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Applications of native and modified corn starch (a review)

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Abstract

Native or modified starches are known to change the physical properties of different foods. For instance, native and modified corn starch can be used as a thickener, texturizer, fat replacer and stabilizer as well as for gel preparation and moisture retention. Corn starch applications include non-food such as in the paper industry and the medical filed. The chemical structure and functional multiplicity makes corn starch suitable for different applications. Nonetheless, native starch utilization is hindered due to the instability of the gels "retrogradation". This can be addressed by physical, chemical or enzymatic modifications. These modifications improve starch functional properties and expand its utilization. Specific starch applications include dairy, bakery, extruded, batters, sauces, gravies, salad dressing, and meat products.

Keywords: Starch, modification, pasting, texture, applications

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1. Introduction

Starch is a biopolymer made primarily of two major components, amylose (AM) and amylopectin (AP). The building unit of both components is D-glucose. Amylose is a linear polymer of glucose linked by α-1-4 glycosidic bond while amylopectin is branched at α-1-6 glycosidic bond in addition to the linear chain (Boyer, 2019; Sasaki et al., 2000; Whistler et al., 2012).

1.1. Amylose

Amylose is considered to be basically linear polymer composed nearly exclusively of α-1,4-linked D-glucopyranose. However, recent evidence suggested that some branches are present on the amylose polymer (Vilaplana et al., 2012). Simplified models for the structure of amylose are illustrated as a straight chain structure, but amylose is actually helical, where the interior of the helix is hydrophobic due to the hydrogen atoms which allow amylose to form a complex with free fatty acids, glycerides, and iodine (Zhu et al., 2011; Curá et al., 1995). Iodine binding is a significant diagnostic tool for quantitative and qualitative starch characterization. Amylose binding with lipids is dependent on various factors such as pH, temperature, mixing time and the molecular structure of the fatty acid or the glyceride. The resulting amylose-lipids complex can alter starch pasting properties such as gelatinization temperatures, change the textural and viscosity profile of the starch paste, and limit retrogradation.

Amylose is well known to play a critical role in starch gel formation after starch gelatinization, i.e., after heating starch in appreciable amount of water. This phenomenon is obvious in the behavior of amylose-containing starches, therefore, corn, wheat, rice, and particularly high-amylose corn starch are considered gelling starches. Gel formation is a result of amylose molecules networking via hydrogen bonding i.e., amylose retrogradation. This network is formed right after starch solubilization at 95°C and cooling to 50°C.

1.2. Amylopectin

Amylopectin is primarily branched glucose polymer that is much larger than amylose. Amylopectin is composed of α-1,4 glycosidic bonded glucose segments branched by α-1,6-link. It has been assessed that about 4–6% of the bonds of the amylopectin molecule are α-1,6 linkages which represents (Zhu, 2018; Hood, 1982) more than 20,000 branches in an average molecule. Studies suggest a bimodal size distribution of starch polymer chains, namely a mix of small and large chains (Robin, 1974; Bertoft et al., 2016; Hizukuri, 1986). The small amylopectin chain is represented by an average degree of polymerization (DP) of about 15, whereas the larger chains are around 45. Amylopectin structure is organized in crystalline structure within the starch granule, whereas amylose occupies the amorphous part of the granule. Due to the highly branched structure of amylopectin, its properties contrast from those of amylose. For instance, given the size of the starch molecule structure, retrogradation can be slower and gel network formation can either be delayed or prevented. Therefore, gels prepared from starches that predominantly amylopectin (waxy starches) are considered to have a cohesive and gummy texture due to the low retrogradation of amylopectin, whereas high amylose starches gels have strong gel with hard texture.

Amylose from different sources has a DP of about 1,500–6,000, whereas amylopectin molecule has a DP of about 300,000–3,000,000(Lin et al., 2016; Zobel, 1988). Based on these numbers, the MW of amylose can range from about 243,000 to 972,000 and amylopectin can range from about 10,000,000 to 500,000,000. Plant source is the main reason for the differences in the MW of amylose an amylopectin, but the method of isolation and MW determination are a source of variation as well. The functionality of starch in different food formulations is very dependent on the ratio of amylose/amylopectin. Because the ratio of amylose to amylopectin and their structure affect starch granule size, compactness of the granule, gelatinization and pasting properties as well as the textural attributes of the formed gel. The approximate amylose and amylopectin contents of corn starch is 25/75, waxy 1/99, tapioca 17/83, potato 20/80, high amylose corn 75/25, wheat 25/75, rice 19/81. These ratios can be manipulated by using classical or sophisticated breeding techniques. Numerous hybrid starches contain basically all amylose, all amylopectin, or amid number of ratios.

1.3. Starch granules

Starch granule is semi-crystalline structure of tightly packed amylose and amylopectin molecules, where amylose represents the amorphous part and amylopectin the crystalline region. Based on its source, starch granules can take different sizes, shapes, and structures. For example, cereal starches are polygonal oval 5-30 µm, potato starch polygonal round 5-100 µm, and rice starch 1-3 µm. In addition, large, oval granules are designated as type A (approximately 35 µm) whereas smaller, more spherical granules are type B (3 µm in diameter). Oats and rice granules organize together in groups where many small granules clustered in an organized geometric fashion. Therefore, despite of the common building unit of the starch granules, native starches are diverse in properties and functionality. The miner components of starch include proteins (0.10 to 0.35%), lipids (0.10 to 0.80%), moisture (12%), and ash (<0.5%) (Rayas-Duarte et al., 1995; Greenwell and Schofield, 1986; Acker, 1982).

2. Starch testing, modification and application

2.1. Starch testing

Many methods were utilized for starch testing and analysis for the purpose of designating starches for specific application based on their properties. The data collected using these methods led to a better understanding of the effect of starch structure on the physical changes that take place when starch is heated in the presence of enough amount of water. Each of the following instruments is used to study one of the structural or pasting properties of starch. Light microscopic and x-ray diffraction analysis have been used to study the structure and the crystalline structure of the granule (Jane et al., 1994; Bowler et al., 1980; Hoseney et al., 1977; Hoseney, 1994). In addition, Rapid Visco-analyzer and Amylograph are utilized to measure viscosity changes in controlled conditions where the swelling power, starch content, starch damage, and the amylose/amylopectin contents of starch or starchy food samples can be assessed.

2.2. Starch modification

2.2.1. Chemical modification

Two of the most important properties of starch termed “gelatinization and pasting” which are the result of changes in starch granules size and viscosity that takes place when starch is heated with water. These physical changes are irreversible and dependent on the amount of heat, stirring speed, accessible amount of water and time. Under these conditions, starch granules are solubilized and consequently able to contribute to the texture, viscosity, and moisture retention of the surrounding components of the food system. Another important property of starch is retrogradation which involves re-association of amylose molecules and occurs during cooling of the system. The frequency and degree of retrogradation are also dependent on gelatinization conditions as well as on the ratio of amylose/amylopectin. These two properties are associated with native starches but they can encounter major changes via chemical, physical, or enzymatic modification of starch.

A number of common types of chemical and enzymatic of starch modification are based on the treatment of native starch with small quantities of approved chemicals and specific type of enzymes. The purpose of these modifications is to alternate starch functionality. The chemical modification is made possible by the presence of appreciable amounts of hydroxyl groups of the glucose, the building unit of the starch polymer. Starch modification (*derivatization*) can be summarized as esterification, oxidation of the glucose hydroxyl groups to carbonyl or carboxylic groups, in addition to acid or enzymatic hydrolysis of glycosidic bonds. Different governmental agencies are responsible for regulating the quantities and the types of the chemicals used in starch modification.

Crosslinking is the most applied type of starch chemical modification where one to two chemicals can be used to crosslink starch granules by binding two hydroxyl groups of the glucose units of the same or different granules. Cross-linked starch granules are reinforced and can endure high processing conditions such as high temperatures or shearing as well as low pH (Whistler et al., 2012). Therefore, crosslinking limits granular swelling, the first step of starch gelatinization and viscosity buildup. This type of modification has direct use in food processing where high temperatures are applied and the need for starch to control the final texture of the product at specific stage of the process is required. A number of chemicals are used for starch crosslinking such as phosphorus oxychloride (starch ester), sodium trimetaphosphate (dis starch phosphate), and acetic anhydride (acetyl group) (Kou and Gao, 2018; Atwell et al., 1980; Kruger and Lineback, 1987). These reactions take place at high pH (8-11.5), because at high pH starch granules are swollen and the chemicals can penetrate into the granule. Starches can gelatinize when subjected to high pH without heating; therefore, salts such as sodium chloride and sodium sulphate are added to protect the starch by reacting with the water. It is known that gelatinization requires appreciable amount of water. The properties of the cross-linked starch are a function of time and reagents concentration. Highly cross-linked starches can show peak viscosity much lower than that of native starch, but in some situations, low crosslinking can produce starch with higher peak viscosity compared to its native starch.

Another form of starch modification is “substitution” which is in contrast to crosslinking lowers starch gelatinization temperature and prevents re-association of amylose during gel cooling, i.e., inhibits retrogradation. Substituted starches find applications in predominantly refrigerated or frozen foods. The utmost practiced starch substitution is the starch acetylation at 0.5–2.5% acetyl groups (Golachowski et al., 2015; Fennema, 1985). About 2.5% acetyl groups are permitted according to the Food and Drug Administration (FDA) regulation. Acetylation reaction is carried out by slowly adding acetic anhydride to starch slurry at pH 7.5–9.0. The pH should be maintained throughout the reaction because acetic acid is a by-product of the reaction; therefore, a steady addition of alkaline solution should be maintained to the end. At the end of the reaction the pH of the slurry should be adjusted to neutral pH and modified starch should be washed before drying. Due to its stability and clarity, acetylated-cross-linked starch is used mainly as food thickener.

To expand starch utilization in primarily hydrophobic food products, starch is substituted with 1-octenylsuccinic anhydride (OSAn), or succinic anhydride (Han et al., 2019). These products are effective as emulsion stabilizers. The reaction for making OSAn starch is basically the same as for acetate, with the exception of the use of hydrophobic cyclic anhydride and the pH of the reaction around 7-9. The properties of OSAn treated starches are similar to those of other substituted starches i.e., lower gelatinization temperature and the propensity of the gel formation is reduced, rather a rubbery mass is produced. OSAn-treated starch is used as a stabilizer in beverages, spoonable salad dressings, or as flavor encapsulater.

2.2.2. Starch conversion

For the food products that require high starch content such as candies, the starch product of choice is the converted starch. The product of starch conversion is usually reduced molecular weight polymers and viscosity. Common conversion methods include acid hydrolysis, oxidation, and enzyme treatment (Atwell et al., 1980; Kruger and Lineback, 1987). Acid hydrolysis and oxidation are performed in dry environment whereas enzyme conversions are done in aqueous starch slurry (Han et al., 2019). The extent of starch conversion is dependent on the applied method, starch source and the reaction time. Hydrochloric acid and sodium hypochlorite are the common chemicals used in acid hydrolysis and starch oxidation, respectively, whereas the enzymes include α–amylase, β-amylase, and Pullulanase.

2.2.3. Physical modification

Physical modification is another way of treating starch to alter its native properties and introduce new form of starch with specialized functionality. The most popular physical method is dry pre-gelatinize starch, where the granule is completely destroyed (Kaur et al., 2012; BeMiller and Huber, 2015; Hedges, 1992; Pitchon et al., 1986; Stute, 1992). This type of starch is used as a thickener for products that receive low heat treatment. Another type of physical modification that produces cold water swelling starches or instant starches which have application in products that receive no heat treatment. These starches are modified by heating starch beyond the gelatinization temperature but in low moisture content. This process does not lead to starch gelatinization but granules will swell and the crystalline part of the granule remains intact. Pre-gelatinization can be done using drum dryers, spray cooking and solvent-based treatment.

2.2.4. Starch enzymatic modification

The digestion of starch has been subjected to many investigations, typically involving in vitro measurement of the susceptibility of starches to attack by different enzymes, rather than measuring actual in vivo experiment (Dona et al., 2010). The enzymatic digestion of starch is a complex multiple chemical process, which can be partially quantified by several measures which differ from one another depending on the enzyme(s) and reaction conditions used in the hydrolysis. These measures include the rate of starch depletion, rate of glucose release, and the rate of the produced oligosaccharides. Subtle differences in the structure of starch granules with similar amylose content can influence α-amylolysis and the mechanism of hydrolysis, these differences are the main cause of the degradation degree (Blazek and Copeland, 2010). Therefore, the ratio of amylose to amylopectin, as well as, the degree of interaction between starch chains within the amorphous domains in the native granules as shown by XDR, are the determinant factors of hydrolysis α-amylolysis (Zhou et al., 2004). The only known enzyme that can hydrolyze starch is a-amylase. After the granule attack by a-amylases the product is dextrins which can be further degraded to glucose by β-amylases. Gelatinized starch is a mix of amylose and amylopectin. The enzymatic breakdown of amylose and amylopectin by a-amylases from different sources such as human digestive enzymes involves salivary and pancreatic a-amylases (a-1, 4-glucan-4-glucanohydrolases; EC 3.2.1.1), which are calcium-containing enzymes that belong to a family of endo-amylases that catalyze the cleavage of a-D-(1,4) glycosidic bonds. These enzymes occur ubiquitously and play a dominant role in starch breakdown in microorganisms, plants and animals (Kandra, 2003). The a-D-(1,6) glycosidic bonds are broken by amyloglucosidase (EC 3.2.1.2). Other enzymes that may also play a role in the breakdown of starch by various plant and microbial species are b-amylase (EC 3.2.1.2), an exo-amylase that cleaves maltose units from the non-reducing end of a-D-(1,4) glucan chains; isoamylase (EC 3.2.1.68), which acts as a debranching enzyme; and amyloglucosidase (EC 3.2.1.3), which hydrolyses a-D-(1,4) and a-D-(1,6) glucosidic bonds (Blazek and Copeland, 2010; Butterworth et al., 2011).

2.2.5. Starch gelatinization and pasting

Starch slurry is insoluble in water and has no specific function, but when heated to about 95°C for five minutes with water it develops unique viscoelastic and textural behavior useful for many food applications (Chiu et al., 1998). This behavior is a sequence of events that take place as follows; viscosity increase due to granule swelling, amylose leaching out of the granule, granule rupture and drop in viscosity, and upon cooling to 50°C viscosity increases again. The first increase in viscosity is due to control of water movement in the system and the drop in viscosity is due to free water movement, whereas the second increase in viscosity is because of the amylose retrogradation. During retrogradation, amylose molecules form a network via hydrogen bonding between the hydroxyl groups. This network is capable of controlling water movement once again thus increases viscosity. Gelatinization is irreversible process whereas retrogradation can be reversed by heating the product. This network can be weakened when starch gel or starchy product is stored at refrigerator temperature. This process is called syneresis which is the separation of water due to amylose re-association and the disruption of the network.

Starch gelatinization profiles vary as a function of pH where extreme pH value has negative effect on native and modified starch pasting properties. Although extreme pH can induce early starch gelatinization, but this can have processing implication in some situations or it can be a processing aid in other circumstance. Therefore, early gelatinization can produce starch with lower peak viscosity. Shearing is a basic step in food processing. High shear has intense effect on starch pasting properties where starch granules start breaking sooner(Whistler and BeMiller, 1997). Whenever starch is exposed to processing condition there is a likelihood of changes in pasting properties to take place. It is well established that food systems are complex, therefore, anytime starch is added to a food system some of the food ingredient may interact with starch granules or compete for the available water and in both cases the pasting properties of starch will be negatively affected (Fallahi et al., 2016).

2.2.6. Starch and hydrocolloids blends

The addition of different gums is common practice in the food industry including starchy foods. The pasting properties of starch are expected to change because the hydrophilic gums will change the water dynamics in the system. Reports in the literature showed that the dynamic rheological properties revealed increase in the magnitude of the moduli (G′ and G″) as a function of angular frequency without any crossovers which indicates system stability. The blend exhibited increase in elasticity and decrease in viscosity (lower consistency coefficient of the power law). Flow behavior index (*n*) data showed that starch-gum blends are pseudo-plastic and revealed shear thinning behavior which further increased by increasing concentration of xanthan, fenugreek, flaxseed and okra gums. Gums increased the gel hardness of the blends after overnight storage except for xanthan (Shahzad et al., 2019; Qiu et al., 2015; Shaari et al., 2017; Li et al., 2017).

3. Starch applications

Starch is used in different foods for diverse reasons. In some cases it is used for viscosity build up, binding, water retention, or film development. The source of native starch is the most important factor to consider when choosing starch for specific application. For instance, native potato and tapioca starches produce clear weak high viscosity gels suitable for cake making or dry soups, whereas corn starch and starches with high amylose content (hard gels) are good for gummy candy products. Therefore, food processing companies need to choose the appropriate type of starch for their application. Nonetheless, when native starch properties are not suitable for specific application, different types of applications can be employed as mentioned above (Chiu et al., 1998). There are many factors to consider when choosing starch type for specific application such as sensory requirements, pH, shearing, food formulation, processing conditions, and conditions during transportation and storage. For some of these conditions native starch can be selected, but for others modified starches are more suitable.

3.1. Baked products

The role of starch in baked products starts after the product is taken out of the oven which is critical in maintaining the volume of the product. This is true for the existing native starch in the base flour and the added modified starches. In addition, modified starches can also increase moisture retention in baked products which is needed because baked products are low moisture products. This will extent shelf life and improve product texture. Cakes and brownies are emulsions of proteins fats, starch, eggs, and sugars. Starch plays crucial role in the quality of these products because of the appreciable amount of water in their formulation. Upon heating, starch granules swell by absorbing water and gelatinize. This will increase the viscosity and the texture of the cake. The increase in viscosity allow for air bubbles entrapment leading to volume increase. Therefore, starch gelatinization has to happen at the right time, because delayed gelatinization can reduce the cake volume. Early gelatinization on the other hand may cause high cake volume at the beginning then it will collapse before the end of baking process. One way to control starch gelatinization is by adjusting the amount of sugars in the formulation where higher sugar content delays gelatinization and the opposite is true.

3.2. Cookies

Cookies formulations are very different compared to cakes due to the high sugar content and low moisture. It has been shown that starch remains un-gelatinized after cookies baking because of the low moisture content of the system which limits the amount of water needed for gelatinization in addition to the high amounts of sugars that compete with the starch for water. Therefore, starch in cookies system plays the role of a texturizer. Damaged starch is expected to absorb water needed by other ingredients which has direct effect on the most important cookies quality “cookies spread”. Waxy starch is usually added to cookies ingredients to introduce chewy texture, retain moisture, and improve dough handling during cutting.

3.3. Spoonable salad dressing

Salad dressing is a very unique system with high oil content and very low pH. These types of dressings are produced at high shear and moderate temperatures. Therefore, the selected modified starch should undergo modification to survive these processing conditions. Because of the unique formulation, salad dressing must contain common and waxy modified starches to provide the needed extended texture to play stabilizing role in the final product. Amylose is responsible for the spoonability of the salad dressing, whereas waxy starch provides viscosity and stability of the dressing. The proper modification for these starches is crosslinking to varying degrees so that to endure the shear and the low pH.

3.4. Meat products

Modified starches found application in emulsified meat products such as frankfurters and bologna and different meat loaves. A combination of cross-linked and substituted starches are often used. The main role of starch in meat products is to either increase viscosity in products such as bologna or absorb released water during frankfurters cooking (Forrest et al., 1975). These roles are critical for good quality and extended shelf life of these products. In addition, these starches play important role in freeze-thaw and slice ability of the above mentioned meat products (Lawrie and Ledward, 2014).

3.5. Fat replacers

Modified starches are used in different food products as fat replacer. Beside the functionality, the most obvious value of starch fat replacers is the low calorie compared to lipids. Fat replacers properties include appropriate molecular weight, dispersibility, and water-binding capacity (Abbas et al., 2010; Richter et al., 1976). These types of starch ingredients are usually hydrolyzed starches or converted starches like maltodextrins. Starch fat replacers applications are many including salad dressing, bakery products, mayonnaise, sauces, and catsup. Some of these starches can be used as emulsion stabilizer, where the key to their effectiveness is the correct molecular weight that can remain in between the water and the oil interface. Some of these starches find wide application in nonalcoholic beverages and salad dressing prepared from OSAn treated starches (Trubiano, 1986).

4. Examples of common problems associated with starch selection

Some problems present in starchy products due to wrong starch selection or processing conditions. Here are some examples of the indications, possible cause, and the proposed solution to these problems

1. Bread: low loaf volume is caused by low gas retention. Suggested solution is adding waxy starch to the bread formulation.
2. Cake: lack of preferred moistness, which is can be due to loss of moisture and can be addressed by increase in the water content of the raw material.
3. Cake: low cake volume could be caused by early starch gelatinized and could be avoided by increasing sugar content in the formulation or by selecting a starch with higher degree of crosslinking.
4. Cake: low cake volume can be due to inadequate starch gelatinization and can addressed by reducing the sugar content, increase oven temperature, or reducing the baking time.
5. Meat: when meat products, such as frankfurters, suffer poor water-holding it can be because of the lack of water-binding capacity ingredients or low freeze- thaw stability. This can be handled by adding substituted starch or by using starch with higher water-holding capacity.
6. Sauce and dressing: too thick or viscous sauce could be a result of extreme starch swelling or gelatinization. This drawback can be handled by reducing starch content, increase water content, or by adjusting the cooking time and/or temperature.

5. Conclusion(s)

Starch is a biopolymer with unique important physical properties that can be used to stabilize food systems viscosity, stabilize emulsions, and the overall texture of foods. Nonetheless, native starches have some drawbacks that can be overcome by different chemical, physical modification or both. Gelatinization is one of the most important starch properties which can be accomplished by heating starch in appreciable amount of water for specific time at 95˚C. This process is a three steps process, granule welling, increase in viscosity, granule disruption, loss in viscosity and increase in viscosity upon cooling of the paste. The second increase in viscosity is called retrogradation where amylose molecules are networked and trap the water freed from granule disruption. This phenomenon is important during starch paste or starchy food storage or product transportation. Native starch contain varying amounts of amylose which is the most determining factor on designating starch for specific application, but some starches are amylose free. Native and modified starches are utilized in many food formulations such as meat products, bakery, soups, sauces, and dairy. It can be used as fat replacer and emulsion stabilizer, as well.

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