

Some Aspects of Developmental Trends in Chemical Modification and Transformation of Starch: Products Preparation and Potential Applications

Bode Daramola

Department of Food Technology, Federal Polytechnic, Ado-Ekiti, Ekiti State, Nigeria

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Abstract. Starch, a non-depleting bioresource has a myriad of applications both in the food and non-food industries. These applications are made possible by starch modification technology. Chemical method of starch modification, the most versatile tool in accomplishing the preparation of copious starch speciality products or by-product which could serve as feed stock or precursor for the preparation of allied products is reviewed. The applicabilities of the speciality starch produced by chemical modification presented in many research papers are surveyed and pooled together and reviewed in this paper. This study suggests the myriads of opportunity that exist using chemical method of starch modification and transformation that have immense applications in both, food and non-food industries. A projection on the future of chemical method of starch modification is highlighted. This review will motivate readership to seek accurate detail knowledge on chemical method of starch modification and transformation for technological and economic advancement.

Keywords: chemical modification, starch speciality products, transformation

Introduction

Starch is the most important reserve carbohydrate and one of the most abundant organic chemicals on earth (Jane *et al.*, 1994). It could be found in the leaves of green plants in the plastids, more importantly, starch is synthesised in any plant and stored abundantly in seeds, grains, roots and tubers of many plants. The principal commercial sources of starch are roots and tubers (cassava, potato and arrow root), cereals (maize, rice and wheat), fruits (banana, plantain and breadfruit) and pith of plants (sago palm). Starch is not region-selective, as a result all countries are endowed with the possibility of abundant supply of starch provided there is vegetation. The abundance of starch spurs scientists to search for food related and non-food applications of starch. Unfortunately, starch in its native form has limited industrial applications whether in food and non-food industries. Interestingly, the properties of native starch can be altered using minor modification such that positive attributes can be greatly improved and/or negative characteristics diminished by slight and relative simple modifications (BeMiller, 1997). The primary reasons for starch modification have been tabulated by BeMiller (1997). Yaacob *et al.* (2011) reported that from 1969 to 2001, there have been more than 23,000, scientific articles in food science and technology. Therefore, it is

E-mail: daramola_bode@yahoo.co.uk

vivid that a comprehensive review of chemical aspect of starch modification for food and non-food applications cannot be accomplished within the limited space of this article. However, it is important to make a list of some texts notably, Wurzburg (1986); Mentzer *et al.* (1984) and Rutenberg (1980) that could furnish pioneer technology details and lead references on starch modification. Beyond the content and period of the cited references, a lot of research progress has been reported in many articles. Therefore, it would be informative and educative to pool some of these articles into one piece in a review.

This study aimed at brief review of developments in chemical method of starch modification and transformation for both food and non-food applications, and some of the manipulations employed to enhance or conferred the product-value-addition. This will motivate readership to seek further knowledge on details of technological accomplishment for preparation of value added products and organic-compliant substitute from starch.

Chemical method of starch modification. Inherent properties of native starch could be changed for industrial compilation and the basic modification types practiced in the US is presented in Table 1. However, of all the methods listed, chemical process offers the highest number of modification opportunities, hence focussed herein.

Table 1. Modification methods and probable conferred attributes

Types of modification	Probable attribute conferred
<i>I. Chemical modification</i>	
<i>A. Derivatisation</i>	
1. Monostarch substitution (etherification and esterification, including polymer grafting)	Improved paste clarity
2. Cross linking (via distarch esterification)	Increase paste stability, lower tendency to retrograde, increase water solubility, improved water solubility.
<i>B. Acid thinning/hydrolytic depolymerisation</i>	
	Increase clarity/increase in digestibility
<i>C. Dextrinisation (depolymerisation and trans-glycosylation)</i>	
	Increase in digestibility
<i>D. Oxidation (bleaching and depolymerisation)</i>	
	Increase in clarity
<i>E. Hydrolysis (malto-dextrins, glucose syrup, glucose etc. - both acid and enzyme-catalysed.</i>	
	Increase in digestibility
<i>II Physical modification</i>	
<i>A. Pre-gelatinised process</i>	
	Cold water solubility
<i>B. Preparation of cold-water swelling starch</i>	
<i>III Genetic</i>	
<i>A. Waxy starch</i>	
	Variable quality profile
<i>B. High-amylose starch</i>	

Source: BeMiller (1997).

The characteristics cooks of native starch, irrespective of the source are undesirable for many industrial applications. This is because, they are susceptible to retrogradation, syneresis, unwanted viscosity as a result of their inability to withstand the typical industrial processing conditions such as extreme temperature, pH, high shear rate, and freeze thaw variation encountered during manufacture of food and allied products. Some of the positive attributes conferred by modification of starch in foods are reported in a review by Daramola and Falade (2006). Since this article captions chemical method of starch modification, it is necessary to explain in brevity the chemical aspect of starch modification outlined in Table 1.

Acid thinning. Acid thinning involves hydrolysis of starch by applications of both organic and inorganic acids to break starch molecular chains namely: amylose and amylopectin. Some of the inorganic acids used are

hydrochloric acid, sulphuric acid and phosphoric acid (Whistler *et al.*, 1984), and organic acids anhydride used include succinic acid anhydride, acetic acid anhydride, (Wang *et al.*, 1997; Agboola *et al.*, 1991).

Oxidation. This involves the use of reagents such as sodium hypochlorite, potassium permanganate and sodium chlorite. All can be used in both acidic and alkaline medium (Kweon *et al.*, 2001).

Derivatisation. As listed in Table 1, derivatisation can be divided into 2 sub-groups:

(1) Starch monosubstitution in nature of etherification and esterification as well as forms of polymer grafting. Any substitution of the hydroxyl moiety on the molecular chains of starch by alkoxide and alkanoate is referred to as etherification and esterification, respectively. Examples of this type of modification is acetylation of starch (Daramola and Adegoke, 2007; Lawal, 2004).

(2) Another example is starch citrates (Agboola *et al.*, 1991) and propyl-etherified starch (Teramoto *et al.*, 2003). In addition, starch ethers could be cationised or anionised, a described procedure has been reported by Kweon *et al.* (1997). Also, preparation of starch succinates by reactive extrusion has been reported by Wang *et al.* (1997). Starch can be modified to carry charges positive (cation) or negative (anion) or both. When cation and anion are combined on a single starch it is termed amphoteric starch. Amphoteric starches, could be etherified, esterified, or grafted starches which simultaneously, contain cationic groups and anionic groups. Generally, the cationic groups could be amino, ammonium, sulphonium or phosphonium. Presently, tertiary amino groups or quaternary ammonium groups are the most important industrial positive group (moiety). Anionic groups are usually carboxyl groups, phosphate groups or sulphonate groups (Yang *et al.*, 2007). A cheap reagent such as alum (double salt) has been used to modify starch as reported in an earlier study by Daramola and Aina (2007).

Starch cross-linkage. Starch cross-linkage could be accomplished using bi-functional compounds, which are capable of reacting simultaneously, with two or more hydroxyl groups in starch forming cross-linked starch. Examples of such compounds are phosphorus oxychloride, epichlorohydrin and sodium trimetaphosphate used mostly for food grade cross-linked starches (Radley, 1976). Cross-linkage facilitates intra and intermolecular bonds at random locations in the starch granules for their stabilisation. As a result of the intra and intermolecular

linkages, paste of cross linked starch are more resistant to shear, and acidic conditions (Majzoobi *et al.*, 2009). All the starch derivatives have amazing technological applications as illustratively summarised in Table 2.

Fundamental factors affecting starch modification using chemical method. The factors affecting starch modification using chemical method can be divided into three classes:

(1) The primary factors which include processing variables such as temperature, solid solvent ratio, stirring rate, concentration of solvent, time and pressure.

(2). The secondary factors are type or chemical nature of solvent (e.g. acid, alkanol, alkaline, esterification and etherification reagents). Nature of chemical is majorly affected by the chemical or inherent functional groups. Added to these methods of processing are: use of reactive extrusion (Wang *et al.*, 1997), microwave heating (Shogren and Biswas, 2006) and use of ionic liquids among others. Also in this group, the use of catalysts, initiator, promoters and modifiers.

(3) The tertiary factors involves: high technology, involving manipulation of active site in molecular chains and granules of starch and combination of chemical method for modification of starch. For example, it is possible to combine cross-linkage method with ionic method in one of the modification. Another one is chemical modification of starch in solvent free environment (Aburto *et al.*, 2005).

Instrumentation in chemical method of starch modification. The commonest analytical instruments for characterisation of modified starch accomplished using chemical method are viscosity analyses (RVA). RVA profiles, the pasting characteristics such as peak viscosity, set back viscosity, final viscosity, pasting temperature and time of starch. Their technological interpretation signifies the extent of conferred modification (Meadow, 2002; Delcour *et al.*, 2000; Deffenbaugh and Walker, 1990; 1989).

Similarly, the thermal characteristics could be studied using a differential scanning calorimeter (DSC). Some of the evaluated parameters are: onset temperature, peak temperature, completion temperature and gelatinisation enthalpy. With the understanding that the two molecular chains, amylose and amylopectin are folded into granule and the fact that there are no two starch granules that are exactly same in terms of size, shape and configuration. Therefore, starch morphological characteristics are studied

using scanning electron microscopy (SEM) (Jane *et al.*, 1994; Jing-ming and Sen-lin, 1990). Besides morphological characteristics, SEM gives insight to location and conformation of hilum that contain the cavity through which chemical moiety passes into the amylose and amylopectin chains. Other importance of SEM on starch granules involves revelation on integrity of starch granule to hydration and dehydration and vapour pressure. It also reveals relationship between starch granules disruption and physicochemical properties of starch.

Structural characteristics of starch could be evaluated using fourier transform-infrared (FTIR). FTIR is important in revealing degree of substitution and the substituent chemical moiety. Other analytical instruments include; x-ray diffraction analytics, and nuclear magnetic resonance. Convectional tests carried out on starch are paste clarity, swelling capacity, solubility, tensile strength, stress, elongation at break, and tear strength. Other assessed parameters are apparent viscosity, freeze thaw stability, gel strength and thermal stability analysis (Chung *et al.*, 2004).

Preparation of starch noodle. Besides the additives application of starch in food preparations, where it could function as binding or adhesion, clouding and dusting agents. Other functions include flowing aid, antistaling and gelling agents. Starch is also used to glaze, mould, shape and thicken during food preparations. Examples of food in which starch performed the itemized functions have been tabulated by Ihekoronye and Ngoddy (1985), as reviewed by Daramola and Falade (2006).

Beyond the uses of speciality starch as additives as previously explained, food can be produced using whole starch. Noodles can be produced from starch. Although, starch is void of gluten, pregelatinised starch is used as binder mixed with ungelatinised starch to facilitate extrusion or sheeting to produce noodles. Basic protocol for the commercial production of bion-type noodles can be found in literature (Tam *et al.*, 2004).

Food noodles can be prepared from flour or starch, provided the product has noodles qualities that are defined by visual attributes, cooking and eating qualities, transparency and glossiness. In cooked starch noodles, the noodles should remain firm and not sticky on standing after cooking. These characteristics have positive correlation to noodles texture and mouth feel acceptance.

Starch transformation. Precursor of starch sweeteners and other organic chemicals. Sweetener can be produced from starch using varieties of acids (Daramola and Falade,

Table 2. Starch derivatives and potential applications

Modified starch/description	Modification type	Domain of application	Leading references
Complexes of oppositely charged ionic starches e.g., polyelectrolyte complexes	Amphoteric	Medicine: dialysis, ultrafiltration anti-thromobogenic agent	Willett, 1995
Oxidized starch	Oxidation H_2O_2 Cu^{2+} ($CuSO_4$) catalyst Fe^{2+} ($FeSO_4$)	Paper industry: surface sizing coating and binding	Parovuori <i>et al.</i> , 1995
Carboxymethylation of starch propyl-etherification of starch	Etherification alkaline Sodium-mono chloroacetate 1-bromo propane	Biodegradable polymer for coating for food and pharmaceutical products	Yaacob <i>et al.</i> , 2011; Teramoto <i>et al.</i> , 2003
Amphotenic starches	Amphoteric starches: Etherification, Esterification, Grafting	Paper making additives, for retention, and strength properties	Yang <i>et al.</i> , 2007
Cross-linked starch	Cross-linkage phosphoryl chloride	Food additives: thickeners, colloidal stabilizer, water retention, agents for food and Non-food waste H_2O treatment	Majzoobi <i>et al.</i> , 2009; Wang <i>et al.</i> , 2005
Cross-linked, cationised anionised amphoteric	Esterification, Etherification	To bind heavy metals from waste water waste treatment	Carmona-Garcia, <i>et al.</i> , 2009
Cross-linked hydrophilic polymers super absorbent	Graft co-polymeric cation	Surgical pad pharmaceutical, domestic, sanitary use, soil condition	Xiao <i>et al.</i> , 2010; Liu <i>et al.</i> , 1996
Complexation of modified starch with pigment	Complexation with pigment	Improvement of optical and pant ability performance of water	Kuuti <i>et al.</i> , 2010
Etherification and cross-linkage	Cationization graft-copolymerization	Water treatment as flocculant in place of alum	Yang <i>et al.</i> , 2007; Sharma <i>et al.</i> , 2006
Cross-linkage of starch	High performance elastomer (Tyre-making)		Song <i>et al.</i> , 2010; Qing <i>et al.</i> , 2006
Aerogels based microcellular foams	Microcellular starch-for production of synthetic foam	Alterative material	Xu <i>et al.</i> , 2005; Glenn and Irving, 1995

2006). Some of the obtained products are glucose, maltose, dextrin and maltose. These sweeteners are superior on the basis of dearth of physiological abnormalities associated with sweetener of synthetic origin.

Starch sweeteners have been produced from starch using acids such as hydrochloric acid, sulphuric acid and phosphoric acid. Each of the acids has its advantages and limitation. For instance, hydrochloric acid is an inorganic acid and it hydrolyse starch and the hydrolysis is complete in comparison to hydrolysis carried out by using phosphoric acid. Nevertheless, sweeteners obtained from hydrochloric acid hydrolysed starch require treatment and other purification processes. However, phosphoric acid hydrolysed starch can be used directly for biological production of ethanol without purification. The application or use of phosphoric acid rather than hydrochloric acid presents some advantages. Phosphoric acid is non-volatile and safer to handle in comparison to hydrochloric acid. Since, phosphoric acid is less severe in comparison to hydrochloric acid, it could be speculated that the application of phosphoric acid should be accompanied by lesser by-products. The hydrolysed starch or sweetener can be diluted on addition to foods or beverages, the phosphoric acid concentration falls to values as low as 0.01-0.05% resulting to a pleasant taste of acidity at pH values of about 3.0. More importantly, if the hydrolysate is to be used in fermentation, there is no need to eliminate the phosphoric acid. Interestingly, neutralisation with ammonia leads to ammonium phosphate, an important supplement for fermentation growth (Fontana *et al.*, 2008). The products from starch hydrolysis, called hydrolysates are made of molecules of different length, consequently, in addition to neutralisation and purification, the hydrolysates are fractionated using chromatographic techniques. Three distinct products namely, glucose, maltose and oligosaccharides fractions are recovered. This is one of the starch processing methods patented (Masuda *et al.*, 1995). Besides being used as sweetener, the hydrolysate is also an ingredient for formulation of tablet coats (Czarnecki and Belniak, 2009).

Aside, from application of acids to hydrolyse starch, alkaline such as sodium hydroxide, potassium hydroxide can be used to depolymerise starch at high temperature approximately 240 °C for a period not less than 60 min to yield organic compounds such as glycol and oxalic acids (Verendel *et al.*, 2011). It is important to state that some of the end-products of starch hydrolysis notably glucose and maltose could be further modified and

transformed to organic chemicals such as ethanol, hydroxyl methyl furfural (Zhang *et al.*, 2012), and fructose (Roman-Leshkov *et al.*, 2010), lactic acid and other feedstock chemicals.

Some miscellaneous modified starch products: Modified starch has applications in many different industries (Table 3) that range from food, drug and medicine to non food industries such as mining, building and electronic industries. Some of these are illustrated hereunder: other than cooking, native starch can be treated or modified to become granular, cold water soluble. The preparation of this kind of speciality of starch using alcoholic-alkaline treatment had been reported by Chen and Jane (1994). Another procedure that used liquid ammonia and ethanol was also described by Jackowski *et al.* (2002). Other novel product include functional modification of starch by esterification of the hydroxyl group by introduction of a chromophoric moiety leading to development of a thermostable and photo-responsive system on starch. A procedure of this kind had been reported by Chandran *et al.* (2012). A starch benzyl ether of high degree of substitution has a unique property of being not gelatinised when cooked at 100 °C. However, when prepared at super atmosphere in a steam injection cooker at 150 °C, dispersion fluid sol results, which when cast gives resistant films.

Most chemical modification of starch is based on material science properties. Starch could also be modified for exhibition of certain nutritional functionality other than dietary fibre. Starch could be conjugated to non-starchy substances thereby, lending significant changes in starch nutritional functionality. This was demonstrated by the work of Hatton *et al.* (1995), that changed the functional properties of carboxymethyl potato starch conjugated with whey proteins. The covalently linked carboxymethyl potato starch-whey was characterised by improved thermal stability and reduced retrogradation in comparison to unmodified starch. Also the conjugated starch-whey product possessed retinol binding ability present in β -lactoglobulin present in whey and α -lactalbumin present in whey known to participate in lactose synthetase reaction. One of the reasons for turning to starch for synthesis of starch-materials is its biodegradability. This is expressed in the capability of microorganisms to decompose polymeric materials to low molecular compounds, such as carbon dioxide and nitrogen, so that carbon returns to the ground/soil or atmosphere. Beyond this, today research is focussing on disassembling the blocks coupled within functionalised starch. This claim has been demonstrated in the research of Auzely-Velty and Rinaudo (2003), for the synthesised starch-

Table 3. Spectrum of modified starch utilising industries with example of application

Industry	Application
Food processing	Pie filling, padding, mixes, fruit juice sources, bulking agent, molds, fluidifying agent maintenance of viscosity in acid foods e.g., fruit juice, decrease syneresis in ice-cream or refrigerated foods. Hard candy gum drops
Paper/board/corrugating	Pigment retention on paper (wet-end addition), as surface sizing agent coating
Brewing	as adjunct
Textile/warp sizing	Text finishing agents to add weight, smoothness and stiffness
Pharmaceuticals	Cosmetics: tooth paste, body cream or lotion Pharmaceutical tablets; binder, filler, disintegrant Body powders
Building pots	Binder for foundries
Agriculture	Soil conditioners
Adhesives	Corrugated boards paper bag Guming applications
Crude oil mining	Oil drilling mud
Briquetting	Domestic and industrial heating
Packaging	Plastics High temperature stable hybrid nylon e.g., meat roasting nylon; Edible films Preparation of surgeon gloves

betaine derivatives using disopropylcarbodiimide and 4-dimethylaminopyridine as coupling agents in an aprotic polar solvent, which carry cleavable cationic groups derived from naturally occurring glycine-betanine. The improvement in this study, lies in lower toxicity and larger biodegradability in comparison to the traditional cationic surfactant compounds.

Some modification enhancement manipulations. Although BeMiller (1997) in an earlier review predicted that there could not be approval of new reagents for derivation of starch, for safety concerns. However, as knowledge expands, new reagents with special attributes

are discovered and other process enhancement manipulation. Two examples shall be discussed in brevity.

Use of ionic liquids. For example, effort on the use of ionic liquids as solvent for reaction-medium for starch has started to receive attention. Ionic liquids are a new technology considered to be green chemistry because of their biodegradability, and low toxicity. Added to this, ionic liquids have a spectrum of compound characteristics through a broad selection of anions and cations combinations. Other advantages inherent to ionic liquids are non-flammability and thermal stabilities and enhancement of reaction rates with higher selectivity, an example of such study is an early work of Stevenson *et al.* (2007) on changes in structure and properties of starch of four botanical sources dispersed in ionic liquid. Besides, acting as solvent, ionic liquids have been reported to exhibit catalytic property. This was demonstrated by acylation of maltodextrin in ionic liquid (Biswas *et al.*, 2009). This process obviates the use of catalyst during acylation of maltodextrin with its economic and technical advantages.

Application of enhanced microwave heating. Starch can be hydrolysed using microwave field. The advantage of this form of heating lies in dissipation of heat inside the medium, which raises the energy of the molecules rapidly. This heating mode is different from convectional heating because all the molecules in the heated system receive same amount and rate of heat readily energized and resulting to higher reaction rates and greater selectivity. The afore-described process could be enhanced by the addition of metallic halides such as sodium chloride, potassium chloride, iron III chloride to the microwave heating solvent or medium. The importance of the inorganic salts could be demonstrated by the amount of (88-109 wt %) glucose hydrolysed from starch using hydrochloric acid for a period of 240 s at a temperature of 145 °C, while the control sample without salt (all other conditions were same), yielded less glucose (78 wt %) not earlier than a period of 600s as demonstrated in the study of Kunlan *et al.* (2001).

Future prospects of chemical method of starch modification. Since chemical modification offers the most versatile opportunities of tailoring starch granules to fit for a particular properties/purpose/application, the future appears bright regarding the relevance of chemical modification of starch for products or preparation of speciality starch for food and non-food applications than is known presently. Another important reason for good prospects for continuous progress or advancement in

chemicals modification of starch is the peculiarities of starch as a bioresource as outlined in Table 4. Additional projection on the future of chemical method of starch modification and prospective application is as follows: The future of chemical method of starch modification would be addressed from the two broad domain of application namely: (1) food application and (2) non-food application. Regarding food application perspective, there are no indications that new chemicals would be approved for modification of starch to be used in food processing. This is in agreement with the prediction of BeMiller (1997). However, any new chemical to be used for modification of starch for food would undergo strict examination to have passed safety test for approval. Beyond this, chemical modification processes for starch could be enhanced by combination with use of novel solvents such as ionic liquid as medium of reaction and catalytic agent (Biswas *et al.*, 2009). Also chemical modification could be combined with physical process such as irradiation. Regarding chemical modification of starch for application in peripheral food and non-food applications, there exists an open end opportunity. Chemical modification of starch in preparation of edible packaging materials used in fast foods and institutional catering and short-time, and self degradative packaging that could be used as packaging materials in bottling of table water and flocculating agents. Such products could be prepared using starch and long chain fatty acids of different unsaturation and alkylation. Polymeric materials have inexhaustive applications list in bioprocessing. The aim of this section is to articulate the need and the possibility of using starch to replace the other materials produced from non-starchy or petrochemical products. Most especially, that biodegradability is of priority in material science, and polymer technology in present day technology. In separation technology, molecularly imprinted polymers (MIPs) have been applied in adsorptive

Table 4. Starch bioresource peculiarities

Starch sources is non-regional specific
Starch is abundant
Renewable/sustainability
Ecofriendly or non-toxic
Amenable to modification in comparison to cellulose and chitin much available bioresource
Inexpensive
Biodegradable
Availabilities of many reaction sites
Modification is not high technology
Procedure is less labourious and operational hazard
Non-depleting

separation as selective chromatographic materials and in the field of solid phase extraction. MIP is a synthetic porous polymer with selective and specific recognition ability of the binding cavities to target molecules by non-covalent interactions such as hydrogen bonding, electrostatic interactions π - π and hydrophobic forces as reported by Seechamnaturakit and Suede (2012).

In addition, verse opportunities await application of starch modified to meet application as immobilised enzymes with respect to reversibly soluble-insoluble polymer. Presently, all the polymers used in enzyme immobilisation are synthetic (Dourado *et al.*, 2002) consequently, it would be more friendly to use biodegradable polymer of starch origin. Finally, chemically modified starch would find place in other stimuli-responsive polymers, sometimes referred to as smart or intelligent polymers which are presently dominated by synthetic polymers. Stimuli-responsive polymers have a series of biological applications, which include tissue engineering, drug release systems, biological sensors, temperature and light responsive films or optical sensors, intelligent microfluidic switches and diagnostic devices (Milichovsky, 2010) consequently an important tool in automation of bioprocess.

Conclusion

The admirable potentials of chemical modification technology to produce speciality starch with both, food and non-food applications are reviewed. This by no means exhaust the modification and transformation of starch for both food and non-food industrial applications. It is anticipated that this review would motivate readership to seek detail and accurate technology knowledge on know-how-accomplishment to develop domestic starch for import substitution for technological and economic benefits.

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