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Chemical Properties of Starch and Its Application in the Food Industry

Henry Omoregie Egharevba

Abstract

Starch is an important food product and a versatile biomaterial used world-wide for different purposes in many industrial sectors including foods, health, textile, chemical and engineering sector. Starch versatility in industrial applications is largely defined by its physicochemical properties and functionality. Starch in its native form has limited functionality and application. But advancements in biotechnology and chemical technological have led to wide-range modification of starch for different purposes. The objective of this chapter is to examine the different chemical reactions of starch and expose the food applications of the modification products. Several literatures on starch and reaction chemistry including online journals and books were analyzed, harmonized and rationalized. The reactions and mechanisms presented are explained based on the principles of reaction chemistry. Chemical modification of starch is based on the chemical reactivity of the constituent glucose monomers which are polyhydroxyl and can undergo several reactions. Starch can undergo reactions such as hydrolysis, esterification, etherification and oxidation. These reactions give modified starches which can be used in baked foods, confectionaries, soups and salad dressings. This chapter discusses the different chemical reactions of starch, the associated changes in functionality, as well as the applications of chemically modified starches in the food industry.

Keywords: reactions of starch, hydrolysis, esterification, etherification, baked products, confectioneries, gravies, soups and sauces, mayonnaises and salad dressing

1. Introduction

Starch also known as amyllum, is an important food product and biomaterial used world-wide for different purposes. Though traditionally used in the food industry, technological advancement has led to its steady relevance in many other sectors such as health and medicine, textile, paper, fine chemicals, petroleum engineering, agriculture, and construction engineering [1]. It is used in the food industry either as food products or additives for thickening, preservation and quality enhancer in baked foods, confectioneries, pastas, soups and sauces, and mayonnaises. Starch is a polysaccharide of glucose made of two types of α -D-glucan chains, amylose and amylopectin. Starch molecules produced by each plant species have specific structures and compositions (such as length of glucose chains or the

amylose/amylopectin ratio), and the protein and fat content of the storage organs may vary significantly. Therefore, starch differs depending on the source. This inherent functional diversity due to the different biological sources enlarges its range of industrial uses [2, 3].

The structural and compositional differences in starches from different sources determine its properties and mode of interactions with other constituents of foods that gives the final product the desired taste and texture. In the food industry, starch can be used as a food additive to control the uniformity, stability and texture of soups and sauces, to resist the gel breakdown during processing and to raise the shelf life of products [2]. Starch is relatively easily extractable and does not require complicated purification processes. It is considered to be available in large quantities in major plant sources such as cereal grains and tubers. These sources are generally considered inexpensive and affordable and serve as raw materials for commercial production [4].

Starch from *Zea mays* (corn, **Figure 1**) account for 80% of the world market production of starch. Maize starch is an important ingredient in the production of many food products, and has been widely used as a thickener, stabiliser, colloidal gelling agent, water retention agent and as an adhesive due to its very adaptive physicochemical characteristics [5]. Starches from tubers of roots such as potato tubers (**Figure 1**), which are considered non-conventional sources have found usefulness in providing options for extending the spectrum of desired functional properties, which are needed for added-value food product development.

The stability of native starch under different pH values and temperatures varies unfavorably. For instance, native starch granule is insoluble in water at room temperature and extremely resistant to hydrolysis by amylase. Hence native starch has limited functionality. In order to enhance properties and functionality such as solubility, texture, viscosity and thermal stability, which are necessary for the desired product or role in the industry, native starches are modified. The widening vista of application possibilities of starches with different properties has made research in non-conventional starches and other native starches more imperative [2, 6, 7]. Recent studies on the relationship between the structural characteristics and functional properties of starches from different sources have continued to provide important information for optimizing industrial applications.

Modification has been achieved mostly by physical and chemical means. Enzymic and genetic modifications are biotechnological processes which are increasingly being explored [8]. While physical modification methods seemed simple and cheap, such as superheating, dry heating, osmotic pressure treatment, multiple deep freezing and thawing, instantaneous controlled pressure-drop process, stirring ball milling, vacuum ball milling, pulsed electric fields treatment, corona electrical discharges, etc., chemical modification involves the introduction of new functional moieties into the starch molecule via its hydroxyl groups, resulting in marked

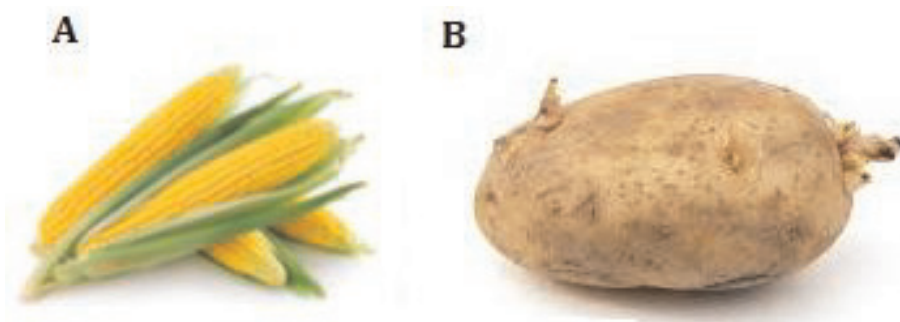


Figure 1.
Corn (A) and potato tuber (B) [2].

change in its physicochemical characteristic. The functional characteristics of chemically modified starch depends on a number of factors including the botanic origin of the native starch, reagent used, concentration of reagent, pH, reaction time, the presence of catalyst, type of substituent, degree of substitution, and the distribution of the substituents in the modified starch molecule. Modification is generally achieved through chemical derivatization, such as etherification, esterification, acetylation, cationization, oxidation, hydrolysis, and cross-linking [7]. This chapter discusses the chemical properties of starch and how they determine its application in the food industry.

2. Amylose and amylopectin

The chemical behaviour of starch is dependent on the nature of its constituent compounds. Starch is a homopolysaccharides made up of glucose units. However, the homopolysaccharide are of two types namely: amylose, which is a linear chain consisting of about 500–2000 glucose units, and amylopectin, which is highly branched and consist of over 1,000,000 glucose units. The two types of homopolysaccharides constitute approximately 98–99% of the dry weight of starch [2]. The ratio of the two polysaccharides usually varies depending on the botanical origin of the starch. Botanic source reports that starch chain generally consist of 20% amylose and up to 80% amylopectin by mass. It is believed that starch with up to 80% amylose can exist [7]. Some classification categorize starch containing <15% amylose as 'waxy', 20–35% as 'normal' and greater $\geq 40\%$ as 'high' amylose starches [9].

Amylose and amylopectin have different physiochemical properties which impact on the overall properties of the starch. Hence it is often important to determine the concentration of each individual component of the starch, as well as the overall starch concentration [10]. The physicochemical (e.g., gelatinization and retrogradation) and functional (e.g., solubility, swelling, water absorption, syneresis and rheological behaviour of gels) properties determine the potential uses of starches in the food industry. These properties depend on the molecular and structural composition of amylose and amylopectin, percent composition and arrangement of these two homopolysaccharides in starch granules which often determine the granule size and shape depending on other genetic factors as a result of the particular species of plant [2].

In food products, the functional roles of starch could be as a thickener, binding agent, emulsifier, clouding agent or gelling agent. In the food industry, native starch is usually reprocessed and modified through chemical processes to improve its functionality for the desired purpose. Chemical modification involves the introduction of new functional groups into the starch molecule which produces in a modified starch with markedly altered physicochemical properties. Such modified starch shows profound change in functionality such as solubility, gelatinization, pasting and retrogradation [11].

The chemical reactivity of starch is dependent on the reactivity of the constituent glucose units [11]. The chemical and functional properties achieved following such modification depends largely on the reaction conditions such as modifying reagent(s), concentration of the reactants, reaction time, type of catalyst used, pH, and temperature. The type of substituents, degree of substitution and distribution of substituents in the starch molecule affects the functional properties.

2.1 Amylose

Amylose is a linear polymer of α -D-glucose units linked by α -1,4 glycosidic bonds (Figure 2). The linear nature of amylose chain and its percentage content in starch,

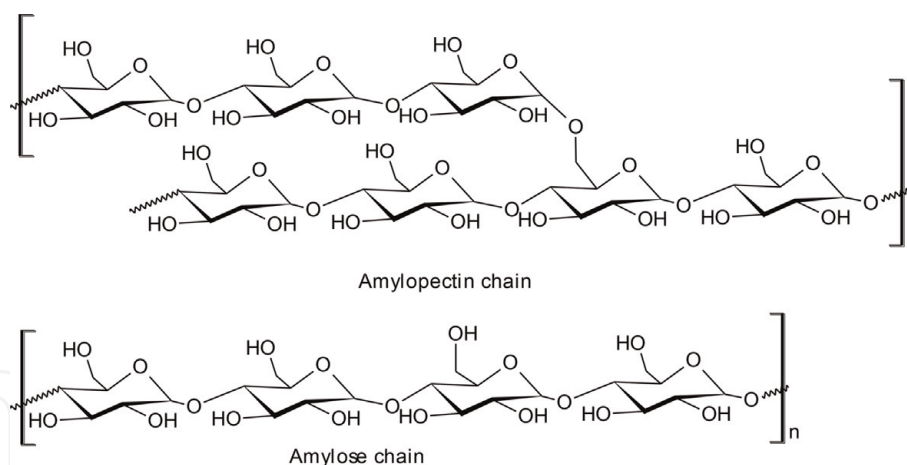


Figure 2.
Chemical structure of amylopectin chain and amylose chain.

and the relative molecular arrangement with amylopectin affect the overall functionality of the starch. Hence starch varies greatly in form and functionality between and within botanical species and even from the same plant cultivar grown under different conditions. This variability provides starches of different properties, which can create challenges of raw materials inconsistency during processing [12].

2.2 Amylopectin

Amylopectin is a branched polymer of α -D-glucose units linked by α -1,4 and α -1,6 glycosidic bonds (**Figure 2**). The α -1,6 glycosidic linkages occurs at the branching point while the linear portions within a branch are linked by α -1,4 glycosidic bonds. In comparison to amylose, amylopectin is a much larger molecule with a higher molecular weight and a heavily branched structure built from about 95% (α -1,4) and 5% (α -1,6) linkages. Amylopectin unit chains are relatively short with a broad distribution profile, compared to amylose molecules. They are typically, 18–25 units long on average [13, 14].

3. Physicochemical properties of starch

Physical properties are those properties exhibited without any change in chemical characteristics of starch and do not involve the breaking and creation of chemical bonds such as solubility, gelatinization, retrogradation, glass transition, etc. On the other hand, chemical properties changes due to chemical reactions and usually involve the breakage and creation of new bonds. Examples of such chemical processes in starch include hydrolysis, oxidation, esterification and etherification. Research strongly indicates that the molecular weight and branching attributes of starch which play important roles in the shape and size of granules can potentially be used for predicting some of its functionality such as texture, pasting, retrogradation, etc. [12, 15]. Amylose has more proportional relationships with pasting and gel textural properties, while amylopectin which are predominant in regular and waxy corn starches, has higher proportional relationship with firmness.

3.1 Solubility and gelatinization

When unprocessed or native starch granules which are relatively inert are heated in the presence of adequate water, usually during industrial processes, swelling of the

granules occur and the amylose dissolves and diffuses out of the swollen granules which upon cooling forms a homogenous gel phase of amylose-amylopectin. The swollen amylopectin-enriched granules aggregate into gel particles, generating a viscous solution. This two-phase structure, called starch paste, is desirable for many food applications where processed starches are used as thickeners or binders [2, 16].

3.2 Retrogradation and shear

Retrogradation of starch is a phenomenon that occurs when the disordered arrangement of the polymer molecules of gelatinized starch begins to re-align into an ordered structure in the food product [15]. Preventing retrogradation affects the freeze-thaw stability and textural characteristics and helps to elongate the shelf life of the food product. Starch modification through chemical means, such as, hydrolysis and esterification are generally used to produce starches that can withstand retrogradation. Preventing retrogradation of starch is important for starch used in frozen foods because it is accelerated at cold temperatures, producing an opaque, crystallized, coarse texture as a result of the separation of the liquid from the gel or syneresis [17, 18]. Crosslinked oxidized starches have been reported to be more stable against retrogradation [15].

Amylose linear chain dissolves in water at 120–150°C and is characterized by high thermostability, resistance to amylase, high crystallinity and high susceptibility to retrogradation. Amylopectin, which is the branched chain is however, slow to retrogradation, with crystalline forms appearing only on the outside of the globule and characterized by a significantly lower re-pasting temperature of 40–70°C and an increased susceptibility to amylases activity than amylose. Retrogradation of starch is affected by botanical origin of the starch, amylose content, length of the amylopectin chains, density of the paste, paste storage conditions, physical or chemical modifications and the presence of other compounds. Recrystallization of starch applies only to amylose chains, and it occurs most readily at temperatures around 0°C, and also at temperatures above 100°C [8]. Physical modification process such as repeated freezing and thawing of the starch paste aggravate retrogradation. The resulting starch thus produced is resistant starch that exhibits resistance to digestibility by amylase enzymes and can be used as an alternative nutrient source for diabetic patients and as a rate controlling polymer coat in controlled drug delivery systems [8].

Starch granules swollen with water are predisposed to fragmentation if exposed to physical severe pressure change. This becomes of major concern where the integrity of the granules is required to maintain viscosity. Shear is the disintegration phenomenon of swollen starch granules or gel. Starch shear arises from the shear stress which builds up during the process of retrogradation and/or gel drying of the gelatinized starch [19]. The stress acting in opposite directions creates a fault-line that causes the material to open up or tear apart. Shearing generally depends on the fluid (gel) viscosity and flow velocity [20]. Starch granules in their raw unswollen forms are not susceptible to damage by shear even in the slurry before cooking. But once cooked or gelatinized, starch granules become susceptible to shear, resulting in loss of viscosity and textural stability [19].

4. Chemical properties of starch

The chemical properties of starch are dependent on the reactivity of starch which is a function of the polyhydroxyl functional groups in the constituent glucose monomers. The hydroxyl groups at position C-2, C-3 and C-6 which are free from the glycosidic

bond linkages and pyranose ring formation, are usually free for substitution reactions involving either the attached hydrogen or the entire hydroxyl group. While the —OH at C-6 is a primary alcoholic hydroxyl group, those at C-2 and C-3 are secondary alcoholic hydroxyl group. Hence starch can undergo hydrolytic cleavage of its chains at the glycosidic bonds; oxidative reaction with the —OH or C—C bond creating carbonyl groups; and other reactions with various functional and multifunctional reagents to produce esterified and etherified starches. Most of the reactions require activation of the hydroxyl of glucose units in acidic or basic media [7].

4.1 Reactions of starch

The reactivity of starch is dependent on the hydroxyl functions of the constituent α -D-glucan polymers (**Figure 2**). Thus starch is able to undergo the following reactions.

4.1.1 Hydrolysis

Hydrolysis is an addition reaction and simply involves the addition of a water molecule across a bond resulting in the cleavage of that bond and formation of the cleavage products, usually with hydroxyl group or alcohol functionality. Hydrolysis of starch can be achieved by chemical or enzymatic process. Chemical process of hydrolysis usually employs heating starch in the presence of water or dilute hydrochloric acid (**Figure 3**). Hydrolysis is also used to remove fatty substances associated with native starches. Hydrolysis under acidic condition is called roasting, resulting in acid modified starch. Treatment of starch with sodium or potassium hydroxide results in alkaline modified starch. Hot aqueous alkaline solutions can be used, and this improves the reducing value of that starch [21–23].

The products of starch hydrolysis include dextrin or maltodextrin, maltose and glucose. Dextrins are mixtures of polymers of D-glucose units linked by α -(1 \rightarrow 4) or α -(1 \rightarrow 6) glycosidic bonds. The percentage of products obtained depends on the conditions used for the reaction such as duration and strength/amount of reagents used. Enzymic hydrolysis uses the enzyme malto-amylase to achieve hydrolysis and this is the process that usually occurs in starch digestion in the gastrointestinal tract [9]. Dextrins are white, yellow, or brown water-soluble powder which yield optically active solutions of low viscosity. Most of them can be detected with iodine solution, giving a red coloration. White and yellow dextrins from starch roasted with little or no acid are called British gum. The properties of dextrinized starch is dependent upon the reaction conditions (moisture, temperature, pH, reaction time) and the products characteristics vary in its content of reducing sugar, cold water solubility, viscosity, color and stability.

Hydrolytic processes have been used in the food industry to produce starch derivatives with better functional properties and processing applications [2]. Acid and alkali steeping are the two most widely used methods for starch isolation in the

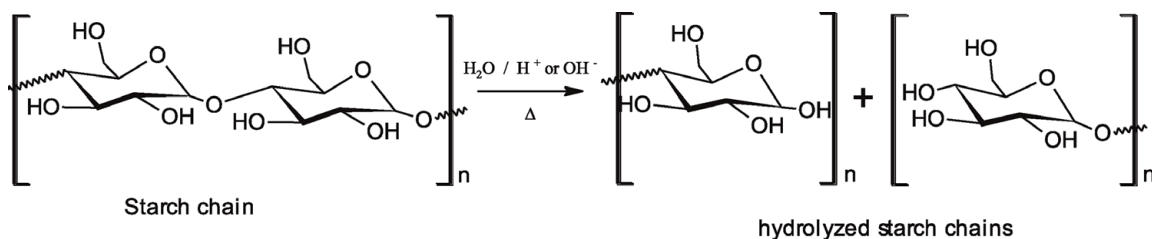


Figure 3.
Hydrolysis of $\alpha(1 \rightarrow 4)$ glycosidic bond.

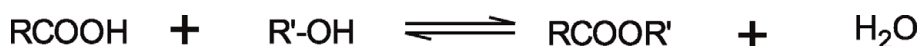


Figure 4.
 Esterification reaction of carboxylic acids and alcohols.

food industry, with numerous modifications. Thermo-alkali isolation method known as nixtamalization has been used in Central America since pre-Hispanic times. Acid and alkali isolation processes affect the amylose/amylopectin, protein and lipid content as well as the granule size and shape of the final product [23].

4.1.2 Esterification reaction

The condensation of an alcohol and carboxylic acid usually under acidic condition, to produce an ester and water, is called esterification [24]. Basically, the reaction is between the carboxylic acid group and the alcohol group with the elimination of a water molecule (**Figure 4**). When the acid anhydride is used, an alkaline condition is preferred in the reaction.

The reaction is usually reversible and the forward reaction is favoured under low pH and excess of alcohol while the reverse is favoured under high pH. Removal of one of the product during the reaction will also favour the forward reaction.

For starch, the reaction is between the carboxylic acid group (—COOH) of fatty acids or —COCl of fatty acid chlorides and the alcohol group (—OH) of the glucose units. Esterification is generally used to introduce more lipophilic groups into the starch molecule making it more lipophilic and for producing crosslink starch when polyfunctional compounds or multifunctional or reagents capable of esterification or etherification are used [15]. Esterification weakens the inter-molecular bonding that holds the granules together and hence alter the granule shape and sizes as well as other functional properties of the starch. The degree of substitution (DS) is dependent on the concentration of reagent used, the type of reagent used, the catalyst and the duration of reaction [25].

4.1.2.1 Acetylation of starch

Starch can be acetylated by reacting it with acetic anhydride to produce acetylated starch (**Figure 5**). The hydroxyl group of the glucose units are esterified with the acetyl groups from the acetic anhydride to give starch with glucose units with acetate function. The DS of the hydroxyl group with acetate group is dependent on the reaction conditions. Acetylated corn starch of DS 0.05, 0.07 and 0.08 have been obtained using 4, 6 and 8% (starch d.w.) acetic anhydride respectively and aqueous sodium hydroxide as catalyst [25].

The introduction of the more bulky acetyl group compares with hydroxyl group causes steric hindrance to the alignment of the linear chains. This allows for easy water percolation between chains thus increasing the granule swelling power and solubility resulting in lower gelatinization temperature [25]. The steric hindrance of

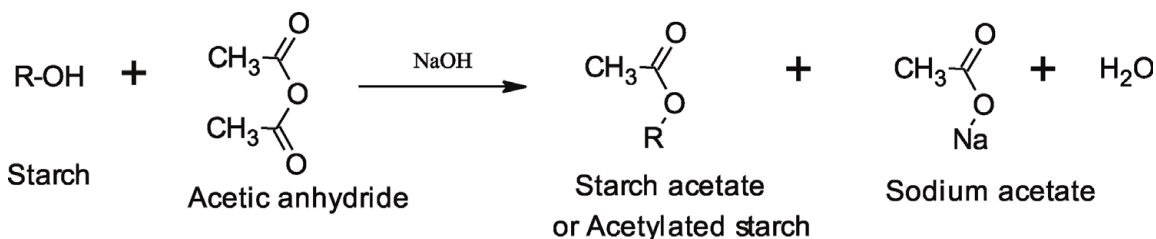


Figure 5.
 Acetylation of starch with acetic anhydride.

less polar acetyl group also reduces the amount of inter-molecular hydrogen bond formation, and weakens the granule structure, preventing molecular re-association and realignment required for retrogradation. However, depending on the DS and the interplay between the a weakened granular structure as result of interruption of the inter- and intra-molecular bonds, and reduced bonding with water molecules as a result of the hydrophobicity of the acetyl groups, the viscosity of the final product can be enhanced.

Acetylation improves paste clarity and freeze-thaw stability of starch. Starch acetates of low DS are commonly used in the food industry for quality consistency, and as texture and stability enhancers. The Food and Drug Administration (FDA) maximum DS of acetylated starches for food application is 0.1 [19]. Starch acetate of high DS exhibit high degree of hydrophobicity and thermoplasticity and are soluble in organic solvents like chloroform and acetone, and are mostly used in non-food applications [25]. At 0.0275 DS, corn starch exhibit lower paste gelling, which is practically lost at 0.05 DS. Most commercial starch acetates have <0.05 DS [19].

Acetylated distarch adipate, is a monosubstituted starch obtained by treating starch with acetic anhydride and adipic anhydride (**Figure 6**). It has been used since the 1950s due to desire for improved stability of product in cold and freezing weather conditions. It is a good temperature change resistant agent used in foods as a bulking agent, stabilizer and thickener. It improves smoothness and sheen of soups and sauces [19]. The improved freeze-thaw stability of acetylated cross-linked waxy maize starch has led to its use in frozen sauces in vegetables, appetizers and pastries. Hydroxypropylation of cross-linked starch also dramatically improves the stability quality of puddings and frozen sauces [19].

4.1.2.2 Succinylation of starch

When starch granule is esterified with succinic anhydride, it produces succinyl starch, and the process is commonly referred to as succinylation of starch. Succinylation of starch was earlier achieved in the presence of aqueous pyridine and under reflux at 115°C (**Figure 7**). However, environmental concerns have led to the development of more green synthetic routes. Thus succinic ester of starch have been prepared by mixing starch with succinic anhydride solution in acetone and refluxing at 110°C for 4 h [25]. Sui et al. [26] was also able to induce a reaction by drop-wise addition of succinic anhydride to a water suspension of starch while maintaining pH at 8.5 by drop-wise addition of sodium hydroxide.

Succinyl group weakens the inter-molecular bonding of starch polymeric chains in the granules, facilitating swelling, solubilisation and gelatinization at lower temperatures. Paste clarity is enhanced and retrogradation is reduced. However, there

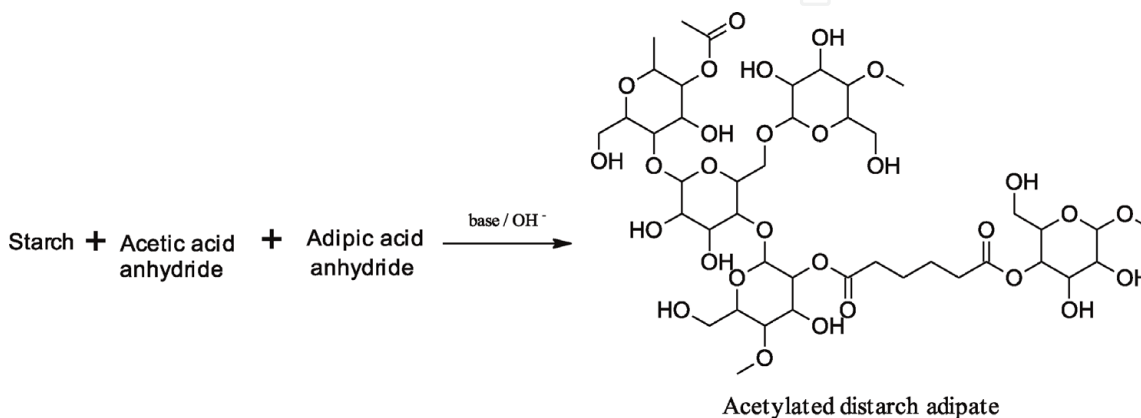


Figure 6.
Esterification of starch with acetic anhydride and adipic anhydride.

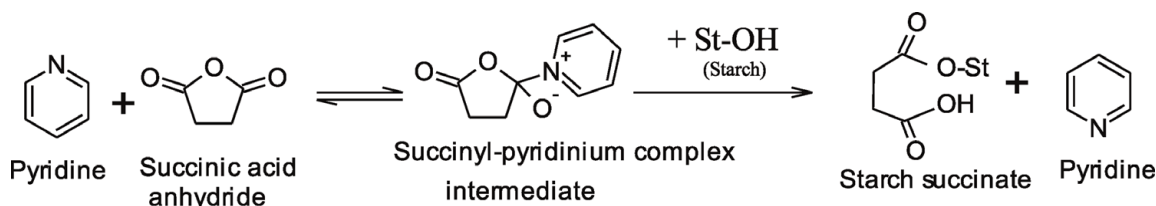


Figure 7.
Succinylation reaction of starch.

may be reduced stability against shear at high temperature and during cooling. Starch succinate is ionic and acts as polyelectrolytes. At low degree of substitution (DS), the succinate makes the starch more hydrophilic and viscous in solution [8, 25]. For its viscosity enhancing effect, succinylated starches could find application in production of non-gelling custard creams, and for its increased hydrophilicity, it could be used for enhancing the juicy/smooth taste of meat and fried products. Starch succinates can also be used in soups, snacks, and frozen/refrigerated food products as thickening or stabilizing agents.

Esterification of starch with octenylsuccinic anhydride (OSA) or octenylsuccinic acid in the presence of an alkali yields starch octenylsuccinate (**Figure 8**), while esterification with dodecyl succinic acid yields starch dodecyl succinate. The octenyl or dodecyl group introduces a reasonable level of lipophilicity to the product, making it have dual functionality which can be used in emulsification and flavour encapsulation. OSA-treated starches are used to stabilize oil-in-water food emulsions associated with beverage concentrates containing flavor and clouding oils [19]. It helps to protect emulsified and spray-dried flavour oils against oxidation during storage. FDA allows a DS of 0.02.

Commercial production of acetylated starch dodecyl succinate, di-substituted starch of low dodecyl succinate residue, employs acetic anhydride reagent at alkaline pH [15]. An alkali-starch complex forms first, which then interacts with the carboxylic anhydride to form a starch ester with the elimination of a carboxylate ion and one molecule of water [15]. Starch succinate offers freeze-thaw stability, high-thickening, low-gelatinization temperature, clarity of paste, good film-forming properties and resistance to retrogradation.

4.1.2.3 Phosphorylation reaction

Inorganic esters also exist, for instance, esters of phosphorous acid (H_3PO_3) and phosphoric acid (H_3PO_4). When starch granules are reacted with phosphorylating agents such as phosphoric acid, mono- or di-starch phosphate is formed (**Figure 9**). The resulting starch has increased stability at high and low temperatures, more

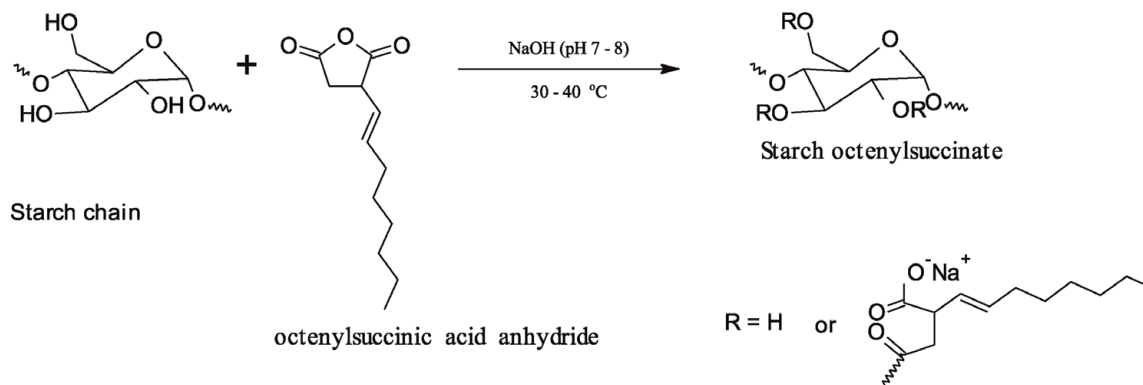


Figure 8.
Esterification of starch with octenylsuccinic acid anhydride.

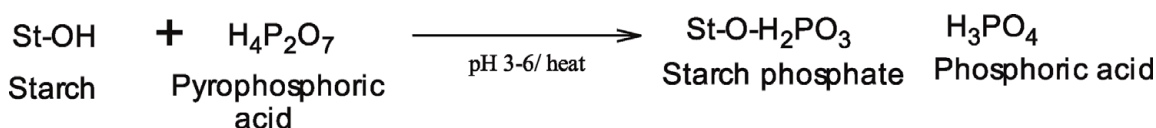


Figure 9.
Phosphorylation reaction of starch.

resistant against acidic condition, and is applicable as a thickening agent. Ortho-phosphate and pyrophosphate has been used to achieve phosphorylation of starch under slightly acidic and high temperature conditions [27].

Phosphoryl trichloride (**Figure 10**), sodium tripolyphosphate (**Figure 11**) and sodium trimetaphosphate (**Figure 12**) have also been used under higher pH to obtain monostarch phosphate and di-starch phosphate [15, 28]. Phosphorylation reactions produce either monostarch phosphate or distarch phosphate which is a cross-linked derivative. However this depends on the reagents and reaction conditions. Usually, monoesters, rather than diesters, are produced with a higher degree of substitution [8]. Steric hindrance as a result of the introduced phosphate groups

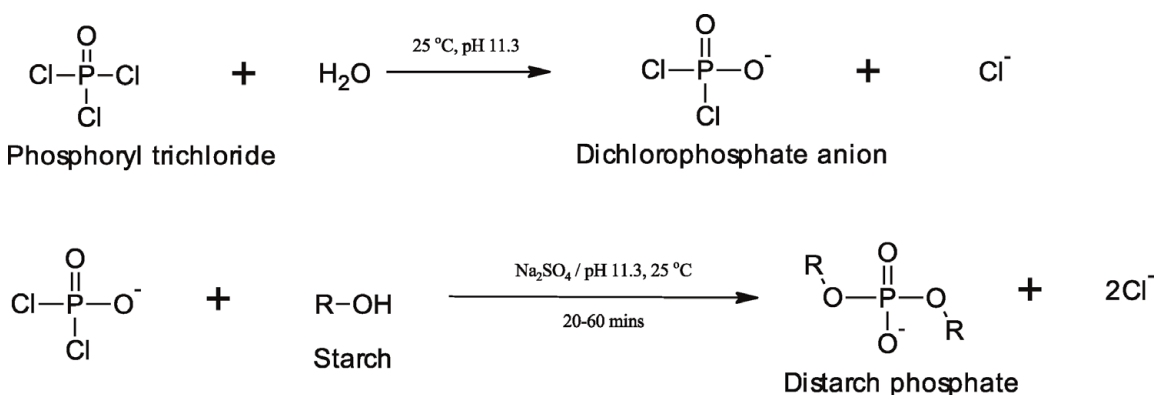


Figure 10.
Phosphorylation of starch with phosphoryl trichloride.

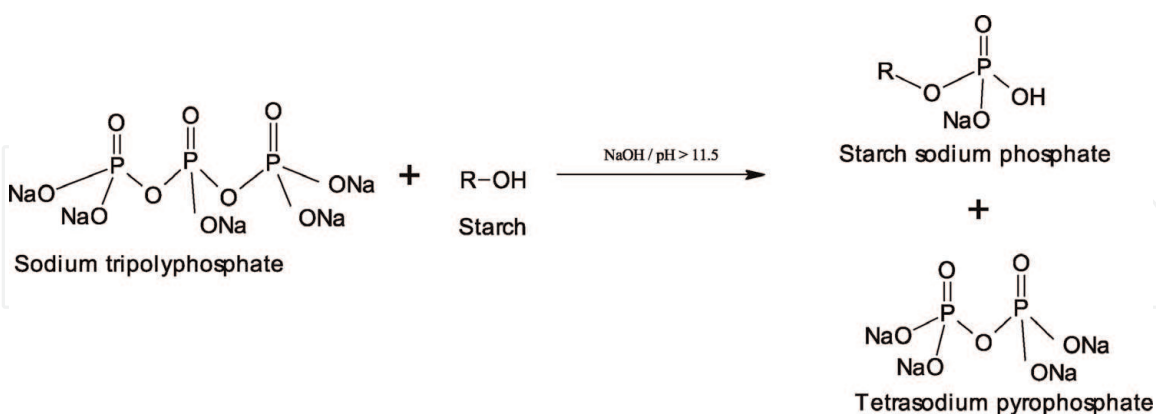


Figure 11.
Phosphorylation of starch with sodium tripolyphosphate.

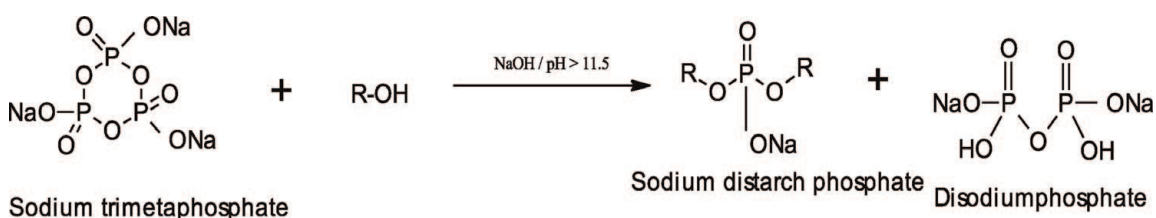


Figure 12.
Phosphorylation of starch with sodium trimetaphosphate.

inhibits the linearity of amylose or the outer branch of the amylopectin chain where it reacted. This weakens the inter-molecular association and creates chains disaggregation, which leads to better paste clarity [8].

Distarch phosphate has the phosphate group esterified with two hydroxyl groups of two neighbouring starch polymer chains [29]. The phosphate bridge or cross-linking strengthens the mechanical structure of the starch granules. Phosphate cross-linked starches exhibit stability against high temperature, low pH and shear, and improved firmness of the swollen starch granule as well as improved viscosity and textural characteristic. Distarch phosphate is used as thickener and stabilizer and provides stability against gelling and retrogradation and high resistance to syneresis during storage [8].

In solution, several specie of the phosphate ion can exist and anyone may be responsible for the phosphorylation reaction depending on the reaction conditions. Phosphorylation has been demonstrated to mostly occur at the C-3 and C-6 of the glucose units, and the degree of phosphorylation depends on distribution of the chain length of the starch polymers [30]. Blennow et al. [31] also demonstrated that phosphate groups may play important role in the size distribution of the amylopectin side chains of phosphorylated starches. Some researchers have reported that about 60–70% of total phosphorus of starch monophosphate is located at C-6 while the rest is located at C-3 of anhydroglucose units. Most phosphate groups (88%) are on chain β of amylopectin [9].

Landerito and Wang [32] reported that phosphorylated starch prepared by the slurry treatment exhibited a lower gelatinization temperature, a higher peak viscosity, a lesser degree of retrogradation, and improved freeze-thaw stability compared with those prepared by the dry-mixing treatment. They believed that phosphorylation probably occurred in both amylose and amylopectin chains, and the amount and location of incorporated phosphate groups varied with starch types, which may be due to their different amylose and amylopectin contents. Waxy starch was more prone to phosphorylation, followed by common and high-amylose starches. Enzymic phosphorylation of starch has been reported [33]. Extrusion condition of 200°C, sodium tripolyphosphate concentration of ≥ 1.4 g/100 ml and pH 8.5 have been used to obtain starch phosphate with high degree of substitution [34].

4.1.3 Etherification

Generally, alcohols (—OH) groups condenses with one another at high temperatures under acidic conditions to form ethers (**Figure 13**). The reaction mechanism is through a proton transfer from the catalyst to one of the molecule to form a cation, which loses the proton by extracting the —OH of the second molecule to form an ether and water.

Etherification of starch is usually done by use of epoxide reagents as depicted in **Figure 14** and **15**. The epoxides are first reduced to diols through a nucleophilic ring opening of the epoxide (cleaving the C—O bond under aqueous, acidic or alcoholic condition) before the eventual condensation of one of the —OH group with that of starch [24]. Some etherification reactions occur under alkaline condition. Like esterification, etherification helps to mostly introduce lipophilic alkyl groups into

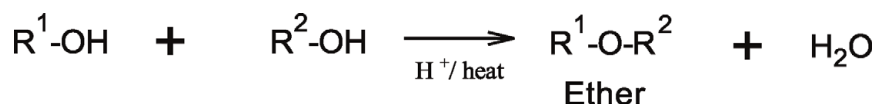


Figure 13.
 Etherification reaction.

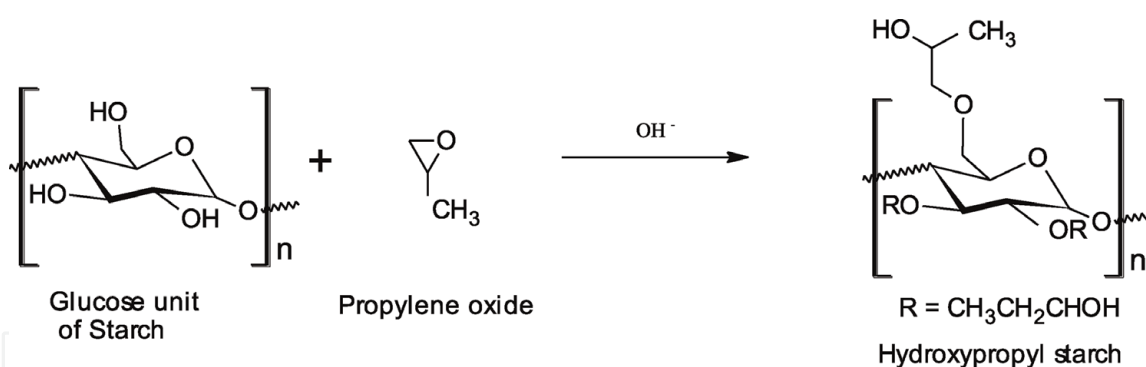


Figure 14.
Etherification of starch with propylene oxide.

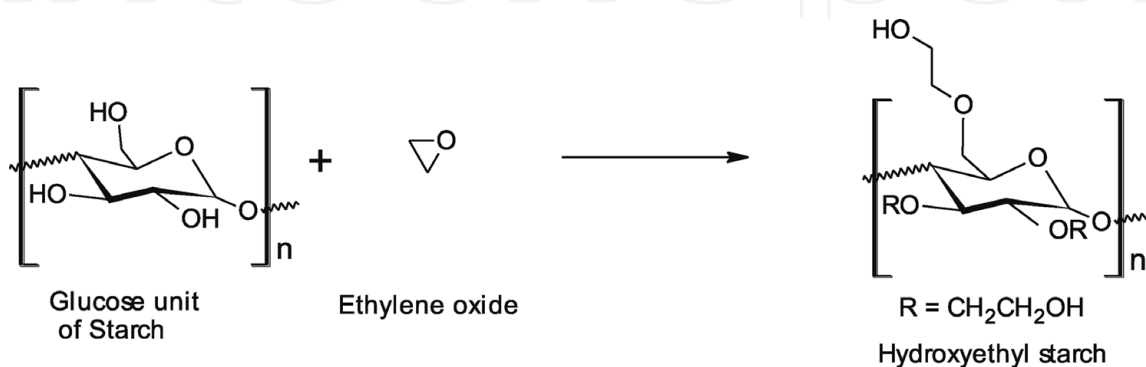


Figure 15.
Etherification of starch with ethylene oxide.

the starch chains thereby reducing the hydrophilicity and the degree of inter- and intra-molecular hydrogen bonding [8].

4.1.3.1 Hydroxypropylation of starch

This reaction process produces hydroxypropylated starch (HPS), which is a starch ether produce by reaction of starch with propylene epoxide in the presence of an alkaline catalyst (**Figure 14**). HPS is used for enhancing stability and viscosity of food products. The hydroxypropyl groups introduced into the starch chains affect the inter- and intra-molecular hydrogen bonds, thereby allowing for more ease of displacement of starch chains in the amorphous regions [8]. HPS is more stable to prolonged high temperatures than starch acetate especially at pH 6, and has improves freeze-thaw stability. It is mostly used in refrigerated or frozen foods and in the dairy industry. The FDA allowable DS for HPS is 0.2 [19].

4.1.3.2 Hydroxyethylation of starch

Hydroxyethylation of starch is performed by reacting starch with epoxyethane or ethylene oxide to produce the starch ether, hydroxyethylated starch (HES) (**Figure 15**). The health concerns of hydroxyethylated starch are limiting its use in the food industry. However they are mostly used in medicine and pharmaceuticals as plasma volume expander and extracorporeal perfusion fluids [35].

4.1.3.3 Carboxymethylation of starch

This is an etherification reaction process where starch is reacted with sodium chloroacetate or chloroacetic acid under certain conditions to produce

carboxymethylated starch (CMS) (**Figure 16**). The reaction involves refluxing chloroacetic acid with dry starch (anhydroglucose units) in the presence of sodium hydroxide in a solvent mixture of ethanol/isopropanol (ratio 3:5). Anhydroglucose unit can be obtained from acid hydrolysed starch [36].

4.1.3.3.1 Cationization of starch

Another etherification reaction is cationization of starch in which starch react with electrophiles or electron-withdrawing reagents such as ammonium, amino, imino, sulfonium, or phosphonium groups to produce cationic starches (**Figure 17–19**), which are important industrial derivatives [15]. Cationic starches are usually prepared under alkaline conditions, and they exhibit higher dispersibility and solubility with better transparency and stability.

Cationic starches containing tertiary amino or quaternary ammonium groups are the most important commercial derivatives, however they are mostly used in the textile and paper industry.

For the production of sulfonium starch, halogenoalkyl sulfonium salts (e.g., 2-chloroethyl-methyl-ethyl sulfonium iodide or any β -halogenoalkyl sulfonium salt), vinyl sulfonium salts and the epoxy alkyl sulfonium can be used (**Figure 19**). Usually R^1 is unsaturated group like alkylene, hydroxyalkylene, aralkylene, cycloalkylene, and phenylene group, while each of R^2 and R^3 can be alkyl, aryl,

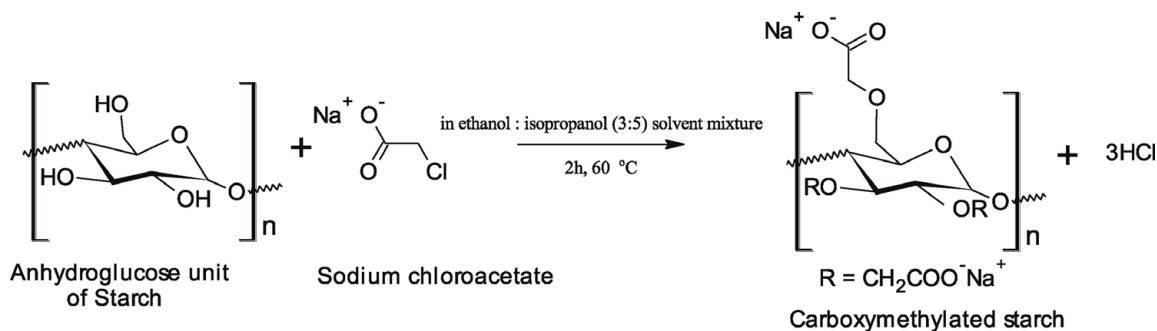


Figure 16.
Etherification of starch with sodium chloroacetate.

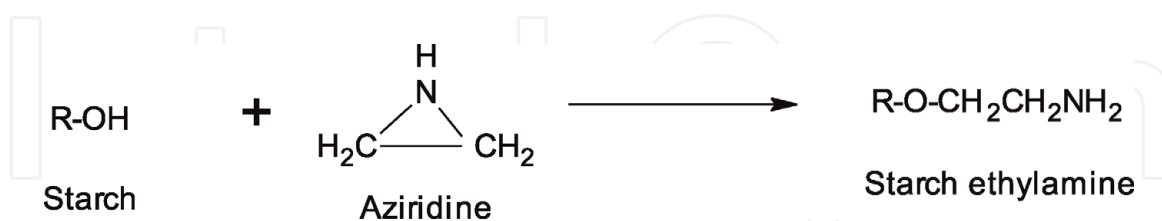


Figure 17.
Reaction of starch with aziridine to produce amino-ethylated starches [15].

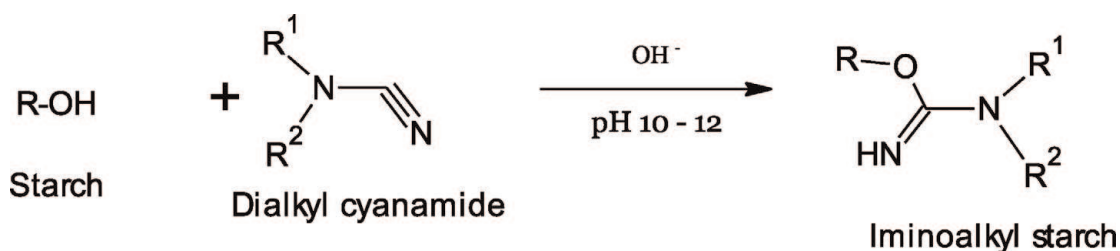
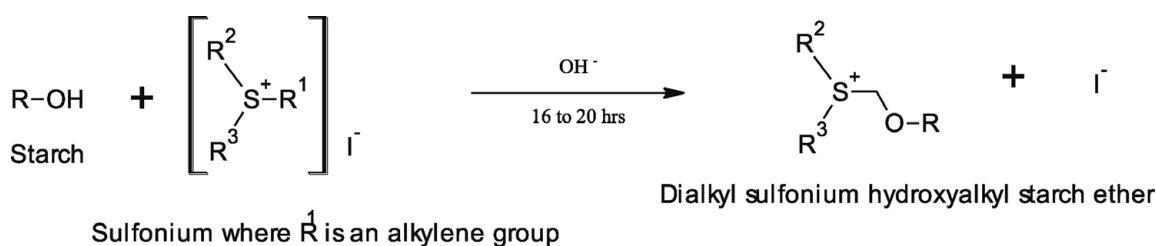


Figure 18.
Reaction of starch and dialkyl cyanamides to produce aminoalkyl starches [15].

**Figure 19.**

Etherification of starch with sulfonium salt to produce a sulfonium cationic starch.

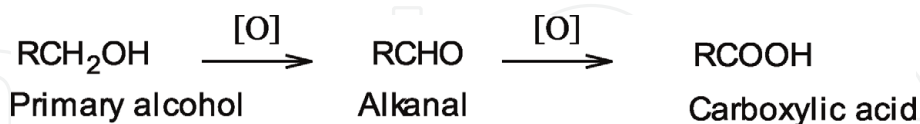
aralkyl, cycloalkyl and alkylene sulfonium groups and may also contain ether oxygen linkages and amino groups [37]. Factors such as reagent used and temperature, affect the reaction period which usually takes about 16–20 h.

Sulfonium starch display positive charge and can be used as thickeners in the form of aqueous dispersions or pastes. These dispersions are made by heating the suitable amount of sulfonium starch and water to a temperature of approximately 93°C. Upon cooling, the resulting dispersion becomes considerably clearer and more resistant to viscosity change compared to the untreated starch. Starch succinate and starch citrates which are obtained through esterification reactions have also been observed to exhibit high cationic properties [8].

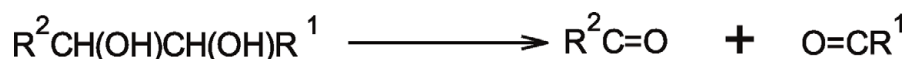
4.1.4 Oxidation

Oxidation of starch with strong oxidizing agents mimics reaction of primary alcohols and diols. Primary alcohol —OH functions are oxidized (**Figure 20**) to its corresponding carbonyls (aldehydes and carboxylic acid), while vicinal diols (**Figure 21**) are cleaved by strong oxidants like periodic acid into its corresponding carbonyl compounds (aldehyde and/or ketones) [24]. Oxidation of secondary alcohol —OH produces ketones (**Figure 22**). Oxidation may result in breakage of some intra- and inter-molecular bonds and partial depolymerization of the starch chains [38].

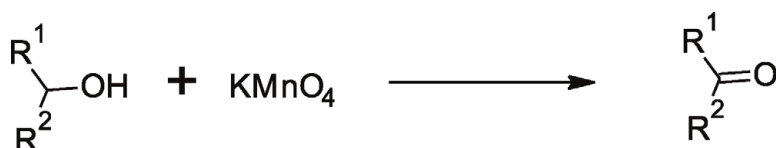
Starches treated with oxidants fall into two broad classes: oxidized and bleached.

**Figure 20.**

Oxidation reaction of primary hydroxyl groups of alcohols.

**Figure 21.**

Oxidation reaction of vicinal hydroxyl groups of alcohols.

**Figure 22.**

Oxidation reaction of secondary hydroxyl groups of alcohols.

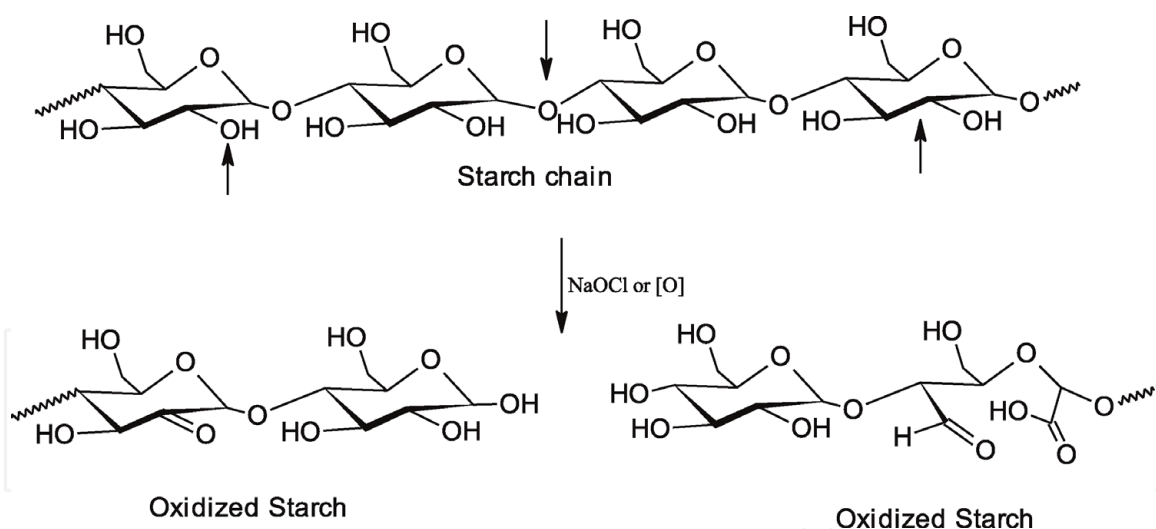


Figure 23.
Oxidation reaction of starch to produce oxidized starch.

Oxidized starches are starches treated with oxidizing agents like sodium hypochlorite (NaOCl). The oxidizing agent can attack the glycosidic bonds hydrolysing them to alcohol (—OH) functions or/and C—C bonds of the glucose unit, oxidizing them to carbonyl functions of aldehydes, ketones and carboxylates (**Figure 23**). Higher pH favors formation of carboxylate groups over aldehydes and ketones. Some depolymerization usually occurs in the process. Introduction of carboxylate groups provides both steric hindrance and electrostatic repulsion. Oxidation is usually carried out on whole granules and it causes the granule to dissolve, rather than swell and thicken [19]. The reaction can introduce up to 1.1% of carboxyl groups in the granule [39]. Oxidation with chlorine or sodium hypochlorite reduces the tendency of amylose to associate or retrograde. The reaction rate of starch with hypochlorite is remarkably affected by pH, which tends to be higher at about pH 7 but becomes very slow at pH 10 [40]. Oxidized starches are used where intermediate viscosity and soft gels are desired, and where the instability of acid-converted starches is unacceptable [41]. Hence, pastes of oxidized starches have a lower tendency to gel compared to those of thin-boiling (or acid hydrolyzed) starches of comparable viscosity.

Other oxidants such as chlorine, hydrogen peroxide and potassium permanganate, dichromates and chlorochromates, etc. are less commonly used. Oxidized starches are reported to give batters improved adhesion to meat products and are widely used in dough and baked foods [41].

Bleached starch is obtained from oxidation of starch with lower concentrations of oxidizing agents like hydrogen peroxide, sodium hypochlorite, potassium permanganate or other oxidants used to remove color from naturally occurring pigments. Bleaching is done to improve the whiteness and/or eliminate microbial contamination. Reagent levels of about 0.5% are usually used, and loss of some starch viscosity due to hydrolysis usually occurs.

4.1.5 Cross-linking of starch

Cross-linking of the starch polymer chains with reagents that could form bonds with more than one hydroxyl group of molecule results in cross-linked starch. Such reactions randomly add inter- and intra-molecular bonds at different locations in the starch granule which helps to strengthen and stabilize the polymers in the granule. Such processes may employ hydrolysis, oxidation, esterification, etherification, phosphorylation or combinations of these methods in a sequential or

one-mix procedure to achieve the desired product that meets the required physico-chemical characteristic of gelatinization, viscosity, retrogradation, and textural properties for food applications. In some instances, multifunctional reagents capable of forming either ether or ester inter-molecular linkages between hydroxyl groups on starch molecules are used. Reactions usually take place at the primary —OH group of C-6 and secondary —OH of C-2 and C-3 of the glucose units. Epichlorohydrin monosodium phosphate, phosphoryl trichloride, sodium trimetaphosphate, sodium tripolyphosphate, a mixture of adipic and acetic anhydride, and vinyl chloride are the main agents used to cross-link food grade starches [15]. Di-starch phosphate (**Figure 12**) which is a phosphorylated starch is an example of a crosslinked starch. Acetylated distarch adipate (**Figure 6**), hydroxypropyl distarch phosphate, hydroxypropyl distarch glycerol are other examples of crosslinked starch [8]. The FDA specify that not more than 0.1, 1 and 0.12% DS (w/w of starch) of phosphoryl chloride, sodium trimetaphosphate and adipic-acetic mixed anhydride, respectively, should be used for food grade starch [19].

Cross-linked starch exhibit increased resistance to processing conditions such as high or low temperatures and pH. Cross-linking reduces granule rupture, loss of viscosity and the formation of a stringy paste during cooking, providing a starch suitable for canned foods and products. Cross-linked starch shows smaller swelling volume, lower solubility and lower transmittance than native starch [15]. While oxidation may increase retrogradation, crosslinking reduces it. Hence a combination of the two chemical modification methods can be used to get the starch with desired balanced characteristics.

4.1.6 Approaches to modification of starch

As mentioned in the introductory section, native starches are modified to improve their physicochemical properties due to different reasons. Different approaches have been reported including physical, chemical, enzymatic and genetic approach. But the most widely used is the chemical approach. For instance, since starch must be gelatinized for it to be digestible in human diet and nutrition, and the process of gelatinizing native starches usually takes appreciable amount of time for granule to swell and form paste of gel as obtained in cooking rice and corn flour porridge, it can be modified to reduce gelatinization time by physical methods such as extrusion, spray-drier and drum dryer, which promote fast starch gelatinization to produce pregelatinized starch [42–44]. Pre-gelatinized starch exhibit reduced gelatinization temperature and time. The modified starches are usually dries to obtain flours and/or pre-gelatinized starches of long-term stability and quick preparation [9]. Pregelatinized starches are partially or totally soluble in cold water and readily form pastes [45]. It absorbs more water and disperses readily in water than the untreated starch, forming gel at room temperature and less prone to deposit [46]. Using gelatinized starch in food products affects the food qualities and properties, such as, bread volume and crumb [47]; pastas elasticity and softness, lusciousness and digestibility, tolerance in the properties of beating and cake mixtures, ice creams, doughnuts, growth of sugar crystals in food products [48]; texture, volume, shelf-life and stability during thawing of cakes and breads [49]. Liquefaction, partial hydrolysis and dextrinization may occur during pregelatinization depending on the processing conditions [42–44].

The process of physical modification does not involved any chemical reaction of starch with a modifying reagent and is referred to as physical modification of starch and the products are known as physically modified starches. However, most modifications of starches are performed through chemical processes. The chemical

reactions of starch (hydrolysis, esterification, etherification, oxidation and cationization) are generally exploited in the industry to produce converted or modified starches fit for different purposes in the industry.

According to the Food and Nutrition Program (FNP) of the FAO [50], a modified starch is a food starch which has one or more of its original physicochemical characteristics altered by treatment in accordance with good manufacturing practice by one of the reaction procedures such as hydrolysis, esterification, etherification, oxidation and cross-linking. For starches subjected to heating in the presence of acid or with alkali, the alteration (mainly hydrolysis) is considered a minor fragmentation. Bleaching is also essentially a process resulting in the colour change only. However, oxidation involves the deliberate creation of carboxyl groups. Treatment of starch with substituting reagents such as orthophosphoric acid etc., results in partial substitution in the 2-, 3- or 6-position of the anhydroglucose unit (AGU) unless the 6-position is occupied for branching in amylopectin chain. For cross-linked starch, where polyfunctional substituting agent, such as phosphorus oxychloride, connects two chains, the structure can be represented by Starch—O—R—O—Starch, where R is the cross-linking group and Starch refers to the linear and/or branched structure [50].

Evolving biotechnological innovations are progressing with enzymatic and genetic modification of starch as a greener alternative to chemical modification due to environmental concerns. Enzymatic modifications basically employ hydrolytic enzymes found in certain bacteria. For instance amylomaltases or α -1,4- α -1,4-glucosyl transferases from *Thermus thermophilus* and cyclomaltodextrinase (CDase 1–5) from alkalophilic *Bacillus* sp. [48]. While α -1,4- α -1,4-glucosyl transferases breaks existing α -1,4 bonds and make new ones to produce modified starch used in foods and non-foods applications, CDase 1–5 can be used to produce starches which are low in amylose content without changing the amylopectin distribution. The granule of starch-cyclomaltodextrin complex produced special tastes and flavours, as well as light, heat and oxygen-sensitivity stability. Transglucosidase, maltogenic α -amylase and β -amylase have been used to produce resistant starches of various degrees of digestibility [8, 51, 52]. On the other hand, genetic modification employs biotechnology to targets the starch biosynthetic process. Genetic regulation of enzymes such as starch synthetase and branching enzymes, involved in starch synthesis through starch synthase genes are used to produces cereal crops that yield amylose- free starch, high-amylose starch and altered amylopectin structure in starch [8].

5. Starch functionality and its applications in food

The reactions of starch explained above are exploited to create different types of modified or converted starched to obtain starches with appropriate physicochemical characteristics such as gelatinization, retrogradation, heat stability, solubility, transmittance, colour, texture, etc., for different industrial applications. The food industry is very mindful of safety of chemical residues hence not all types of modified starched are used in foods. Generally, modified starches are used for adhesion and as binder in battered and breaded foods, formed meat and snack seasonings; as dustings for chewing gum and products produced in the bakery; as crisping cover for fried snacks; fat replacer and juiciness enhancement in ice cream and salad dressings; flavour encapsulating agents in beverage clouds; emulsion stabilizers in beverages, creamers and canned foods; foam stabilizer in marshmallows; gelling agents in gum drops and jelly gum; and as expanders in baked snacks

and cereal meals [19]. **Table 1** gives a summary of the chemical modification processes and their food application.

5.1 Baked products (bread, pies, samosas, wafers, biscuits and sausages)

Baked products like biscuits, pies, bread, cakes wafers and sausages are high density products requiring heat resistant starches. Hence crosslinked starches are used since they are more resistant to oven baking temperatures of $120 \geq 230^{\circ}\text{C}$. Gelatinized starches are also used in ready-to-eat cereal meals such as corn-flakes, etc. The temperature, humidity and degree of stirring determine the texture and quality of the product.

5.2 Confectionery (candy, sweets and sweetmeat)

Oxidized starches have high clarity or transmittance, low viscosity and low temperature stability. It is frequently used in confectioneries for coating candies and sweets since they easily melt.

5.3 Gravies, soups and sauces (soups, sauces, tomato paste or ketchup)

Etherified and crosslinked starches are mostly used. Crosslinked starched have higher stability for granules-swelling, high temperature resistant, high shear stability and acidic conditions stability. They are used as viscosifiers and texturizers in soups, sauces, gravies, bakery and dairy products. Etherified starches have improved clarity of starch paste, greater viscosity, reduced syneresis and freeze-thaw stability. Crosslinked starches are used in wide range of food applications such as gravies, dips, sauces, fruit pie fillings and puddings.

5.4 Mayonnaises, salad dressing, ice cream, spreads and beverages

Hydrolyzed and esterified starches are mostly used in salad dressing and beverages. Hydrolyzed starch (acid-modified starches) has lower paste viscosity under cold and hot conditions. Hence they are used in mayonnaises and salad dressing [19]. Esterified starches have lower gelatinization temperature and retrogradation, lower tendency to form gels and higher paste clarity, and are used in refrigerated and frozen foods, as emulsion stabilizers and for encapsulation of beverage clouds. OSA starch is used as emulsifiers in mayonnaises and salad dressings.

5.5 Pasta (spaghettis, macaroni, others)

Pregelatinized and crosslinked starches are mostly used in pastas. Gelatinized starch affects pastas elasticity and softness, delectableness and digestibility. Crosslinking gives the needed structural firmness to the pasta.

5.6 Puddings (custard, pap, others)

Pregelatinized starches are used in puddings, instant lactic mixtures and breakfast foods to achieve thickening or water retention without employing heat. They are also used in ready-to-use bread mixtures. They are used where little or no heat is required and the increased absorption and retention of water improves the quality of the product; as an agglutinant in the meat industry; and as a filling for fruit pies [9, 49].

Chemical process	Specific treatment	Products	Function	Food application	References
Hydrolysis	Acid treatment	Acid-hydrolyzed starch, acid thinned or thin-boiling and fluidity starches	Reduced hot-paste viscosity, improved gelling or gel strength. Enhanced textural properties	Gum, pastilles, jellies	[19]
	Acid treatment	Dextrinized starch	Increased solubility and gel stability, reduced viscosity and improved emulsification properties. Encapsulate volatiles aromatic compound such as limonene, isoamyl acetate, ethyl hexanoate and β -ionones	Fat replacer in bakery and dairy products, bakery glazes, protective coating in confectionery. Flavour encapsulator in seasonings	[1, 19]
	NaOH or KOH treatment	Alkaline hydrolysed starch	Increase viscosity		[22]
Oxidation	Sodium hypochlorite oxidized starch	Oxidized starch	Lower viscosity, improved whitening of granules, high paste clarity, low temperature stability, and increased adhesion. Reduces retrogradation of cooked starch pastes	As binder in battered meat and breading, film former and binder in confectionery, crispy coating in various fried food stuffs, texturizer in dairy products	[15]
Esterification		Monosubstituted starch (starch acetates, starch hydroxypropyl ethers, starch monophosphate esters)	Freeze-thaw stability, improved emulsification properties	As emulsion stabilizers and for flavor encapsulation in refrigerated and frozen foods	[15, 19]
	Acetylation with acetic acid anhydride	Starch acetate	Increased lipophilicity emulsion stabilizer. Improves quality of any fat/oil-containing products. Reduces rancidity by preventing oxidation. Increase viscosity	Bulking agent in snack foods, stabilizer and thickener in most foods, improves smoothness and sheen of soups and sauces. Cholesterol-free salad dressings, and flavor encapsulating agents in clouding agents, creamer and beverage. Substitute to gum arabic, egg yolk and caseinates	[1, 15, 19]
	Succinylation with succinic acid anhydride	Starch succinate	Improved viscosity and juice taste. Freeze-thaw stability	Soups, snacks, and frozen/refrigerated food products. As thickener and in non-gelling custard creams. Meat and fried products to improve juicy or smooth taste and retain flavour	[25]

Chemical process	Specific treatment	Products	Function	Food application	References
	Succinylation with OSA	OSA starch	Increased paste viscosity, emulsion stabilizer and lower gelatinization temperature. Reduces glycemic response after consumption of beverages	Beverage emulsion stabilizers, and mayonnaises. Flavour encapsulating agent for battered meat and meat products	[19, 25, 53, 54]
	Treatment with adipic anhydride	Starch adipate	Higher paste viscosity, clarity and stability	Thickening agent in foods	[25]
	Phosphorylation	Starch phosphate	Better paste clarity, lower gelatinization temperature, higher viscosity, reduced retrogradation, and improved freeze-thaw stability	Frozen foods	[8]
		Distarch phosphate	Stability against high temperature, low pH and shear, and improved firmness of the swollen starch granule as well as improved viscosity and textural characteristic, resistance to syneresis during storage	As a thickener and stabilizer in foods such as soups and sauces	[8]
Etherification		Etherified starches	Improved clarity of starch paste, greater viscosity, reduced syneresis and freeze-thaw stability	As stabilizer in wide range of food applications such as gravies, dips, sauces, fruit pie fillings and puddings. Flavour encapsulating agent in beverages clouds	[15]
	Carboxymethylation	CMS	Cold-water solubility	Candy foods, sweets	[1]
	Hydroxypropylation	HPS	Improves freeze-thaw stability, water-holding properties, lowers the swelling/pasting temperature, increases paste clarity and reduces gel formation. More stable to prolong high temperatures. Increase solubility	Salad dressing, ice creams, refrigerated and frozen foods, and dairy products	[19]
	Cationization	Sulfonium starch	Higher dispersibility and solubility with better paste clarity and stability		[19]

Chemical process	Specific treatment	Products	Function	Food application	References
Crosslinking		Crosslinked starches	Higher stability to granules swelling, high temperature, high shear and low pH. Better viscosity and freeze-thaw stability. Volume expander. Delays retrogradation and reduce paste clarity	As thickener and texturizers in soups, sauces, gravies, bakery and dairy products. Filling in fruit pies and canned foods. In bread and dough products as expander and to improve rheological properties	[9, 15, 53, 55]
		Crosslinked-hydroxypropylated starch	A smooth, viscous, clear thickener and freeze-thaw stability	Gravies, dips, sauces, fruit fillings and puddings	[15]
Pre-gelatinized starch			Cold-water solubility and thickening	Instant soups, sauces, dressing, desserts and bakery mixes. Thickener in food that receive minimal heat processing such as pastas	[15, 19]

Table 1.
Application of chemically modification starches in foods.

6. Conclusion

The importance of starch as a biopolymer continues to be on the upward trend due to its versatility. It has transformed from its traditional use as energy-source food to more sophisticated food and non-food applications. Its growing relevance in modern technological application is as a result of its susceptibility to modification, which transforms the native properties into more desirable and malleable characteristics fit for different purposes. These modifications are only possible due to the chemical reactivity of the constituent glucose monomers of the starch chains. Though the starch granule is inherently almost unreactive, it is however easily activated for reaction by certain conditions such as high or low pH, higher temperature, presence of a catalyst, etc. Under the right condition, starch molecules can undergo hydrolysis, oxidation, esterification and etherification reactions to produce products of improved organoleptic, textural, mechanical and thermoplastic properties of desirable foods and non-foods application. Modified starches like starch acetate, starch phosphate, HPS, CMS, sulfonium starches and their crosslinked derivatives are used for various applications in the food industry. However, concerns for chemical residues in these products and environmental considerations for hazardous chemicals used in some of the process, have led to more studies for greener modification processes. Though biotechnology has evolved enzymic and genetic modification processes for production of some modified starches, they are still highly limited and sometimes uneconomical, hence chemical modification remains the most versatile and mostly used.

Conflict of interest

The author declares no conflict of interest.


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