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Modification of starch by novel and traditional ways: influence on the structure and functional properties

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Starch, a polymeric carbohydrate widely present in plant biomass, has gained popularity owing to its functional characteristics, lower cost and ability to completely decompose without any toxic byproducts. Native starches have the fewest applications among the food and non-food sectors. Thus, modifications to eliminate their shortcomings, viz., low pH, reduced viscosity, easy retrogradation, gelling, and syneresis during cooking, will prove to be useful through application extension. Physical modifications are simple and less expensive. Meanwhile, chemical modifications involve the extraction of the hydroxyl group from the starch molecule, yielding the desirable outcome for the extensive use of starch. With the advent of green chemistry, considerable attention has been paid to the development of novel physical modifications with the advantages of high efficiency, environmentally friendly operation, and ease of starch modification. High hydrostatic pressure (HHP) processing, microwave processing, pulsed electric field (PEF), and cold plasma are some of the tactics that govern this modification accordingly, keeping in mind the environment suitability and application broadness as well. Recently, there has been increasing interest in the chemical alteration of starches by means of oxidation, succinylation and acetylation to explore new horizons to improve their utilization potential beyond food, viz., pharmaceuticals, textiles and other fields. Increases in the solubility features, *in vitro* digestibility terms, resistant starches proportion and application extension are the selected traits discussed herein.

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1 Introduction

Starch is a natural storage polysaccharide found in abundance in plant roots, stems/stalks, and seeds, and is considered the second major biomass found on Earth.¹ Chemically, it is a polymeric carbohydrate constituting amylose (linear molecule) and amylopectin (branched molecule) units joined by glycosidic linkages.² Due to structural differences, these two units are distinct molecules in both physical and chemical nature.

The biochemical processes involved in the synthesis of starch include the production of glucose molecules by plant cells through the process of photosynthesis. It is formed in the chloroplasts and amyloplasts in green leaves. These are organelles involved in the synthesis of starch stored in cereal grains and tubers. Owing to its abundant presence, starch is extensively employed in different sectors as a raw material, such as papermaking, adhesives, bookbinding, corrugated board, plastics, textiles, construction, paints/varnishes, chemicals, pharmaceuticals, oil fields, and others.^{3,4} In addition, it is widely used in food, including ice creams, soups/curries/gravies/batters, bakery items, dairy items, and meat-based products as a stabilizer, thickener, and processing ingredient.⁵ Its broadened suitability as an ingredient and additive governs and regulates the homogeneity, texture variability, and stability of liquid foods, resists the breakdown of gels all through processing treatment, and extends the storage stability of products.⁶ Starch is also utilized in biodegradable packaging, thin-films, alcohol-containing fuels, and thermoplastics having enhanced thermal and mechanical activity.⁷

Native starch granules are usually modified to enhance the beneficial properties and eliminate shortcomings, such as low pH, reduced viscosity, easy retrogradation, gelling, and syneresis during cooking, thereby enhancing their applications in the food and non-food sectors. Starch processing is an ever-evolving

industry, and there are many opportunities to create novel starches that possess innovative functional and value-added terms. Different starch modification methods include physical, chemical, and combination of methods/dual modification⁸ (Fig. 1). The starch oxidation, acetylation, succinylation, acid/alkali treatment, and cross-linking correspond to chemical modifications, while high hydrostatic pressure (HHP) processing, microwave processing, pulsed electric field (PEF), and cold plasma are novel and environmentally friendly operations. However, annealing (hydrothermal) and pre-gelatinization (thermal) are categorized as traditional physical modification methods.⁹ Different modifications/processing treatments also lead to alterations in the functional properties of starch. Depending on the requirements, various starch processing methods are used at the industrial level. Thermal processing treatment of starch in an aqueous environment has been shown to induce a shift from amorphous to crystalline starch, causing starch gelatinization.¹⁰ Chemical methods are often highly effective in modifying starch, but their disadvantages are related to chemical costs, chemical residues, time, and waste.¹¹ Moreover, current novel physical methods through the use of moisture, thermal energy, radiation energy, high pressure, and cold plasma have progressively attracted interest due to their advantages of greater efficiency, simple operation, and generation of no chemical by-products. In addition, these physical and chemical starch modification methods can be used to design tailor-made food and non-food items containing starch and its derivatives.¹² Focusing on the importance of starches and their modification, the present review is an in-depth discussion of the same, summarizing the various novel and traditional physical and chemical methods used to provide them with quality attributes through functional and structural terms. A discussion about the beneficial properties of altered starches compared to the native one qualifies their potential beyond food application, and thus may direct future upcoming research studies accordingly. Selection of starches from lists of sources *i.e.* tubers, cereals, coarse cereals and pulse crops were subjected to traditional to novel, cum physical to chemical reformations govern their existing potential to much broader application terms.

2 Modification of starch by different processes

Native starches have complex granular and crystalline organizations that vary in size among plants. Different parameters have an impact on the physical, chemical, structural, and functional characteristics of starch. Any alteration/variation in the molecular structure of starch through the environment, operations, and processing treatments is called starch modification. These changes can be beneficial or non-beneficial to the structure and function of starch molecules.¹³ Native starches show diversity in their properties. Thus, to improve the quality of these starches and achieve better results in various food and non-food applications, the scientific community has committed to modifying the starch structure in different ways.

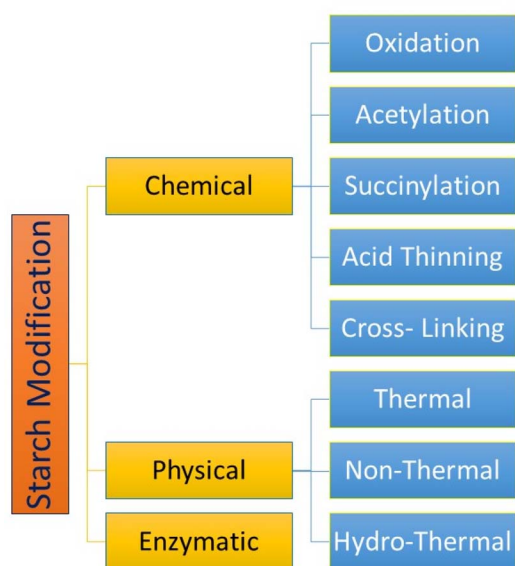


Fig. 1 Methods of starch modification.



2.1 Physical processes for modification of starches

The physical modification of starch is the alteration of starch properties caused by physical treatment. It does not result in chemical changes in the starch, other than the cleavage of a few glycosidic bonds.¹⁴ These are novel starch modification methods, which can be used to obtain environmentally friendly starch, called green technology. Generally, pre-gelatinization tactics are the common adopted method to carry out modifications among starches of any origin. Besides this, high hydrostatic pressure (HHP) processing, microwave processing, pulsed electric field (PEF) processing, and cold plasma technology¹⁵ are other non-conventional/green starch modification means that can achieve novelty among starches, as presented in Table 1.

2.1.1 Novel physical starch modification methods

2.1.1.1 High hydrostatic pressure (HHP). HHP processing is also known as cold gelatinization. Unlike the thermal treatment of starch, HHP processing can change the native granular

organization of starch into a gelatinized structure. Starch gelatinization can be more simply achieved through HHP processing than thermal ways under defined settings.¹⁶ The main features of gelatinized starch processed through HHP processing is a partly disintegrated grain structure, transformed crystalline starch organization and lower viscosity of starch solution as compared to the thermal gelatinization of starch.¹⁷ A schematic view of HHP processing of starchy food is presented in Fig. 2. Generally, the effect of HHP processing on the level of starch gelatinization depends on the type of starch, water and pressure level, processing temperature, and time. Cereal-based starch shows high sensitivity to HHP treatment, while the legume and tuber starches are less sensitive.¹⁸ HHP offers many advantages over the thermal processing methods: (a) starch retrogradation is slower than the thermal process; (b) increase in the swelling and solubility of starch; (c) changes in the thermal and pasting characteristics; (d) alteration in the amount of fast/slow or resistant starch.¹⁹ Moreover, HHP of

Table 1 Starch modification by novel non-thermal methods

Modification type	Raw material	Findings	References
High hydrostatic pressure (HHP) processing	Mung bean starch	Complete gelatinization at 600 MPa for 30 min HHP lowered the gelatinization temperature, gelatinization enthalpy, swelling capacity and solubility of starch	Li <i>et al.</i> (2011) ¹⁸
	Lotus seed starch	Decrease in the starch solubility and swelling power at 85 to 95 °C while an increase was observed in same at 55 to 75 °C	Guo <i>et al.</i> (2015) ⁷⁸
	Quinoa starch	Increase in the water holding capacity and particle volume upon treatment at pressure (0.1 to 600 MPa) and temperature (25 to 75 °C)	Ahmed <i>et al.</i> (2018) ⁷⁹
Microwave processing	Waxy maize starch	α -(1,6) Glycosidic linkages were destroyed readily, as compared to the α -(1,4) glycosidic linkages of starch Microwave treatment for 5 min led to degradation of the internal chain (amorphous area), while external chains (crystalline area) were destroyed at 10 min treatment	Yang <i>et al.</i> (2017) ³⁴
	Potato starch	The gelatinization temperature of starch was higher in the microwave-treated sample High peak viscosity, breakdown viscosity, and amylose content of microwave-treated sample	Xia <i>et al.</i> (2018) ³⁵
Pulsed electric field (PEF)	Aqueous starch suspension (wheat starch)	PEF treatment with field strength (25 kV cm ⁻¹) and total specific energy input (50 kJ kg ⁻¹) showed a great impact on wheat starch (fractures on the granule surfaces, lowering of peak apparent viscosity, & creating firm gels), therefore beneficial for 3D printing of starch	Maniglia <i>et al.</i> (2021) ⁴
	Pea starch	Increase in resistant starch from 11.73% to 12.24%, and rapidly digested starch increased from 50.88% to 59.40% upon PEF treatment	Li <i>et al.</i> (2019) ⁴¹
	Potato starch	Improved emulsion stability after PEF treatment of potato starch acetic anhydride system	Hong <i>et al.</i> (2018) ⁸⁰
Cold plasma	Corn starch	Dielectric barrier discharge plasma led to molecular oxidation, and degradation of starch molecules Decreased crystallinity was observed upon plasma treatment	Bie <i>et al.</i> (2016b) ²³
	Parboiled rice (<i>Oryza sativa</i>)	Enhanced cooking quality of plasma-treated rice Improved textural properties with a decline in hardness and stickiness with an increase in time and power	Sarangapani <i>et al.</i> (2015) ⁴³



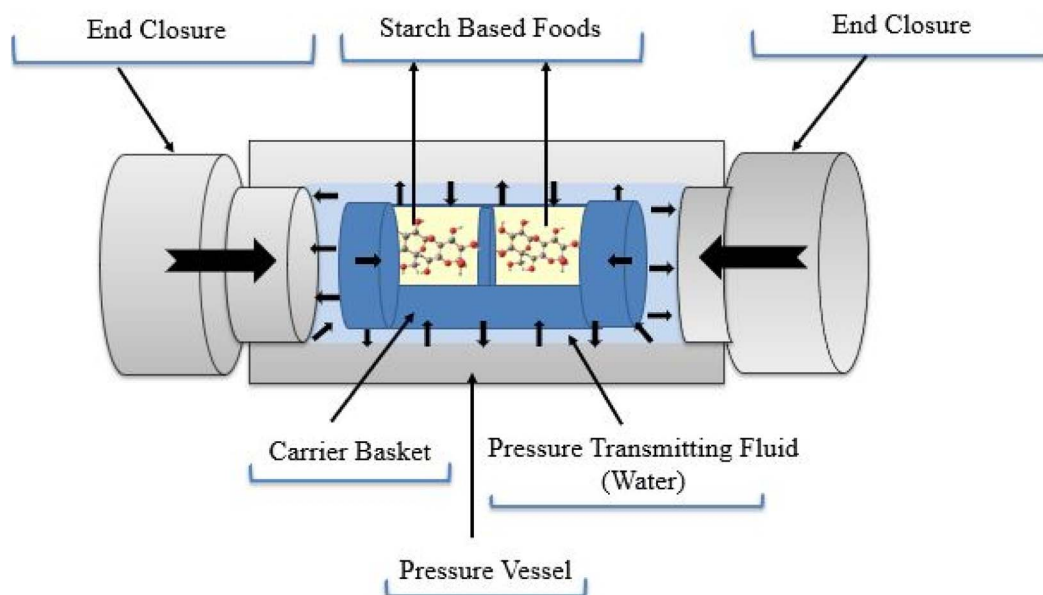


Fig. 2 Schematic view of high hydrostatic pressure (HHP) processing.

starch is helpful in its utilization in films. It was observed that HPP led to improvement in the physical attributes and water-resistance of the films.²⁰

For instance, HPP processing at a pressure of 600 MPa for 30 min led to complete gelatinization of mung bean starch.¹⁸ The lowering of the gelatinization temperature and gelatinization enthalpy was also noticed through a differential scanning calorimeter. Another study reported an upsurge in the slowly digested starch content of waxy wheat (31.12%) upon HPP retrogradation treatment at 600 MPa. The processing treatment also led to a decrease in the enthalpy of gelatinization, the relative crystallinity, and the peak viscosity of the waxy wheat starch samples. Moreover, changes in the *in vitro* digestibility, physico-chemical and structural characteristics of waxy wheat starch were noticed upon HPP retrogradation treatment.¹⁶ For the preparation of the starch-based film, buckwheat and tapioca starch were gelatinized using HPP treatment at 600 MPa, 20 °C for a period of 20 min. As a result, films made with HPP showed higher tensile strength and elongation at break than films made with thermal processing, regardless of starch type.²⁰

Regarding the changes in the structural properties of starch upon HPP treatment, limited research has been conducted on the alterations in the molecular structure of starch upon HPP. However, studies have shown that the modification in the molecular structure under high pressure is closely linked to the origin of starch. Nonetheless, further studies are needed to know whether amylopectin chains could be more susceptible to breakdown by high pressure.¹

In terms of the relative crystallinity of the starch molecules, it can be reduced with high pressure in HPP.^{20,21} The rationale behind the reduction in starch crystallinity is that HPP encourages the penetration of water molecules into the starch granules. It thus weakens the double helices in the crystalline

area and destroys the internal crystal assembly, leading to a decrease in relative crystallinity.²²

Studies on the influence of HPP on the starch granule morphology showed that the shape of sorghum starch remains intact with only some surface cracks upon the processing treatment with HPP at 120–360 MPa. However, when the processing pressure reached 480 MPa, the starch granules swelled and collapsed. Meanwhile, further increasing the processing pressure to 600 MPa led to deformation and fusion of the starch granules.²³ Likewise, similar results of HPP treatment were obtained for corn starch²⁴ and mung beans.¹⁸ Hence, HPP processing could be utilized to obtain desired starch properties without much alteration to the structure and functionality of starch.

An HPP-driven investigation on cassava starch²⁵ showed transformation from crystallinity to an amorphous state. HPP-induced gelatinization (500 to 600 MPa) with a decrease in flour concentration and increase in holding time favors an increase in rapidly digestible starch with decreased resistant starch fraction. In general, high pressure processing increases the swelling power and solubility if subjected at 55–75 °C, but decreases these properties if subjected 85–95 °C. Starch granules also swell on pressure processing at 500 MPa. However, they are completely ruptured as the pressure increases, while keeping the birefringence intact.²⁶

2.1.1.2 Microwave processing. Microwave processing technology is well-known for its applications in several food technology operations. The energy created by the microwave generates electric and magnetic fields having spectral frequencies ranging from 300 MHz to 300 GHz. When exposed to microwaves, polarized or charged atoms have a tendency to align with components of the microwave electric field that rapidly change the direction of the microwaves (Fig. 3).



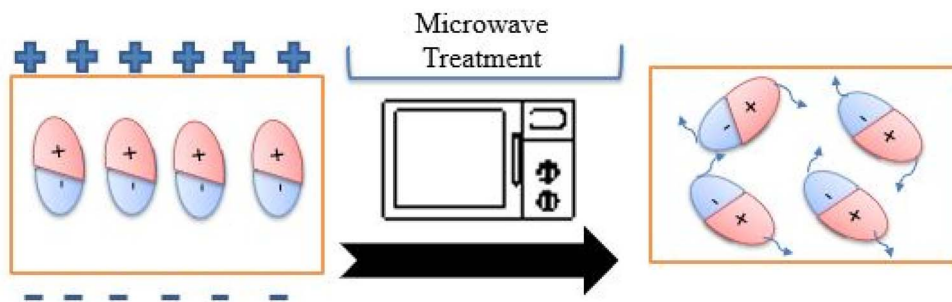


Fig. 3 Mechanism of microwave processing.

Microwaves can create pores, bumps, and cracks in the starch granules to improve the efficiency of extraction. For example, microwave-treated granules of potato starch prior to acetylation processing exhibited more apparent pores than those without microwave processing, and further roughness after the acetylation process. The moisture level of starch is also an important factor that affects grain morphology.²⁷ High moisture levels of food starch are very sensitive to microwave irradiation because water allows microwave energy to penetrate, causing pores to form and starch to collapse.²⁸ However, regarding the mechanism of starch processing by microwaves, there is presently no definite explanation. Nonetheless, it is usually believed that the impact of microwave irradiation is mainly dependent on the dielectric heating causing the rapid dipole reorientation of the polar molecules of starch, thus leading to the development of structural variations.²⁹

A number of researchers worked on checking the influence of microwave processing on starch characteristics. For instance, Xie *et al.*³⁰ reported that the molecular weight of potato starch granules decreased with longer microwave treatment. The variation in the morphology of starch is also strictly associated with the exposure time of the microwave. Research done by Oyeyinka *et al.*³¹ described that pores are formed on the starch granules of Bambara groundnut subsequently after 10 seconds of the microwave, and collapsed after 60 seconds. Cracks or holes in the surface might occur due to the higher internal vapor pressure caused by water upon the quick heating process, and the collapse may be caused by the destructive action on the internal assembly of starch.³²

Ma *et al.*³³ argued that all of the physical characteristics of the potato starch–water system, including the polarization-cross, thermal properties, and particle size, are influenced by microwave heating. The precise influence of microwave is important in the initial phases of gelatinization, but the thermal influences have a greater effect in later phases. Furthermore, Yang *et al.*³⁴ detected a decrease in starch viscosity, enthalpy, and synergism of starch after microwave processing. In addition, α -(1,6)-glycosidic bonds were more effortlessly disrupted during microwave processing than α -(1,4)-glycosidic bonds. They also investigated the chain length profile of waxy maize starch using a high-performance anion exchange chromatography pulsed amperometric detector, and determined that the A-chain content was altered by microwave

irradiation. The B-chain content increased with increasing microwave time, although a short irradiation time (5 minutes) exposure had little effect. The outer/external A-chains reside predominantly in crystalline domains that form double helices in starch granules, while the inner/internal B-chains are found predominantly in amorphous regions.³⁵ Therefore, it is conceivable that starch modification by microwave chiefly encompasses the disruption of amorphous regions (inner B-chains) in the initial step, and crystalline regions (outer A-chains) mainly in the subsequent steps.³⁴

Furthermore, intense microwave radiation can change the crystallographic construction of starch. A study done by Nawaz *et al.*³⁶ showed that microwave processing of lotus (*Nelumbo nucifera*) seed starch led to changes in the morphology from the C-type crystalline edifice to a mixed morphology; for example, a blend of type C and type A, or else a mix of type C and type B crystal structure. Likewise, the crystal organization of microwave-treated potato starch (type B) was converted to type A.³⁷

2.1.1.3 Pulsed electric field (PEF) processing. Pulsed electric field (PEF) treatment is a physical modification that has gained much interest from researchers due to its green technology and other benefits, such as environmental friendliness, cost-effectiveness, profitability, and energy-saving. PEF processing is primarily done on the liquid materials by passing high-intensity electrical pulses (more than 10 kV cm^{-1}) in a short duration of time (usually microseconds) for carrying out processes like pasteurization, inactivation of enzymes, recovery of biological constituents/extraction, modification at the molecular level, and enhancing the chemical process.¹ Furthermore, PEF helps in modifying the morphological characteristics of the starch granules.³⁸ PEF can cause modification in the starch characteristics by reducing the relative crystallinity, gelatinization and enthalpy temperature, viscosity and gelatinization temperature. Relative crystallinity exhibits a noteworthy correlation with the strength of PEF.³⁹ In a recent study, tapioca starch processed with PEF at 30, 40 and 50 kV cm^{-1} exhibited a decrease (24.2% to 18.1%, 11.4%, and 7.2%, respectively) in the relative crystallinity of the processed tapioca starch.⁴⁰ On a similar note, the variations in the lamellae structure of starch also show dependence on the electric field strength. This is due to the steady decrease of the scattering peak as the PEF strength increases.³⁹



Additionally, regarding the starch particle morphology, the literature showed that PEF treatment leads to enhanced roughness and formation of cracks, gaps, holes, corrosion or small deposits on the surface of starch granules.¹ PEF can modify digestible starch content, although it sustains resistant starch content. Li *et al.*⁴¹ showed that the PEF treatment increased the fraction of resistant starch from 11.73% to 12.24%, and the content of rapidly digested starch increased by 50.88% to 59.40%.

Furthermore, it has been reported that PEF treatment substantially alters the microstructural and macromolecular linkages between biomolecules under non-thermal conditions. In contrast, a recent study by Zeng *et al.*³⁹ reported that PEF processing was unable to disturb the starch chains. No significant change in the molecular size distribution was observed for waxy rice starch upon PEF processing at 30, 40, and 50 kV cm⁻¹. Regarding the combinational methods of starch modification, PEF-assisted succinylation increased the degree of substitution of modified starch. The pasting temperature at 2–6 kV cm⁻¹ also decreased to 7.6–15.1 °C for PEF-assisted starch esterified with octenyl succinic anhydride. Nonetheless, it was only 3 °C for the non-PEF-treated esterified starch compared with native starch.⁴² Therefore, PEF can be utilized as an appropriate green processing technology for starch modification.

2.1.1.4 Cold plasma processing. Plasma processing obeys the simple physical principle that the added energy is supplied to the gas by electric discharge, turning the gas into a high-energy plasma state, which is the fourth state of matter. The plasma is composed of positive and negative charged ions, free electrons, free radicals, and intermediate extremely reactive atoms, molecules, and UV photons having a clear neutral charge.⁴³ These reactive species favor diffusion into the surface, and endure multiple physical and chemical modifications.⁴⁴ Cold plasma processing of foodstuffs possesses various beneficial effects, such as extended shelf life, increasing germination rate of seeds, shortening of rice cooking time, starch modification, microbial and enzyme inactivation, and changes in hydrophilic/hydrophobic effects.⁴⁵ The experimental setup utilized in existing studies revealed that the exposure of starches with low-temperature plasma or glow discharge plasma induces starch crosslinking among the existing molecular pattern of starches. It is directly involved with the activation of free radicals, and hence accelerates the leaching of amylose. It also decreases the

relative crystallinity because of the depolymerization of the active plasma species. In summary, plasma processing alters the physical and functional aspects of starch (Fig. 4). This technology improves the pasting properties and viscosity, but reduces the tendency of retrogradation.^{15,43} Cold plasma treatment combined with microwave assistance on starches imparts elevated solubility features, and the same can be attributed to amylose leaching after treatment for hours.⁴⁶

Studies have shown that plasma-modified starch may cause little or no change in the starch crystallization morphology. However, it may induce changes in the relative crystallinity.¹⁵ Nonetheless, it must be noted that the amorphous region of the starch is more sensitive as compared to the crystalline region for two probable reasons: (a) the branched chains of starch molecules in the amorphous region are organized in a loose manner and easily compatible to interact with the reactive species of plasma,⁴³ and (b) the effect of plasma is usually restricted to the limited nanometer layers inside the starch granules and does not modify the overall activities of starch.⁴⁷

A literature survey indicated a decline in the relative crystallinity of cassava starch (8% decrease) upon treatment with helium glow plasma, whereas a significant decrease of 12% was observed upon treatment with oxygen glow plasma under identical experimental settings. Correspondingly, Thirumdas *et al.*¹⁵ reported a decrease in the relative crystallinity of rice starch from 43.06% (with no treatment) to 37.47% (40 W, 10 min air plasma treatment). Hence, it appears that the lowering of the relative degree of crystallization is substantially dependent on the type/kind of starch, as well as the plasma type and duration of treatment. Regarding the lamellar structure of starch, Zhang *et al.*¹¹ observed that helium and nitrogen glow plasma treatment enhanced “*d*” (which is the lamellae repeat distance) and “*d_c*” (average crystalline lamellae thickness), while it marginally decreased “*d_a*” (average amorphous lamellae thickness) in potato-based starch. Moreover, the treatment with glow plasma led to polymerization or crosslinking between the starch molecules. The study also suggested that starch modified with the glow plasma could assist as a potentially highly safe thickening or gelling agent for different food products. Thus, starch processing can be performed by cold plasma as a new technique. However, more studies need to be conducted to verify the applications of plasma-modified starch in current food systems.

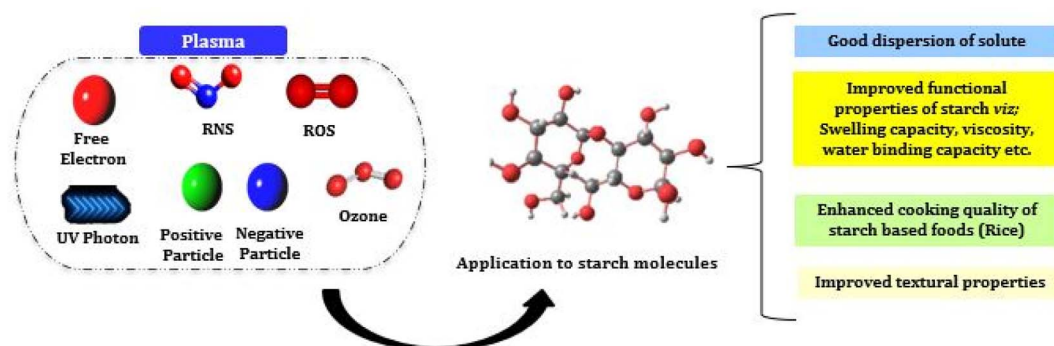


Fig. 4 Effects of plasma treatment on the properties of the starch molecules.



2.1.2 Conventional physical starch modification methods

2.1.2.1 Pre-gelatinization. Pre-cooking is a physical starch modification technique that turns natural starch from insoluble in water to a fully soluble form at room temperature termed as pre-gelatinized starch or instant starch.⁴⁸ Pre-gelatinized starch can be employed in ready-to-eat foods without cooking, and also has the benefit of reducing the cooking time. In pregelatinized starch obtained through extrusion, starch granules having moisture levels of 13–20% are exposed to high temperatures (up to 200 °C) along with high pressures (more than 10 MPa), and sheared during the extrusion process. As a result, the starch molecules are severely damaged and decomposed, causing low water absorption and viscosity.⁴⁹ Yan and Zhengbiao⁵⁰ also studied the effect of extrusion and drum drying on the morphology of pre-gelatinized starch molecules by scanning electron microscopy (SEM). Granules of pre-gelatinized starch made by extrusion technology showed irregular stones, shapes and holes under 300× magnification (Fig. 5). In contrast, the pregelatinized starch granules formed through the drum drying process showed an irregular laminar structure, while entirely losing the common granular shape (Fig. 6). This is attributable to the higher temperature during the development of pre-gelatinized starch. During the process, degradation of starch occurs and the intermolecular hydrogen bonds are broken by high temperature, which can gelatinize the starch and also destroy its crystallinity.

Taro starch was adopted for dry heating with carboxymethyl cellulose and sodium alginate. It was then analysed in comparison with potato and sweet potato, and showed remarkable features of high solubility, least transmittance, color diffraction and swelling intensity as ruptured starch granules.⁵¹ Banana starch exhibits 50% high water binding properties on treatment with hydroxyl-propyl on exposure to an elevated gelatinization temperature of 90 °C.⁵²

2.1.2.2 Hydro-thermal methods. Hydro-thermal processing is a method that alters starch, while preserving the intact grain structure. This method involves maintaining the starch molecules in a mobile state above the glass transition temperature (T_g) and below the gelatinization temperature (T_{gel}).⁵³ Annealing and heat moisture temperature are examples of hydrothermal treatment. Annealing is a hydrothermal treatment of starch granules in the presence of heat and water (40–76% w/w) between the temperature of commencement of gelatinization

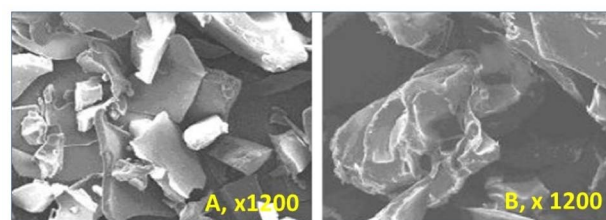


Fig. 6 SEM illustration showing the pre-gelatinized starch from drum drying.

and the glass transition temperature.^{54,55} The parameters that are required for annealing to occur are moisture content, time, and temperature. Changes in these conditions alter the scope of treatment. Other properties of modified starch are reduced solubility, retrogradation, increased enzymatic hydrolysis and crystallinity. Heat-moisture treatment is a combination of heat and moisture treatment that changes the physicochemical attributes of starch. This processing method is comparable to annealing, except it is done at low moisture (<35% w/w), usually between 15 minutes and 16 hours, and at 80–140 °C. Heat-moisture treatment modifies the physicochemical properties without destroying the granular structure of starch.⁵⁴ It also improves the weak functional property of native starch, which contributes to a variety of applications in food industries.

The hydrothermal methods of starch modification show a wide range of effects on the functional properties. Hoover⁵⁵ reported that the swelling property of starch granules was reduced due to heat-moisture treatment. Chung *et al.*⁵⁶ studied the modification of pea, lentil, and navy bean starch by heat-moisture treatment, annealing, and dual modification (heat moisture-treated starch subjected to annealing) & (annealing subjected to heat-moisture treatment). The study showed that both swelling power and amylose leaching of native, annealed, heat-moisture treated and dual-modified pea, lentil and navy bean starch were in the order of pea > lentil > navy bean. The heat moisture treatment decreases the swelling and amylose leaching of starch. In addition, the heat-moisture treated starch subjected to annealing displayed the lowest swelling and amylose leaching. According to a study done by Adebawale *et al.*,⁵⁷ the swelling power and solubility of Bambara groundnut starch were reduced by both heat-moisture treatment and

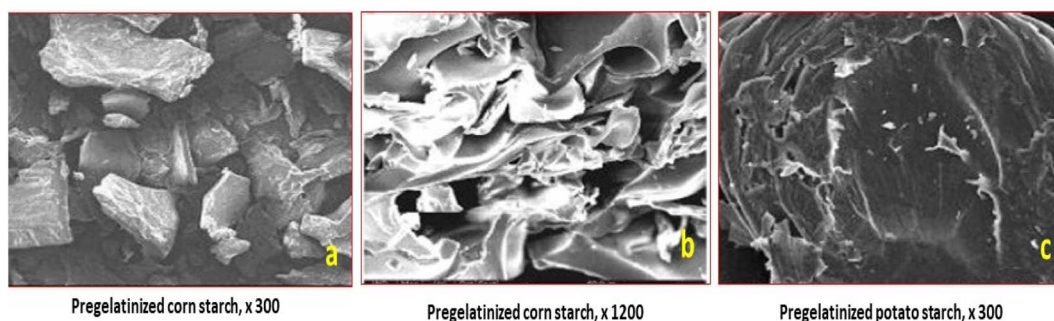


Fig. 5 SEM illustration showing the pre-gelatinized starch from extrusion.



annealing treatment. A study by Simsek *et al.*⁵⁸ exhibited improvement in the swelling power of black bean starch and pinto bean starch upon annealing treatment.

Regarding the effect of hydrothermal treatment on the gelatinization temperature, it is reported that the enthalpy of gelatinization either remains unchanged or decreases with heat-moisture treatment.⁵⁵ Simsek *et al.*⁵⁸ reported a decrease in the gelatinization temperature range and an increase in the transition temperatures (onset, peak and conclusion temperature) of black bean and pinto bean starches. Annealing also increases gelatinization enthalpy of black bean and pinto bean starches as compared to their native forms. Güzel *et al.*⁵⁹ reported a significant increase in the transition temperatures of borlotti bean, white kidney bean, and chickpea on heat-moisture treatment. A significant decrease in gelatinization enthalpy was observed in white kidney bean, yet there was no significant decrease in chickpea and borlotti bean. Legumes, on its exposure through physical modification means (heat-moisture treatment), undergo a significant increase in resistant starch proportion.⁶⁰

The pasting property of starch is greatly influenced by hydrothermal treatment. With an increase in pasting temperature and thermal stability, a decrease in peak viscosity and either decrease or increase in the setback of starches were reported.⁵⁵ Likewise, Adebawale *et al.*⁵⁷ also stated that the pasting temperature on Bambara groundnut starch increases on heat moisture treatment, whereas annealing has no significant impact on the pasting temperature. The peak viscosity of Bambara groundnut starch is reduced by hydro-thermal treatment. According to Simsek *et al.*,⁵⁸ annealing treatment of black

bean and pinto bean starch results in lowering the peak viscosity, hot paste viscosity, cold paste viscosity, breakdown and setback. Meanwhile, annealing of bean starch shows an increase in the pasting temperature.

2.2 Chemical processes for modification of starches

The chemical modification of starch involves the transformation of starch, which is usually attained by introducing or blocking a functional group through the processes of etherification, oxidation, esterification, crosslinking, succinylation, and acid thinning. Owing to the presence of abundant hydroxyl groups in the starches, several chemical modifications could be carried out. In comparison with other modification methods like genetic engineering and physical methods, the chemical ways of starch modification offer wide possibilities for starch functionalization. Thus, the range of applications are greatly expanded, particularly due to emergent chemical methods.³ The following section describes some of the frequently used chemical modification techniques of starch (Table 2).

2.2.1 Oxidation. Commercial preparation of oxidized starch includes a reaction between native starch and a specific oxidant under controlled conditions, and results in the introduction of carbonyl and carboxyl groups. The hydroxyl groups contained in starch are sequentially oxidized, first to a carbonyl group and then to a carboxyl group.⁶¹⁻⁶³ Oxidation of starch can be done by using different oxidants, such as hydrogen peroxide, peracetic acid, sodium hypochlorite, potassium permanganate, ozone, nitrogen dioxide, and chromic acid.⁶¹ The level of starch oxidized can be determined by the carboxyl and carbonyl

Table 2 Recent studies on the chemical modification of starch

S. no.	Modification type	Raw material	Key findings	Reference
1	Starch modification by esterification and acid alcohol	Rice bean (<i>Vigna umbellata</i>) starch	Alterations in the physicochemical, pasting, particle size, and morphological action of rice bean starch Lowering of the amylose content of rice bean starch and swelling power	Thakur <i>et al.</i> (2021) ⁸¹
2	Starch modification by acetylated distarch adipate	Cassava root starch	Improved water binding activity (89.69%) and solubility (80.33%)	Jankar <i>et al.</i> (2020) ⁸²
3	Met extrusion of alkali-treated starch	High amylose corn starch	Increase in NaOH-treated starch elongation at break Improved tensile strength (10.03 MPa) and thickness (0.229 mm) were observed at 2% NaOH treatment	Qian <i>et al.</i> (2019) ⁴¹
4	Esterification (acetylation) & process Etherification (carboxymethylation) process Succinylation process	African star apple fruit starch	Enhanced oil absorption capacity (2.00%), swelling capacity and solubility Improved water absorption capacity (1.49%), swelling capacity and solubility	Ahmed <i>et al.</i> (2019) ⁸³
5	Succinylation process	White sorghum (<i>Sorghum bicolor</i>) starch	Increased swelling capacity and solubility Succinyl groups led to improved swelling power Lowered rearrangement of leached-out amylose units	Mehboob <i>et al.</i> (2015) ⁶⁹
6	Cross-linking (sodium trimetaphosphate and sodium tripolyphosphate)	Tapioca starch	Enhanced thermal stability of cross-linked starch Better textural and sensory quality of soups	Wongsagonsup <i>et al.</i> (2014) ⁸⁴



content, and the degree of oxidation depends on conditions, such as pH, time of reaction, and the oxidizing agent.⁶³ The oxidizing agents popularly used for the oxidation of starch are sodium hypochlorite and ozone.^{58,63} Starch oxidation usually reduces its swelling capacity, viscosity during pasting, and enthalpy change during gelatinization, while increasing the melting point of the retrograded starch.

Oxidation processes have a wide impact on the starch properties. Adebowale *et al.*⁵⁷ oxidized the starch of Bambara groundnut (*Voandzeia subterranean*) and reported an increase in water absorption. The water absorption capacity of the native starch form was $2.00 \pm 0.10 \text{ g g}^{-1}$, but the oxidized starch showed a water absorption capacity of $2.40 \pm 0.01 \text{ g g}^{-1}$. Ogungbenle *et al.*⁶⁴ reported that the percentage of water-binding capacity of native starch obtained from pumpkin seeds, white melons, yellow seeds, benni seeds, and bulma cotton seeds were 85, 81, 78, 83, and 80, which when oxidized changed to 96, 94, 92, 90 and 89, respectively. Likewise, Lawal and Adebowale⁶⁵ also reported on similar results of oxidation on jack bean starch. They concluded that the water absorption capacity of modified starch is much higher than that of the native jack bean starch, and the oxidized jack bean starch showed the highest water absorption capacity. Oladebeye *et al.*⁶⁶ oxidized starches obtain from pigeon pea, lima bean, and jack bean by gaseous ozone. Ozone-oxidized starches exhibited higher swelling power than their native forms. The solubility of pigeon pea and lima bean also increased upon ozonation. However, the jack bean exhibited lower solubility after 15 minutes of ozone-generation time.

In the previous research, it has been shown that the oxidation of jack bean starch improves the oil absorption capacity. Modified starch shows a much higher oil absorption capacity than native jack bean starch, and oxidized jack bean starch shows the highest oil absorption capacity compared to other starches.⁶⁵ Comparable findings were reported for Bambara groundnut starch by Adebowale *et al.*⁵⁷ Bambara native starch has 1.76 ± 0.10 oil absorption capacity, which on oxidation shifted to the higher value of 3.04 ± 0.18 .

Enthalpy of gelatinization decreases on oxidation of starch. In a study, it was observed that the native jack bean starch exhibited a gelatinization value of 0.75 J g^{-1} , which on oxidation decreased to 0.4 J g^{-1} .⁶⁵ A study by Wojcicchowski *et al.*⁶³ found that the enthalpy of gelatinization of oxidized common bean starch is lower than its native form, and the values of onset temperature and mid-point temperature do not change. According to Adebowale *et al.*,⁵⁷ the oxidation of starch lowers the gelatinization temperature. Oladebeye *et al.*⁶⁶ reported that the highest onset temperature at 5 minutes of ozone generation in lima bean was $76.61 \pm 0.06 \text{ }^\circ\text{C}$, and that for jack bean was $77.22 \pm 0.02 \text{ }^\circ\text{C}$. However, it was found that pigeon pea starch had no change in onset temperature. Lima starch also showed a slight difference in conclusion temperature.

Pasting temperature, peak viscosity, hot paste viscosity, and cold paste viscosity of native Bambara groundnut (*Voandzeia subterranean*) starch were reported to be higher than its oxidized form. Moreover, oxidized Bambara starch showed higher stability and lower setback than native Bambara starch. It was

also revealed in previous literature that the setback viscosity decreases on oxidation.⁵⁷ In contrast to the Bambara starch, the oxidized common bean starch showed higher peak viscosity, hardness, and adhesiveness than the native starch form.⁶³ A study by Lawal and Adebowale⁶⁵ showed that the pasting temperature, peak viscosity, hot paste viscosity, viscosity after 30 min of holding, and cold paste viscosity of jack bean starch decreased by oxidation. Oladebeye *et al.*⁶⁶ reported an upsurge in the pasting properties, such as peak viscosity, cold paste viscosity, and hot paste viscosity of pigeon pea, lima bean and jack bean upon ozonation. With an increase in ozone generation time, the setback viscosity decreased. However, in the case of jack bean at 5 minutes of ozone generation time, the setback viscosity initially increases, but then decreases on further ozone generation time.

Swelling capacity and solubility of starches are usually associated with temperature. The swelling power of all native and oxidized starches increases with an increase in temperature. On oxidation, the swelling power of Bambara groundnut starch decreases and has values lower than its native form. The swelling power of native Bambara groundnut starch at $65 \text{ }^\circ\text{C}$ was 138.50%. On further heating at $75 \text{ }^\circ\text{C}$, $85 \text{ }^\circ\text{C}$, and $95 \text{ }^\circ\text{C}$, it increases to 249.30%, 456.90%, and 498.70%, respectively. The swelling power of oxidized starch at temperatures of $65 \text{ }^\circ\text{C}$, $75 \text{ }^\circ\text{C}$, $85 \text{ }^\circ\text{C}$, and $95 \text{ }^\circ\text{C}$ was in the order of 126.30%, 210.30%, 390.90%, and 452.90%, respectively.⁵⁷ Likewise, Vanier *et al.*⁶² reported that upon oxidation, the swelling power of starch granules decreases and the solubility increases. Wojcicchowski *et al.*⁶³ reported that common bean starch has the maximum swelling power at $90 \text{ }^\circ\text{C}$. In a comparison of native and modified common bean starch, dual-modified (oxidized-acetylated) starch showed superior swelling properties over oxidized and native starch. Modified starches have more stability terms, and are known for their high water and oil binding capacities. Native starch and oxidized starch reveal high (26.02 ± 0.04) and low (15.46 ± 0.12)% syneresis, respectively thus able to produce more stable starches.⁶⁷

Regarding the solubility of starch, it is well known that heating leads to an increase in the solubility of Bambara groundnut starch. The oxidized starch has the highest solubility percentage as compared to other acetylated and modified starches. Studies also showed that hypochlorite oxidation increases solubility by weakening the internal structure of starch granules. According to Adebowale *et al.*,⁵⁷ the solubility of oxidized starch is more than that of the native starch. Following the order, the percent solubilities of oxidized and native forms at $65 \text{ }^\circ\text{C}$ are 2.90% and 2.70%, respectively. Bambara oxidized starch shows the highest solubility of 16.70% at $95 \text{ }^\circ\text{C}$. Wojcicchowski *et al.*⁶³ reported that the solubility of oxidized common bean (*Phaseolus vulgaris* L.) starch is greater than that of the native forms. The low solubility value of native starch could be due to its gelatinization, which starts at a temperature near $70 \text{ }^\circ\text{C}$.

2.2.2 Acetylation. Acetylation involves the reaction of starch with acetic anhydride and vinyl acetate, and could be done in the presence of an alkaline catalyst (sodium hydroxide), water or organic solvent.⁶⁴ The amylose content increases steadily with an increase in the degree of substitution of the



hydroxyl group of sugar with the acetyl group. The high amylose content of acetylated modified starch may induce a beneficial effect on human health, such as reduction of glycemic load and insulin impact, owing to the fact that amylose gets digested more slowly.⁶⁸ The United States Food and Drug Administration has authorized a 0.2 substitution level of acetylated starch for applications in the food and pharmaceutical sector. These acetylated starches act as a thickener, binder, stabilizer, texturizer, and film-forming agent. Meanwhile, acetylated starches are used in baked foods, sauces, frozen items, salads, baby food products, and other products.⁸

Acetylation influences the functional properties of native starch. With the acetylation process, the water absorption capacity of starch also increases. Since the native starch granules are closely interrelated, they have lower water-binding capacity. By the process of acetylation, the acetyl groups are introduced. This may reduce the compactness of the starch polymer, provide steric hindrance, facilitate access of water to the amorphous domain, and increase the water absorption capacity. According to Olagunju *et al.*,⁶⁸ the water absorption capacity of native pigeon pea starch was 1.13 mL g⁻¹, which increased to 1.93 mL g⁻¹ on acetylation. Similarly, Adebowale *et al.*⁵⁷ reported a water absorption capacity of 2.10 g g⁻¹ in the acetylated Bambara groundnut (*Voandzeia subterranean*) starch. Ogungbenle *et al.*⁶⁴ reported that the percent water-binding capacities of native gourd seed, white melon, yellow seed, benniseed starch, and bulma cotton seed were 85, 81, 78, 83, and 80, which increased to 95, 91, 90, 88 and 86 on acetylation, respectively. Hence, it is well demonstrated that the acetylation process led to the enhancement in the water absorption capacity. The modified starch enhances the water absorption capacity, which may improve the textural property, thickening property bulking, and gelling properties, and thus contribute to increasing the industrial application of legume starch.⁶⁸

According to Lawal and Adebowale,⁶⁵ acetylation of jack bean starch improves the oil absorption capacity. On a similar note, Adebowale *et al.*⁵⁷ reported an oil absorption capacity of 1.76 ± 0.10 in the native Bambara groundnut starch, which shifted to a higher value of 2.55 ± 0.21 on acetylation.

In the context of gelatinization, the enthalpy of gelatinization (ΔH) decreases on acetylation.⁶⁵ Native jack bean starch exhibited a gelatinization value of 0.75 J g⁻¹, which decreased to 0.56 J g⁻¹ on acetylation. A study by Wojcickowski *et al.*⁶³ stated that in the case of acetylated common bean, the values of ΔH and onset-temperature (T_o) decrease. According to Adebowale *et al.*,⁵⁷ the acetylation process lowers the gelatinization temperature of starches.

The previous research showed that the acetylation process led to a decline in the pasting properties of the starch. Pasting temperature, peak viscosity, hot paste viscosity, and cold paste viscosity of native Bambara starch were observed to be higher than those of its acetylated form. Acetylated common bean starch has the lowest value of breakdown viscosity.⁶³ A study by Lawal and Adebowale⁶⁵ stated that the pasting temperature, the peak viscosity, hot paste viscosity, viscosity after 30 min of holding, and cold paste viscosity decreased upon acetylation of jack bean starch.

Acetylation of starches led to an upsurge in their swelling properties. Acetylated starch has more swelling power as compared to oxidized starch and native starch.^{58,63} An increase in heating also increases the solubility of Bambara groundnut starch. As per the study done by Adebowale *et al.*,⁵⁷ the solubility of starch is in the order of oxidized > native starch > acetylated. Following the order, the percent solubility of oxidized, native, and acetylated forms at 65 °C was 2.90%, 2.70%, and 2.50%. Bambara oxidized starch exhibited the highest solubility of 16.70% at 95 °C, while the acetylated and native form of Bambara starch has a solubility of 12.50% and 14.59%, respectively, at the same temperature. Wojcickowski *et al.*⁶³ observed that in the case of common bean (*Phaseolus vulgaris* L.), the solubility of native and modified starch is in the order of oxidized – acetylated (dual modified) > oxidized > acetylated > native starch.

2.2.3 Succinylation. Succinylation is done by esterification of native starch with succinic anhydride. Starch succinylation takes place under alkaline conditions, resulting in the addition of hydrophilic, negatively charged succinyl groups, which give hydrophilicity to the starch. Therefore, starch succinate delivers a variety of attractive properties, such as greater consistency, improved thickening, lower gelatinization temperature, and improved stability during refrigeration/cold storage.⁶⁹ Succinylation of starches is approved by the United States Food and Drug Administration for use in the food sector with a processing level of 4%. The starch succinates are basically known for their low gelatinization temperature, swelling capacity in cold water, cryogenic stability, outstanding viscosity stability, enhanced clarity of starch paste, low retrogradation effects, as well as their stability for acid/alkali. These properties of starch succinate are an asset for their candidature for several foods or non-food usage. In certain studies, the succinylation process is carried out through octenyl succinic anhydride.⁷⁰ Starches modified with octenyl succinic anhydride are used to stabilize oil or water-based emulsions. The glucose portion of the starch is bound to water and the lipophilic octenyl part is bound to the oil, thus preventing the parting of the oil and water phases. The succinylation process also impacts the physical and functional characteristics of the native starch. The next section presents some changes in starch upon succinylation.

According to research done by Bushra *et al.*,⁷¹ the swelling power of native mung bean starch is enhanced by succinylation and increases continuously as the temperature increases. A decreasing solubility trend was reported with the effect of succinylation upon the increase in temperature. Bushra *et al.*⁷¹ stated that the water absorption capacity of native mung bean starch increases following succinylation. By the introduction of a succinyl group, there is a reduction in the starch retrogradation, which leads to improvement in the water holding capacity and water binding capacity. The oil absorption capacity of native mung bean starch also decreases on succinylation.⁷¹

On succinylation, the transition temperatures (onset, peak and conclusion temperature) of native mung bean starch decrease. Enthalpy of gelatinization also decreases on succinylation of mung bean.⁷¹ Acetylation and succinylation in comparison to their application reformation among taro starch



brings about a decrease in viscosity and increase in viscosity characteristics, respectively.⁷² Octenyl-succinylated anhydride esterification improves emulsifying characteristics, and is suited well to A-type starches provided with the least degree of substitutions.⁷³

2.2.4 Acid thinning. Acid-thinned starch is prepared by treating a concentrated slurry of native starch with an acid, such as hydrochloric acid, nitric acid and sulphuric acid, below the gelatinization temperature for a specific time depending upon the viscosity or degree of conversion.⁶¹ The starches employed for the preparation of gum candies are often treated with hydrochloric acid, and therefore are known as thinned starches. This type of starch is widely utilized in the food, textile, as well as paper industries. During acid hydrolysis, the hydroxonium ion reacts with the oxygen atom of the glycosidic bond and then hydrolyses the bond. Before entering the starch interior, an acid first acts on the surface of the starch granules. Acidic modifications substantially alter the structural and functional effects of starch without affecting its grain morphology.⁸

According to Lawal and Adebawale,⁶⁵ the water absorption capacity of native jack bean starch is reduced by following acid thinning treatment. This may be due to an increase in crystallinity, which probably restricts the entry of water into granules of acid-thinned starch. The study also revealed that the acid thinning of jack bean starch causes a reduction in the oil absorption capacity of native jack bean starch.

In a study, the pasting temperature of native jack bean starch increased, but the peak viscosity, hot paste viscosity, viscosity after 30 min of holding, and cold paste viscosity decreased on acid thinning. The setback value also increases on acid thinning. Citric acid addition among banana starch carry out gelatinized modification in them with enhanced functional attributes hence make their way to consume it as routine meal to reduce body fat and also to favor the healthy microflora count.⁷⁴

2.2.5 Cross-linking. Cross-linked starch is rigid with low swelling power and solubility, and can withstand severe processing conditions without breaking. Sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin (ECH), and phosphoryl chloride (POCl_3) are the commonly used cross-linking agents. During the crosslinking process, the new covalent bonds are introduced with pre-existing hydrogen bonds between the starch particles. Crosslinking leads to improved acid, heat, and mechanical resistance of starch.⁷⁵ Cross-linking of carboxymethyl starches with multifunctional carboxylic acids, for example citric, tartaric, malic, and many more offers a significant swelling capacity, which is helpful in forming stable hydrogels. The strength of cross-linked starches is based on the length of the spacer and the presence of functional groups. Among all, citric acid forms the utmost distinct network structure.⁷⁶

Cross-linking affects the functional properties of the native starch. Cross-linked starch has low solubility because of the reinforcement of the structure starch granules, which limits the mobility of the starch chain in the amorphous region and limits the water absorption capacity.⁶¹ Cross-linking also decreases the water-binding capacity of legume starch.⁶²

A group of researchers studied the cross-linking of the kudzu starch (a vine of the leguminous plant) by treating it with sodium tri-metaphosphate at varying time, temperature, and concentration, where the swelling capacity and solubility of the modified starch decrease as the degree of cross-linking increases compared to the native form. A reduction in the swelling property of starch may occur due to structural rearrangement of amylose and amylopectin, and a decrease in solubility may be due to the fact that the cross-linking bonds are stronger than the hydrogen bonds. As a result, the granules of starch become hard to dissolve.⁷⁷ Likewise, Sharma *et al.*⁷⁵ also mentioned a decrease in both swelling capacity and solubility on crosslinking of faba bean starch by STMP, while the swelling capacity and solubility decrease progressively with an increase in cross-linking. According to Güzel *et al.*⁵⁹ there is a decrease in the swelling power, but an increase in the solubility of borlotti bean, white kidney bean, and chickpea starch upon cross-linking.

Cross-linking of starch leads to an increase in the starch transition temperatures (onset, peak, and conclusion temperature) and enthalpy of gelatinization.⁷⁵ On a similar note, Güzel *et al.*⁵⁹ reported a significant upsurge in the onset gelatinization temperature of borlotti bean, chickpea bean, and white kidney bean on STMP cross-linking. Peak and conclusion temperature also increase on crosslinking, but the gelatinization enthalpy of all three starches decreases on cross-linking. With the addition of STMP, the retrogradation property of cross-linked starch increases. Native kudzu starch was reported to take 48 h for its maximum retrogradation, while modified kudzu starch takes 12 h to reach the maximum.⁷⁷

In a recent study, it was reported that the cross-linked kudzu starch has high freeze-thaw stability and a lower syneresis rate.⁷⁷ It was also stated that the cross-linked starch with the addition of STMP (12%) at a reaction temperature of 55 °C could be frozen and thawed three times.

Peak viscosity and breakdown viscosity of faba bean starch decrease on cross-linking treatment. Studies have reported that with an increasing degree of crosslinking treatment, the peak viscosity decreases. However, the final viscosity and setback of native starch increased at lower levels of crosslinking, while the starch shrinkage of native faba bean starch decreased as the degree of crosslinking increased from 1% STMP. An increase in pasting temperature is observed as the level of cross-linking increases.⁷⁵

3 Conclusion

Starch is one of the vital yet versatile food ingredients, possessing value-added properties for a multitude of industrial usages both in food and non-food sectors. Innovative functional and value-added properties boosted among modified starches. Modified achievements in starch through thermal application induce transition characteristics from amorphous to crystalline, resulting in its gelatinization. Etherification, oxidation, esterification, crosslinking, succinylation and acid thinning are the processes involving the introduction or blocking of functional groups under chemically driven modification. Furthermore, physical modification of starch carries out changes in the



properties of starch resulting from physical processing. Pregelatinization, annealing and heat moisture temperature treatments are some conventional physical treatments, while some non-conventional treatments, *viz.*, high hydrostatic pressure (HHP) processing, microwave processing, pulsed electric field (PEF) processing, and cold plasma technology provide environmentally friendly alternatives to the starch modification. These green technologies can produce starch with broadened properties that are useful in food and non-food fields. The present review summarizes the physical and chemical techniques adopted on starch isolated from various sources, and revealed significant variations in properties that benefit society. However, these novel physical approaches that carry out starch alterations in turn possess broad application traits. These highlighted practices even demand much more exploration in terms of the optimization of the process parameters, revealing more sources for starch, and application extension to pharmaceuticals and textiles. To some other miscellaneous fields, they still demand more research studies in the same direction.

Conflicts of interest

There are no conflicts to declare.

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