

Review Article

Chemically Modified Starch and Utilization in Food Stuffs

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Abstract: Starch consists of two main components: mainly linear amylose and highly branched amylopectin, and is stored as discrete semicrystalline granules in higher plants. Among carbohydrate polymers, starch is currently enjoying increased attention owing to its usefulness in different food products. Green leaves of plants contain chlorophyll, which is able to absorb light quanta and utilize the energy to catalyze the formation of glucose and oxygen from carbon dioxide and water. In general, modified food starches are used to provide functional attributes in food applications that native starches normally cannot provide, as starch is abundant and readily available and starch can provide an economic advantage in many applications where higher priced items such as gums otherwise must be used. Herein we discuss the chemically modified starch and reviewing its utilization in food stuffs.

Keywords: Modified Starch, Amylose, Amylopectin, Cationization, Oxidation, Stabilization, Conversion

1. Introduction

Starch composed of two main components: mainly linear amylose and highly branched amylopectin, and is stored as discrete semicrystalline granules in higher plants. Starch granules range from 1 to 100 μm in size and their structures are dependent on botanic origin. Semicrystalline starch granules display a hierarchical structural periodicity, have a layered organization with alternating amorphous and semicrystalline radial growth rings of 120 – 400 nm thickness emanating from the hilum. The semicrystalline rings are formed by a lamellar structure of alternating amorphous and crystalline regions with a regular repeat distance of 9 – 10 nm. The crystalline regions are thought to be formed by double helices of amylopectin side chains packed laterally into a crystalline lattice [1].

Among carbohydrate polymers, starch is currently enjoying increased attention owing to its usefulness in different food products. Starch contributes greatly to the textural properties of many food stuffs and is widely used in food and industrial applications as a thickener, colloidal stabilizer, gelling agent, bulking agent and water retention agent [2].

Native starches have been widely used in some industries; however, their disadvantages found in reality have also greatly limited their applications in some industrial food applications such as insolubility in cold water, loss of viscosity and thickening power after cooking, low shear resistance, thermal resistance and high tendency towards retrogradation. These shortcomings of native starch could be overcome [2-4].

Since their development in the 1940s, modified food starches have become a vital part of the food industry.

Starch gelatinization is the collapse or disruption of molecular orders within the starch granule (fig. 3), manifested in irreversible changes in properties such as granular swelling, native crystallite melting, loss of birefringence, and starch solubilization.

Starch retrogradation is a process that occurs when the molecules composing gelatinized starch begin to reassociate in an ordered structure. Starch modification usually affects these phenomena, and can include hybridization as well as physical and chemical modification of native starch [5].

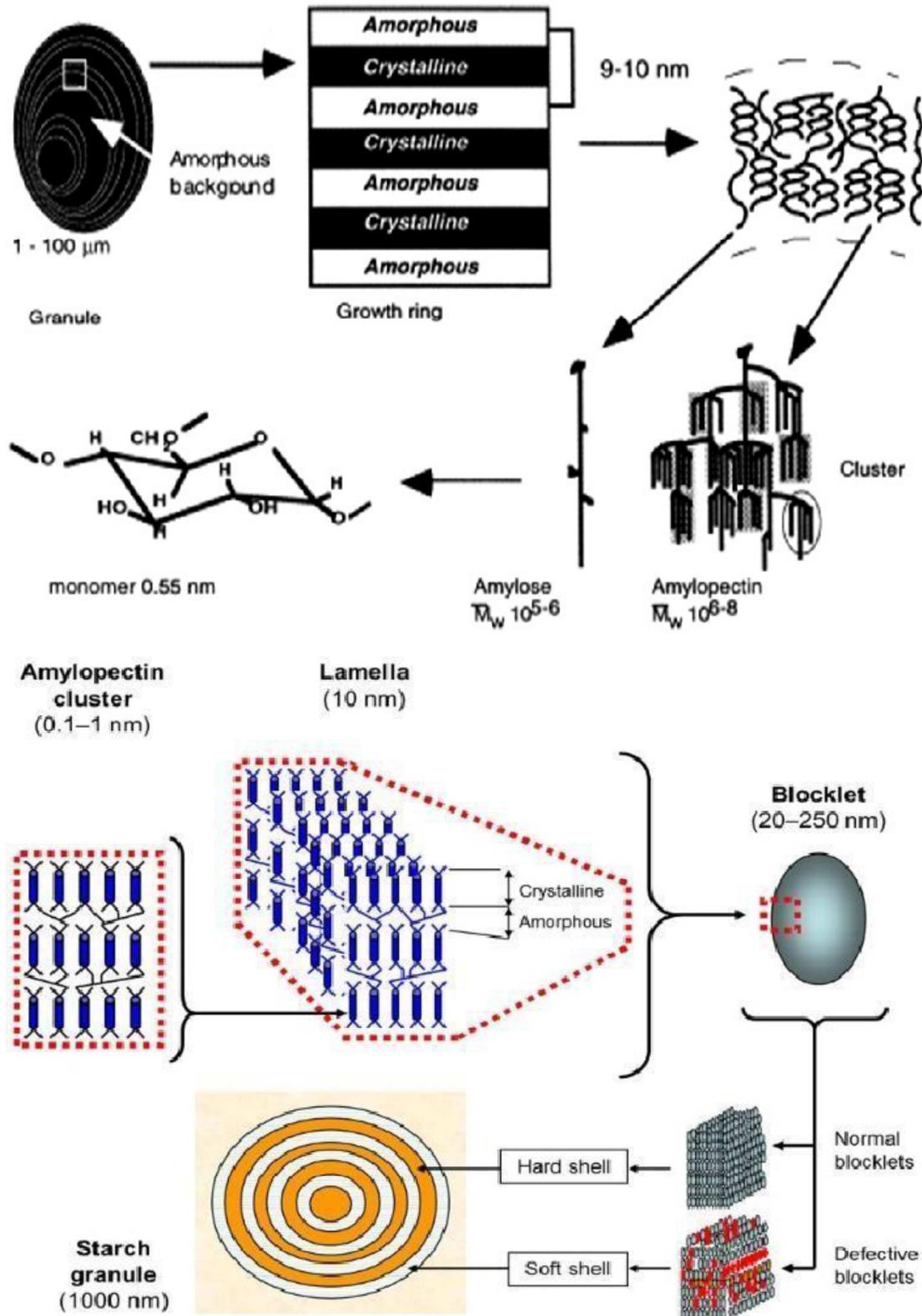


Fig. 4. Schematic representation of the different structural levels of the starch granule and the involvement of amylose and amylopectin [5].

2.3. Chemically Modified Starches

Food grade starches are chemically modified mainly to increase paste consistency, smoothness, and clarity, and to impart freeze-thaw and cold storage stabilities [2, 8].

Modified starches with desirable properties and degree of substitution can be prepared by critically selecting a suitable modifying agent and a native starch source. The distinguishing factors that affect the efficiency of modification are the starch source, amylose to amylopectin ratio, granule morphology, and type and concentration of the modifying reagent [2].

The effects of chemical modifications on thermal, morphological and pasting/rheological behaviour of starches may be quantified using instrumentation such as differential scanning calorimetry (DSC), scanning electron microscopy (SEM), Viscoamylograph/Rapid Visco Analyser (RVA) and dynamic rheometer, respectively [2].

The rate and efficiency of the chemical modification process depend on the reagent type, botanical origin of the starch, size and structure of its granules.

The knowledge about the structural changes in starch granules, caused by modification with chemical reagents, can be of importance for understanding the altered functional properties, and for developing chemically modified starches with desired properties [2].

2.4. Chemical Modification Process

2.4.1. Conversion

Conversion is the process used to reduce the viscosity of raw starches. Its main objectives are to allow the use of starches at higher percentages, increase the water solubility, control gel strength or modify the stability of starch. Typically, native starch cannot be used at much more than 6% solids because it imparts such a high viscosity. However, in the confection industry in a product such as a soft gum candy, a low viscosity starch at high solids is needed to obtain the

desired gel structure and set. Thus, a converted starch is required. Methods of conversion include acid hydrolysis and oxidation. Each method of conversion provides starch products with distinctive functionality. Other chemical modifications fall in the area of derivatization, including crosslinking, stabilization, and the addition of unique functional groups [5, 9].

2.4.2. Stabilization

The process in which, the blocking groups react with starch polymers to inhibit retrogradation, the alignment of polymers that causes a change in the structure of the food product. Inhibiting retrogradation imparts textural, and freeze-thaw stability, thus prolonging the shelf life of the food product. This modification is the most important step in frozen foods, since retrogradation of starch polymers is accelerated at cold temperatures, leading to an opaque, gelled, and/or chunky texture with eventual syneresis or “weeping” of liquid from the gel [5, 6].

2.4.3. Addition of Lipophilic Groups

In addition to stabilization, derivatization of the starch molecule can also include the addition of other functional entities such as lipophilic groups to starch molecules. The derived starch products are used in encapsulation and emulsion stabilization [5].

Chemical modification of starch is generally achieved through derivatization such as etherification, esterification, cross-linking, oxidation of starch. The chemical modification involves the introduction of functional groups into the starch molecule, resulting in markedly altered physico-chemical properties. Such modification of native granular starches, profoundly alters their gelatinization, pasting and retrogradation behavior [2].

The most common chemical modification includes: oxidation, crosslinking, esterification, and etherification. Table 1 presents different starch modification types and preparation techniques.

Table 1. Different starch modification types and preparation techniques [2].

Modification Types	Preparation techniques
Etherification	Hydroxypropyl starch Esterification with propylene oxide
Esterification	Starch acetate Esterification with acetic anhydride or vinyl acetate. Acetylated distarch adipate Esterification with acetic anhydride and adipic anhydride. Starch sodium octenylsuccinate Esterification by octenylsuccinic anhydride.
Cross-linking	Monostarch phosphate Esterification with ortho-phosphoric acid, or sodium or potassium orthophosphate, or sodium tripolyphosphate Distarch phosphate Esterification with sodium trimetaphosphate or phosphorus oxychloride. Phosphated distarch phosphate Combination of treatments for monostarch phosphate and Distarch phosphate.
Oxidation/bleaching	Treatment with peracetic acid and/or hydrogen peroxide, or sodium hypochlorite or sodium. Chlorite, or sulphur dioxide, or potassium permanganate or ammonium persulphate.

2.4.4. Oxidation

Starch oxidation has been practiced since the early 1800s, and various oxidizing agents have been introduced, for instance, hypochlorite, hydrogen peroxide, periodate, permanganate, dichromate, persulfate, and chlorite. The major

reactions of hypochlorite oxidation of starch include cleavage of polymer chains and oxidation of hydroxyl groups to carbonyl and carboxyl groups (Fig. 3). The reaction rate of starch with hypochlorite is remarkably affected by pH; the rate becomes rapid around pH 7 and very slow at pH 10 [2].

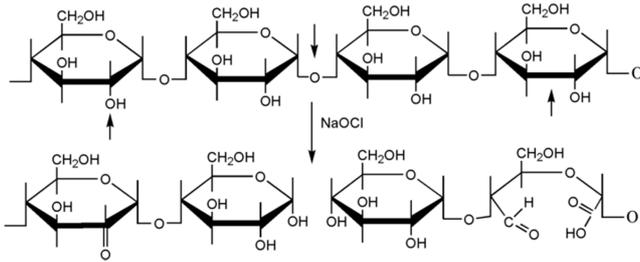


Fig. 5. Hypochlorite oxidation of starch, showing carbonyl and carboxyl formation [3].

The main uses of oxidized starch are paper and textile industries. The application of oxidized starches in the food industry is increasing because of their low viscosity, high stability, clarity, and binding properties. Oxidized starch for food use is mainly produced by the reaction of starch with sodium hypochlorite [3].

2.5. Cross-Linking

This is a treatment, whereby, small amounts of compounds that can react with more than one hydroxyl group are added to the starch polymers. Cross-linking yields starch granules with increased resistance to overcooking and other variations in processing conditions. Its main purposes are to provide a short texture for cooked dispersions of starch and to impart resistance for processing conditions such as temperature, acidity, and shear [5].

Cross-linking treatment is intended to add intra- and inter-molecular bonds at random locations in the starch granule that stabilize and strengthen the granule [2, 10]. Restrict water uptake could also be achieved by cross-linking method, due to the increased density of crosslinks in the starch structure [10]. Starch pastes from cross-linked starches are less likely to break down with extended cooking times, increased acidity or severe shear. Cross-linking minimizes granule rupture, loss of viscosity and the formation of a stringy paste during cooking, yielding a starch suitable for canned foods and products [2].

Cross-linking is generally performed by treatment of granular starch with multifunctional reagents capable of forming either ether or ester inter-molecular linkages between hydroxyl groups on starch molecules.

Sodium trimetaphosphate (STMP), monosodium phosphate (SOP), sodium tripolyphosphate (STPP), epichlorohydrin (EPI), phosphoryl chloride (POCl_3), a mixture of adipic acid and acetic anhydride, and vinyl chloride are the main agents used to cross-link food grade starches. Jane et al. (1992) found that cross-linking of starch chains occurred mainly in amylopectin. Another factor that may influence the extent of crosslinking is the size distribution of starch granule population. During cross-linking small size granules have been reported to be derivatized to a greater extent than the large size granules [2].

Starch contains two types of hydroxyls, primary (6-OH) and secondary (2-OH and 3-OH). These hydroxyls are able to react with multifunctional reagents resulting in cross-linked starches, Fig. 6.

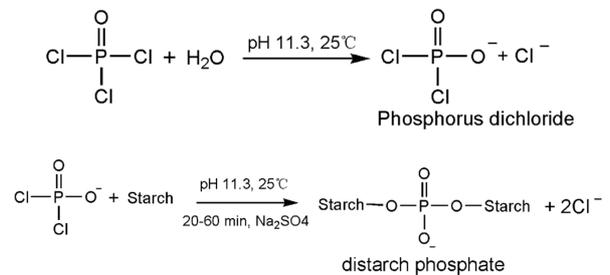


Fig. 6. Starch crosslinking by phosphorous dichloride [3].

Cross-linking is performed to restrict swelling of the starch granule under cooking conditions or to prevent gelatinization of starch. Cross-linking is often employed in combination with other methods (Fig. 5 & 6) for starch modification, such as oxidation, hydrolysis, etherification, and esterification to provide appropriate gelatinization, viscosity, and textural properties for food applications [2].

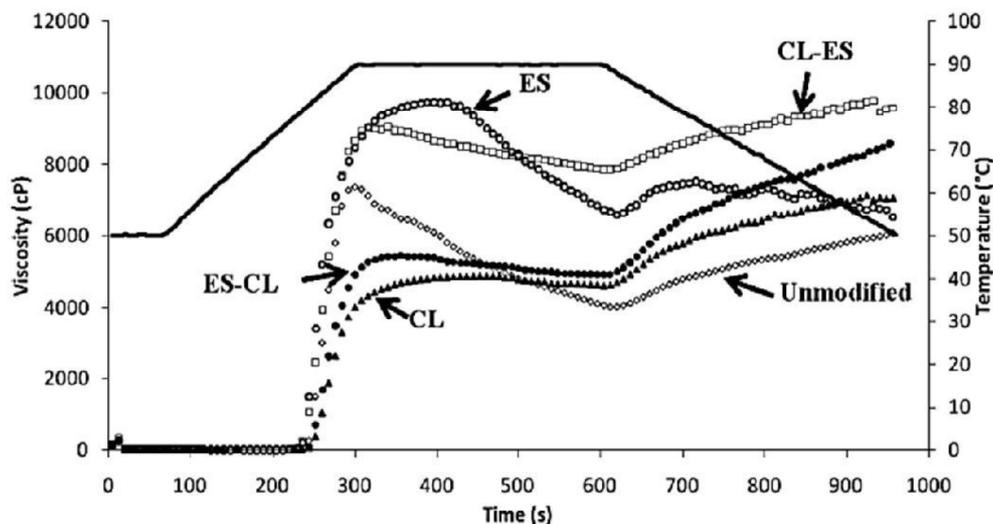


Fig. 7. Viscosity of unmodified and chemically modified banana starches: Cross-linked (CL), esterified (ES), esterified-cross-linked (ES-CL), and cross-linked-esterified (CLES) [12].

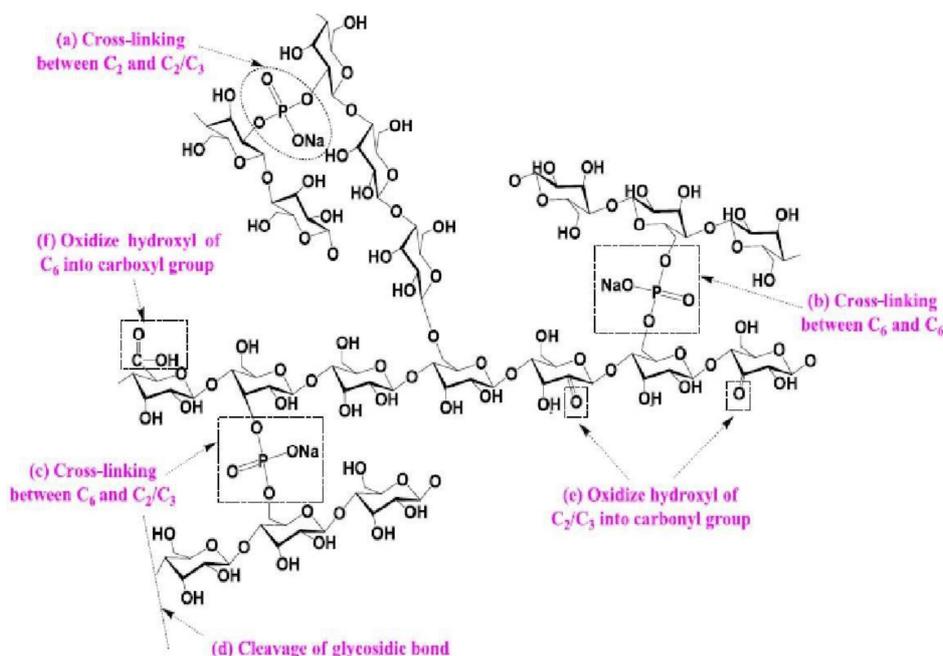


Fig. 8. Possible structure of cross-linked oxidized maize starch [13].

Chemical modifications (esterification and cross-linking) altered the digestibility and physicochemical characteristics of banana starch. The chemical modifications altered the structural order in banana starch, resulting in decreased temperature and enthalpy of gelatinization and retrogradation. In the pasting properties, the ES and CL-ES showed higher peak viscosity, whereas CL and ES-CL samples had lower peak viscosity. Chemical modifications can be used to modify digestibility properties of starch, Fig. 7.

2.6. Esterification

Starch ester is a kind of modified starches in which some hydroxyl groups have been replaced by ester groups. Esterification can impart hydrophobicity to starch products by the substitution of free available hydroxyl groups [11].

Acetylated starch with a low dodecyl succinate is commonly obtained by the esterification of native starch with acetic anhydride in the presence of an alkaline catalyst [2]. Acetylation of starch in aqueous suspension by acetic anhydride at alkaline pH is used commercially to produce starch acetates of low dodecyl succinate. Under alkaline conditions, starch is indirectly reacted with a carboxylic anhydride. An alkali starch complex forms first, which then interacts with the carboxylic anhydride to form a starch ester with the elimination of carboxylate ion and one molecule of water [3].

Starch esters are synthesized with various reactants, such as acid anhydrides, Octenyl Succinic Anhydride (OSA), dodecenyl succinic anhydride (DDSA) fatty acids and fatty acid chlorides [2].



Fig. 9. Starch acetates prepared by reacting starch with acetic anhydride [4].

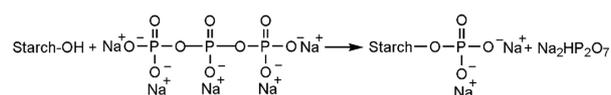


Fig. 10. Phosphate monoester of starch prepared by reacting starch with sodium triphosphate [3].

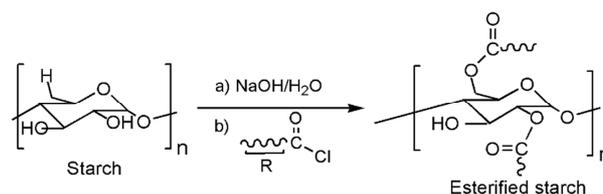


Fig. 11. Scheme for reaction of starch with fatty acid chlorides (R: C8, C12, C16) [14].

The esterification of starches using fatty acid chlorides (Fig. 9), has several advantages in comparison to previous classic methods, including: (a) utilizing water as a green solvent instead of organic solvents, (b) the reaction time is very short and is completed just over several minutes, and (c) the hydrophobically modified products are precipitated in water and are separated without any need for a nonsolvent. The chemically modified starch, through this method, has an amphiphilic character and could be used for the preparation of starch nanoparticles utilizing a dialysis method [14].

2.7. Etherification

The food grade hydroxypropylated starches are generally prepared by etherification of native starch with propylene oxide in the presence of an alkaline catalyst. The hydroxypropyl groups introduced into the starch chains are capable of disrupting the interand intra-molecular hydrogen bonds, thereby weakening the granular structure of starch, leading to an increase in motional freedom of starch chains in

3.3. Reduction of Blood Glucose Concentration

The *in vivo* glycemic response of HOSA-starch (Heated Octenyl Succinic Anhydride starch), showed a delayed appearance of blood glucose peak and a significant reduction (32.2%) of the peak glucose concentration, further confirmed its slow digestion property. Amylopectin debranching analysis revealed HOSA-starch had the highest resistance to debranching enzymes of isoamylase and pullulanase [14].

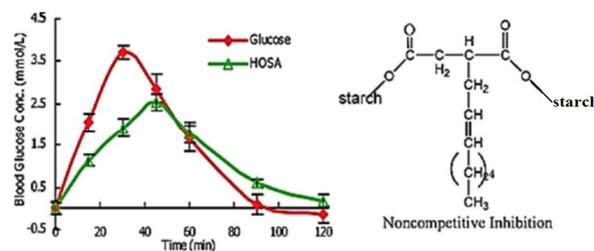


Fig. 17. The mechanism and molecular structure of the slowly digestible waxy maize starch prepared by Heated octenyl succinic anhydride (HOSA).

Table 2. Some properties and applications of modified starches [2].

Types	Properties	Applications
Oxidation/bleaching	Low viscosity, high clarity, and low temperature stability	Used in batters and breading for coating various food stuffs, in confectionery as binders and film formers, in dairy as texturizers.
Etherification	Improved clarity of starch paste, greater viscosity, reduced syneresis and freeze-thaw stability	Used in wide range of food applications such as gravies, dips, sauces, fruit pie fillings and puddings
Esterification	Lower gelatinization temperature and retrogradation, lower tendency to form gels and higher paste clarity	Used in refrigerated and frozen foods, as emulsion stabilizers and for encapsulation
Cross-linking	Higher stability of granules towards swelling, high temperature, high shear and acidic conditions	Used as viscosifiers and texturizers in soups, sauces, gravies, bakery and dairy products

4. Conclusion

Progress in understanding the high value of chemically modified starches has encouraged the starch industry to produce modified starches using different modification reagents and starch sources. Some factors such as starch composition, concentration and type of reagent, and reaction conditions may affect the reactivity of starch during chemical modifications like acetylation, hydroxypropylation and crosslinking. The heterogeneity of the granule population within a single starch source may also affect the extent of modification. The changes observed in the physico-chemical, morphological, thermal and rheological properties of the starches after modification may provide a crucial basis for understanding the efficiency of the starch modification process at industrial scale and make starch an important functional ingredient for numerous food systems.

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