Scholars International Journal of Chemistry and Material Sciences
Abbreviated key title: Sch. Int. J. Chem. Mater. Sci.
A Publication by "Scholars Middle East Publishers"
Dubai, United Arab Emirates
ISSN: 2616-8669 (Print)
ISSN: 2617-6556 (Online)

Chemical modification of Grains' starch for Improved Functionality

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Original Research Article

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Article History
Received: 04.06.2018
Accepted: 25.06.2018
Published: 30.06.2018

DOI: 10.36348/sijcms.2018.v01i01.002

Abstract: Grain starch in general has wide array of applications in industry, food preparation, paper surface coating and textiles. Many of the important functional properties of starch including the emulsion capacity, water and oil absorption, least gelation concentration and foaming capacity can be substantially improved from physical and chemical modifications. In this review, current and advances in grain starch modification technology was examined and the functional properties compared with the unmodified sample. Chemical modifications such as crosslinking starch granules with variety of cross-linkers such as citric acid improved the functional properties of *acha* starch significantly. The least gelation concentration (LGC) increased from 6% to 8% and the pasting viscosity also decreased to 25Cp Other chemical modification techniques examined include oxidation and acid treatment or mild hydrolysis. Several starch oxidizing agents were reviewed and the effect of sodium hypochlorite (3% active chlorine) on *acha* starch was compared to the native starch. Oxidation further reduced the pasting viscosity of native sample from 30Cp to 20Cp whilst the least gelation concentration was also reduced to 6%. Acid treatment affected the pasting viscosity of *acha* starch substantially (15Cp) whilst the LGC increased to 14%. The scanning electron microscopy (SEM) of modified samples showed effects on starch granule morphology.

Keywords: Chemical modification, crosslinking, oxidation, acid treatment, least gelation concentration (LGC) and pasting viscosity

INTRODUCTION

Unmodified starches generally are less desirable for many industrial applications, because of their tendency to degrade under industrial processing conditions such as high temperature, diverse pH, high shear rate, and freeze thaw variation [1]. Starches are good binding materials and good disintegrant for pharmaceutical applications [2]. When starches are modified, they find technical applications as super absorbent hydrogels, preparation of bio-polymer based flocculants and drug-release, better binder and disintegrant and also as good fillers in textile and paper industries.

A good number of starches produced today are from crops that serve as sources of staple foods. This development has necessitated research on alternative means of sourcing starch for domestic and industrial uses. Focus on underutilized plants for starch production has stimulated research on crops such as mucuna beans, bambarra groundnut, new cocoyam, black Gram, Great Northern Bean, sago, pigeon pea, yam bean, field pea, lentil, Tiger nuts, Tacca tubers and jack beans[3].

Acha (*digitaria exilis)*, is greatly underutilized. It provides cheap source of nutrients for some impoverished population and ready feeds for livestock. Unmodified native starch has its limitation in food and general industrial applications. Some of the disadvantages include:

- Loss of viscosity at low pH values
- High processing temperature or mechanical treatment.
- Long texture
- Retrogradation-syneresis

Some reported studies on Acha starch focused on proximate chemical composition [4-6] Chemical modifications of acha starch including oxidation, acid treatment and cross-linking of the hydroxyl functional groups was extensively explored. Such modifications greatly improved its functional properties and other physico-chemical characteristics [7].

Chemical Modification by Cross-Linking

Cross-linking of starch is performed by treating granular starch with multifunctional reagents such as monosodium phosphate (SOP), sodium trimetaphosphate (STMP), sodium Tripolyphosphate, epichlorohydrin, phosphoryl chloride ($POCl_3$), a mixture of adipic acid and Acetic anhydride and a mixture of succinic anyhydride and vinyl acetate [8-10].

The most common method of modification is cross linking. When you cross link starch, a chemical bond takes place between the starch chains and cross-linking reagent. By cross linking starch some functional properties (compared to native starch) are greatly improved. These include:

- Shorter texture
- Stability at low pH values
- Heat/shear stability

The gelatinization temperature is higher in a cross-linked starch than in the native starch and at the same time the relatively high breakdown is no longer seen. The viscosity, especially after cooling, is also significantly higher than in native starch. During the holding period at 95^0C it is furthermore evident that the cross-linked starch is stable when stirred. By cross linking the starch you can produce a starch that under normal circumstances has almost no viscosity. If this starch is subject to low pH, high temperature, heavy mechanical processing or all of these at the same time, the starch will, however, give some viscosity. Heavily cross-linked starches therefore “demand” a heavy treatment in order to give higher viscosity whereas other starches subject to the same conditions will collapse with a weak or no viscosity.

As a low cost natural polymer, starch is widely used in paper, food, adhesive, and many other industries. In order to improve the performance of starch, cross linking is often conducted either in the processes of starch modification or during the application processes. Many cross linkers have been developed in the past for cross linking starch. Ammonium zirconium carbonate (AZC) is one of the common cross linkers for cross linking starch in aqueous solutions, having been widely used as a starch cross linking agent in paper surface coating for more than 20 years.

However, the mechanisms of starch cross linking with AZC have not been well studied. In order to optimize the cross linking chemistry of starch and find new paths for the utilization of starch in papermaking, a better understanding of the starch cross linking mechanism is necessary. Several researches focused on the fundamental study of starch cross linking in an aqueous solution and its applications in fiber surface grafting, filler modification, and starch nano-particle formation.

It was reported that starch cross linking could facilitate the reduction of starch particle size during reactive extrusion. However, the mechanism of the particle size reduction by starch cross linking was not illustrated. The reason that the cross linking can cause the particle size reduction of starch during extrusion is fundamentally interesting. The effects of extrusion conditions, including temperature, screw speed, torque, starch-water content and cross linker addition, on the particle size have been studied. It was found that the addition of cross linkers could significantly increase the shear force (torque), and consequently facilitate the reduction of the particle size. The results indicate that the starch particle size decreased with the increasing temperature. At 100 degree Celsius, the starch particles with a size of 300 nm could be obtained. With the addition of appropriate cross linkers (glyoxal), the starch particle size could be reduced to around 160 nm, even at a lower extrusion temperature of 75 degree Celsius.

Cross-linking is a common approach to improve the performance of starch for various applications. Starch and starch products have been cross-linked with cross-linking agents, such as phosphorus oxychloride, sodium trimetaphosphate, sodiumtripolyphosphate, epichlorohydrin, and 1, 2, 3, 4-diepoxybutane, in order to improve the mechanical properties and water stability of starch products [12-14]. In addition to cross-linking, blending starch with synthetic polymers has also been considered to improve the performance of starch products. Films have been developed from starch blended with low-density polyethylene, and polyvinyl alcohol (PVA) [15- 17]. The mechanical properties and dissolution of the blend films showed substantial improvement compared to the non-cross-linked films. However, the chemicals used for cross-linking starch are relatively toxic, expensive or do not provide the desired improvement in properties. Blending synthetic polymers with starch at high temperatures could damage starch and lead to poor properties of the materials developed. Poly carboxylic acids, such as citric acid, are inexpensive and non-toxic chemicals that have been used to improve the performance properties of cellulose and proteins in textile applications [11].

Although cotton and silk fabrics have been cross-linked with carboxylic acids, mainly to improve their appearance and resistance to wrinkling, it has also been shown that the mechanical properties and water stability of regenerated protein fibers can be improved by cross-linking with poly(carboxylic acids). A schematic of the conventional cross-linking of cellulose with carboxylic acids is shown in fig.1. As seen from the scheme, carboxylic acids cross-link the hydroxyl groups in cellulose and the cross linking reaction is reported to occur at temperatures between165 and 175 °C. [9,11]. The mechanism of conventional cross linking of cellulose occurs mainly through the hydroxyl groups.

Since starch also contains considerable amounts of hydroxyl groups and starch is more easily accessible to chemicals than cellulose, poly (carboxylic acids) can be expected to crosslink starch and improve its properties. This was demonstrated by the successful cross linking of native tapioca starch with citric acid as coating for the development of controlled release fertilizer [18]. It has been reported that citric acid can form strong hydrogen bond interactions with starch and improves its thermal and water stability and inhibit retro-degradation [19]. However, incorporating citric acid substantially reduced the tensile stress of the products. Citric acid was also used as an additive to starch–Polyvinyl Alcohol (PVA) films, due to the antibacterial effects of citric acid. It was reported that adding citric acid decreased the strength of the starch–PVA film but provided better strength than glycerol-added starch–PVA films.

The better strength of the citric acid-added starch–PVA film compared to glycerol-added starch–PVA films was attributed to the better hydrogen bonding between citric acid and starch–

PVA molecules compared to glycerol and starch–PVA molecules [20].

This author [9] successfully used citric acid to cross-linked Acha starch and improve its physico-chemical properties. Proximate compositions of the native starch was improved upon modification. The moisture content of the samples ranged between 7.98% and 11.45%. The ash content and ether extract (fat content) ranged from 0.20% to 0.50% and 0.25% to 0.35% respectively. The protein content was in the range of 1.31% to 0.87%, while the crude fiber content ranged between 0.65% to 1.05%. The carbohydrate content was in the range of 85.34% to 89.71%.

The modified samples exhibited low moisture content compared to the native acha starch, whilst the least moisture content of 7.98% was found with the acid treated sample. These low values of moisture content following modification are advantageous especially in terms of shelf life and reduced spoilage under various storage conditions. Both the native acha starch and modified samples were dried under the same conditions. Therefore, the reduction of moisture content may be due to the substitution of the hydroxyl groups on the starch molecules.

The ash content also shown a similar pattern of reduction with the least ash content observed with the acid modified starch. The reduction of the total ash content may be attributed to the washing away of the mineral contents of the starches during acid treatment, acetylation and oxidation processes. It was reported [21] that ash content of modified jack jean starch reduced considerably after modification and they reported this observation to washing away of the starches mineral contents.

The crude fiber and ether extract (fat content) were also reduced following modification of the native acha starch.

All forms of modification including cross-linking (acetylation) oxidation and acid treatment reduced the protein content of the native acha starch. These low values showed the purity of starches following modification. The least protein content was observed with the cross-linked sample of 0.87%. The carbohydrate content following modifications increased from 85.34% to 89.71% observed with the native acha starch and acid treated starch respectively. The highest carbohydrate content of 89.71% was observed with the acid thinned sample, since the carbohydrate content was obtain by difference, reduction in other parameters led to increase in carbohydrate content of modified samples.

Modification by Acid treatment

In certain applications a high content of starch is desirable for appropriate gel formation as seen in wine gums and liquorice. When unmodified starch is used as the gelling agent the paste would become too viscous during heating as a very high starch concentration is required to form a gel. In such application you can use the thin boiling starches. Thin boiling starches have a low viscosity. In other applications, such as instant soups, thin boiling starches are often used as filler without any specific technical function. The thin boiling starches have been degraded. The most common methods of degrading the starches are oxidation, acid treatment, and enzymatic degradation.

When starch is degraded through acid treatment, the starch chains are broken almost the way they are when oxidized. The difference is that the starch is not stabilized as it is with the oxidation. This shows in a much higher end-viscosity than with oxidation. The oxidized starch has a much lower end-viscosity than the acid hydrolyzed starch, which is due to the earlier mentioned carboxylic acid groups stabilizing the starch. When acetylated, the oxidized starch results in a more stable starch.

Products from hydrolysis of starch such as maltodextrin, corn syrup, glucose syrup and high glucose syrup have a wide application in the food, textile, brewing, and pharmaceutical industries [22]. These products are mainly derived from corn, barley and potato starch. In Malaysia, sago starch is considered as one of the most important sources of starch. Wang *et al*. reported that about 60 million tonnes of sago starch extracted from sago palms are produced per annum in South-east Asia. However, the raw sago starch exists as large granules with compact crystalline structure. As a result, the enzyme reaction rate and yield of products from raw sago starch was reported to be too low for industrial application [19].

The bioconversion of sago starch was limited by the resistance of the raw granule to enzymatic hydrolysis. It has been reported that treatment of raw starches with acid at below its gelatinization temperature would enhance its digestibility by enzymes. Therefore, in order to increase the susceptibility of raw sago starch to enzymatic hydrolysis and improve glucose production, sago starch was treated with acid below its gelatinization temperature. The effect of acid treatment on the production of glucose using raw starch as the substrate was studied.

Swelling power, solubility and water binding capacity of starches decreased following acid modification. The morphological properties revealed hydrolysis of starch granules due to attack of acid on amorphous regions, which come in contact with the acid leading to fusion of granules. After modification, starch granules tended to appear fused and less smooth than the native starch granules. The acid modified starches reported slightly higher pasting temperature compared to their native counterparts. The acid modification reduced thickening ability of starches that is based on swollen capacity of undamaged granules as revealed by pasting properties. The syneresis increased with acid modification of starches.

Acha starch was modified [23] by acid treatment using 36% HCl and reaction allowed to proceed for 1 hour at 45^0C in a shaking water bath. The reaction was then stopped by neutralizing the solution media with 1M NaOH. The slurry was subsequently transferred into 50ml centrifuge tube and centrifuged at 3500rpm for 5 minutes. The supernatant collected and the precipitate washed with 50% ethanol until neutral to litmus. The acid treated starch was filtered using Whatman No. 1 filter paper and dried in an oven at 40^0C.

The gelation properties of unmodified acha starch, cross-linked, oxidized and acid thinned samples are presented in table 1. The least gelation concentration varied from 6 % to 14 %. The value increase from 6 % (native acha stach) to 8 % for cross-linked sample and 14% for acid thinned sample. The least gelation concentration for oxidized sample remained unchanged at 6%

Cross-linking introduced bulky functional groups during modification which minimized intermolecular interaction and caused electrostatic repulsion amongst the starch molecules thereby increasing least gelation concentration values. Gelation property of starch is a phase phenomenon resulting from aggregation of starch molecules. Since acid treatment of starch is resulting from break in the glycosidic bond linkages of starch molecules leading to increase in smaller molecular weight distribution, significant increase was observed in the least gelation concentration following acid treatment of native acha starch.

The pasting properties presented on table 1 also show wide variation, especially after acid treatment. These are shown as viscosities (Cp) at room temperature using Brookfield Viscometer The pasting viscosities of modified samples were reduced from 31.5 centipoise for native acha starch to 25.0 centipoise for cross-linked sample through 20.2 centipoise for oxidized sample and 15.1 centipoise for acid treated sample. The pasting viscosity reduced by over 50% on Acid treatment modification. Little wonder, acid treated starch are referred to as 'Thin boiling starches', for desired applications where low viscosity is important. In such instances where high content of starch is desirable er for the starch to form a gel as in wine gums and liquorice the pasting property of native starch would be too viscous during heating. In such applications, we can take advantage of the acid treated samples. Also in instant soups compositions, thin boiling starches are often used as filler.

Oxidation using Sodium Hypochlorite

Oxidation is the only type of modification where two different opposing forms of functional properties alterations take place simultaneously: degrading and stabilization like the acetylation. The oxidized starches are characterized by very low viscosity during boiling and very high viscosity during cooling due to the high content of dry matter.

Native starch is treated with a variety of oxidizing agents to obtain oxidized products. Oxidized starch is composed of amylose with shorter chain lengths than native starch. It improves whiteness and reduces microbiological contents. In addition, the hydrogen bonding reduces the tendency to retro-gradation. Producing soft-bodied gels of high clarity. Oxidized starches are the best thickeners for applications requiring gels of low rigidity. This improves adhesion in batters and breading.

Oxidized starches have found many applications in industry. Examples of common applications include the use of oxidized starch in the paper industry, for instance in coatings or surface sizing, the adhesive industry, the textile industry, and the food industry.

The preparation of oxidized starches is conventionally carried out by oxidation with an alkali metal hypochlorite, which is a relatively cheap oxidizing agent.

The main factors controlling the oxidation reaction are the amount of alkali metal hypochlorite used, the pH, the temperature and the use of metal and/or bromide ions as catalyst [24]. It has been proposed that dissociation of the hypochlorite in solution and the presence of radicals in the reaction mixture determine the reaction mechanism. Despite the extensive research done, the exact mechanism of the hypochlorite oxidation of starch is, however, still not entirely clear.

As stated above, the course of the oxidation reaction using an alkali metal hypochlorite depends much on the pH during the reaction. This dependency has been widely addressed in literature. The highest reaction rates are found at neutral pH, while the reaction rate decreases with increasing pH. At acidic pH (<5), chlorine is formed, which, for evident reasons, is to be avoided in an industrial process. Thus, from the view of the reaction rate, it would be desirable to perform the oxidation reaction at or around a neutral pH.

During the oxidation of starch with an alkali metal hypochlorite, different reactions occur. These reactions lead to an introduction of carboxyl and carbonyl groups, and to the degradation of the starch molecule. The pathway(s) of all these reactions, and the exact balance between the carbony- and carboxyl-functional groups, determine the properties of the oxidized starch. The relative amount in the oxidized starch of carboxyl and carbonyl groups and the extent of degradation of the starch molecule are dependent on the pH during the oxidation reaction.

The degradation of the starch molecule during oxidation leads to a lower viscosity of a solution (or dispersion) of the oxidized starch, which is usually desired of an oxidized starch. It has been found that the degradation occurs to a farther extent at neutral pH of about 7 to 7. 5 than at alkaline pH such as pH of 9 or higher. In other words, in order to obtain an optimal yield of oxidized starch providing a solution or dispersion of low viscosity, the oxidation reaction should preferably be carried out at neutral pH.

However, the viscosity in solution (or dispersion) is not the only important property of an oxidized starch. The viscosity of the solution (or dispersion) should remain stable during storage.

Carboxyl groups that may be introduced in the starch during the oxidation reaction, provide the desired stability of the viscosity of an oxidized starch solution or dispersion. The higher number of carboxyl groups, the better the viscosity stability. Contrary to the degradation of the starch, the amount of carboxyl groups introduced in the starch during oxidation with an alkali metal hypochlorite is small when the oxidation is carried out at neutral pH The pH at which a high number of carboxyl groups are introduced lie around 10.

Besides choosing the oxidation reaction conditions so that a high number of carboxyl groups are introduced, the stability of the viscosity of solutions (or dispersions) of oxidized starch may be increased by introducing ether or ester groups in the starch.

The number of carbonyl groups introduced in the starch during oxidation negatively affects the stability of the viscosity of the oxidized starch in solution (or dispersion). It further leads to a more brown-yellow color of a solution or dispersion of the oxidized starch, which is usually not wanted. The amount of carbonyl groups introduced is also dependent on the pH during the oxidation reaction. At neutral pH, a relatively high number of carbonyl groups are introduced. At a higher pH, less carbonyl group will be introduced during oxidation.

From the foregoing therefore, it is clear that the choice for the pH at which conventional oxidation reactions of starch using an alkali metal hypochlorite are performed, constitutes a compromise between efficient starch degradation and stability of the viscosity. of the oxidized starch,

Conventionally, the pH during oxidation of starch using an alkali metal hypochlorite is chosen at 8.5 or higher, dependent mostly on the desired viscosity.

The amylopectin type starch is subjected to oxidation, enzymatic treatment, acid hydrolysis or thermo-chemical conversion. When oxidation process is performed at pH 9.5, the obtained oxidation product may be used as a finishing agent in papermaking.

As has been indicated above, for reasons of stability, the oxidation process is usually carried out at a pH higher than 8. 5. Higher pH adversely affects the reaction rate. Also, carrying out the oxidation process at this pH has the effect that relatively high amounts of oxidizing agent are necessary to achieve the desired viscosity. As the oxidizing agent is usually an alkali metal hypochlorite, the more oxidizing agent is used, the higher the risk that a certain amount of chlorine ends up in the oxidation product. The presence of chlorine is highly undesirable with respect to (public) health and the environment.

When small amount of an alkali metal hypochlorite is used as an oxidizing agent, much smaller amounts of chlorine are present in the oxidized starch and the oxidation process can be achieved in less time.

Amylopectin consists of very large, highly branched molecules having an average degree of polymerization of 1, 000, 000 or more. The commercially most important starch types (maize starch, potato starch, wheat starch and tapioca starch) contain 15 to 30 wt. % amylose. Of some cereal types, such as barley, maize, millet, wheat, milo, rice and sorghum, there are varieties of which the starch granules nearly completely consist of amylopectin.

Calculated as weight percent on dry substance, these starch granules contain more than 95% amylopectin. The amylose content of these cereal starch granules is thus less than 5%. The above cereal varieties are also referred to as waxy cereal grains, and the amylopectin starch granules isolated therefrom as waxy cereal starches.

For instance, potato starch granules isolated from potato tubers usually contain about 20% amylose and 80% amylopectin (wt. % on dry substance). During the past 10 years, however, successful efforts have been made to cultivate by genetic modification potato plants which, in the potato tubers, form starch granules consisting for more than 95 wt. % (on dry substance) of amylopectin. It has even been found feasible to produce potato tubers comprising substantially only amylopectin.

Problems regarding odor and foaming, which, because of the lipids and/or proteins, may occur when using waxy cereal starch products (native and modified).

The oxidation of starch is carried out with an alkali metal hypochlorite as oxidizing agent. Preferably, sodium hypochlorite is used as an oxidizing agent. Alkali metal hypochlorite is relatively cheap and possesses a relatively potent oxidizing power, thus leading to a very efficient and fast oxidization process.

The amount in which the oxidizing agent is added may vary between 0. 001mole and 0. 4 moles of alkali metal hypochlorite per mole starch, preferably between 0.0025 and 0. 15 moles of alkali metal hypochlorite per mole starch. The alkali metal hypochlorite should be added to the starch in a controlled manner. It is one of the advantages of this process that significantly smaller amounts of oxidizing agent are sufficient.

The temperature at which the starch is treated with an oxidizing agent is preferably chosen between 20 and 50°C, more preferably between 25 and 40°C.

The oxidation reaction may be carried out as a suspension or solution reaction in water. Preferably, the reaction is carried out as a suspension reaction in water, as this leads to a granular oxidized starch. To this end, the starch to be oxidized is suspended in water in an amount ranging between 0. 5 and 1.5 kg of dry starch per liter water.

Optionally, a catalyst or a combination of catalysts may be used in the oxidation reaction. Suitable catalysts include bromide, cobalt, iron, manganese and copper salts.

Surprisingly, it has been found that the alkaline treatment has a highly beneficial effect on the properties, especially the viscosity stability, of the oxidized starch. An oxidized starch may be stored at increased temperatures, e.g. 80°C, for prolonged periods of time without substantially any change in the viscosity of the product being observed.

An oxidized starch may also be used as a protective colloid for providing the desired stability.

In the textile industry, oxidized starch may be used to improve the weaving operation or weaving efficiency by warp yarn sizing. This results in an improved abrasion resistance of the warp yarns during the weaving process and less warp-end breakages. The oxidized starch may further be applied as finishing agent to give a smooth and firm hand to fabrics. It may also be used for the coating of glass fibers. In addition, it may be used as blanket adhesive in the textile printing industry.

In the food industry, Arabic gum may be replaced in confectioneries by an oxidized starch. The excellent stability of the oxidized starch, leads in these applications to a more clear food product.

The list of applications of oxidized starches is highly extensive and many more applications of oxidized starches are conceivable.

Oxidation of acha starch using sodium hypochlorite (3.5% active chlorine) was carried out [25] by dissolving 25g of native starch in 100ml of distilled water and the pH of starch solution adjusted to 10-11 with sodium hydroxide solution. The starch slurry was heated to a temperature of 30^0C and 20ml of sodium hypochlorite solution (3.5% active chlorine) added to the starch solution dropwise over a period of 20 minutes with stirring. During the addition of the reagent and the course of reaction the pH of the slurry was maintained at the desired value with 0.1M NaOH or 0.1M HCl solution. The mixture was stirred under defined conditions and then terminated after 2 hours by addition of sodium metabisulphite.

Oxidation improved water and oil absorption capacity of native acha starch, emulsion capacity and foaming property. This may be attributed to the incorporation of carboxyl functional groups on the starch molecules which enhanced binding capacity more than the native starch, while cross-linking and acid treatment reduced the water absorption capacity.

The reduction in water absorption capacity of acid treated sample might be due to increase in starch crystallinity that probably restricted the access of water into the starch granules of the acid thinned starch. See Figs. 2, 3 and 4 for scanning electron microscopy (SEM) of starch granule morphology. In the same vein, reduction of water absorption capacity of acetylated cross- linked sample may be attributed to the incorporation of hydrophobic acetyl group into the starch molecule The increase in water absorption capacity following oxidation is very important especially in the application of this starch either as a drug carrier or disintegrant in tablets and capsule formulation.The result of oil absorption capacity of native acha starch and modified sample are presented in table 2. The values expressed as parent vary from 122 observed with native acha starch to 112 observed for acid thinned sample, there was a general reduction of native acha starch. This may be attributed to the functional groups incorporated onto the starch molecule following chemical modification. This is in agreement that acetylation and oxidation do not improve oil absorption capacity of great northern bean. This modification in starch structural granules restricted access of oil into the granule of the starch. This is because chemical modification is thought to occur in the amorphous region of the starch molecules leading to increase in starch crystallinity.

The pH of starch slurries of native and modified acha starch are presented on table 2. The pH values varied from 6.45 to 7.80. A reduction on pH value was observed following modification by cross linking (acetylation) and oxidation. The value, however, increased to 7.80 following acid treatment

The reduction in pH values of acetylated and oxidized samples may be attributed to the incorporation of acetyl functional group to the starch molecule thereby increasing the acidity of starch molecules.

The bulk density of native acha starch and modified sample are presented on table 6. The bulk density values were in the range of 0.39 to 0.50.A reduction of bulk density was observed with all chemical modifications of the native acha starch. The least bulk density was observed with the acid thinned sample (0.39). The reduction in bulk density might be attributed to increased crystallinity following chemical modification. Increase crystallinity is characteristic of more ordered state and this might impact greater stability on the modified samples. Thus retrogradation of native acha starch as well as seneresis may be improved unpon modification. This improved physical property following chemical modification of native acha starch is desirable in food and pharmaceutical applications as good dispersant and preparation of biopolymer based flocculants.

The result of foam capacity of native acha starch and modified samples are presented on table 2. The foam capacity of acetylated (cross linked) and oxidized sample were reduced to 3.0% and 3.2% respectively. The acid thinned sample increase in foam capacity to 10%. Reduction in foam capacity following crosslinking and oxidation could find suitable application as an emulsifier in the food industries [25].

The emulsion capacity of native acha starch, cross linked, acid treated and oxidized samples are presented on table 2. The emulsion capacity increased in all the modified samples from 36% to 40% in the acid thinned sample. This suggests that chemically modified acha starch are better emulsifying agent due to the introduction of functional groups in the starch molecules increasing the binding force of the starch granules.

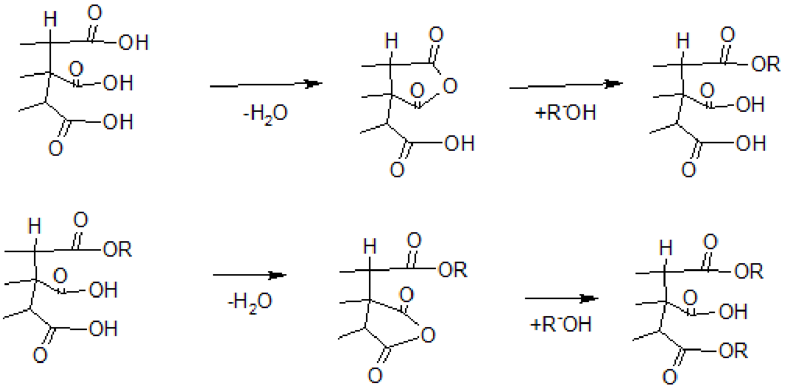


Fig-1: Mechanism of cross-linking using carboxylic acids. The R-OH represents starch or cellulose [11].

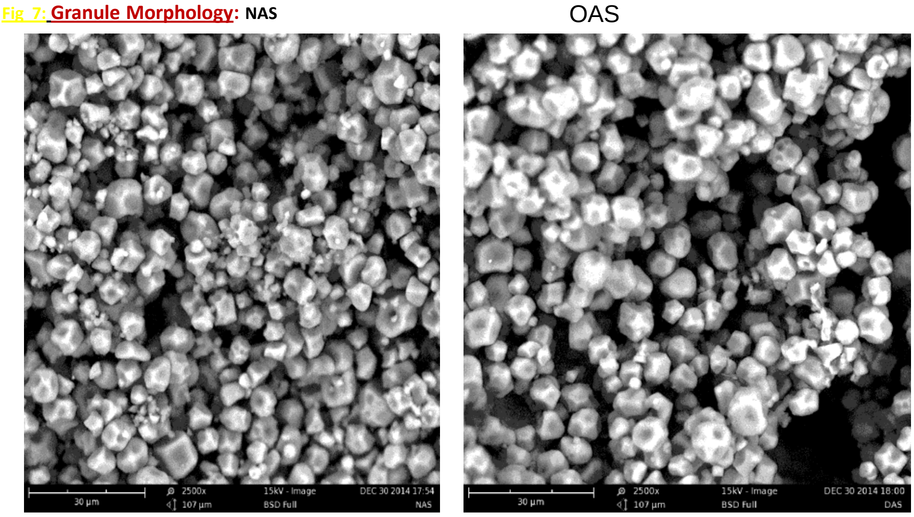


Fig-2: Comparison of Granule morphology native acha acha starch (NAS) and oxidized sample (OAS)

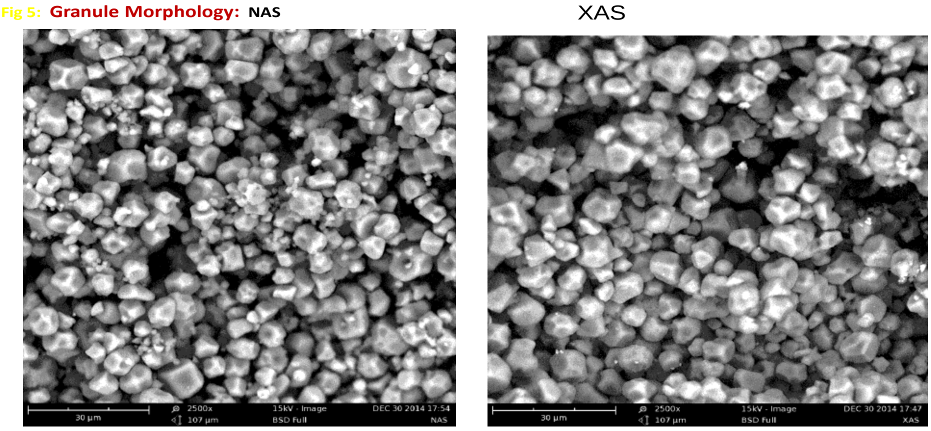


Fig-3: Comparison of Granule morphology native acha starch (NAS) and cross-linked (XAS)

Fig 6: **Granule Morphology**: **NAS** HAS

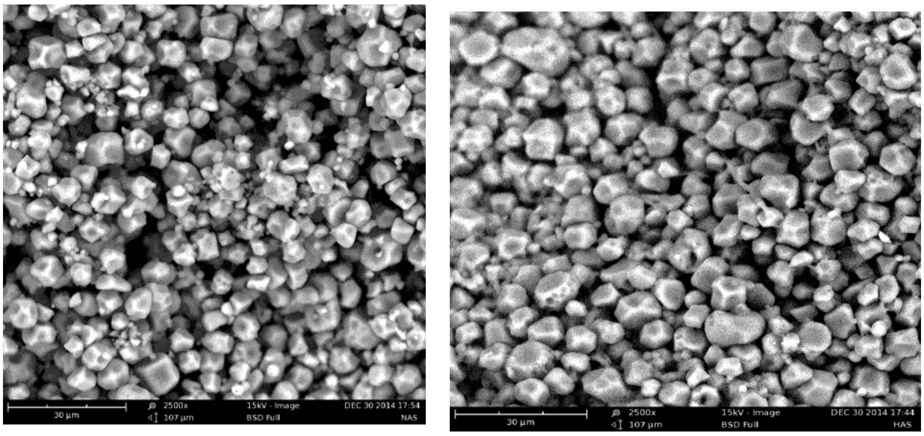


Fig-4: Comparison of Granule morphology of native acha starch (NAS) and acid treated sample (HAS)

List of Tables

Table-1: least gelation concentration: NAS refers to unmodified or native acha starch; XAS refers to crosslinked sample OAS is oxidized sample while HAS refers to Acid treated sample

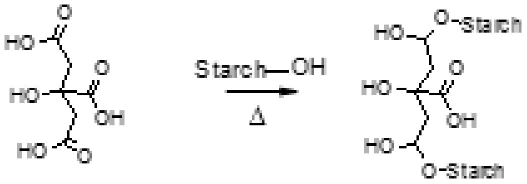
CONCENTRATION%	NAS	XAS	HAS	OAS
2	Viscous	Viscous	viscous	viscous
4	Viscous	Viscous	Viscous	Viscous
6	Gel	Viscous	Viscous	Gel
8	Gel	Gel	viscous	Gel
10	Gel	Gel	Viscous	Gel
12	Gel	Gel	Viscous	Gel
14	Gel	Gel	Gel	Gel
16	Gel	Gel	Gel	Gel

Table-2: Functional properties of native starch and modified samples

Starch	Water Abs Capacity	Oil Abs Capacity	Emulsion Capacity	Foam Capacity	Bulk Density	pH
NAS	488	122	36	4.00	0.50	6.85
XAS	465	116	48	3.00	0.41	6.45
HAS	315	112	40	10.00	0.39	7.80
OAS	499	115	39	3.20	0.44	6.40

NAS = Native Acha starch; XAS = Cross linked Acha starch; HAS = Acid treated Acha starch; OAS = Oxidized Acha starch.

TOC Graphics



Supporting Information

Included is supporting information for review outlining the relevance and originality of work and a TOC graphics.

CONCLUSION

Chemical modifications of an underutilized Acha grains enhanced its functional properties including emulsion capacity, water and oil absorption capacities. Rheological properties expressed as paste viscosities were altered on modified samples. The viscosities of cross-linked, oxidized and acid treated samples were reduced.

Potential applications of modified acha starch include good emulsifying agent, starch thickened sauces, soups, paper binding and pharmaceutical drug carriers and disintegrants. Modifications improved stability and retrogradation.

RECOMMENDATION

For commercial exploitation of modified acha starch, especially for such important industrial applications as paper binder and pharmaceutical drug carrier for tablets and capsule formulation and disintegrants, it is recommended that the bond strength and tensile strength are further investigated. The thermal stability and enthalpy of gelation (phase transition) should be investigated.

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