

Chemical Modifications of Starch; A Prospective for Sweet Potato Starch

Dhiya Eddine Bensaad¹ , Mohammed Saleh^{1*} , Khalid Ismail¹ , Youngseung Lee²  and George Ondier³ 

¹ Department of Nutrition and Food Technology, The University of Jordan, 11942, Amman, Jordan

² Department of Food Science and Nutrition, Dankook University, Republic of Korea

³ Taylor Laboratories, Houston, TX, 77041, USA

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ABSTRACT

The current review presents the potential chemical modifications and applications of sweet potato starch in food and non-food industries. Native starch in general and particularly sweet potato starch characteristics have several functional features and applications in biomedicine as well as in the food industry. Modified starch is expected to enhance such characteristics as discussed in this review. For instance, due to the polymeric and branching nature of starch; the starch is usually less soluble, absorbs less water and oil, and shows a strong ability to bind to iodine. Also, native starches have significantly lower digestibility values under enzymatic treatment. Starch modifications, therefore are designed to enhance one or more of the above-mentioned limitations; thereby, modification of starch can alter the physicochemical characteristics of the native starch to improve its functional characteristic. Starches can be modified using physical methods (annealing, heat moisture treatment, pre-gelatinization, and other non-thermal processes), chemical methods (etherification, acetylation, acid modification, cationic linking, esterification, cross-linking, and oxidation), enzymatic modification methods, genetic alteration process or combination of them.

Keywords: Modified starches, Chemical modification, Cross-linking, Physicochemical properties, Sweet potato.

INTRODUCTION

Sweet potato (*Ipomoea batatas* L.) is a starchy crop that grows around the world. It is a dicotyledonous plant that is a member of the Convolvulaceae family. The plant

has vast, nourishing store roots and develops white and purple sympetalous blooms due to the different compositions of phenolic compounds and the variety of pigments found in their root tubers (Mu & Singh, 2019). Sweet potatoes may be a more stable food source while being easier to grow and maintain and currently the principal crop of grains and legumes in many parts of the

* Corresponding author. E-mail: misaleh@ju.edu.jo

world, including the roots and tubers (Mu & Singh, 2019). In 2019, the annual global production of sweet potatoes was 91,820,929 tons whereas China produces about 90% of the world's sweet potatoes (Vithu *et al.*, 2019). Despite its high nutritional value, sweet potato is very under-utilized because of its short shelf-life, short cycle of production, and limited consumer acceptance due to its higher degree of sweetness (Saleh *et al.*, 2018).

Starch plays an essential role in developing food products and is used in foods due to its excellent gelling and thickening performance (Kolaric *et al.*, 2019). Starch also referred to as the polysaccharide, is usually employed as a food additive including thickening, stabilizer, or texture enhancer. In addition, it improves the quality of stored products (moisture retention), and as a result, it regulates the movement of water in food. Moreover, starch has the potential to be employed as a delivery vehicle for chemicals of interest to the food and pharmaceutical sectors, such as antioxidants, colorants, flavors, and pharmaceutically active proteins, among other things (Abegunde *et al.*, 2013).

However, its low resistance to shear, high retrogradation, and poor freeze-thaw stability limit starch to use in various industrial applications. Fortunately, these natural shortcomings can be overcome by different methods of modification, rather than chemical modification, physical, enzymatic, and genetic techniques can be used (Tang *et al.*, 2020). Although physical treatment of starch granules generally destroys or causes changes in the packing arrangements of the polysaccharide molecules contained within the granules; such structural changes can alter the properties and functions of the starch, including the characteristics of its hot pastes and gels and their digestibility (Punia, 2020). More specifically, physical treatments can produce starches with properties similar to that obtained by chemical modifications (i.e., lightly cross-linked starches that are known to increase tolerance to low pH, high temperatures, and high shear). However, the changes are not as dramatic and as thermo-stable as those produced by chemical modification (BeMiller, 2018). This review presents the potential chemical modifications and

applications that can be applied to sweet potato starch to enhance its applications in food and non-food industries.

Composition

The main component of the sweet potato root is starch, which can make up around 80% of the dry mass (Zhu & Wang, 2014). Sweet potato consumption has different health advantages because it contains reasonable amounts of bioactive compounds such as dietary fiber, carotenoids, phenolic acids, anthocyanins, vitamins and minerals, and protein (Gastelo *et al.*, 2014). Furthermore, Sweet potato has a high moisture level comparable to other roots and tubers and comparatively low dry matter content. The average dry matter range is about 30%. However, the moisture content of sweet potatoes depends widely on cultivars, planting location, climate, soil type, and cultivation. The sugar content of sweet potatoes in dry matter ranges from 13.6 to 37.1 percent (Nandutu, 2004).

In regards to protein content, sweet potato encompasses around 1.73%-9.14% dry base. Protein derived from sweet potatoes is primarily composed of spore mines and has significant amounts of essential amino acids (Mu & Singh, 2019). It has an excellent capacity for gelatinization and emulsifying characteristics leading to being quickly recovered by isoelectric precipitation or processed by ultrafiltration/diafiltration techniques. In addition, sweet potato protein hydrolysates exhibit notable antioxidant activity (Arogundade *et al.*, 2012).

Carbohydrates are the highest nutrient available in sweet potato roots. It accounts for around 80–90% of the total dry matter (Loebenstein & Thottappilly, 2009). The dry matter contents vary depending on the cultivars, cultural practices, and climate and are reported to range from 13 to 48% (Bradbury and Holloway, 1988; Cereda *et al.*, 1982). The carbohydrate in sweet potato roots comprises starch, cellulose, hemicellulose, pectins, and sugars. Starch accounts for 60–70% of the dry matter, although varieties having much less starch content are also reported (Cereda *et al.*, 1982; Truong *et al.*, 1988). Sweet potato has 49.7% fiber, pectin (39.5%), cellulose, hemicellulose, and lignin. Also, sweet potato dietary fiber

has significant physicochemical and functional properties (Mu & Singh, 2019). Sweet potato starch is the most abundant storage polysaccharide in plants and one of the most affordable and readily available organic biologic materials (Wang *et al.*, 2020). Sweet potato dry matter is made mainly of amylose and amylopectin with values in the range between 13.33% and 26.83% and from 73.17% to 86.67%, respectively (Mu & Singh, 2019).

Sweet potato is a source of polyphenols, of which more than 70% are chlorogenic acids and their derivatives, and 10% to 20% are flavonoid compounds (Cheng Wang *et al.*, 2017).

Also, sweet potato phenolic acid is a mixture of caffeic acid and caffeoylquinic acids typically present in all parts of the sweet potato plant (Mu & Singh, 2019).

Anthocyanins are other compounds having chemoprotective properties. Their presence is evidenced by the purple color of the flesh and jacket of the sweet potato. Cyanidin and peonidin are major aglycones (Jung *et al.*, 2011).

Starch Extraction

Starch is usually extracted from various starch-rich crops via wet separation techniques. For example, according to Kolaric *et al.* (2019), sodium chloride (1 mol. / L solution) isolates starch in sweet potatoes. In summary, the aliquot of sweet potato is usually cut into small pieces measuring 1 cm x 1 cm and homogenized for 1–2 minutes with the appropriate solution. A 1: 2 ratio of sweet potato to a saline solution is usually used. The slurry is usually filtered using sieves of varying sizes (750, 250, and 200 m). Starch was then washed with distilled water several times for a continuous wash. The precipitated starch is dried at room temperature before grinding into a fine powder. The following figure presents the extraction method of starch from sweet potatoes according to (Kolaric *et al.*, 2019).

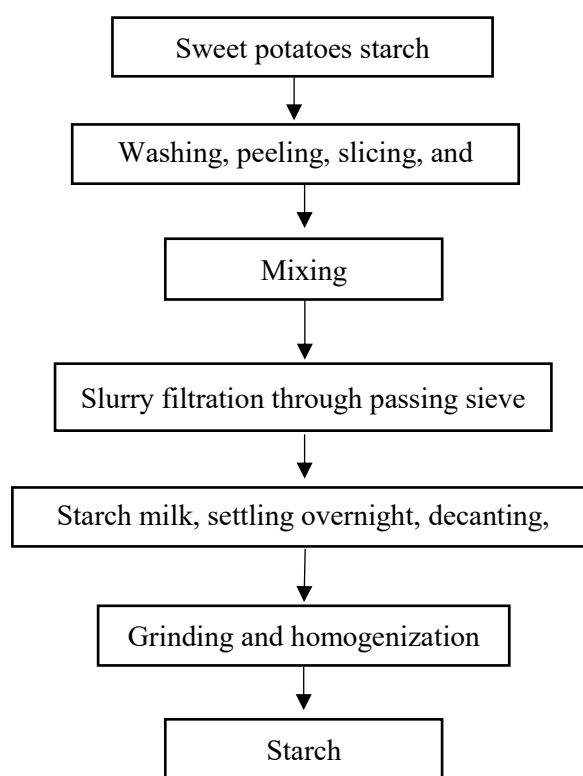


Figure 1: method of starch extraction from sweet potato with modification (Kolaric *et al.*, 2019).

Characterization of native starch

Sweet potato starches have a high digestibility, syneresis, swelling power, and solubility (Mu & Singh, 2019). Starch also has several functional features and applications in biomedicine and industry, relying on its compact structure. Because of the polymeric and branching nature of starch; the starch is significantly less soluble, less able to absorb water and oil, and strongly binds to iodine (Haq Nawaz & Dure, 2020). Native starches, on the other hand, have significantly lower digestibility values under enzymatic digestibility. The use of several physical and chemical modifications to increase their nutritional, biological and industrial enhance functional characteristics (Haq Nawaz & Dure, 2020). The following figure presents the glycosidic linkage bonds in starch

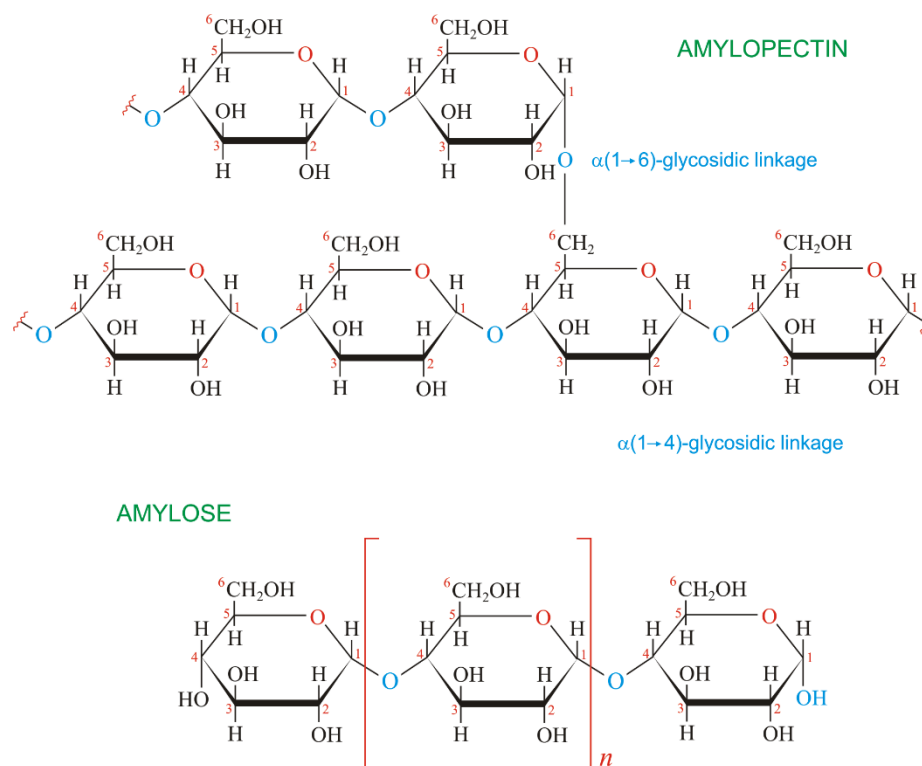


Figure 2: Structure of amylose and amylopectin in starch (Haq Nawaz & Dure, 2020).

Sweet Potato Chemical Modifications

Native sweet potato starches are very limited in usage by the food industry. It has a higher viscosity, is highly cohesive, and is more stable at low temperatures, while unstable when applied in foods more acidic. Modification techniques of sweet potato starch can be carried out by modifying its physical and chemical from native (Patria *et al.*).

Chemical modification

Chemical modification is the most frequently used starch modification method, such as etherification, esterification, oxidation, hydrolysis, and cross-linking.

The chemical modification incorporates functional groups (carboxylic, ester, ether, and amino groups) into starch molecules, significantly altering considerable improvements in starch molecules' physicochemical properties while leaving the molecules unchanged in form or size (Obadi & Xu, 2021).

Chemical modification includes altering the physicochemical characteristics of starch by adding new chemical or functional groups in starch without any physical alteration in the shape and size of the molecule. The glucose units in amylose and amylopectin have three reactive hydroxyl groups, the main sites for chemical modification in starch. The chemical modification modifies starch's physical behavior, including retrogradation, salting, and gelatinization that function by

stabilizing starch granules' intermolecular and intramolecular binding (Haq Nawaz & Dure, 2020).

These techniques are limited to use because of many problems concerning consumer safety and the environment. There has been an increasing tendency to combine several chemicals to produce novel modifications (Zia ud *et al.*, 2017).

Figure 3 shows the recent technique for modification in sweet potato starch based on the reagent used for chemical modification.

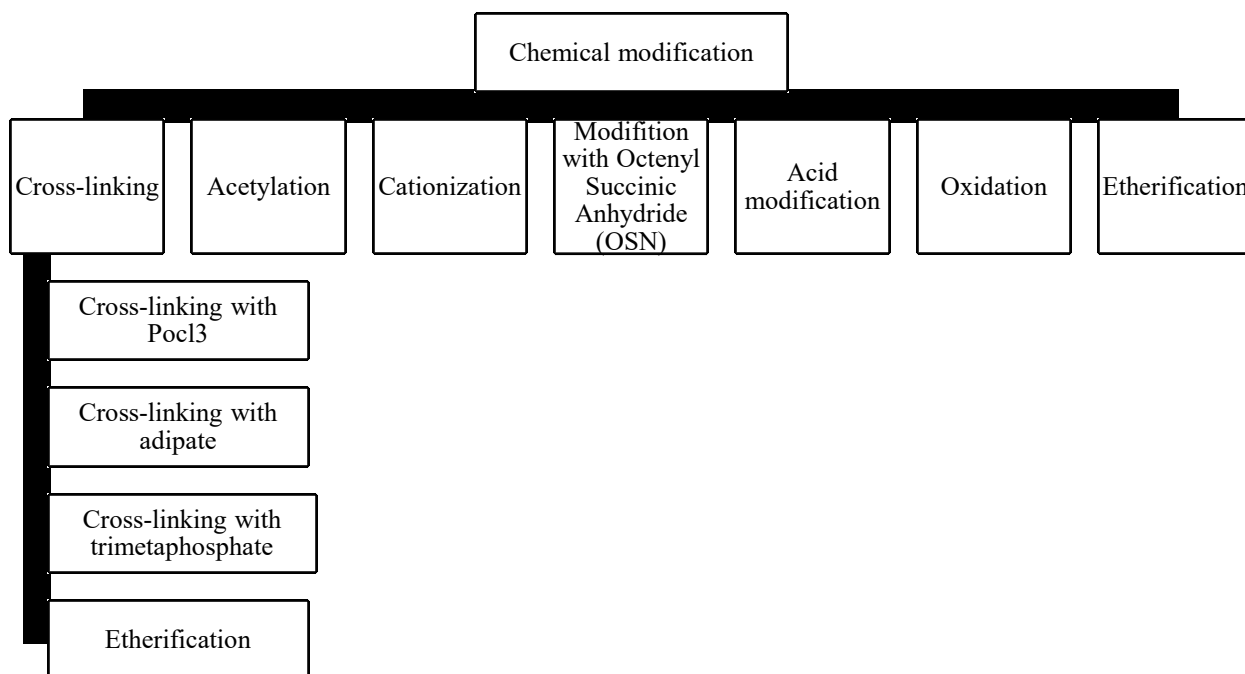


Figure 3: Recent methods of modification of sweet potato starches

Cross-linking

In the food industry, cross-linked starch to stabilize the granular structure restricts and has nutritionally beneficial effects (Koo *et al.*, 2010). The modification of native starch with various cross-linking reagents such as phosphorus oxychloride (POCl_3), epichlorohydrin (EPI), sodium tripolyphosphate (STPP), and sodium trimetaphosphate (STMP) (Siroha *et al.*, 2020) is a consequence replace the OH group with various functional groups, including an ether group, an ester group or a phosphate group (Subroto *et al.*, 2020).

Sodium trimetaphosphate (STMP), one of the essential food additives with low toxicity, is an effective crosslinking agent among these reagents (Gui-Jie *et al.*, 2006). One type of cross-linked starch is di-starch phosphate produced by reacting starch granules with STMP or POCl_3 under alkaline conditions (Zia ud *et al.*, 2017).

Crosslinking modified starch alters the properties of natural starch by enhancing its solubility, mechanical shear pressures, and paste stability (Subroto *et al.*, 2020). The cross-linking of starch has also been affected by

numerous factors, including the reagent's chemical composition, reagent concentration, pH, reaction time, and temperature (Mirmoghtadaie *et al.*, 2009). Wang *et al.* (2020) Reported cross-linked starch to have an essential role in increasing the functional characteristics, freeze-thaw, the cold storage stability of the molecular solubility of starch, thermo-mechanical shear stability, and stability of pastes. Due to the unique qualities of cross-linked starch, in the food sector used as (1) a thickener and stabilizer effect on canned foods, (2) used to improve the freeze-thaw or cold-storage stability of frozen foods, and (3) used in the preparation of pastry to improve the mouth-feel and storage resistance

Crosslinking of starches with POCl₃ under ultra-high pressure

Starch and phosphorus oxychloride quickly react into starch phosphate. However, this crosslinking reaction is dependent on the pH used when the high pH for the crosslinking reaction is an efficient pH of around 11. Therefore, it is necessary to make phosphorous dichloride fast and directly in response, which diffuses into starch granules to obtain optimal results from cross-linking modifications (Subroto *et al.*, 2020). Kim *et al.* (2012) proposed a technique of crosslinking POCl₃ starches. For crosslinking starch with POCl₃, first dissolve anhydrous sodium sulfate (10.0% w/w) in 80 mL of double-distilled water, as per this technique. Next, suspend starch (20 g, w/w, db) in a quick stirring solution. A 0.1% w/w POCl₃ is usually added to the thick slurry and pH is adjusted to approximately 11.5 with 1 M NaOH. After carrying out the reaction at 45°C for 120 min. The slurry is typically neutralized bulk to pH 5.5 with 1 M HCl. the polymer can then be separated and dried before use (Shah *et al.*, 2016). In the same manner, Kim *et al.* (2012) proposed an ultra-high-pressure separation of modified starches with a POCl₃ crosslinked reaction taking place within 15 minutes at 400 MPa.

Crosslinking with sodium trimetaphosphate

Sodium trimetaphosphate (STMP) is a chemical reagent that is still safe for starch. However, because the

reagent and starch interact slowly, sodium sulfate can increase the pH and thus accelerate the reaction rate (Subroto *et al.*, 2020).

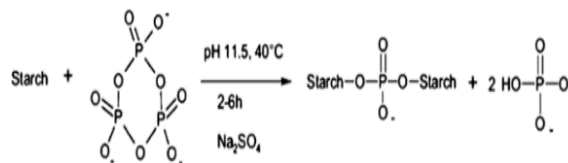


Figure 4: Crosslinking of starch with sodium trimetaphosphate (Shah *et al.*, 2016).

Crosslinking with adipate reagent

The crosslinking reaction between starch and adipate reagent was rapid with an optimum pH of around 8 with anhydrous acetic acid to preserve the pH of the starch solution (Subroto *et al.*, 2020). Adipate can allow a rapid crosslinking reaction with starch at pH 8. The pH solution for starch can be maintained by adding acetic/adipic acid anhydride. Often, along with crosslinking of adipate, acetylation of hydroxyls also occurs (Shah *et al.*, 2016). These two processes produce a double-modified starch (Singh *et al.*, 2012). Although the extent of crosslinking is exceedingly difficult to evaluate, the use of ³¹P-NMR can be used to quantify the degree of cross-linkage for cross-linkages with phosphorylating chemicals (Shah *et al.*, 2016). Figure 4 explains the mechanism of cross-linking of starch with adipate

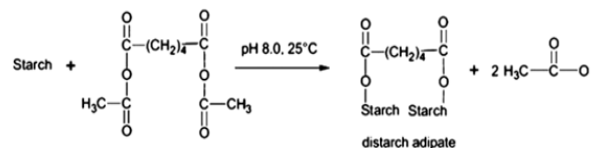


Figure 5: Cross-linking of starch with adipate (Shah *et al.*, 2016).

Crosslinking with epichlorohydrin

Epichlorohydrin produces a multifunctional reaction with starch. As the reaction proceeds, a single crosslink forms, consuming either one or two molecules of epichlorohydrin. Diester and diglycerol molecules form cross-linked starch molecules (Shah *et al.*, 2016).

Characteristic of cross-linked starch

Cross-linked starches exhibit more excellent thermal stability than their native counterparts, as seen by a reduction in weight loss (Wongsagonsup *et al.*, 2014). In addition, cross-linked starches are better suitable for various industrial applications due to their more resilient granular structure. The most intriguing property of cross-linked starches is that they degrade rapidly but leave a more significant amount of residues than untreated starches (Zia ud *et al.*, 2017). Although the number of cross-linked starches decreases when assessed as a function of temperature, the solubility increases with an increase in the degree of cross-linking (Koo *et al.*, 2010). Moreover, no variation in crystallinity pattern was observed between modified corn starch and native corn starch (Zia ud *et al.*, 2017).

The decreased retrogradation rate and increased gelatinization temperature observed with cross-linked starch are due to the reduced mobility of amorphous chains within the starch granule as a result of intermolecular bridges, and cross-linked starch exhibits more pronounced syneresis than native starch due to the ordered structure of the starch paste, resulting in a higher gelatinization temperature (Mirmoghtadaie *et al.*, 2009).

Acetylated (Ac) starch

Acetylated starches are produced using acetic anhydride and an alkaline catalyst such as sodium hydroxide. Part of the glucose molecule's hydroxyl groups is usually replaced by an acetyl group that results in a modified molecular starch structure (Bello-Pérez *et al.*, 2010). Acetylation of starch is an essential substitute for starch, which provides the necessary thickening in food applications. Acetylation of starch is a granular starch ester with a low-temperature CH_3CO group providing starch with improved functionality over the native form by enhancing its stability and retrogradation resistance. Acetylated starch was reported to acquire enhanced gel viscosity, solubility, swelling factor, hardness, cohesiveness, adhesiveness, and translucency (Mirmoghtadaie *et al.*, 2009).

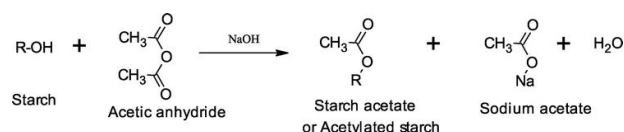


Figure 6: Acetylation of starch with acetic anhydride (Omoregie, 2019).

Characteristic of acetylated starch

The addition of acetyl groups weakens the connection between starch molecules, increasing the modified starch's swelling power and solubility. Hydrogen bonding is restricted in acetylated starches due to the starch molecule's inter- and intra-molecular electrostatic repulsion (Ashogbon *et al.*, 2014). Acetylated starches served a variety of purposes depending on their degree of substitution. These starches with a low degree of substitution of approximately (0.01-0.2) can be used as an adhesion, thickening, texturizing, binding, stabilizing, and film-forming agents in baked goods, sauces, frozen meals, canned pie fillings, baby foods, snack foods, and salad dressings. Acetylated starches with an intermediate degree of substitution (0.2-1.5) and a high degree of substitution (1.5-3.0) have been highly soluble in acetone and chloroform and thus suitable for the use of thermoplastic materials (Luo & Shi, 2012).

Two possible explanations exist for the acetylated starches' poor viscosity. To start, the introduction of acetyl groups during the modification process degraded and dissolved the native starch's orderly structure (Saartrat *et al.*, 2005). Next, the acetylation reaction depolymerized the starch samples. Depolymerization resulted in a fall in the molecular weight, which resulted in a decrease in viscosity (Sun *et al.*, 2016). However, research conducted on the acetyl content of rice starch resulted in increased crystallinity but gradually decreased its diffraction peak as a result of disruption of the intermolecular hydrogen bonding (Siroha *et al.*, 2020).

Cationic starch

Cationic starches are important industrial derivatives developed using functional groups such as ammonium, imino, amino, sulphonium, or phosphonium by

introducing a positive ionic charge, in another hand, the native starches' hydroxy group changes with an ionic charge by using 2,3-epoxypropyltrimethyl ammonium chloride (ETA) as a cationic monomer under wet, dry or intermediate processes (Zia ud *et al.*, 2017).

The wet method is the most frequently utilized of the three. The process occurs in the forward direction during the wet cationization of starches by combining starch with water to generate a homogenous solution with a 40 percent concentration and regulating the pH with a chemical cationizing agent within 11-12. Starch will be entirely cationized in 12–16 hours, with all these reaction conditions and temperatures between 40–45 °C (Heinze *et al.*, 2004). In the dry method of cationization (lack of liquid phase), the reagent is sprayed onto dry starch. At the same time, the extrusion process repeats the same procedure and the mixes are thermally treated during the semi-dry processing (Zia ud *et al.*, 2017). The main advantage of these processes is that they are environmentally friendly. However, a by-product produced with the wanted product is likely, and it can also be expensive to separate the two (Radosta *et al.*, 2004). In addition, the dry cationization procedure would result in thicker starch compared to the wet cationization approach. However, for wet cationic starch, greater molar masses are produced than in the dry approach (Zia ud *et al.*, 2017).

Cationic starch is produced by starch's reaction with amino, imino, ammonium, sulphonium reagent, or phosphonium groups (Santacruz, 2014). Cationic monomers such as 2,3-epoxypropyltrimethyl ammonium chloride (ETA) or 3-chloro-2-hydroxy propyl trimethyl ammonium chloride (CTA), or processes between the two procedures, usually change the free hydroxyls of the native starch (Heinze *et al.*, 2004). In dry-cationization methods (procedures without a liquid phase), the reagent is sprayed onto the dry starch during extrusion; in semi-dry methods, the reagent is sprayed onto the starch mixtures after they have been thermally treated. Both strategies contribute to the reduction of pollutants in the environment. Nonetheless, the necessary products can be obtained Radosta *et al.* (2004), as well as the net product,

can be expensive to separate from the by-products. In the wet cationization procedure, dimethyl sulfoxide (DMSO) is homogeneous, or aqueous alkaline solution is heterogeneously (Heinze *et al.*, 2004). The illustration reaction scheme is shown in figure 6.

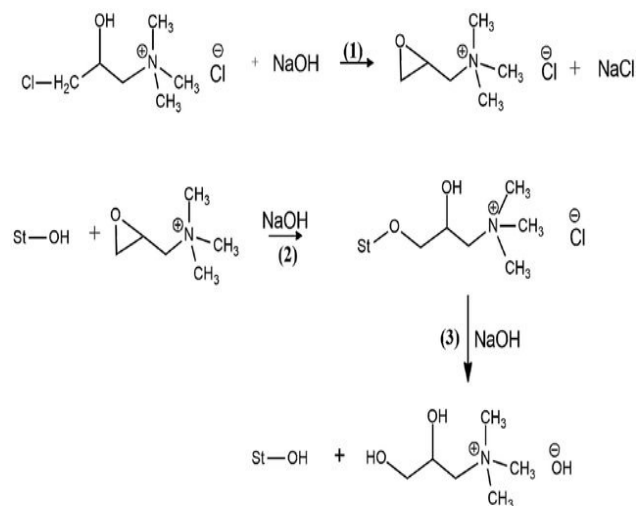


Figure 7: Illustration of cationization starch chemical scheme reactions (1) epoxidation formation, (2) cationic starch formation, and (3) hydrolysis reaction with an excess of NaOH (Md Nasir et al., 2020)

Characteristic of cationic starch

Among the three processes, the wet approach is the most frequently employed. Starches' wet cationization is accomplished by mixing starch and water to generate a homogenous suspension with a 40% concentration and changing the pH to 11-12 with a chemical cationizing agent. Starch will eventually be cationized if these reaction conditions are maintained together with a temperature of 40–45 °C for 12-16 hours (Heinze *et al.*, 2004). The primary advantage of these two procedures is their being environmentally friendly. However, there is a possibility that the by-product will be manufactured concurrently with the desired product, and it may also be costly to separate the two (Radosta *et al.*, 2004). The altered morphology of the cationic corn starch granules was attributed to the cationic reagent penetrating its

interior, resulting in subsequent granule enlargement and disintegration (Pi-xin *et al.*, 2009). In addition, the loss of crystallinity is attributed to the modification's aqueous alkaline environment (Ashogbon *et al.*, 2014). In their contribution, Kuo and Lai (2009) revealed that the changes in the pasting and heating properties of cationic corn starches related well with the increase of the degree of substitution, combined with the features of granular morphology. Kuo and Lai (2009) also found a progressive decrease in cationic starches' structural and molecular integrity with a rising degree of substitution up to 0.04311. At the same time, significant physicochemical and morphological modifications happened when the degree of substitution increased to 0.1215.

Octenyl Succinic Anhydride (OSA)

Octenyl Succinic Anhydride (OSA) starches stabilize the emulsion's oil-water interface. The glucose portion of the starch binds the lipophilic water, while the octenyl portion binds the oil, preventing oil and water separation. Modified OSA starches are used in many foods, pharmaceuticals, and industrial oil-in-water emulsions, including drinks and salad dressings, flavor embedding agents, clouding substances, processing aids, body powders, and lotions (Siroha *et al.*, 2020). The illustration reaction scheme is shown in figure 7

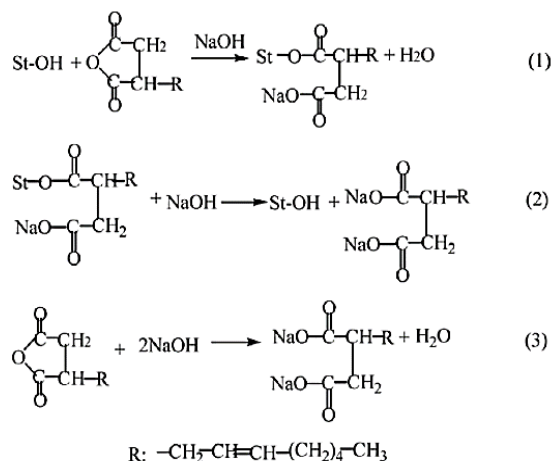


Figure 8: Chemical reactions during OSA modification (Hui *et al.*, 2009).

Characteristics Octenyl Succinic Anhydride (OSA) starch

The degree of substitution of OSA-modified starches was evaluated using various methods. Raised amylose content was detected in the small and large granule fractions when the pH was increased, with the maximum amylose concentration recorded at pH 8. This might be because amylose reacts rapidly with OSA under higher acidic conditions. Starches' pasting characteristics are also altered due to the modification (Olayinka *et al.*, 2011). It found a reduction in paste viscosities that did not follow the substitution sequence, and showed that changes in pH during modification substantially influenced the pasting properties of small and large starch fractions, with the peak of viscosity (PV) being reduced at pH 4 and 6 relative to their natural counterparts (Siroha *et al.*, 2020). Arueya and Oyewale (2015) concluded that no apparent differences were observed in the native and succinylated starch morphology. The deformation of the granular starch structure following modification, which they thought was caused by the very alkaline conditions employed to modify the starch. After succinylation, the deformation of starch granules has also been seen in yam starch (Lawal, 2012). The quantity of deformation and aggregation of modified starch granules increased in direct proportion to the amount of succinic anhydride supplied. The degree of substitution (DS) is defined as the average number of substitutions per anhydroglucose unit, which did not exceed the standard value of 3 (Siroha *et al.*, 2020).

Acid modification

Acid modification using HCl or H₂SO₄ solutions is another standard method for modifying starch characteristics. However, sweet potato starch is the most acid-resistant compared with certain other starches hydrolyzed (Campanha & Franco, 2011). In addition, this technique may be counteracted by new genotypes that abound in short amylopectin unit chains, which lead to more structural defects in the granules and thus more rapid amylopectin degradation (Genkina *et al.*, 2009).

Acid hydrolysis is a vital chemical modification method because it can substantially impact starch's structural and functional properties without altering its granular form (Wang & Copeland, 2015). Starch acid hydrolysis was performed by incubating starch at gelatinization temperatures in acidic solutions. One of the main aims of acidic starch hydrolysis is to generate a product with a low viscosity of the starch paste. Products from acid hydrolysis or acid starch pyrolysis above gelatinization do not technically belong to acid-modified starch (Zia ud *et al.*, 2017).

The acid hydrolysis mechanism involves attacking the hydroxonium ion of the glycoside oxygen atom of the native starch to cleave and depolymerize the starch chains. Acid starch hydrolysis proceeds by breaking both α -(1,4) and α -(1,6) links and lowering the chain length with time. Acid penetration and hydrolysis are more accessible to the α -(1,4) link and α -(1,6) amorphous regions (Hoover, 2000). The acid modification process attacks the starch granules in two stages. During the early phases of hydrolysis, acid targets both amylose and amylopectin but preferentially attacks the amorphous portions of the starch granule in the first stage, followed by the crystalline and amorphous sections at a similar rate (Wang *et al.*, 2020).

Characteristic of acid-modified starch

Many hypotheses discussed the reasons that acid hydrolysis results in enhanced crystallinity. First, the cleavage of some of the amylose chains that run through the amorphous regions may allow the freshly released chain ends to be rearranged into a more crystalline structure. Next, the reorganization of the crystalline structure during acid hydrolysis increases crystallinity by partial filling of water channels in crystallite cavities with double helices. Finally, increased crystallinity may be caused by the retrogradation of hydrolyzed free amylose into double helices, which reorganize into acid-resistant crystalline areas (Atichokudomchai *et al.*, 2004).

Acid-hydrolyzed starch may also possess other functional properties such as a decrease in intrinsic viscosity, hot paste viscosity, and an increase in gel

strength, water solubility, and film-forming ability. Such functional characteristics would enable acid-modified starches to be used as a gelling agent in the manufacture of gum candies and processed cheese loaves, as a fat substitute/fat mimetic in low-fat butter spread/margarine, low-fat mayonnaise, low-fat milk-type products, and low-fat ice cream and as a resistant starch-rich powder in slowly digestible cookies (Wang & Copeland, 2015).

Oxidation modifications of starches

Oxidation is an efficient method for modifying the physicochemical properties of starch. The use of oxidative agents would in modifying starch through the formation of new functional molecular groups. Hypochlorite oxidations or, more infrequently, potassium permanganate are among the procedures that are employed (Zhang *et al.*, 2012). These methods involve the conversion of the primary hydroxyl group to the carboxyl group. However, since oxidation is an exothermic reaction, care must be taken to limit the reaction temperature so that no further breakdown of the polymer chain occurs (Tharanathan, 2005).

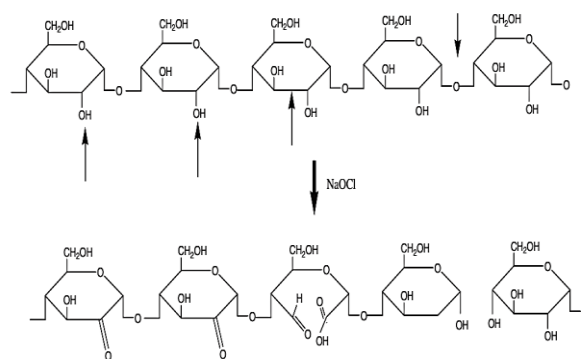


Figure 9: Sodium hypochlorite oxidation of starch, showing carbonyl and carboxyl group formation in the α -1, 4-D-glucose chains of amylose and/or amylopectin (Vanier *et al.*, 2017)

Characteristics of Oxidized starches

When performed on gelatinized starch dispersion; oxidation is faster than when conducted on granular suspensions. Carbonyl groups introduced during oxidation contribute to the stability of starch dispersions.

Oxidation depolymerizes the starch and introduces the functional group carboxyl and carbonyl. Oxidized starches are used in lemon curd, salad cream, and mayonnaise, requiring neutral-tasting, low-viscosity starch (Tharanathan, 2005). Additionally, increased viscosity and altered thermal properties due to oxidation affect the swelling ability properties of the starch derivative, affecting its ability to absorb water, making derivatives ideal for use in the majority of oral formulations, including hydrogels, tablets, and various other devices (Neeraj & Bisht, 2018).

Etherification modifications of starches

When hydroxyl groups in starch molecules react with cationic, anionic, amphoteric, or nonionic starch; starch ethers are usually produced. The physicochemical features of etherification starch (i.e., thermal stability, ion activity, greater reaction efficiency, and thixotropy) are somewhat superior to those of native starch. Starch ethers are used in multiple areas, such as coatings, additives, medication delivery, papers, and much more. Cationic starch is an important modified starch, in which the positive ionic charge has been produced by introducing sulfonium, ammonium, amino, imino, or phosphonium groups (Kuo & Lai, 2009).

Application

The industrial utilization of native starches is limited because of their inherent imperfect nature, such as water insolubility and their enduring syneresis. Physical, chemical, enzymatic, and biotechnological agents or their combinations can change the functioning of starch and stabilize starch granules during processing and make starch acceptable for food and industrial applications (Ashogbon *et al.*, 2014).

An essential utilization of starch in the food industry is baking flour. Cakes and bread are the most essential among bakery products due to their high consumption. Starch is one of the components responsible for the structure and properties of the final products in the formulations of the baking industry. Other industrial processes include starch as a food ingredient or a

thickener and gelling agent in small quantities. Starch is also utilized in manufacturing several types of pasta in noodles and for extrusion and in instant food and fried food formulations (Alcázar-alay *et al.*, 2015).

Starch for non-food applications has emphasized the versatility of starch and introduced it to new markets, new processing techniques, and the demands for biodegradable and renewable resources. Starch is also a chemical feedstock for conversion into many products with significant value (Ellis *et al.*, 1998). Starch is used as an excipient in the pharmaceutical industry, a bonding agent for active drugs. Due to its amylose content, starch can form an inclusion complex with many food ingredients, such as essential oils, fatty acids, and aromas. Also, starch is known for its capability to produce films in food packaging applications (Jiménez *et al.*, 2012).

Edible and biodegradable starch films can be formed from native starch or its Amylose or Amylopectin components using two primary techniques: a wet method with a starch suspension and a subsequent drying or a dry procedure with a thermoplastic procedure (Paes *et al.*, 2008). Film manufacturing is also available with modified starch (Alcázar-alay *et al.*, 2015).

Starch has been studied in recent years in nanostructures such as nanocrystals resulting from the breakdown of the amorphous area in semicrystalline starch granules by hydrolysis of acid or in the production of gelatinated starch nanoparticles (Déborah *et al.*, 2010). These nano-compounds have unique features as compared to conventional materials because of their nano-size. Full material in filtering and practical barriers for flexible packaging can be used for nanoparticles (Bondeson *et al.*, 2006).

8. Toxicological aspect

Many modified starches made for food use contain only small substituent groups and have been used as safe food ingredients. The degree of added mono-substitution groups is relatively low during acetylation and hydroxyl-population of food-grade starch. The maximum allowed substitution levels are 2.5, 0.4, and 10 percent for starch acetates, starch phosphates, and hydroxyl-populated

starch respectively. Likewise, cross-related starches having a cross-related substitute group per 1000 or more anhydrous-glucose units are considered safe. Legislative approval of new starch derivatives is now under discussion in processed food formulations, However various custom-manufactured starch derivatives with several changes are being developed and analyzed (Tharanathan, 2005). Some of the compounds of starch are being employed as fat substitutes or fat substitutes, these compounds are either partly or entirely undigested. Many investigations have shown that chemically

modified starches have physiological effects influenced by the type of modification (Singh *et al.*, 2007).

The chemical change in starch by acetylation increases food's satiating, glycemic, and insulinemic qualities. Phosphorylated/cross-linked starches are slowly digested and provide human nutritional advantages. Modified starches can also be utilized to treat specific medical modalities (e.g. glycogen storage and diabetic Mellitus) by slow digestion (Singh *et al.*, 2007).

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التعديلات الكيميائية للنشاء، تطلعات حول نشاء البطاطا الحلوة

ضياء الدين بن ساعد¹، محمد اسماعيل صالح¹، خالد السماعيل¹، يونغسونغ لي² وجورج اوندير³

¹قسم التغذية والتصنيع الغذائي، كلية الزراعة، الجامعة الأردنية، الجبيهة، عمان الأردن

²قسم الغذاء و التغذية جامعة دانكوك ، جمهورية كوريا الجنوبية

³مختبرات تايلور تكساس ، الولايات المتحدة الأمريكية

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ملخص

يعرض البحث الحالي التعديلات والتطبيقات الكيميائية المحتملة لنشاء البطاطا الحلوة في الصناعات الغذائية وغير الغذائية. النشاء الأصلي بشكل عام وخصائص نشاء البطاطا الحلوة بشكل خاص لها العديد من الميزات والتطبيقات الوظيفية في الطب الحيوي وكذلك في صناعة الأغذية. من المتوقع أن يعزز النشاء المعدل مثل هذه الخصائص كما تمت مناقشتها في هذه المراجعة. على سبيل المثال، بسبب الطبيعة البوليمرية والمتفرعة للنشاء؛ عادة ما يكون النشاء أقل قابلية للذوبان، ويمتص كمية أقل من الماء والزيت، ويظهر قدرة قوية على الارتباط باليود. أيضا، النشويات الأصلية نسبة الهضم لها أقل بشكل ملحوظ تحت العلاج الأنزيمي. لذلك، تم تصميم تعديلات النشاء لتعزيز واحد أو أكثر من القيود المذكورة أعلاه؛ وبالتالي، فإن تعديل النشاء يمكن أن يغير الخصائص الفيزيائية والكيميائية للنشاء الأصلي لتحسين خصائصه الوظيفية. يمكن تعديل النشاء باستخدام الطرق الفيزيائية ((التلدين (ANN) ومعالجة الرطوبة الحرارية (HMT)، والعمليات المسبقة الجيلاتينية والعمليات غير الحرارية الأخرى)، والطرق الكيميائية (الأثير، والأسئلة، والتعديل الحمضي، والربط الكاتيوني، والأسترة، والربط المتبادل، والأكسدة)، وطرق التعديل الأنزيمية أو عملية التغيير الجيني أو مزيج منها.

الكلمات الدالة: النشاء المعدل، التعديل الكيميائي، الربط المتبادل، البطاطا الحلوة، الخصائص الفيزيائية والكيميائية.