

REVIEW ARTICLE

Starch modification techniques: an overview

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ABSTRACT

As technologies and processes increase the use of residues, starchy vegetal biomass is becoming an important alternative material in many applications because of its versatility, low cost, and ease of use when altered in its physicochemical properties. A growing number of industrial applications and renewable energy sources employ starch. Several ways have been devised to manufacture a variety of modified starches with various properties and applications. Physically modified starches can be created without chemicals or even biological agents, making them easy and affordable to utilize. Contrarily, starches include many hydroxyl groups that have been used for over a century to create starch esters and ethers as well as other more subtle adjustments, such as adjusting the structure of starches for particular purposes, it is possible to modify them chemically. Thus, the purpose of this review is to summarize recent developments and advances in starch modification. This study discusses enzymatic modification, dual modification, and physical modification techniques. The degree of change in starch characteristics reveals a starch's resistance or susceptibility to certain chemical changes. By carefully choosing an appropriate modifying agent and a native starch supply, modified starches with desired characteristics and levels of substitution can be created.

Keywords: Starch granules, chemical modification, physical modification, enzymatic modification, productions, dual modification

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INTRODUCTION

Food and non-food industries use starch, an important biomacromolecule in nature. There are two major components to starch: amylose, which is almost linear, and amylopectin, which is very branched. Depending on the amylose content and amylopectin structural parameters, starch has different properties, which determine its application (Kong et al., 2008). The native starch however, exhibits some limitations, including a lower thermal resistance, increased thermal decomposition and shear resistance, and the tendency to retrograde (Ahmed and Auras, 2011).

The native form of starch is rarely consumed intact and is commonly used by industry. Due to their instability with respect to temperature, pH and shear forces, native starches are limited in their direct applications. Decomposition and retrogradation

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are characteristics of native starches (Liu et al., 2011). Further, some starch granules are inert, water insoluble at room temperature, highly resistant to enzymatic degradation, and thus do not function properly. Modifications of native starches are often used to improve their properties, including solubility, texture, adhesion, and tolerance to high heating temperatures (Singh et al., 2007; Sweedman et al., 2013).

The production of modified starches with a variety of characteristics and applications has been developed by several methods. By modifying starch polymers in these ways, the polymers become flexible, and their physicochemical properties and structural attributes are modified to make them more useful for food and non-food industries (López et al., 2010). In terms of starch modification, the industry is constantly evolving. Yadav et al. (2013) describe physical, chemical, and enzymatic modifications of starch. Physical methods are heat and moisture, while chemical modifications introduce functional groups into the starch molecule via derivatizations (e.g., etherification, esterification, crosslinking) or degradation reactions (e.g., hydrolysis and oxidation) (Singh et al., 2007).

Starch has been modified through a variety of methods in the last few decades to produce functionalities relevant to a range of industrial applications. A modification can be chemical, physical, enzymatic, or genetic in nature. There are a number of review articles available on the subject of starch modification. In the last decade, researchers have been increasingly interested in developing new methods for modifying starch, with an emphasis on enzymatic, physical, and genetic methods. Hence, this paper aims to present all the new changes that have occurred in the last decade.

PRODUCTION/ MODIFICATION TECHNOLOGIES

The process of modification is properties characteristic to changes for native starch with the use of physical, chemical, genetic or enzymatic methods.

Physical modification

Water solubility of starch and reduction in the size of its granules can be improved through physical modifications. To treat the native granules by physical methods, have various combinations of pressure, moisture, temperature, irradiation and shear. This method is cost-effective, safe and easy to implement. These methods are favoured whereas the product is planned for consumption of human because these methods do not need any biological agents or chemicals (Neelam et al., 2012; Ashogbon and Akintayo, 2014; Alcazar-Alay and Meireles, 2015). Illustrates the examples of various kind of research studies on the modification of starch given in the Table 1.

Pre-gelatinized starch

It is that starch which undergone a process of cooking until complete gelatinization and process of drying also happening at the same time. Drying method can be spray drying, drum drying or extrusion. These treatments results the breakdown of granular structure, absenteeism of birefringence properties and also, end up with the complete granular fragmentation. Increase in swelling properties, cold water depression and solubility are the principal properties of PGS. Cooking conditions, the starch source and drying are collectively responsible for the PGS functionality (Ashogbon and Akintayo, 2014; Alcazar-Alay and Meireles, 2015). As per physically modified starches, PGS is mainly utilized in various instantaneous products that includes baby foods, soups and desserts as a thickener agent because of its property to get dissolve in cold water to form pastes. PGS does not depend upon heating to form paste due to this it is favoured in sensible foods (Majzoobi et al., 2011).

Hydrothermal treatment

Heat moisture treatment (HMT) and Hydrothermal treatments viz. annealing (ANN) are type of physical modifications that bring changes in the starch's physicochemical properties without breaking its granule (Tester and Debon, 2000; Chung et al., 2010; Jyothi et al., 2011; Chung et al., 2012). In these two treatments, it is important to control the temperature and time required for heating, also, treatments are dependent on starch to moisture ratio. When excess of moisture/water (>40%) is present, annealing take place and HMT is always carried out under control conditions- restricting the moisture content (10–30%) and at higher temperature (90-120°C) (Zeng et al., 2015; Raigond et al., 2015; Alcazar-Alay and Meireles, 2015). Brumovsky and Thompson (2001) has found that through partial acid hydrolysis of high amylose corn starch, heat stable granular can be obtained and resulting to raise the effect of hydrothermal treatment. HMT is carried out at restricted moisture levels below 35% and moisture content for ANN is higher or equal to 40%. HMT as a physical modification technique is safer with comparison to chemical modification because it is natural. RS level is increased by both hydrothermal treatments without breaking starch's granular structure. The combination of gelatinization and melting at 40 to 60% moisture level results the breakdown of granular structure. The temperature must be below down the gelatinization temperature to save the actual granule structure and this process is popular as Annealing treatment. Due to the consequence of enhanced granule stability generated by hydrothermal treatments, a high RS content is expected (Thompson, 2000).

Crystallinity degree increases, crystalline granular forms get strengthen also, starch chains in crystalline and amorphous layer get in an order because of the annealing treatment. Components of starch interact and increases the granule stability. Due to this, starch's solubility and swelling capabilities gets reduced and granule resistance towards the activity of amylolytic enzymes increases (Raigond et al., 2015). Lee et al. (2012) treats waxy potato starch (0% amylose) at 20 to 25% moisture for 1, 5 and 9 hours at 110, 130 and 150°C temperature treatment. The development of crystallites, binding of amylose chains and ordering in the amorphous region causes the reduction in the degree of swelling and resistance to amylolytic enzymes increases when heat moisture treatment of maize starch having high amylose is done at 100°C temperatures, also, moisture content is kept below 35% (Hoover and Manuel, 1996). Rise in the Resistant Starch yield of pea (2.3%), corn (7.7%), and lentil (5.6%) was recorded after HMT by Chung et al. (2009). The effect of heat moisture treatment and annealing treatment on production of RS content was compared by them (Chung et al., 2010). Through annealing, RS content was increase by 0.3%, 1.3% and 1.6% while due to heat moisture treatment, increase of 1.7%, 4.7% and 5.0% in gelatinized starch of navy bean, pea and lentil was observed. Many changes on amylose leaching, granular surface, swelling factor, X-ray diffraction, granular surface, gelatinization parameters of starch were reported from an extensive a range of HMT conditions and range of botanical sources (Gunaratne and Hoover, 2002; Adebawale et al., 2005a; Adebawale et al., 2005b; Watcharatewinkul et al., 2009).

Mostly for the preparation of RS-3, high amylose starch of corn is utilized (Dimantov et al., 2004). Because of the amylose retrogradation, resistant starch-3 resists amylase digestion and amylose retrogradation supply α -1, 4 glycosidic linkages inaccessible to amylase. The common methods that are used to increase the RS-3 yield are annealing, repeated freeze-thawings and acid hydrolysis of amylo maize starch (Thompson, 2000; Raigond et al., 2015). After annealing, the increase in the RS content of the pinto and black beans were 39.7% and 19.7% respectively and samples were treated for 24 hours at temperature 50°C with 50% moisture, observed by Simsek et al. (2012). Higher RS content was produced with Heat moisture treatment and annealing treatment in gelatinized samples when used in combination. Heat moisture treatment (25% moisture, 100°C, 16 hour) of normal corn and waxy corn, potato starch and rice raised the RS in waxy corn starch from 27 to 40.3%, as the same treatment reduce the content in potato, rice and normal corn starch by 4.7 to 29.7% (Jiranuntakul et al., 2011; Raigond et al., 2015).

To improve the potential health benefits of the whole wheat flour by increasing its RS content, an experiment was conducted by Arcila and Rose, (2015). To whole wheat flour in water (1:15 %w/v), they gave zero to seven cycles of (boiling) cooking and freezing (-18°C for 23 hour). They observed that during in vitro starch digestion there was increase in the RS content from 1.03 to 8.07% along with the upsurge of cooking-freezing cycles. Apart from this, with increasing cooking–freezing cycles leads to increase in the short chain fatty acids, usually propionate during in vitro fecal fermentation (Arcila and Rose, 2015).

During dry heating of starch at high temperature with or without the addition of acid leads to the dextrinization of starch (DeMan, 1999). The botanical origin of the starch and dextrans obtained under specified conditions demonstrate the properties of RS obtained during this process. The resistance of dextrans to enzymatic hydrolysis is greater degree of dextrinization and time of process is higher (Wang et al., 2001). The linkages 1, 3 and 1, 2 between glucoside residues of dextrans increases with elongation of dextrinization process. During dextrinization, free glucose generates and attached to the chain to form various linkages between glucoside residues by the amylolytic enzymes of gastrointestinal tract of human. α 1,3 glycoside linkages could only be disturbed by glucoamylase. The longer glucan chain complexes are formed through the interaction of lipids and fatty acids with amylose content and these complexes are resistant to amylolytic enzymes and are called as RS-5. These complexes can also be formed in small intestine of humans because here, fatty acids form complexes with the product of partial starch hydrolysis and upsurge the content of non-digested RS that pass to large intestine, also, these complexes can form at 37°C (Crowe et al., 2000; Leszczynski, 2004). The production of water-soluble RS with non-starch linkages has been recognised by Pyro dextrinization (Laurentin and Edwards, 2004) this can be considered as soluble dietary fibre. To reduce the cholesterol level in blood, soluble dietary fibre is well-known. Earlier, Cholesterol lowering effect of non-viscous soluble dietary fibre (wheat starch based low digestible carbohydrates) was also evaluated (Juhel et al., 2011; Raigond et al., 2015).

Other physical modification methods

Grinding

Cereals such as wheat need grinding to extract starch at large scale. During grinding, significant granule damage happens and shear forces are produced that pressed the granule structure. The damage to the granule is observed through splits in the starch's surface. It lowers the crystallinity of the amylopectin molecule. Restrictions on the swelling capacity are eliminated due to the fragmentation of the amylopectin molecule, through facilitating subsequent gelatinization. After grinding, the easy gelatinization of the starch granules reduces parameters (T₀ and enthalpies) in the final starch product (Alcazar-Alay and Meireles, 2015).

Extrusion

It is one of the food processing techniques which is used widely to produce food. It is primarily used to make food products of various shapes and involves high temperature short time (HTST) process (Camire et al., 1990; Raigond et al., 2015; Alcazar-Alay and Meireles, 2015). Due to Extrusion, there is an increase in the T gel of starch, changes in the molecular extension and its associations such as the amylose-lipid complex structure. This process can reduce the RS content, also, affects starch digestibility (Martínez et al., 2014; Alcazar-Alay and Meireles, 2015). It is not only a processing technique but have the potential to raise the RS content into food stuff up to certain limits, proved by researchers. This may happen because of the high shear force in extruder that causes depolymerisation followed by thermal cleavage of the starch molecule, that generates

straight chains which are more prone for precipitation (retrogradation) into RS-3 (Agustiniano-Osornio et al., 2005; Raigond et al., 2015).

During process; the RS content is affected by the screw speed, shear force, type of starch and barrel temperature. However, moisture content of starches has lesser impact with comparison to other parameters (Dupuis et al., 2017; Raigond et al., 2015). There was no Significant effect on rise in resistant starch content at moisture level of 12-18% in maize starch whereas at moisture level Upto 20% the RS content was increased after extrusion, reported by Bello-Perez and Paredes-Lope, (2009). The origin of starch is important factor in extrusion just like other techniques for RS production. For increase in RS content through extrusion process, banana starch is most efficient among the various plant origins because of high gelatinization temperature (76.6°C) and content of amylose (Bello-Perez and Paredes- Lope, 2009). After extrusion a small rise in enzyme RS content for normal maize starch from 1.5% to 2.1% and wheat starch (from 0.8% to 2.8%) was observed by Chanvrier et al., 2007. After the extrusion of barley, Huth et al. (2000) obtained 2–3% of RS. It is important to note that the observations on the effect of extrusion on resistant starch content are conflicting. Various researches described a reduction in the content of RS (or increased digestibility) after extrusion, described this due to the rupture of granular structure because of various treatments such as high pressure, thermal treatment and shear forces (Alsaffar, 2011). This confliction may be through the interactions among food components in different food matrix that may differ according to food formulation, extrusion processing condition/s and ingredient/s composition. The normal corn starch of acid-modified effect of extrusion (twin-screw) on the RS content was examined by Hasjim and Jane, (2009). The RS content in the Normal corn starch is 11.0% and the RS content increased to 19.0% and 20.0% after hydrolysis of acid followed by low / high shear extrusion conditions respectively.

Extrusion, the production of RS3 can be achieved by processing the starch at temperature treatment 90, 100, 120, 140, or 160°C, having moisture content 20%, 25%, 30%, 35%, or 40%, and with engine speed presses 60, 80, or 100 rpm. Storing it 4 ° C for 24 hours before drying, such combination treatments can increase the levels RS3 (Faraj, Vasanthan and Hoover, 2004). For process optimization, the extrusion product from corn starch can be increased by complex amylose-fat. The structure of starch could be affected by Microwave irradiation which turned into soluble from an insoluble. But quantitatively, it does not affect RS levels.

Non-thermal modification

A few processes that include thermal treatments to increase or prolong the life of a product are applied in the food production. Thermal treatments include boiling temperatures for seconds or minutes (Table 2). There were some disadvantages of conventional treatments such as alterations in the organoleptic properties, damage of some nutrients and vitamins. The one of the option or alternative to conventional process to eliminate spores and pathogenic microorganisms is the Non-thermal modification. The use of ultrasound, high pressure, and microwaves, electric pulses are used in Non-thermal techniques (Anderson and Guraya, 2006; Mollekopf et al., 2011; Hódsági et al., 2012; Braşoveanu and Nemtanu, 2014; Alcazar-Alay and Meireles, 2015). In industry, the pressure is from 400 to 900 MPa is used in high pressure technology. The swelling capacity is generally restricted by High pressure and also decreases paste viscosity. Several times pressure below atmospheric pressure (vacuum pressures) is used in other technologies; for starch granule modification, is the most recent technology used where technology uses gas in a plasma state modification (Deeyai et al., 2013; Wongsagonsup et al., 2014). An ionized gas is plasma consist of various active ionic species types: excited atoms, ions, protons and electrons (Bogaerts et al., 2002; Alcazar-Alay and Meireles, 2015). For this particular treatment, the gases utilized in plasma state includes ammonia, ethylene, methane, oxygen, air, hydrogen or argon. This treatment modifies the hygroscopicity, degree of oxidation and polymerization

of starch in various ways (Wongsagonsup et al., 2014; Alcazar-Alay and Meireles, 2015). Use of microwaves to modify starch involves number of interacting mechanisms, namely furnace dimensions, irradiation, also, the characteristics of the starch. The most necessary factors are temperature and moisture that impact the dielectric properties of the starch in the microwave irradiation process (Braşoveanu and Nemtanu, 2014; Alcazar-Alay and Meireles, 2015). By the modification with microwaves results from the rearrangement of starch molecules which generates changes in enthalpies, solubility, Tgel, rheological behaviour and swelling capacity (Iida et al., 2008; Zuo et al., 2012; Yu et al., 2013; Alcazar-Alay and Meireles, 2015). Modification by microwave also generates differences in the crystallinity in the granule and its morphology which depends on the moisture and starch source (Braşoveanu and Nemtanu, 2014; Alcazar-Alay and Meireles, 2015).

Utilization of ultrasound is observed as a physical modification treatment. Starches that are in suspension and starches which have undergone previous gelatinization are treated with this process-Ultrasound (Iida et al., 2008; Alcazar-Alay and Meireles, 2015) Ultrasound maintain the granule's shape and size but primarily affects the amorphous region. The properties are solubility, swelling capacity and viscosity of the paste are modified and the surface of starch becomes porous (Luo et al., 2008). The frequency, sound, process time, temperature and the starch suspension properties decide the Ultrasonic modification (i.e., botanical source of starch and concentration) (Zuo et al., 2009; Alcazar-Alay and Meireles, 2015).

Table 2: Studies on different type of modification with references

Type of modification	Source of starch	Results	References
Non hydrothermal modification	Tapioca	During modification, reactions occurred, depolymerisation and crosslinking of the starch which can replace the chemical reactions.	Wongsagonsup et al., 2014
	Potato starch	With the help of ultrasound starches treated showed depolymerization of the granules. Modification of the paste properties. The better medium was water for starch modification.	Sujka and Jamroz, 2013
	Wheat starch		
	Corn starch		
	Rice starch		
	Ginger (Zingiber officinale R.) Turmeric (Curcuma longa L.)	SFE treatment did not alter granule morphology or amylose/amylopectin ratio. The process of modification reduced Tgel and the maximum viscosity in ginger. The opposed behaviour was showed by Turmeric starch.	Braga et al., 2006

Chemical Modification

It is modification in which involves functional group on the molecule of starch, which is not affecting the size distribution or morphology of granules (Lopez et al., 2010; Simsek et al., 2012; Alcazar-Alay and Meireles, 2015). The chemical reagents block the access of the enzyme and form atypical connexions during the chemical modification of starches and escape digestion. Changes in molecular structure contribute to the production of a high RS content during the chemical treatment of starch (Lopez et al., 2010). Cross-linking is commonly used for enhancing flexibility and freezing starch paste's thaw and cold storage stabilities. Cross-links incorporate inter-and intra-molecular connexions to spontaneously stabilise and reinforce the granule of starch (Acquarone and Rao, 2003; Singh et al., 2007). Seib and Woo (1999) and Woo and Seib (2002) have identified the use of the chemical modification of cross-linking (CL) for RS production through the use of standard starches from several botanical sources. Granular starch is treated with a multifunctional reagent for preparing cross-linking starches,

which can form either or links between the groups of hydroxyl starch on the starch molecule (Singh et al., 2007). The chemical modifications are as mentioned in table 3

Cross linking

Cross linking is the polymer happen when chains (linear or branched) are covalently interconnected. This is also knows as cross ligation or cross linking. There are two methods which are utilized in food industry of starch such as Cross-linking and substitution of starch (Jyothi et al., 2006). In the starch molecules, there are reagents which is used in ester or ether bonds with group of hydroxyl (Singh et al., 2007; Alcazar-Alay and Meireles, 2015). The substitution chemical modification can also produce high level of RS. Chemically altered starches are less susceptible to enzyme hydrolysis, either in the native granular form or in the gelatinized state (Lehman and Robin, 2007). It is modification in which the polymer rigidity increase by formation three dimensional network. It increase the molecular mass and degree of polymerization; starch molecules are soluble in organic solvents. There are many agents which are used in crosslink native starch such as sodium tripolyphosphate, sodium trimetaphosphate, phosphoryl chloride and epichlorohydrin and many others (Woo and Seib, 2002; Alcazar-Alay and Meireles, 2015). Depend upon the reagents those are used for crosslinking, the end product are classified into three types are by starch esterification monostarch phosphate reacts with sodium or potassium orthophosphoric and orthophosphoric acid; when native starch distarch phosphate reacts with sodium tripolyphosphate or phosphoryl chloride and in last, phosphated distarch phosphate, resulting from combination of monostarch and distarch phosphates treatments (Gunaratne and Corke, 2007; Jyothi et al., 2006). Starch digestibility is decreased by substitution of starch hydroxyl groups with octenylsuccinyl, acetyl hydroxypropyl and citryl (Xie and Liu, 2004; Heacock et al., 2004; Han et al., 2007; He et al., 2008; Chung et al., 2008). The numerical decrease digestibility of starch liked to a phosphate bridge is reported by Sang et al., 2006. Whereas Chung et al. (2008) and Wolf et al. (1999) reported minor or no changes. The differences in the origin and properties of starch as well as the conditions used for modifying starch can be attributed to the contradictions in the reports for different workers. The production of cross-linking stomach is based on biologically or polyfunctional reagents are oxychloride phosphorus, trimetaphosphate sodium and mixed acetic acid anhydrides and dicarboxyl acids. Starch is linked to phosphate and sulphonate hydroxyl groups (Jyothi et al., 2006; Sajilata et al. 2006). For crosslinking glucans in the production of RS reagents (sodium triphosphate or its mixture with sodium tripolyphosphate) can be used (Kahraman et al., 2015). Chemical as well as functional properties of starches of cross-linked depends on the reaction conditions (time, pH and Temperature etc), source of starch and the concentration of cross-linking reagents (Wang et al., 2002; Singh et al., 2007). A reaction time is positively associated with resistant starch content of cross-linking wheat starch (Woo and Seib, 2002). Acids such as hydrochlorine, orthophorous and sulfuric acids based on the dry weight of starch can be adjusted with starch. Starch with 49.5% indigestible starch (RS), can be made with HCL at 1/160 native starch and 90° C for 1 hour, from native Lima bean starch (Tester et al., 2004).The RS content of crosslinked maize and wheat starch is increased by temperature and pH. Cross-linking is more subjective to pH than changes include by temperature. The resistant starch content was 80.4% and 83.9% of cross-linked maize and starch of wheat respectively (Futch, 2009). Cross-linking weed starch production conditions were 38° C and pH 12 as well as a 70°C and pH 12 cross-linking weed starch (Kahraman et al., 2015). The increased in RS content (21.49% to 29.14%) with double modification of banana starch by cross-linking esterification (Carlos-Amaya et al., 2011).

Gelatine starch can be seen as swelling granules, combined of starch fragments with dispersed starch molecules (DSM) and fully DSM according to the degree of gelatinisation. The RDS (Rapidly Digestible Starch), SDS (Slowly Digestible starch), and RS content in cooked starches are the determinants of the rate of starch Gelatination and structure of the starch through physical or chemical treatment (Juansang et al., 2012). There are other uses of chemically synthesized starches, such as

thickness, food additives and gelling agents and fat substitutes (López et al., 2010; Alcazar-Alay and Meireles, 2015). Chemically modified starches are fully digested and their accessibility to amylolytic enzymes depends on the origin of the starch and degree of chemical substitution (Wolf et al., 1999). Modified starch is typically inaccessible to amylolytic enzymes after chemical alteration. Di-starches are immune modified starch with a high DF content ($\geq 70\%$ w/w). The resistance also increases with the degree of their replacement in the event that di-starch is involved in amylases (Woo and Seib, 2002). Because of its amylolysis resistance, acetylated back-starch is considered to be one of the form of RS. The degree of replacement and raw material used for esterification and mainly affected its properties (Zeiba et al., 2013). As well as acetylation, hydroxypropylation, glycine rusting and cross-connection with epichlorohydrine can increase the starch resistance to amyloses (Juansang et al., 2012). Ohkuma et al. (1995) identified the development, by heat treatment of potato starches in the presence of acid followed by rationing, of indigestible dextrin or pyrodextrins in the patented processes.

Acetylated starch

It is a type of chemical modification of polymeric molecules of starch by adding functional acetylated groups which create and react a specific ester with free hydroxyl groups found in the starch polymer branch chains (Sweedman et al., 2013; Alcazar-Alay and Meireles, 2015). It is the modification that is more widespread and which leads to the use of reactive reagents (vinyl acetate or OSA and anhydrous acetic acid) as the product of native starch esterification in the alkaline catalyst presence ($\text{Ca}(\text{OH})_2$, NaOH, Na_2CO_2 , KOH) (Wang et al., 2002; Alcazar-Alay and Meireles, 2015).

OSA modified starch is an important emulsifier in the nutritional, cosmetic and pharmaceutical industries. It adds hydrophobic chains in this modification of hydrophilic starch structure (Chen et al., 2014; Alcazar-Alay and Meireles, 2015). The formation of acetyl groups decreases contact resistance between the molecules of the starch. The solubility and swelling capacity of acetylated starch is increased by comparison with native starch (Berski et al., 2011; Alcazar-Alay and Meireles, 2015). In acetylated starch there are restricted hydrogen bonds due to the electrostatic repulsion forces of the starch molecule. Hydroxyl groups and glucose anhydrous were converted into acetylated groups in acetylated starch (Huang et al., 2010; Alcazar-Alay and Meireles, 2015). Low-replacement acetylated starch (0.01-0.2) has some applications in thickeners, conforming films, encapsulation agents, adhesives, texturizers, and stabilisers (Elomaa et al, 2004).

Cationic starch

They are mostly produced by reacting starches with components containing tertiary ammonium or quaternary ammonium, imino, amino and sulphuric or phosphate groups. Cationic monomers like 2,3-epoxypropyl trimethyl ammonium chloride or 3-Chloro-2-hydroxypropyl ammonium chloride in dry/ wet processes have been commonly used to alter free hydroxyl ions of the native starch molecule. In the dry cationic transition, the reactive is sprayed on the dry starch during extrusion within the absence of a liquid phase. A mix of starch and spray reagent before thermal treatment is used for semi-dry cationization. Wet cationization involves an in alkaline solution, heterogeneous reaction or a dimethyl sulfoxide homogeneous reaction. The physicochemical properties (starch) and therefore the granular structure are modified after the cationic process, especially the method requires a high degree of substitution. The cationic reaction decreases the temperature of the paste, increases the height viscosity and leads to different changes in starches from various sources. The cationic starch materials of the textile industry are favourites among modified starch materials since the positive changes within the molecular chains correspond to the electrostatic links between cellulose fibre negative charges (Hubbe, 2006). There are many applications in the treatment of

cationic starches (i.e., flocculants and clothing additives), preferable for low costs, excellent safety, biocompatibility and rapid deterioration (Zhang, 2001; Alcazar-Alay and Meireles, 2015).

Table 3: Different type of chemical modification with researches

Type of modification	Chemical	Sources of starch	Observation	References
Cationization		Waxy maize starch	Reduction in fragmentation and starch granule size. Esterification reaction is produced on the granule surface.	Liu et al., 2015
		Commercial potato starch	Studied that in cationization reactions the effects of amine groups. Due to sensible amine structures, temperatures which is lower have better results.	Anthony et al., 2013
Crosslinking		Commercial corn and wheat starch	Studied the application of parameters (temperature and pH to produce RS). RS production was increased for corn as well as wheat starches at higher pH.	Kahraman et al., 2015
		Oat starch	Reduction in the amylose content due to alkaline conditions; increase in the swelling capacity of starch granules; viscosity increase at high temperatures; and rapid development of viscosity at cooling temperatures.	Berski et al., 2011
Acetylation		Commercial starches from oat, corn, wheat, banana rice, and potato.	RS production was $\leq 100\%$ in all studied materials. RS produced was less water-soluble at 95 °C and increased the Tgel and enthalpies of starch paste.	Woo and Seib, 2002
		Commercial corn starch	Improved performance of starch for textile applications. Reduction in surface tension, impregnation, wetting and diffusion of starch in textile fibers.	Zhang et al., 2014
		Commercial corn starch	Pre-treatment increased the swelling capacity of granules and the peak of viscosity. Decrease in paste temperature.	Chen et al., 2014
		Commercial potato starch	Increase in solubility and decrease	Kapelko et al., 2013

	in swelling capacity caused by both pretreatments. Acetylation effects were directly dependent on the pretreatment.	
Oat starch	Reduction in amylose content, temperature of the paste and viscosity at high temperature. Rapid development of viscosity upon cooling.	Berski et al., 2011
Banana starch	Increasing the swelling capacity and solubility of banana as compared to native starch. And also increased the paste viscosity. Decreased the retrogradation tendency.	Bello-Pérez et al., 2000

Oxidation

Oxidation is the starch modification process which is important process. It is a process in which functional groups (carboxyl and carbonyl groups) are found in depolymerize the molecule and the starch molecule (Kuakpetoon et al., 2001; Lawal, 2004; Neelam et al., 2012). During process, it is necessary to maintain the appropriate parameters pH and temperature (Kuakpetoon, 2001). The reactive oxidants used include per-acetic acid, hydrogen peroxide, sodium hypochlorite, nitrogen dioxide, potassium permanganate and chromic acid (Sánchez-Rivera et al., 2005; Sandhu et al., 2008). Currently, starch modified by oxidation has significant utilisation in the industry especially in food to form coatings and adherent surfaces (Lawal et al., 2005).

Acidification

Studies were conducted where autoclaving and then retrogradation of acid modification to increase content of RS was followed (Shin et al., 2004; Koksel et al., 2008). In this case, the acid would first hydrolyse the amorphous portion of the starch granules and then hydrolyse the crystalline region, which would result in the shorter chains production, which would be disorganised by autoclaving, and finally redirected to a more orderly double helix structure during retrogradation that would prohibit hydrolysis of enzyme (Hoover, 2000; Raigond et al., 2015).

Citric acid was followed by chemical treatment of ordinary corn starch and dry heating for 7 hours at 140° C, and then heating at 100° C in a bath with boiling water yields RS 68.3%. In the process of heat treatment, swollen starch chains produced more likely to attack citric acid. Citric anhydride replaces the amylolytic hydroxyl glucans of the starch chains which help digestion. Treatment with thermal acid usually facilitates RS development; however, high intensity of this treatment can destroy an amylolysis digestion-resistant structure. Liu et al., 2014 recorded an increase of 35.62% of the RS prepared by standard maize starch heat and citric acid treatment. The phosphodiester cross-links of starch can generate resistant starch-rich powders with 40-98% RS (Woo and Seib, 2002).

Acid modification it the method which involve the acidic solutions such as most commonly used HCl and H₂SO₄ to form a concentrated paste of solids 35–40% at a temperature below T_g for a specific duration depending upon the conversion degree or desired viscosity (Amaya-Llano et al., 2008; Thirathumthavorn and Charoenrein, 2005). The mechanism of acid modification is also known as acid hydrolysis (Amaya-Llano et al., 2008).

Hydrolysis is generated randomly, the polymeric chain is shortening and breakdown the linkages α -1, 4 and α -1,6 links. It develops in two different stages: an early stage in which hydrolysis preferentially attacks the amorphous regions of granules at a high reaction rate and a subsequent stage in which hydrolysis occurs in the crystalline region at a slower rate (Wang and Wang, 2001). The rate of hydrolysis and modification of starch are in amylose: amylopectin ratio proportion, as well as to the conformation and size of granules (Hoover, 2000). After hydrolysis, decreases the molecular mass of the starch, and increases crystallinity (Zuo et al., 2014).

The reduction of amylose content in starch, this reflects increase in gelatinization enthalpies and paste temperature (Lawal, 2004). Dilute acid solutions are used for starch modification which gel consistency are improved and viscosity of paste reduced due to depolymerization of the starch (Pérez and Bertoft, 2010; Ulbrich et al., 2015).

Table 4: Different type of chemical modification with observation from various sources

Type of modification	Chemical	Sources of starch	Observation	References	
• Oxidation		Sorghum	Decrease in swelling capacity and viscosity of the paste.	Ali et al., 2014	
		Commercial potato starch	Decrease in the viscoelastic properties of the paste due to oxidation. Microwave uses are not significantly difference from the conventional method.	Ptaszek et al., 2013	
		Oat Starch	Apparent increase in linear molecules due to amylopectin depolymerization. Reduction in viscosity at high temperature and faster development of viscosity upon cooling.	Berski et al., 2011	
		Corn Starch	Decreased the amount of SDS and Increased the RS but, pregelatinized corn starches had an increase in RDS.	Chung, Shin, and Lim, 2008	
	• Acid hydrolysis		Yam starch	Increase in swelling capacity and granule density. Breakdown or fragmentation of granules.	Falade and Ayetigbo, 2015
			Sorghum	Granule surface was highly porous, reducing its swelling capacity.	Ali and Hasnain, 2014
			Peas (38% starch) Potato (25% starch) Wheat (30% starch)	Hydrolysis reduced granule size and paste viscosity. The amylopectin depolymerization increased the quantity of linear chains similar to amylose, favoring gel formation and its strength.	Ulbrich et al., 2014
	Potato, corn, wheat, peas and tapioca (Acid are used HCl, HNO ₃ , H ₂ SO ₄ and H ₃ PO ₄)	H ₃ PO ₄ produced a lower hydrolysis rate, whereas HCl and HNO ₃ resulted in a higher reduction in molecular mass and consequently a higher hydrolysis rate.	Singh and Ali, 2000		

Dual Modification

It is the modification in which combine various type of modification such as combination of physical and chemical (phosphorylation assisted by high pressures, acetylation assisted by microwave). Especially, dual modification of chemical which include two type of chemical modification such as crosslinking/hydroxypropylation, acetylation/oxidation and crosslinking/acetylation, (Adebowale and Lawal, 2002; Carmona-Garcia et al., 2009; Huang et al., 2010; Alcazar-Alay and Meireles, 2015). This includes methods which the chemical reaction involves in the presence of an enzyme therapy or specific physical environment which can increase the derivatives or, in some situations, increase the level of substitution (Deetae et al.,

2008; Neelam et al., 2012; Ashogbon and Akintayo, 2014) In the dry cycle, microwave assisted esterification for the development of starch melted an efficiency of reaction of upto 98% and a time of reaction under 5 minutes. This is considered an efficient way to esterify starch (Xing et al., 2006; Neelam et al., 2012).

Table 5: Studies on Dual modification with references

Type of chemical modification	Sources of starch	Observation	References
Dual modification	Sorghum	Paste clarity was Increased.	Ali et al., 2014
	Potato peel	Depolymerization of starch was quantified by reducing sugar production. The method of ultrasound in acidified water shown the degree of depolymerization highest.	Hernoux et al., 2013
	Commercial starch	corn	Spier et al., 2013
	Corn and mung bean starch	Combined treatments generated several damages to the surfaces of the starch granules, making them more susceptible to enzymatic hydrolysis.	Karim, Sufha and Zaidul, 2008
	Cassava starch	Significantly different functional properties compared to hydroxypropyl starch prepared with untreated native Starch.	2008
		Reduce the use of chemicals to enhance production.	Jyothi et al., 2005

This modification is utilized widely in frozen foods, salad dressings puddings and canned foods (Jane, 1997; Singh et al., 2007). Jyothi et al., 2005 have also observed the high efficiency of manatee succinylated starch production with microwave support. This is good way to reduce the use of chemical products for increasing efficiency. For sterification of cold-water-soluble carboxymethyl potato starch with octenyl succinic anhydride, ultrasound and microwave irradiation was used. The esterification time was positively cut from a couple of hours to a couple of minutes. The derivatives showed great surfactant performance and emulsifying. A hybrid modification process using rice starch linkage and phosphorylation provided strong freeze thaw stability with modified rice starch. The treatment of native starch with a combination of glucoamylase, fungal α -amylase and propylene hydroxypropilation was carried out in the process of modified corn and mung bean starch (Cizova et al., 2008). This enzymatic partial hydrolyse produces modified starch, with major functional characteristics distinct from that of hydroxypropyl starch produce under normal conditions (Karim et al., 2008; Neelam et al., 2012).

Genetic Modification

Such techniques include transgenic technology that targets the enzymes involved in starch biosynthesis so, as to benefit from chemical or enzymatic alteration which is environmentally harmful after harvest. The conventional plant breeding techniques or biotechnology can be used for genetic modification (Johnson, 1999; Neelam et al., 2012).

(1). Amylose-Free Starch

The simultaneous down-regulation of three starch synthesis genes (Granular bound starch synthetase, starch synthetase II, and Starch synthetase III) was produced through the synthesis of amylose-free starch amylose free waxy starch, which resulted in the waxy starch with short amylopectin chains. Mutant maize is typically cultivated maize, wheat, sorghum and amaranth. This produced waxy starch is commonly used in the food industry, as it gelatinize quickly and creates transparent pastes which are not gel.

(2). High-Amylose Starch

A mutation in the gene encoding starch branching enzyme (SBE) IIB, also known as “amylose extende (ae),” is produced by high-amylose starch in cereals. The discovery of the gene and its degradation in tubers using antisense technologies to made it possible for starch to be developed that have increased the amounts of amylose slightly in potato (Jobling et al., 1999). Nonetheless the production of starches with amylose levels of over 60% must be limited by both SBEI and SBEII (Schwall et al., 2000). Recently a more effective approach was used to inhibit the gene function with domain SBII antibodies to generate starches with higher levels of amylose. The derivative thus developed an important precursor to the production of enzyme-resistant polymers that can be used in the colon targeted delivery of medicines. High-amylosis starches can also be converted into a nutritive advantage of ‘resistant starch’ (Bird et al., 2000).

(3) Altered amylopectin structure

Amylopectin synthesis is regulated by a variety of enzymes, including starch synthetase, ramifying enzymes and debranching enzymes, each with an isoform. Alternative amylopectin structure de-regulate any of single enzyme therefore fails to create a completely new feature of amylopectin. For some rice plants, however inhibition of SS II and SS III isoforms shows low gelatinizing (less than 50 °C) of functional derivative (Neelam et al., 2012).

Enzymatic Treatment

To reduce the molecular mass and also, to debranch the amylopectin, enzymes are used. This is so because RS production can be improved by reducing the molecular mass and by debranching the amylopectin (Reddy et al., 2013). The amount of amylose will be increased through enzymatic treatment of starch which then would form crystalline structure that are tightly packed and so this becomes more resistant to enzymatic hydrolysis. α -1, 6 glycosidic bonds at branch point on the amylopectin can only be breakdown by isoamylase and pullulanase which are debranching enzymes, and this results the starch molecule with higher amylose content. The α -1, 4 glycosidic bonds can also be breakdown by α amylase and β amylase. α amylase and β amylase act on different area of starch molecules. All the α -1,4 glycosidic bonds are broken by the α amylase with an exception of those areas near the branch points and releases glucose monomers while β amylase by act on every other α -1,4 glycosidic bonds from non-reducing end of amylose or amylopectin and releases maltose units. Therefore, to increase the RS content, enzymatic treatment is given to hydrolyze amylopectin branch chain, isoamylase and pullulanase are commonly used with comparison to α and β amylase. High amylose content is produced by debranching of amylopectin which then produces more crystalline structures and at the end increases total RS -3 content. Break all the α -1, 4 glycosidic bonds of starch chain is the major role of the enzyme α -amylase and finally to reduce the viscosity of starch paste at faster rate. This is so because starch paste’s viscosity is affected with the addition of α -amylase and therefore, development of crystals is difficult. Viscosity of starch paste will be lesser at higher α -amylase level because movement of linear chains crystal formation will be difficult (Gao et al., 2011). The amount of α -amylase should be sufficient to obtain appropriate yield of RS. To calculate the total dietary fibre content of RS samples, enzymatic treatment has been used and the concentration of α -amylase was found to be more critical than amyloglucosidase (McCleary, 2000) as high α -amylase activity is associated with decrease in RS content. Pullulanase treatment can be used to form resistant starch from corn, potato, tapioca, wheat, oat, sago, barley and arrow root (Sajilata et al., 2006).

CONCLUSION

In recent years, the starch industry has expanded rapidly, and modification processes have increased its versatility. In both the food and non-food industries, starch can be modified physically or chemically to meet different needs. By modifying starches (physically, chemically, genetically or enzymatically), unconventional starches and vegetable residues containing starch can be used more effectively in industry. When appropriate, unconventional starches can replace conventional starch in industrial processes in whole or in part, depending on cost and accessibility. It is necessary to determine the property requirements of starch for each process in order to select the most appropriate modification method based on application requirements, market trends, availability, and structural properties. Starch modification is an industry that is constantly evolving. There are several ways of modifying starch's structure to obtain a functional product with the appropriate properties for specific industrial applications, thus further enhancing its added value. Chemical modification is generally achieved through derivatization such as esterification, etherification, crosslinking, cationization due to the presence of ubiquitous hydroxyl groups on native starches. There is an evolving new trend called dual modification, which involves the combination of physical and chemical methods. Enzymatic treatment reduces the molecular mass and also, to debranch the amylopectin, enzymes are used. Conventional plant breeding techniques or biotechnology can be used for genetic modification. As a result of physical modification, starch can be made more water soluble and the granule size of starch can be reduced. Native granules can be treated physically with combinations of temperature and moisture, pressure, shear, and irradiation. Physical modification is simple, inexpensive and safe. Chemical or biological agents can be harmful to health, so these modification techniques are preferred.

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