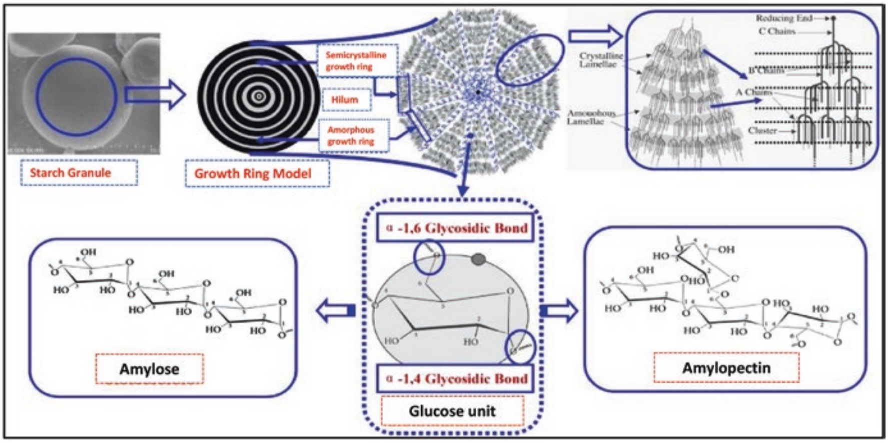

Fig. 2 Schematic diagram of the starch structure. Adapted from Liu et al. (2017)

Table 1 Characteristic features of amylose and amylopectin

Characteristic	Amylose	Amylopectin
Structure	Linear	Branched
Linkages	α-1,4	α-1,4 and α-1,6
Molecular weight	<0.5 million	50–500 million
Gel formation	Firm	Soft
Color with iodine	Blue	Reddish brown

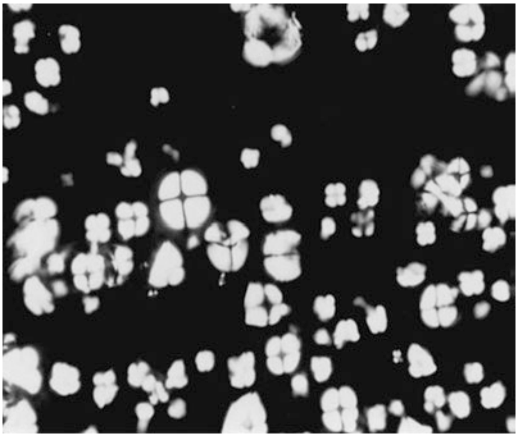

Fig. 3 Maltese cross in starch granules observed under polarized light

Amylose and amylopectin molecules are packaged into semi-crystalline aggregates and these aggregates are systematically packaged into starch granules. In these tightly packaged starch granules, the starch molecules have little affinity for water and are not functional (Blanshard 1987). The amylose content of starch varies: waxy, normal, and high-amylose starch consist of 0–8%, 20–30%, and more than 40% amylose, respectively (Li et al. 2008a, b). Branch chains of amylopectin form double helices and contribute to the crystalline structure of the granules, whereas amylose is amorphous and interspersed among amylopectin molecules (Jane et al. 1992).

Amylose and amylopectin do not exist free in nature, but as components of discrete, semicrystalline aggregates called granules. The size, shape, and structure of granules varies among botanical sources (Table 2). The diameters of the granules generally range from less than 1 μm to more than 100 μm, regular (spherical, ovoid, or angular) or quite irregular shapes. Wheat, barley, and rye granules exhibit two separate distributions of granule sizes and distinctly different shapes. Some granules, such as those in oats and rice, have a higher level of structure in which many small, individual granules are cohesively bound together in an organized manner. These are called compound starch granules. Although the major components of all types of starch granules are amylose and amylopectin polymers, there is great diversity in the structure and characteristics of native starch granules.

Table 2 Granule size and shape of starches of different botanical sources

Property	Dent corn	Waxy corn	High amylose corn	Wheat	Rice	Potato	Tapioca
Diameter (μm)	5–30	5–30	5–30	1–45	1–3	5–100	4–35
Shape	Polygonal, round	Polygonal, round	Polygonal, round, irregular	Round lenticular	Polygonal, spherical compound granules	Oval, spherical	Oval, truncated

Adapted and modified from Alexander (1995)

Physicochemical and Functional Characteristics of Starch

Starch when heated in excess of water results in the disruption of crystalline structure, due to breakage of hydrogen bonds, and water molecules form hydrogen bonds to the exposed hydroxyl groups of amylose and amylopectin. This results in an increase in granule swelling and solubility. Swelling power and solubility provide evidence of the magnitude of interaction between starch chains within the amorphous and crystalline domains. The extent of this interaction is influenced by the amylose/amylopectin ratio, and by the characteristics of amylose and amylopectin in terms of molecular weight distribution, degree of branching, length of branches and conformation of the molecules. Amylose-lipid complexes have been shown to restrict swelling and solubilization (Hoover and Hadziyev 1981). Swelling power provides an evidence of non-covalent bonding between starch molecules. Factors that determine the degree of swelling and solubility include amylose-amylopectin ratio, chain length and molecular weight distribution, degree/length of branching and conformation.

Starch Gelatinization and Retrogradation

Gelatinization is an endothermic process resulting in the disruption of molecular order of the starch granules. Double helical and crystalline structures are disrupted in starches during gelatinization. The granules are disrupted with absorption of water, losing their organized molecular structure, to facilitate swelling (García-Alonso et al. 1999). Native starches are insoluble in cold water and gelatinization is essential to facilitate water absorption and enhance their chemical and physical properties, to suit food processing industries. An increase in temperature causes the starch crystallites to break apart and undergo hydration. This results in several changes such as granular swelling, native crystalline melting, loss of birefringence, and starch solubilization (Atwell et al. 1988). Gelatinization is a two-step process, first the starch granules swell due to breakage of hydrogen bonds in the amorphous portions and in the next event, water acts as a plasticizer, resulting in hydration and swelling of the amorphous regions (Wani et al. 2012).Starch gelatinization is normally achieved by heating starch with water, but can also be achieved by heating starch in the presence of plasticizers like glycerol, ethylene glycol, and 1, 4-butanediol, alkaline solutions like NaOH and KOH, in neutral salt solutions like $CaCl_2$ and LiCl, and solvents like dimethyl sulfoxide (DMSO) (Ai and Jane 2015). After gelatinization is complete, the amorphous starch readily absorbs water and forms a paste. Upon cooling, some starch pastes can develop gels.

Gelatinization, an important functional property of starches, varies with respect to the starch composition (amylose-to-amylopectin ratio, and the percentage of phosphorus, lipids, proteins, and enzymes), the molecular structure of amylopectin, granule architecture, granule morphology, and granule size distribution (Tester 1997; Hoover et al. 2010).The temperature of initial gelatinization and the range over which gelatinization occurs depend on the method of measurement, on the starch: water ratio and granule type. To determine the gelatinization temperature of starch, many instruments have been used. These include differential scanning calorimetry (DSC), polarized light microscopy, thermomechanical analysis, and nuclear magnetic resonance spectroscopy, and other methods for the degree of starch gelatinization, such as X-ray scattering and Fourier transform infrared spectroscopy. However, DSC has emerged as the preferred method of choice for the measurement of starch gelatinization and the properties that are reported using DSC include gelatinization onset (To), peak (Tp), and conclusion (Tc) temperatures, peak height index (PHI), and enthalpy (ΔHg). The gelatinization properties of different starches determined by differential scanning calorimetry are presented.

Cooling of gelatinized starch results in the re-association of the leached amylose from gelatinized granules. This process is called retrogradation. Retrogradation causes starch gels to become less soluble during cooling due to recrystallization of starch molecules (BeMiller and Whistler 1996) and is of great interest to food technologists and industries since it profoundly affects quality, acceptability and shelf-life of starch-containing foods (Karim et al. 2000).

Retrogradation, also referred to as setback, occurs with re-crystallization of amylose which is more susceptible to retrogradation than amylopectin. Amylopectin is only minimally involved in starch retrogradation (Mua and Jackson 1998). The re-association and re-crystallization of amylose causes release of the water absorbed and bound during gelatinization, leading to the phenomenon known as syneresis. Retrogradation of gelatinized starch involves formation and subsequent aggregation of double helices of amylose and amylopectin chains, thus governing elasticity, firmness, and textural staling of all starch-containing systems (Atwell et al. 1988). Therefore, changes leading to retrogradation can restrict the starch functional properties making it less desirable for food industries. Cereal starches in general retrograde more slowly, and to a lesser extent, than tuber and root starches (Roulet et al. 1990). Differences in retrogradation behavior might be related to amylopectin fine structure, lipid content, amylose/amylopectin ratio and molecular weights. Avarami equation is frequently used to analyze retrogradation kinetics, however, this analysis implies a single step process. Since retrogradation is more complex, this analysis has therefore limited applicability.

Retrogradation in starches is commonly measured using a DSC, texture analyzer or a rheometer. While the DSC analysis is sensitive to chain ordering of the amylopectin fraction, the mechanical tests are sensitive to chain entanglements with/without the formation of crystallites (Shevkani et al. 2017). Rheological techniques are suited to monitor gel firmness (rigidity) on ageing and are usually carried by measuring the storage modulus (G`). These techniques do not evaluate the role of one component or process only, but the combined effect of all the components of the gel. Karim et al. (2000) have reviewed the methods to study retrogradation of starches. DSC measures retrogradation enthalpy (ΔHret) and transition temperatures for the melting of recrystallized starch. ΔHret is the amount of energy required for dissociation of the re-associated amylopectin. Hence, it provides a quantitative measure of retrogradation, higher ΔHret means higher retrogradation tendencies.

Pasting Properties

Heating of starch continuously in excess of water causes starch granules to swell and burst. Then the amylose leaches out and the granules disintegrate resulting in the formation of a viscous material called paste (BeMiller 2007). Pasting occurs after or simultaneously with gelatinization. Pasting properties of starch are important indicators of how the starch will behave during processing and, starch is generally regarded as the most important constituent of rice in terms of cooking quality and functionality. The pasting properties of starch are used in determining the suitability of starch in different foods and other allied products. The most important pasting characteristic of granular starch dispersion is its viscosity. High paste viscosity suggests suitability as a thickening agent in foods and as a finishing agent in the textile and paper industries. The pasting characteristics of starch are determined either using a Brabender Visco Amylograph or a Rapid Visco Analyzer (RVA) (Wickramasinghe and Noda 2008; Tukomane and Varavinit 2008; Lin et al. 2009). Rheometers (Park et al. 2007; Li et al. 2008a, b) or viscometers, which record viscosity profiles continuously with changes in temperature are also used to measure the pasting properties. RVA is used to determine pasting properties such as peak, final, setback, and breakdown viscosity, pasting temperature, and peak time. In this test, starch is mixed with water and allowed to hydrate rapidly on heating, then held constant for a specific time, and finally cooled to measure the pasting properties. As heating continues, an increase in viscosity can be observed by swelling of starch granules, which reflects the process of pasting. The temperature at the onset of viscosity increase is termed pasting temperature. Viscosity increases with continued heating until the rate of granule swelling equals the rate of granule collapse, which is referred to as the peak viscosity (PV). PV reflects the swelling extent or water-binding capacity of starch and often correlates with final product quality since the swollen and collapsed granules relate to the texture of cooked starch. Once PV is achieved, a drop in viscosity, or breakdown, is observed as a result of disintegration of granules. Breakdown is a measure of the ease of disrupting swollen starch granules and suggests the degree of stability during cooking (Adebowale and Lawal 2003). Minimum viscosity, also called hot paste viscosity, holding strength, or trough, marks the end of the holding stage at the maximum temperature of the RVA test. The cooling stage begins and viscosity again rises (setback) which is caused by retrogradation of starch, particularly amylose. Setback is an indicator of final product texture and is linked to syneresis or weeping during freeze–thaw cycles. Viscosity normally stabilizes at a final viscosity or cold paste viscosity, which is related to the capacity of starch to form a viscous paste or gel after cooking and cooling (Newport Scientific 1998). Other components naturally present in the starchy material or additives interact with starch and influence pasting behavior (Newport Scientific 1998).

Modification of Starch

Native starch, extracted from plants, cannot always withstand the extreme processing conditions, e.g., high temperature, freezethaw cycles, strong acid and alkali treatments, and high shear rates (Hermansson and Svegmark 1996; Wang and Copeland 2015). In addition, retrogradation occurs after loss of ordered structure on starch gelatinization, which results in syneresis or water separation in starchy food systems. Therefore, its use is limited and it unacceptable in many industrial applications. However, these shortcomings of native starch could be overcome, by modifying the starches. Modification of starch alters the properties of starch, including solution viscosity, association behavior, and shelf life stability in final products. Different techniques are used to modify native starch to enhance or inhibit its inherent properties, or to endue its specific properties to meet the requirements of industrial applications. Common modification methods for starches include physical (e.g., high pressure autoclave, osmotic pressure treatment, extrusion, irradiation, etc.), chemical (e.g., oxidation, esterification, etherification, hydroxypropylation), and enzymatic modifications (e.g., dextrin) (Liu et al. 2017). The commonly used methods for starch modification are summarized in Table 4.

Chemical modification is the most widely explored modification method due to the non-destructive nature of a select few of the processes and potential increases in the functionality of the modified starch. Chemical modification is generally achieved through derivatization, such as acetylation, cationization, oxidation, acidhydrolysis, and cross-linking. These methods are however limited due to environmental concerns and consumer safety (Ashogbon and Akintayo 2014). Starches can also be modified physically to improve their solubility and change particle size. The physical modification involves the treatment of native starch granules under different temperature/moisture combinations, pressure, shear, and irradiation and this modification has been gaining wider acceptance because of the absence of chemical reagents in the modified starch. Pre-gelatinization is the simplest of all starch modifications. It is effected by the cooking of aqueous starch slurry and subsequent drum drying (Tharanathan 2005).

Table 4 Common methods of starch modification

Modification	Types	Reference
Physical	Thermally inhibited treatment (dry heating)	Chiu et al. (1998)
	Deep freezing	Szymonska et al. (2000)
	Multiple deep freezing and thawing	Szymonska et al. (2003)
	Iterated syneresis	Lewandowicz and Soral-Smietana (2004)
	Corona electrical discharges	Nemtanu and Minea (2006)
	Mechanical activation-with stirringball mill	Huang et al. (2007)
	Micronization in vacuum ball mill	Che et al. (2007)
	Osmotic-pressure treatment	Pukkahuta et al. (2007)
	Instantaneous controlled pressure drop (DIC) process	Zarguili et al. (2006); Maache-Rezzoug et al. (2009)
	Pulsed electric fields treatment	Han et al. (2009)
	Superheated starch	Steeneken and Woortman (2009)
	Ultrasound	Jambrak et al. (2010); Sujka and Jamroz (2013)
	Dry heating with ionic gums	Gul et al. (2014); Chandanasree et al. (2016); Lim et al. (2002)
	Gamma irradiation	Wani et al. (2014); Gul et al. (2016)
Chemical	Acid hydrolysis	Sanguanpong et al. (2003); Akubor (2007); Rolland-Sabate et al. (2012)
	Acid hydrolysis in alcohol	Ferrini et al. (2008); Cavallini and Franco (2010)
	Alkali treatment	Raja (1992)
	Acetylation	Tran et al. (2007); Osundahunsi and Mueller (2011); Mbougueng et al. (2012)
	Cross-linking	Nabeshima and Grossmann (2001); Jyothi et al. (2006), Tran et al. (2007); Varavinit et al. (2007)
	Cationization	Han and Sosulski (1998)
	Oxidation	Tran et al. (2007); Sangseethong et al. (2009, 2010); Amorim et al. (2011); Klein et al. (2014); Beninca et al. (2013)
	Ozone-oxidised starch	Kesselmans and Bleeker (1997);An and King (2009);Chan et al. (2009)
	Hydroxypropylation	Schmitz et al. (2006); Jyothi et al. (2007)

Recent developments in biotechnology have provided means for the modification of starch during the growth of the plant. Different amylose levels, amylopectin structure, and phosphorus contents from various plant sources can be produced using antisense reduction of enzyme activity of single or multiple enzymes (Jobling et al. 1999). Modifications can be achieved through transgenic means by introducing genes for new enzymes into a desired plant from other plants or novel mutations for enhanced carbohydrates.

Applications of Modified Starches

Starches have found enormous uses in food and other industries. Modification of starch is an ever evolving industry with numerous possibilities to generate novel starches which includes new functional and value added properties as demanded by the industry. Modified starches have wide applications as compared to native starches. Starch modification is primarily carried to overcome the shortcomings of native starch and increase its usefulness for industrial applications (Table 5). Starch can be modified by hydrolysis to serve as a fat replacer. Well-known fat replacer from starch base is maltodextrin beside some other starch hydrolysis products. It is widely used for low-fat butter spread/margarine, low fat mayonnaise, low fat milk type products and low-fat ice cream (Sajilata and Singhal 2005).

Several studies have been reported on the potential use of modified starches as texture improver in the food industry. It can provide crispness of crackers and biscuits, desired chewiness for certain foods, viscosity breakdown resistant for canned foods, and improvement in the quality of extruded products. Modified starches have

Table 5 Starch modifications and their applications

Modification	Outcome	Applications
Cross-linking	Increased cooked granule rigidity and stability, tolerance to high shear and temperature and low pH	Viscosity builders in high temperature and high shear processing (e.g. in canning and retort processing, in applications that require viscosity control during pumping operations
Genetic modification	Waxy, high amylose	High viscosity and potential for RS3 resistant starch respectively
Partial hydrolysis	Depolymerized, reduced viscosity, increased retrogradation	Confectionary, batters, coatings
Pregelatinized and cold-water swelling	Dispersible in cold water	Convenience foods (e.g. Instant puddings)
Oxidation	Depolymerized, reduced viscosity, improved clarity, reduced syneresis, improved cling	Batters and breadings, other coatings
Stabilization/ starch esters	Reduced gelatinization temperature, decreased retrogradation, and a reduced tendency to form gels, improved clarity	Refrigerated and frozen foods, emulsion stabilizers
Stabilization/ starch ethers	Reduced gelatinization temperature, high viscosity, decreased retrogradation and good freeze-thaw stability, improved clarity	Many applications: gravies, dips, sauces, fruit pie fillings, and puddings

Source: Adapted from Singh et al. (2007)

been used to prepare resistant starches which are further used to prepare slow digestible food products for example cookies, muffins and breads. In recent years, modified starches are being used for high shear and temperature stability, and for the encapsulation and controlled release of different pigments, flavors and oils. Other related benefits of modified starches are: stabilizer, emulsifier, thickening agent, dusting agent, drying aids, binder, clouding agent, suspending agent and for freeze-thaw stability (Abbas et al. 2010). Modified starches have also been used to produce biopolymer films (biodegradable films) to partially or entirely replace plastic polymers because of low cost and biodegradability and good mechanical properties (Xie et al. 2005).

Conclusions

Starch is the reserve carbohydrate in plant and plant materials and undoubtedly has been widely researched. The shortcomings in native starches, such as insolubility in cold water, high viscosity, and thickening after cooking, syneresis, tendency to easily retrograde and the loss of ordered structure after gelatinization in starchy food systems can be overcome. Modification of starches is being carried out since long and allows starches to be used in a variety of food applications. The physical, enzymatic and genetic modification of starch has been most promising with a large number of newer methods in starch modification being continuously explored. Though the efforts are large in chemical modification, the health of the consumer and environmental concerns should also be taken into consideration. Starch may be added to foods in order to provide thickening or product stability or potentially to carry flavors. There is still much to learn about starch granules and its modification, although considerable progress has been made in recent years.

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Resistant Starch and Slowly Digestible Starch

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Introduction

In human nutrition, starch plays an important role in supplying metabolic energy, which enables the body to perform its functions. Based on the rate and extent of digestion, starch has been classified into different fractions viz. Rapidly Digestible Starch (RDS), Slowly Digestible Starch (SDS), and Resistant Starch (RS) (Englyst et al. 1992). Starch has been quantified into these fractions using the in vitro Englyst assay: the starch fraction digested within 20 min of incubation has been classified as RDS, the starch fraction digested between 20 and 120 min corresponds to SDS, and the remaining fraction that was not further digested has been classified as RS. RDS induces a rapid increase in the blood glucose and insulin levels, which may cause a series of health complications, such as diabetes and cardiovascular diseases (CVD). SDS is slowly digested in the small intestine, thereby resulting in a slow and prolonged release of glucose into the blood, coupled to the low glycemic response. Thus SDS can be helpful in controlling and preventing hyperglycemia-related diseases. Resistant Starch (RS) is the fraction of starch that is resistant to hydrolysis by α-amylase and pullulanase enzymes in vitro and may be fermented in the colon (Englyst et al. 1982). It is that fraction of starch, which escapes digestion in the GI tract but may be fermented in the colon (Englyst et al. 1996). The end-products of fermentation are carbon dioxide, hydrogen, methane and short chain fatty acids (SCFAs).

RS is measured as the difference between total starch (TS) and the sum of rapidly digestible starch (RDS) and slowly digestible starch (SDS) (Sajilata et al. 2006).

$$\mathrm{RS} = \mathrm{TS} - \left(\mathrm{RDS} + \mathrm{SDS}\right)$$

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RS may escape digestion due to various reasons. The compact molecular structure of starch may limit the accessibility of hydrolytic enzymes (Haralampu 2000). The starch may be physically inaccessible to the hydrolytic enzymes as in grains, seeds and tubers. The starch granules may also be configured in such a manner which prevents their digestion e.g., unripe bananas, raw potatoes, and high amylose maize starch (Nugent 2005). When gelatinized starch is cooled retrograded starch (starch crystals) is formed which is resistant to digestive enzymes. This form of 'retrograded' starch is found in foods like corn flakes, and cooked and cooled potatoes (approximately 5%) (Haralampu 2000). Chemical modifications like esterification, etherification and cross linking of starch also makes it resistant to enzymatic hydrolysis (Lunn and Buttriss 2007). RS has been further classified into five types: RS1, RS2, RS3, RS4 and RS5.

RS1

This form of RS is physically inaccessible to hydrolytic enzymes because it is entrapped within the food matrix such as partly milled grains and seeds. It can be used in a variety of conventional foods as it is stable to most cooking operations (Sajilata et al. 2006).

RS2

The RS2 comprises of native, uncooked granules like raw potato or banana starches, whose crystallinity makes them resistant to enzymatic hydrolysis (Hernandez et al. 2008). These ungelatinized starches are resistant to digestion because of their compact structure (Sajilata et al. 2006). A particular type of RS2 called high amylose maize starch (HAM) is unique because it is stable to most cooking operations (Wepner et al. 1999).

RS3

RS3 is generally called retrograded starch (Wepner et al. 1999). It is formed when starch is first gelatinized and then cooled for retrogradation. During retrogradation the polymer chains reassociate by the formation of inter chain hydrogen bonds to form double helices. The double helices are left handed, parallel stranded and one turn of double helix is 20.8 Å. Retrograded starch has type A crystalline structure (Eerlingen et al. 1993a, b). RS3 content is also affected by degree of polymerization (DP) of amylose, with increase of DP, RS3 content increases, reaching maximum at

100 DP and then remains constant (Eerlingen et al. 1993a, b). DP level of 10–100 is necessary for the formation of double helix (Gidley et al. 1995).

RS4

RS4 is chemically modified starch and include modifications like esterification, acetylation, etherification, phosphorylation or crosslinking. RS4 is further grouped into subcategories based on their solubility in water and the experimental protocols used for analysis (Nugent 2005). Chemical modifications of starch prevent its digestion by blocking the access to hydrolytic enzymes and by the formation of atypical links (Sajilata et al. 2006; Kim et al. 2008).

RS5

Besides structural characteristics, other factors intrinsic to starch rich foods can affect enzyme activity and hence starch hydrolysis. These factors include the amylose-lipid complexes, the presence of native α-amylase inhibitors in starchy foods and non-starch polysaccharides. RS5 is formed by the complexation of amylose with lipids (Fuentes-Zaragoza et al. 2011).

Sources

Naturally cereals, seeds and other starch rich foods are excellent sources of SDS and RS (Charalampopoulos et al. 2002; Gani et al. 2020). Among non processed foods, unripe bananas are the richest source of RS (47–57%). Unripe banana flour was prepared with 17.5% RS, 73.4% total starch and 14.5% dietary fibre (Rodriguez et al. 2008). Tuber starch like potato shows B-type crystallinity which is highly resistant to enzymatic hydrolysis. Raw potato starch contains almost 75% RS (Bednar et al. 2001). Whole grains are rich sources of RS, dietary fibre and oligosaccharides while as flour group contains low concentrations of RS (Slavin 2004). Flour contains two principal components viz. protein and starch, where as whole cereal grain contains the pericarp, aleurone layers and germ that provides the lipids and fibre. Processing of cereal grains alters their chemical composition. The RS content of whole cereal grains was found to be five times higher than their respective flours (Bednar et al. 2001).

Pulse grains contain high contents of RS (Rochfort and Panozzo 2007). RS and total dietary fibre contents of 24.7% and 36.5%, respectively were found in legumes. Various factors are responsible for higher contents of RS in legumes. C-type pattern of crystallinity found in leguminous starches makes them more resistant to hydrolysis as compared to cereals which have A-type crystallinity (Mir et al. 2013). Leguminous starch contains higher levels of amylose as compared to cereal and pseudocereal starches which reflects their high RS content (Mikulíkova et al. 2008). Quick retrogradation of cooked leguminous starch makes it exceptionally resistant to hydrolysis (Tharanathan and Mahadevamma 2003).

RS content varies from a few percent to 80% in the legumes. It may further increase or decrease due to hydrothermal processing, depending on the variety of legumes and parameters of processing (Giczewska and Borowska 2003).

Processing had a great impact on the RS and SDS content of foods, and generally RS contents are reduced by severe and longer periods of processing. RS content of cooked rice reduced from 12% to 5% during grinding where as RS content of oats reduced from 16% to 3% during cooking (Muir and O'Dea 1992). Autoclaving, baking, flaking, and parboiling are known to influence starch digestibility and the yield of SDS (Brand et al. 1985; Holm et al. 1985; Casiraghi et al. 1993; Kingman and Englyst 1994). During pullulanase debranching and cooling treatment of the cooked waxy maize starch, short-term retrogradation occurs as a result of the crystallization of the amylose fraction, leading to maximum SDS formation (Miao et al. 2009).

Formation of Resistant Starch and Slowly Digestible Starch

Different modifications of starch like physical, chemical, enzymatic treatments, irradiation and genetic modifications have been employed for the formation of RS and SDS. Some of these modifications are described as follows:

Physical Modifications

Physical treatments for preparation of SDS and RS include hydrothermal treatments, recrystallization, polymer-entrapment, and extrusion. When starch is heated to various levels, it leads to the formation of RS and SDS. RS was obtained by cooking the starch above its gelatinization temperature and drying simultaneously on heated rolls like drum driers and extruders (Holm et al. 1988). Gelatinization of starch at 120 °C for 20 min, followed by cooling to room temperature also provides good yields of RS (Garcia-Alonso et al. 1999). High yields of SDS (39.3–56.7%) were obtained by dual retrogradation treatment (gelatinization-retrogradation-gelatinization-retrogradation) in rice starch (Tian et al. 2013). Good yields of RS3 were also obtained by various combinations of time and temperature treatments to various sources of native starch. The temperature treatments were autoclaving the starch at 110 °C (Berry 1986), at 121 °C (Sievert and Wursch 1993), at 127 °C (Berry 1986), at 134 °C (Berry 1986), or at 148 °C Sievert and Pomeranz 1989) for periods ranging from 30 min to 1 h. Recently effects of autoclaving temperature

(140–145 °C) and storing time (24, 48 and 72 h) on resistant starch (RS) formation from high amylose corn starch were investigated. High autoclaving temperature (145 °C) and long storage time (72 h) increased the yield of RS (Dundar and Gocmen 2013). Partial acid hydrolysis (PAH) of the high-amylose corn starch can be used to produce granular RS, which is stable to further heat treatment at atmospheric pressure (Brumovsky and Thompson 2001; Ozturk et al. 2011). PAH followed by heat moisture treatment increased the yield of boiling-stable granular RS to the maximum of 63.2%. Pyrodextrinization has been identified as a way of producing RS which is water-soluble and has non-starch linkages (Laurentin and Edwards 2004). Modification of dry starch through heat treatments, with or without addition of acids is referred to as Pyroconversion. The acids include hydrochloric acid at 0.15% (based on starch dry weight) and orthophosphoric or sulfuric acids at 0.17% (Wurzburg 1995). Pyrodextrins are commercially produced by heating dry, acidified starch in a reactor with agitation. During pyroconversion hydrolysis and transglycosidation of starch occurs which can be facilitated by spraying acid on the starch. A wide range of products that vary in available starch, digestibility, cold-water solubility, swelling power, viscosity, color, and stability were produced during pyroconversion (Ohkuma and Wakabayashi 2001).

Shin et al. (2005) reported that when granular sweet potato starch (50% moisture) is heated to 55 °C, the amount of SDS increases by 200%. It has been reported that hydrothermal treatment of granular sweet potato starch alters its structure from C_b type to A-type as a result of the melting of starch crystallites and subsequent recrystallization. This structure change converts a fraction of amorphous amylose molecules into the crystalline form, thereby decreasing enzyme susceptibility. Miao et al. (2009) showed that controlled retrogradation of partially debranched waxy maize starch can be used to make SDS and RS, which occurs due to the formation of imperfect, low-density B-type crystallites (Miao et al. 2009). Controlled debranching of waxy starch results in the formation of great number of short chains of amylose that are available for chain re-alignment, cross-linking and double helix formation, which leads to the formation of more SDS and RS contents. Other studies have shown that retrogradation correlates with the SDS and RS content of mutant maize; this maize has a higher proportion of long amylopectin chains and linear branch chains of amylopectin with DP 9–30. This type of amylopectin probably acts as an anchor point to slow the digestion of branched-chain fractions with $DP > 30$, which as physical entities are the primary constituents of SDS and RS (Zhang et al. 2008). Entrapment or encapsulation of the starch in the structured protein network can be used as a novel method for development of RS and SDS. Starch-encapsulated spheres with 44% SDS were prepared by dropping a homogeneous mixture of 1% sodium alginate (w/w) and 5 g of starch into a 2% $CaCl_2$ solution (w/v) (Hamaker et al. (2007). An SDS product has been generated by using partially gelatinized or plasticized materials to form a low-swelling network of mixed crystallites that consisted of short-chain amylose ($DP < 300$) and basic starch. This network has been formed through cooking or mixing processes, especially extrusion (Innereber and Mueller 2005). In addition SDS has been generated in feed by adding a reducing carbohydrate to comminuted cereal grain, heating the mixture followed by drying (Winowiski et al. 2005). In other words, physical modifications of the starch that affects enzyme binding and the rate of digestion can be used to modulate starch digestibility for formation of SDS and RS.

Enzyme Treatment

Controlled enzymatic treatment of starch with α-amylase, β-amylase, isoamylase, pullulanase and transglucosidase is an alternative approach to change the chain-length of starch supramolecular structure in order to achieve appropriate digestibility and glycemic response (Shah et al. 2018). RS has been prepared from high amylose starch by gelatinization followed by treatment of slurry with debranching enzymes like pullulanase and isolating the starch product by drying/extrusion (Haralampu and Gross 1998). RS products having at least 50% RS content were manufactured by forming a water-starch suspension, heating the suspension in an autoclave at 100 °C so that full starch gelatinization takes place and then cooling to allow retrogradation of amylose. The best results were obtained at a temperature of 134 °C, with four heating-cooling cycles and a starch: water ratio of 1:3.5 (Pomeranz and Sievert 1990). RS was also prepared by gelatinizing the starch (common corn starch and waxy maize starch), followed by treatment with a debranching enzyme, isoamylase or pullulanase and precipitation of the debranched starch. For precipitation, the suspension was allowed to cool at room temperature, which reduced the solubility of the starch and then the precipitate was heated at 70 °C to dissolve a small portion of the precipitate. Reprecipitation was then employed by cooling of the suspension. This repetition of the dissolving and precipitation processes improved the temperature stability of the resulting aqueous dispersion (Harris and Little 1995). Increased yields of RS were obtained by subjecting the starch to enzymatic hydrolysis (pullulanase, 40 U/g/10 h), autoclaving (121 °C/30 min), storing under refrigeration (4 °C/24 h), and lyophilizing (Reddy et al. 2013).

SDS has been prepared by debranching starch using pullulanase or isoamylase (Shi et al. 2003). In the case of waxy starches, shorter debranching time and high concentrations of debranching enzymes are more suitable for debranching starch to form SDS (Guraya et al. 2001b). A low GI maize starch with some branched structure has been developed by partial α-amylase treatment and retrogradation, and the slow digestibility was retained even after cooking (Han et al. 2006). Shorter chains of amylopectin and noncrystalline amylose molecules were rapidly digested, while DP_n 121 chains showed the greatest resistance to digestion, followed by DP_n 46 chains. A similar trend was reported in the formation of SDS from commercial starch by controlling the hydrolysis of gelatinized starch with α-amylase (Hamaker and Han et al. 2006). A novel slowly digestible storage carbohydrate comprising of more than 90% amylopectin was produced by treating a native root or tuber starch with a branching enzyme derived from a microorganism with a branching degree of at least 8.5–9% (Vander-Maarel et al. 2008). Moreover, it was reported that both the increase in branch density and the crystalline structure of starch enhances its slow digestion property through the partial shortening of amylopectin A and B1 exterior chains, as well as linear chains of amylose, through the action of β-amylase and maltogenic α-amylase (Ao et al. 2007). This correlated closely with an increase in the number of α-1, 6 linkages and a simultaneous decrease in the number of α-1, 4 linkages. The enzyme-treated starch consists of B- and V-type crystalline structures, which increases the resistance of starch to digestion. These studies suggested that enzymatic debranching of the exterior chains of amylopectin molecule can change its structure and form higher proportions of SDS and RS.

Chemical Modifications

In many processes, starch is being modified by chemical reagents to improve functionality and create commercially valuable, starch based products. The most common chemical treatments are acid treatment, oxidation, cross-linking and substitution including esterification and etherification. Recently studies have focused on such treatments in SDS and RS production (Zhao et al. 2012; Ashwar et al. 2016; Ashwar et al. 2018). The enzymatic resistance in RS4 is done by cross linking with chemical agents (Haynes et al. 2000). Cross linked starches are obtained by reaction of starch with bi- or polyfunctional reagents like phosphorus oxychloride, sodium trimetaphosphate, or mixed anhydrides of acetic acid and dicarboxylic acids like adipic acid. Cross-linking of rice, wheat, corn, potato, tapioca, oat and mung bean starches using sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin or phosphoryl chloride ($POCl_3$), produced type 4 resistant starch (Seib and Woo 1999; Zhao et al. 2012). These authors explained that the levels of RS in wheat starch cross-linked with 2% $POCl_3$, 12% STMP/STPP, and 2% epichlorohydrin were 85.6, 75.6 and 75.8 g/100 g starch, respectively. Sang et al. (2010) prepared phosphorylated wheat starch with high levels of the RS (68.7%) and SDS (24.4%). Cross-linking when carried out by sulphonate and phosphate groups between starch molecules through their hydroxyl groups brings resistance to enzymatic hydrolysis (Hamilton and Paschall 1967). Cross-linking of starch with mixtures of STMP and STPP under alkaline conditions restricts swelling of starch and imparts increasing resistance to digestive enzymes (Woo and Seib 2002). Simsek et al. (2012) prepared acetylated bean starch with high levels of the RS (44%). Acetylation of starch increased the RS content in bean, as a result of acetyl groups which blocks the action of digestive enzymes (Chung et al. 2008). Modification of starch with octenyl succinic anhydride is known to increase levels of SDS and RS more than other modifications such as acetylation, hydroxypropylation, or crosslinking (Han and BeMiller 2007; Juansang et al. 2012). Esterification with octenyl succinic anhydride (OSA) has been shown to be the most potent method of modifying waxy starch to form SDS, followed by combined modifications like crosslinking-hydroxypropylation, acetylation and crosslinking (Han and BeMiller 2007). The modified starch with attached OSA molecules may act as uncompetitive inhibitors to reduce the enzyme activity and thereby cause slow digestion of starch. As these studies showed, chemical modifications of starch can be used to prepare SDS and RS, but clinical and toxicological trials needs to be performed in order to evaluate the safety and efficacy of SDS and RS consumption.

Genetic Modification

Genetic modification of starch biosynthesis has been used to develop a strategy for generating new cultivars with desired functionality through extensive breeding and characterization of the resulting cultivars. Genetically controlled factors that affect the starch functionality include structure of starch, content of starch, interaction of cell components, and starch granule architecture. Waxy starches may be more suitable for developing SDS, since their fine amylopectin structure (i.e., the distribution of branches and chain length) is more critical for SDS formation (Guraya et al. 2001b). In one study, SDS (long-chain amylopectin starch) was developed from maize by over expressing a particular enzyme involved in starch biosynthesis (Moallic et al. 2006). This starch, with high granule crystallinity, has few short chains of amylopectin and more intermediate and long chains. Other study showed that genetic mutants containing amylopectin molecules with either a high proportion of short chains with $DP < 13$ (particularly A chains with DP 5–9) or a high proportion of long chains with $DP \geq 13$ (particularly intermediate to long B chains with $DP > 30$) contain greater proportions of SDS than wild type (Zhang et al. 2008). According to a study by Benmoussa et al. (2007), development of SDS and RS is positively correlated with the presence of both long and intermediate/short chains, respectively, while it is negatively correlated with the lowest proportion of extremely short chains. They also found that the channels in starch granules can regulate starch digestibility, since starch granules with channels are digested from the interior, and more extensive channelization of starch gives more access to the hydrolytic enzymes (Benmoussa et al. 2006). Therefore, genetic modification has the potential to produce ideal starch with high contents of SDS and RS.

Factors Influencing the Formation of RS and SDS

Various factors have been reported to influence the formation of RS and SDS. These are described as:

Starch Structure

Starch is semicrystalline in nature synthesized mostly as spherical granules in plant tissues. These granules are composed of alternating concentric layers of ordered crystalline and less-ordered amorphous lamellae extending from hilum to the surface