Comprehensive review of the impact of modification on the properties of jackfruit seed starch and its applications

Abstract

Jackfruit belongs to the family Moraceae and is used as a novel source of starch. In the native stage, starch granules are generally insoluble at room temperature, extremely resistant to enzymatic hydrolysis and display an inability to endure processing conditions related to pH, temperature, shear rate and freeze–thawing.

Modification can be carried out using chemical, physical or enzymatic methods, or a combination of these. To solve this problem, modification of starches is usually conducted to alter pasting, gelatinization and retrogradation behavior.

Modified starches have been recognized as a multifunctional excipient in various industries.

This review covers a wide array of topics relating to starch, including: methods of modification; the impact of modification on morphology, crystallinity, viscosity and functionality; and the application of modified starch.

Keywords: Jackfruit, modification, morphology, viscosity, chemical
Introduction

Jackfruit (*Artocarpus heterophyllus* Lam.) is associated with edible bulbs of white to yellow fleshy tissue and seeds, and is widely grown in tropical countries, including India [1–6]. The seeds account for 8–15% of the total fruit weight and they are rich in carbohydrate and protein content [7, 8]. They also contain several minerals, saponins, lignans, phytonutrients and isoflavones [9]. As jackfruit seeds are composed of 63–80% carbohydrate, they can be used for the production of starch. Jackfruit seeds contain 70–85% total starch when dry [10–14].

Jackfruit seed starch (JFS) consists of 25 to 45% amylose content and 45 to 80% amylopectin content [15–19]. The JFS granules are bell-shaped with smooth surfaces. The granular size lies between 5 and 10 µm [18]. JFSs have vast applications in the food industry, mainly being used as a thickening and binding agent, and stabilizer [19]. Several studies have been conducted in the last few years to investigate the properties of JFS and they reported many limitations to their industrial use [10, 15, 18, 19].

However, the native starch has some drawbacks such as water insolubility, limited swelling ability, low granule dispersibility, higher gelatinization temperatures and syneresis [14, 16]. As the modification of starch may help to advance its functionality, researchers have studied various techniques and agents for the modification of starches and have investigated the improvement in their properties and their suitability for industrial applications [18]. However, the properties of the starches may be altered during the modification process. Therefore, recently, there have been a number of studies on the functional and physicochemical properties of JFS after different kinds of modification. Modification of starches can be achieved using enzymatic, chemical (etherification, carboxymethylation, esterification, cross-linking and oxidation), and physical (annealing, heat-moisture treatment or HMT, the microwave oven method, pregelatinization, extrusion and various non-thermal processes) and partial gelatinization techniques [20, 21].

The attributes of the resultant starches differ, as they depend upon the processing conditions, such as time and the temperature of processing. The uses of native starches, however, are mostly fixed to acting as a diluent or filler, owing to the limitations of various characteristics.

The modification of the native starch, by any method, generally resulted in improved functionality. Some studies also reported on the combined effect of two reaction methods on numerous unmodified starches, by various methods including cross-linking and carboxymethylation and so on [22, 23]. Both reagents induced specific changes to the starches after modification. The dual reaction resulted in either an increase in viscosity due to restricted chain movement or a decrease in viscosity with enhanced swelling [23].

This literature survey is going to present the modification processes and the effect on JFSs. This review will summarize the preparation, physicochemical and functional properties of physically and/or chemically modified jackfruit starches, and their applications.

Isolation and modification of JFS

According to Mukprasirt and Sajjaanan-takul [15] and Noor *et al.* [24], the fruit was cut and seeds removed from the bulbs. These seeds were washed with water to take away undesirable parts.

The arils of seeds are removed manually and lye-peeling should be carried out to remove the thin brown spermoderms. Starch from jackfruit seeds can be extracted by either the alkali
method or the distilled water method. In the alkali method, the seed flour is soaked into 0.5% sodium hydroxide solution for 6–8 hours.

Filtration should be carried out followed by washing 3 times with distilled water. This filtrate is left to settle overnight at 4°C. After 24 hours, decant the water and dry at 40–60°C [25]. In the distilled water method, the seed flour is soaked into water instead of alkaline solution. Further processing is similar to the alkali method [10].

Modification techniques

After the extraction of starch from seeds, the obtained starch undergoes modification. Modification of starches is conducted to improve their functional characteristics.

Various techniques have been used to modify the JFS such as acid–alcohol modification, the acid-thinned method, cross-linking, carboxymethyl modification, HMT, hydroxypropylation, pregelatinization, annealing, oxidation, microwave and conventional heating modification and so on [17, 18, 26–33].

**Figure 1** Scanning electron microscope (SEM) images of (A) native jackfruit seed starch (JFS), and JFS modified by (B) acid–alcohol, (C) hydroxypropylation, (D) oxidation, (E) annealing, (F) cross-linking (CL-JF), (G) partial gelatinization and (H) heat-moisture treatment [18, 30, 32–34]

**Effect of modification on recovery yield and granule morphology**

Dutta *et al* [17] reported on the recovery yield of jackfruit seed after modification and they concluded that the recovery after acidic modification decreases as the time of the modification process increases. These researchers worked on starch acid modification in two dimensions; firstly, short-term treatment, and then, long-term treatment, with variations in time and acid concentration. They found that the total minimum recovery of starch was 73% after modification, but it was highest in long-term treatment (LT1) (86.32%) at a 1 M HCl concentration. There is insufficient data regarding recovery for other modification techniques. Babu *et al* [35] reported that the recovery yield of citric acid- and hydrochloric acid-modified sweet potato starch was above 93%, which is greater than that for the JFS.

The granular morphology of starches changes after modification (Fig. 1).

Dutta *et al* [17] reported that native JFS has various shapes, including round, dome-shaped, trigonal and tetragonal, with granular size ranging from 6–12 µm. They have also reported on the effects of different acid treatments on the granular morphology of starch and they found
that the acid degrades the granule surfaces; this effect increases as the time of treatment increases. They also found that the acid treatment had more of an effect on the flat surfaces of all the shaped granules. Therefore, it can be concluded that the surface of the starch granules is affected during modification. Another team of researchers [28] supported the above results, and reported on the effect of acid modification on the starches. They concluded that there was no apparent damage to the starch granule surface when treated with a considerably diluted hydrochloric acid solution (that is, 0.5 M), while a positive result was obtained whereby a smoother surface was observed on the starch granules. At the same time, when starch granules underwent treatment with an increased concentration of acid (that is, 2.0 M), the researchers found that granules became ruptured and broke down into small pieces. This result can be ascribed to the attack of the acid on the amorphous starch, which leads to rupture of the particles [28].

In chemical modification, esterification is achieved using many methods and hydroxypropylation is one of these. After hydroxypropylation, the shape of the granules in the starch was not significantly altered. However, if the concentration of propylene oxide increases, some degradation can occur on some starch granules. Changes in the appearance of starch granules after hydroxypropylation have been reported for different sources of starches, like potatoes, pigeon peas and cassava [36–38].

Kittipongpatana and Kittipongpatana [18] reported that scanning electron microscopy images showed that native JFSs have round and bell-shaped granules with a size ranging from 5 to 10 µm and distorted, wrinkled surfaces. In addition, there was rupturing of granules after modification by pregelatinization and carboxymethylation.

After modification, the shapes of the starches become irregular (Fig. 1).

The sizes of the oxidized JFSs were increased after oxidation [33]. Many studies have reported that after oxidation no change occurs to the surface and shape of the granules in starches such as banana starch, barley starch and corn starch [39, 40]. Hydroxypropylation did not alter the shape of the starch granules significantly [29]. HMT and annealing are physical modification techniques. After HMT and annealing, the granules become more swollen, and granule fusion and surface corrosion have also been observed [30, 32]. This could be the result of partial gelatinization of starch occurring with a combination of high moisture and heat [38, 41].

Impact of modification on granular swelling, solubility and amylose

Several researchers have shown that granular swelling and amylose leaching are reduced, and solubility is increased, upon modification of legume [42] and tuber [43–45] starches. However, in some studies, swelling capacity has been reported to increase after modification [18, 29, 32].

According to Kittipongpatana and Kittipongpatana [18], hydroxypropyl jackfruit starch has the highest solubility and swelling capacity, rather than pregelatinized, cross-linked jackfruit starch. The amylose content of starches is also affected by modification. Kittipongpatana and Kittipongpatana [18] reported that no significant difference was found between native and HMT-modified starches, while Dutta et al [17] demonstrated an effect of acid concentration and the time of treatment. The latter reported that reduced treatment time decreases (due to the rapid initial degradation of amylase by acid) the amylose content, that is, there is higher amylose leaching compared to
a longer treatment time (where degraded amylose fractions recrystallize).
Such changes in the starches are attributed to the following phenomena occurring during modification: A) an increase in crystallinity or disruption of crystallites, B) amylose–lipid interactions and C) amylose–amylose and/or amyllopectin–amyllopectin chain interactions [46].

**Impact of modification on X-ray patterns, peak intensities and crystallinity**

The native jackfruit starch granule exhibits the typical A-type X-ray diffractogram. After modification of the starches, there was no change seen in the X-ray pattern, but different peak intensities were observed [17, 18, 29, 32].

Modification results in minor changes in the peak intensities, and therefore, changes occur in the percentage crystallinity.

Dutta *et al* [17] showed that the amyllopectin content influences the peak intensities of starch. Kittipongpatana and Kittipongpatana [32], applying HMT to JFS with a medium moisture content and temperatures, showed increased intensity of reflection peaks. Naknaen [29] reported a decrease in the degree of crystallinity of the starch as the volume of propylene oxide increased, in a reaction that occurred in the crystalline region of the starch.

On the other hand, an increase in the crystallinity of potato starch was reported by Vermeulen *et al* [47] when it was subjected to HMT at 130°C. This could occur when decoupling of the double helices from the amyllopectin backbone takes place, which renders the double helices sufficiently mobile to become organized in more perfect/larger crystallites [47].

Khunae *et al* [48] reported that the peak intensity increases with an increase in moisture content, due to an increase in the mobility of amylose–lipid complex chains.

XRD analysis of pregelatinized JFS (PG-JF) and carboxymethyl jackfruit starches (n-CMJF) showed a fusion between the peaks and significant loss of distinctive diffraction. This suggests that these are amorphous solids in nature. With carboxymethylation using methanol as a solvent, a slight decrease in the crystallinity of methanol carboxymethyl jackfruit starches (m-CMJF) compared to native starch is seen. Similarly, modification of starch using 1- or 2-propanol as solvents resulted in a noticeable decrease in the diffraction intensity, because of the loss of crystallinity [18].

Koo *et al* [49] reported no significant difference between the XRD of native and cross-linked corn starches. This is because cross-linking predominantly occurred in the amorphous regions of granules, thus having very little effect on the crystallinity of starch.

**Impact of modification on gelatinization parameters**

The gelatinization of starches is a process of order–disorder phase transition of granules in the presence of heat and water that ultimately results in swelling and solubilization of starch granules and loss of their crystallinity [29, 50].

Gelatinization occurs at a specific temperature and is affected by the size of the starch granules, their crystallinity and microstructure, and also, by the amount of amylose and amyllopectin, along with protein, fat and phosphorus content [22, 25, 51–58].

The gelatinization of starches can be measured by various methods, with differential scanning calorimetry being one of these. The thermal phase transitions of the starches are defined as $T_o$ (onset), $T_p$ (peak of gelatiniza-
tion), \( T_c \) (conclusion) and the enthalpy of gelatinization (\( \Delta H_{gel} \)) \([28]\). The gelatinization of native and modified JFSs has been measured by many researchers \([14–16, 28–30, 32, 33]\).

Naknaen \([29]\) had reported that the gelatinization temperatures of hydroxypropyl-modified JFSs were less than those of native JFSs reported elsewhere \([14–16, 32, 59]\). These differences in gelatinization temperatures \( (T_o, T_p, \text{and} \ T_c) \) and the enthalpy of gelatinization \( (\Delta H) \) could be due to disruption of the hydrogen bonds among starch chains. The decrease in the gelatinization temperatures could also be dependent on the nature of the chemicals used in the modifications \([60]\). In this regard, Naknaen \textit{et al} \([33]\) investigated the oxidation of starches with different concentrations of sodium hypochlorite and reported that there was no significant difference in gelatinization temperatures among native and oxidized starches of jackfruit seeds.

However, they did report that oxidized starches had lower onset temperatures \( (T_o) \) than the native starch, which indicates that the oxidized starches had higher gelatinizing and hydrating capacity. This decrease in \( T_o \) is due to the weakening of the starch granules, which ruptures the amylopectin double helices easily \([61]\).

Similar results were also reported by Kittipongpatana and Kittipongpatana \([18]\) for hydroxypropyl- and cross-linked-modified starches, but according to these researchers, pregelatinized JFSs show a significant rise in gelatinization temperatures \( (T_o, T_p, \text{and} \ T_c) \), with a drastic drop in the enthalpic energy required for gelatinization indicating the loss of molecular order, which is also supported by the findings of Singh and Singh \([54]\).

A similar result was reported for the thermal transition of cross-linked corn starch and was proposed to be due to an increase in the free volume of starch chains brought about by the presence of bulky and ionic phosphate groups \([62]\). Modification of starches provides starch with better storage stability in food applications \([51]\).

### Impact of modification on viscosity

Viscosity is one of the most important functional properties of starch as it determines the further application of starches in various usages. Pasting properties can be measured by the Rapid Visco Analyzer (RVA), where the viscosity of starch is measured during the heating cycle of a suspension of starches \([63]\).

This reveals the molecular changes that occur in starch granules that decide the behavior of the JFS during cooking. It shows the minimum temperature required for the cooking of the starches. A higher pasting temperature needs a longer cooking time \([29]\). The pasting properties of starch depend on granule swelling, the resistance between swollen granules, crystallinity, amylose leaching, the degree of gelatinization and the level of molecular breakdown \([64]\), along with the chain length of starch components \([65]\). Naknaen \([29]\) reported a reduction in pasting temperature after modification.

The reduction in pasting temperature was found as hydroxypropyl starch is hydrophilic in nature. This facilitates the penetration of water into the starch molecules and this weakens the starch granules more easily, compared to native starch. The peak viscosity shows the water binding capacity of starches. The peak viscosity and breakdown viscosity were also decreased following modification. Setback viscosity measures the gelling ability or retrogradation tendency of starch, and after modification, setback viscosity also decreases. Zuo \textit{et al} \([28]\) have also reported a drastic reduction in the hot paste viscosity after acid thinning. Acid hydrolysis reduces the swelling and absorption of starch molecules during cooking, mainly in the amorphous region \([44]\). This study also proposed that the change in vis-
osity might be a consequence of an increased degree of amylose recrystallization. Dutta et al.\textsuperscript{[17]} have also reported similar results and far lower viscosity resulting from acid–alcohol modification of JFSs. Similar results have also been found with other starches, such as corn starch and sorghum starch, following modification.\textsuperscript{[65–67]} These kinds of changes in viscosities make the starches suitable for use as fillings in confectionery products.

### Applications in the food industry

Many researchers have developed different methods to modify starches, which require treatments that are either physical, chemical or enzymatic, or a combination of these, that is, duel modification\textsuperscript{[17, 18, 26, 28–33]}. The main reason for the modification process is to improve the properties of the starch; predominantly to enhance water-holding capacity and heat-resistant characteristics, to minimize syneresis, to strengthen binding properties and to bring about superior thickening behavior\textsuperscript{[68, 69]}. Here, various properties of the products, such as structure and texture, appearance, organoleptic properties and shelf stability, are some important parameters that are considered when selecting modified starches for the development of the product (Table 1). In the present day, modified starch is considered to be a food additive and has an upper limit that is based on the type of modification that has been carried out. Labelling is also defined by the US Code of Federal Regulations\textsuperscript{[70]}. Starch can be used as a fat replacement after modification by hydrolysis; for example, maltodextrin is used in low-fat ice cream, low-fat mayonnaise, low-fat milk products and low-fat yoghurt\textsuperscript{[70–73]}. Numerous studies have approved the potential use of modified starches as texture improvers in products within the food industry. They enhance the crispness of bakery products and snacks, improve the textural properties of extruded products, bring de-

<table>
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<th>Modification technique</th>
<th>Parameters studied</th>
<th>Benefit</th>
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<tr>
<td>Pre-gelatinization</td>
<td>100 g starch in 350 ml of distilled water. Temperature and time: 80°C for 15 min, 200 ml methanol.</td>
<td>Improved gelatinization, temperature, water solubility, solution viscosity, swelling ability and water uptake.</td>
<td>[18]</td>
</tr>
<tr>
<td>Annealing</td>
<td>Suspension 20% (w/v); temperature: 45, 50, 55 and 60°C. Time 72 hours.</td>
<td>Increased thermal stability. Increased peak viscosity.</td>
<td>[30]</td>
</tr>
<tr>
<td>Microwave modification</td>
<td>5 g of starch and 10 ml 10% maleic acid. Power: 3 watts; time: 2.5 min; temperature: 35°C.</td>
<td>Higher solubility and swelling power.</td>
<td>[31]</td>
</tr>
<tr>
<td>Heat-moisture treatment</td>
<td>A sample having moisture content of 10, 15, 20, 25, 30 and 35% heated in a hot-air oven set at 60, 90, 100, 110, and 120°C for 6, 12 and 16 hours.</td>
<td>Increased gelatinization temperature as the moisture content was increased in the samples.</td>
<td>[32]</td>
</tr>
<tr>
<td>Acid modification</td>
<td>In the short-term process starch was suspended in concentrated HCl and 70% alcohol (1:2 v/v); hydrolyzed in a shaking water bath at 45°C for 15, 25 and 30 min. Neutralized by 1 M NaOH to pH 7.0. In the long-term process, acid hydrolysis with 1 M HCl in absolute alcohol at 27°C for 1, 5, 10 and 15 days with thorough shaking every 6 hours.</td>
<td>Long-term treatment caused greater loss of crystallinity than short-term. Loss in viscosity. Can be used in confectionery fillings.</td>
<td>[17]</td>
</tr>
<tr>
<td>Acid thinning</td>
<td>0.5 and 2.0 mol/l aqueous HCl reaction was performed in a water bath at 45°C for 3 hours and neutralized with NaOH.</td>
<td>Granules a smaller size. Increased crystallinity. Gelled more easily. Reduced paste viscosity.</td>
<td>[28]</td>
</tr>
<tr>
<td>Hydroxypropylation</td>
<td>Starch suspension (100 g/400 ml water); 20 g of Na2SO4; pH 11.15. Temperature and time: 40°C for 24 hours. Diluted aqueous HCl (0.1 M) centrifuged for 15 min at 5000 rpm.</td>
<td>Molecular substitution (MS) increased with the volume of propylene oxide. The degree of crystallinity. Increased swelling power and solubility. Lowered gelatinization parameters.</td>
<td>[29]</td>
</tr>
<tr>
<td>Cross-linking</td>
<td>Starch suspension 78.5 g of 50% w/w Na2SO4 solution. The JFSC/CA/NaOH/STMP ratios were 1:0.29:0:28:0.07.</td>
<td>Solubility was significantly greater than for native starch.</td>
<td>[26]</td>
</tr>
<tr>
<td>Carboxymethylation</td>
<td>Carboxymethyl jackfruit starches were prepared using different alcoholic solvents methanol, 1-propanol, 2-propanol.</td>
<td>Highest viscosity.</td>
<td>[18]</td>
</tr>
<tr>
<td>Oxidation</td>
<td>40% (w/w) starch slurry, temperature 35°C. Chemical reactant: 6% sodium hypochlorite (NaOCl), 1% hydrochloric acid or active chlorine. pH 8.5.</td>
<td>Improved the whiteness, paste clarity and stability of starch gel at low-temperature storage. Used as a thickener or stabilizer.</td>
<td>[33]</td>
</tr>
<tr>
<td>Partial gelatinization</td>
<td>Starch and distilled water ratio of 3:7 at room temperature. Temperature: 70°C for 20, 30 or 60 min.</td>
<td>A slight change in pasting profile. Higher water-holding capacity. Absorbs or absorbs more moisture to give a higher equilibrium moisture content.</td>
<td>[34]</td>
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sirable chewiness to products and improve the viscosity of canned foods [18, 26, 32, 74–77].

Another application of the modification process is related to resistant starch. As we know, resistant starches are rich in fibre, and this allows nutritional claims to be made with respect to products being high in fibre [78, 79]. Gunaratne et al. [79] reported that modified starches have a high gelling temperature, which is useful for many products. Some researchers have studied the suitability of starches for micro-encapsulation of flavour volatiles and oleoresins to prevent their loss during processing [80–82].

Applications in the pharmaceutical industry

Starches are being modified by various techniques to bring about changes in one or more of their physical or chemical properties. They can be pregelatinized to obtain particles with a larger diameter [83]. They can be modified by cross-linking, where the chains get trapped together like a web, and they can also be heated or exposed to acetic acid or enzymes which cause breaks in the long chain resulting in simple molecules such as polydextrin, maltodextrin and dextrin. Alternatively, the hydrogen of the starches can be replaced by other groups, such as the carboxymethyl group, which changes the physicochemical and functional properties and results in carboxymethyl starch (CMS). The addition of carboxymethyl helps to improve the heat and microbial stability of starches. When other groups are added to the starch for replacement of hydrogen, such as carboxymethyl and carboxyethyl, they reduce the recrystallization tendency of starches. Oxidation of starch (generally, by using sodium hypochlorite) resulted in a higher clarity and a lower viscosity, compared to native starch [84]. Starches have been used as disintegrants, diluents, adhesives, binders, absorbents, for suspending, for film-forming and as emulsifying agents in the pharmaceutical industry; previously, native starch was used for these purposes but there were some problems with respect to the properties, such as poor flowability and restricted solubility [85]. That is why many types of research are currently ongoing to modify starches and check their suitability for use in pharmaceuticals. As the modification of native starches changes their gelatinization, pasting and retrogradation behavior, and thus, changes the binding and flow properties of tablets and so on, pregelatinized and acid-hydrolyzed starch is being used as a multifunctional pharmaceutical excipient [86, 87]. Modified starches like those that are carboxymethyl-modified are generally used in immediate release tablet formulations [88, 89]. Grafted phosphate ester derivatives and acetylated starches are used for the controlled release of drugs for better patient treatment. Modification has also been carried out to alter the hydrophilicity of the native starch by derivatization with acetate, hydroxypropyl and hydroxyethyl to alter self-assembling [90].

Kittipongpatana et al. [26] used cross-linked carboxymethyljackfruit starch (CL-CMJF) (modified JFS) as a tablet disintegrant and found improved water uptake ability, but there were no significant changes in the flowability, compared to native JFS. JFSs can be used as pharmaceutical excipients in various pharmaceutical formulations [91–94].

Conclusions

It is apparent from this review that great attention has been focused on the effect of modification on the structure and properties of native starches. However, there is still some shortage of information on the changes to starch structure and properties during the different modification techniques. Modification of starches improves the colour, swelling power, solubility, paste clarity and sta-
bility of the starch gel during low-temperature storage. Additionally, gelatinization temperatures and crystallinity are decreased. These kinds of unique changes in the properties of modified JFS could potentially result in such starches being used in confectionery and in other areas within the food industry, and also, for making gum candies and so on. Modification improves thickening, stabilizing activity and paste clarity, so these starches could also be useful for products stored at low temperatures, such as ice-cream.

Conflict of Interest
All of the authors declare that they have no conflict of interest.

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