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Application of Starch and Starch-Based Products in Food Industry

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Abstract: Starch is an edible polymer derived from plant basis. It is commonly used in food industry as it offers good stabilising effect. Moreover, starch can be easily modified either physically or chemically making it a very versatile source. For instance, its capability to be easily modified and coming from low cost source making starch as one of the most important ingredient in food preparation. There are currently varieties of commercially modified starch available in Malaysian market. For example, potato, corn, wheat and tapioca starch are presently on the top list. However, there are also numbers of unexplored native starch for example from fruits processing waste. Besides, these fruit by-products are considered as underutilised source of starch. Although there are few existing reported studies on starch extracted from fruits seed and other waste products, more new sources are believed to be explored in future according to particular starch-based products industries and demands. Therefore, this review discusses current starch based-products developments and application of unconventional starch in food industry.

Keyword: Food Industry; Modified Starch; Physicochemical Properties; Starch; Waste.

1. Starch

Starch, which is the most plentiful carbohydrate stored in a plant acts as the key factor in determining quality of food products [1]. Moreover, it is one of the most important polymers that has been extensively used daily in both food and non-food application [2]. It is normally derived from natural source of polymer, available in abundance, low cost and usually consumable and edible by animal or any living creature [3]. According to [4], various functions of most studied biopolymers which are starch basically due to its easily available. Koko Krunch is an example of Malaysian most common consumed cereal grains by kids or even adults in conjunction with a study reported that the main source of energy is coming from starch present in cereal grains [5]. Moreover, it comes from a variety of source worldwide such as barley, corn, potato, wheat, tapioca and rice [6].

Corn, potato, rice, tapioca and wheat are the main available source of commercially produced starches in the market [7]. These five starches have been categorised as gluten-free starch which suits well for people with allergen towards gluten [8]. Hence, making starch as a major raw material for food industrial purpose. A brief explanation on several selected types of food crops including barley, corn, wheat, potato, rice and tapioca containing starch will be described in the following paragraphs.

Barley (*Hordeum vulgare* L.) is a good source of gluten-free flour producing bread with a more compact texture as compared to bread made up of wheat flour containing gluten [9]. Furthermore, malt and beer production is depending on barley produced as its main raw material, while it is also used for animal feed [10]. Livestock energy, human gut health and fermentable sugars in brewing are depending on the degraded functional properties of barley [11]. It has been found by previous study that by substituting wheat with barley bran, capability of dough water absorption was increased up to 71.5% in chapatti production [12].

There are differences between a normal and naked barley or known as hull-less barley which commonly consumed by Tibetan people in Tibetan Plateau. Naked barley easily had undergone threshing process. Threshing is known as a process of separating seeds from its husks or hulls [13]. During retrogradation, barley containing longer chains of amylopectin performs more perfect crystals and a higher peak temperature (Tp) achieved when it has been analysed by using differential scanning

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calorimetry (DSC) [14]. Thus, it supports claim made by recent study that barley is currently on number four of most consumed cereal crop worldwide [15].

Corn starch is as important as any other starch in industrial use. Starch isolated from corn was fused into many baked goods such as cookies, cakes, icings and fillings due to its ability in maintaining moisture content, prevent growth of crystal from sugars and enhanced juiciness [16]. Corn starch also provides consistency and good gelling properties during heating of corn-banana custard paste [17]. Furthermore, 25% of amylose was reported present in normal corn starch granule [18]. [19] reported that 50% from total starch production has been utilised by food industry. According to [20], costs could be saved and at the same time cow's dairy produced could be maintained by supplying cow with low-corn starch based diets. By partially substituting wheat flour with corn resistant starch, a whiter, less yellowish and reddish cake was produced [21]. Another fun fact of corn is that in industries, it comes in two varieties which is normal corn starch and the other one is waxy corn starch. The composition of amylose and amylopectin varies depending on starch origin. Amylose present in a starch molecule in the range of 20 – 30%. Whereas, highly branched glucose polymer present at about 70% in a starch molecule known as amylopectin. This is specifically for normal starch. However, the situation changes for waxy starch when the composition is 100% amylopectin [22].

Wheat, which is scientifically known as (*Triticum aestivum*) has been the oldest and most consumed crop in various forms of food products worldwide such as cake, cookies and bread due to its promising energy supplies and other good constituents [23]. Baking quality of wheat products such as cookies and bread are depending on the starch molecular structure and its properties [24]. Lipids, protein and starch are main component of wheat flour [25]. Despite of being world's leading food component, high consumption of wheat-based product can result in a negative health impact such as obesity and type 2 diabetes [26]. In Malaysia, bran and wheat germ bread produced by Gardenia brand is an example of how wheat by products have been utilised by food industry which accounted 10% from the cereal waste production. Recent study claimed that the wheat bran has been disposed as animal feedstock despite of its rich-antioxidant properties [27].

Potatoes are produced mostly in a mild climate area whereas harvested products will be collected upon reaching autumn season [28]. Despite of its well played role in food industry, potato starch was also found to function well in paper and textile sizing together with stiffening laundered fabrics [29]. Recent study reported that phosphorous which was found in starch of potato at a peak amount may affect functionality of this particular starch [30]. According to [31], potato starch does not respond well to pressure-induced gelatinization. In general, gelatinization is a process occurring in the presence of water and heat. Even though potato is the most consumed food crop worldwide, it has been labelled as contains a high glycaemic index (GI) due to its ability in causing sharp increase of blood glucose level [32]. Starch produced from tapioca and potato have been extensively applied by both food and non-food industries [33]. Therefore, potato is also crucial in food industry for starch production.

Rice (*Oryza sativa* L.) starch which is made up of majority 70 – 80% of branched amylopectin and 20 – 30% of linear amylose, is normally eaten in the form of cooked rice [34]. In Maluku, Indonesia, rice production per annum can only fulfil about 40% of consumer's demand. Starch presence in rice cause it one of the most utmost food crops consumed in Asian countries like Malaysia, Indonesia and Thailand [35]. Recent study stated that food and non-food industries are enjoying benefits obtained from versatility of rice starches [36]. Different region produced different taste and variety of rice. As an example, there are two most common consumed rice varieties known as Basmathi and Irri in Pakistan. Even in Malaysia, people are common with Basmathi rice type imported from Pakistan due to its promising aroma and quality. This is supported by a recent study, which found that the Basmathi rice is pricier but contains more aromas whereas Irri rice is a way cheaper due to its non-aromatic properties [37]. It can be concluded that rice is staple food for Southeast region.

Tapioca (*Manihot esculenta* Crantz) has been processed into sago and starch which could be found abundantly in Tamil Nadu, India [38]. Besides, it is a good source of starch in forming soft and transparent gel despite of its low protein content [39]. Sour starch produced from cassava starch can be used in bread-making and pastry production or as an alternative for gluten-free bread [40]. This is consistent with previous research, which claimed that rice, potato and tapioca starch as the most leading used starches in the production of many gluten-free products in terms of texture characteristics [41]. Recent study stated that tapioca can grow well in low rainfall areas and barren soil thus making it an attractive source of starch [42]. In many food products, thickening and gelling properties were supplied by tapioca starch [43]. There are few benefits of tapioca starch for example contains no smell, clarity of paste and stickiness which is favourable in food industry [44]. Therefore, tapioca or cassava is also as essential as other source of food crops.

Starch is actually an insoluble carbohydrate, which composed of α-glucose polymers [45]. There are two most essential components present in starch compound which are amylose and amylopectin. These two major polysaccharides present in starch supports the characteristics of biodegradable and thermoplastic polymer [46]. In a chain of glucose polymers, there are bonds that joining them, which are α-1,4- and α-1,6-glycosidic linkages [47]. According to [11], it is way much easier to hydrolyse starches with α-1,4-glycosidic bonds than α-1,6-glycosidic bonds. Amylase is the most important enzyme in catalysing α-1,4-glycosidic bonds in a starch polymer [48].

Low molecular weight with several long branches belongs to amylose, whereas a vast number of short branches and highly branched polymers belong to amylopectin [49]. Moreover, within the starch granule, amylose and amylopectin are found in the form of water soluble lamellae and semi-crystalline structure [50]. Normally in starch harvested products, amylose was found to be 20 – 30%, while amylopectin 70 – 80% and this amylose to amylopectin ratio are crucial in determining each different starch physicochemical properties [51].

Biological genetics backgrounds of a starch source have a great influence in amylose and amylopectin ratio [52]. Starch derived from carbohydrates has a wide range of functions in variety of food products [53]. In addition, many different industries have utilised the goodness of starch functions and not only applicable in food industry such as in cosmetics, textile, paper and pharmaceutical industry [54]. On the other hand, cooking, processing, organoleptic capabilities and starchy food digestibility are all influenced by amylose to amylopectin ratio [55]. In a recent study reported that when comparing between amylose-rich starch and amylopectin-rich starch in terms of expanding in size, amylopectin-rich starch did way better [56]. Therefore, starch structural and functional properties depend solely on content and structure of amylose and amylopectin [57]. Table 1 [58] elaborates amylose and amylopectin in starch.

Table 1 Amylose and amylopectin in starch. [58]

Amylose	Amylopectin
Linear polymer	Branched polymer
α-1,4-glycosidic linkages	α-1,4- and α-1,6-glycosidic linkages

Photosynthesis plays important roles in synthesising glucose molecules in plant cells. Higher photosynthetic rate produces greater yield productions. Starch is carbohydrate end product obtained from plants when they perform photosynthesis and each plant have different starch distribution amount depending on its species [59]. On the other hand, fruits are undeniably containing all the goodness of antioxidants and helps in maintaining one’s health and weight management. Nutritionist and dietician will always advise a client under their consultation to consume more fruits due to its promising health benefits. However, recent study on several commonly consumed tropical fruits in Nigeria claimed that for people with type 2 diabetes may not suggested to have high intake of fruits due to starch presence in that particular fruit [60].

Starch will be less functional if it is in its native conditions despite of its sources and origins. This is supported by previous study, which stated few disadvantages of native starch such as sensitive towards pH, low clarity of starch paste, high retrogradation, low in syneresis and decomposition [61]. Besides, starch presence in banana is good for human’s blood glucose control as resistant starch in banana preventing one’s blood glucose level to have rapid increase. However, if banana starch applied in industry requiring this particular starch to swell properly, forming gel and hold moisture, it will not be able to do so in its raw conditions and yet modification still in need fulfilling such demands [62]. Therefore, next section will be discussing on application of starch in food industry and modification of starch.

2. Application of Starch

Starch is the main source of energy in the human diet. Due to its practicality in diverse application of food products, starch is gaining biggest attention as compared to other carbohydrate polymers [63]. Breakfast cereals, bread, cookies, pasta, pastries and noodles are among commonly processed cereal grains [64]. These are among the most common starch containing products available in Malaysia. On the other hand, appearance, grade and shape of foods depending on starch viscosity attributes, retrogradation and pasting elements making starch as the main functional components in food products [65]. Ability of starch in nature to react with itself or other compounds leads to several usage in food systems such as thickener, gelling agent, stabilizing agent or as filler [66].

Normally, it can be found in the plants, where carbohydrate store starch in the amplest amount. According to the Malaysian Food Pyramid, as prescribed by Ministry of Health Malaysia, the base part of the pyramid is made up of carbohydrate food sources such as bread, cereals, and rice [67]. Therefore, starches based food products provide 50 – 55% of the total daily energy of a human being. Moreover, starch is also significant in providing energy for animal feed and feedstock. In the food industry, starch is an essential food additive due to its gel-forming ability, thickening agent and stabilising food products [68, 69]. A study was done to help people with dysphagia, which is difficulty in swallowing starch-based products, by modifying food consistency using sago and tapioca starch that acts as thickener [70]. Different starches source fulfilling various industrial demands. As an example, sago starch is great in terms of elasticity, softness, flexible to use and less adhesive [71]. As compared to tapioca starch that has a very cohesive texture despite of its better cold stability [72].

On the other hand, native starch extracted from tapioca may be potentially applied as a new thickener for fruit fillings [73]. According to [74], food industries consider well on physical, chemical, physicochemical, pasting and thermal properties of tapioca flour and starch. The versatility of starch is not only applicable to the food industry, but also in pharmaceutical use. Starch extracted from water chestnut fruits and pine tree seed or also known as pinhão were tested for their ability to act as excipients or drug delivery [75, 76]. Other than that, starch is crucial in edible film production. For example, rice husk fibre starch was used to produce film [77]. In another case where modified corn starch films were used to coat Red Crimson grapes making longer-lasting of products freshness [78]. On the other hand, starch also provides substitution towards Malaysian oil and gas sector. According to a study reported by [79], bioethanol extracted from Sri Kanji 1 cassava starch is way much cheaper as compared to gasoline fuel. Starch also helps in enhancing paper coating industry [80, 81]. Thus, starch is necessary for food, pharmaceutical, edible film, bioethanol products and paper coating industry.

Table 2 shows commercially available starch and its functions reported by previous studies between 2012 and 2017. Corn, wheat, potato, tapioca/cassava and rice are among the most commonly starch available in the market. Normally starches are added for enhancing quality of products in food industries. For example, corn starch helps in increasing fibre content in cake productions [82]. It also helps in reducing sponge cake texture as compared to wheat flour [83]. [84] reported that corn has been extensively used for syrup production especially high fructose corn syrup for industrial needs. Corn is also a good source of starch for thickening agent in infant formula [85].

Wheat starch, on the other hand, has been used in breadfruit cookies formulation [86]. It was also found to supply gelling properties to food products [87]. Potato starch was found to act as a good pasting and gelling agent at the same time [88]. Potato starch film was also found be able to be produced from potato starch [89]. Tapioca/cassava starch was reported in a previous study to help in risen up the quality of jasmine rice bread gluten-free quality [90]. Besides, tapioca starch is also a good thickening agent in fruit filling production such as blueberry filling in a blueberry cheesecake [91]. In addition, it was also found to increase the quality of soup production [92]. Last but not least, rice starch acts as an emulsion stabiliser [93] and able to improve gelling properties when added with hydrocolloids such as sodium carboxymethylcellulose (CMC) and hydroxyl-propyl methylcellulose (HPMC) [94].

Table 2 Commercially available starch and functions.

Starch source	Function
Corn	Increased fibre content in cake production [82]. Reduce sponge cake texture as compared to wheat flour [83]. Corn syrup production [84]. Thickener in infant formula [85].
Wheat	Breadfruit cookies formulation [86]. Gelling properties [87].
Potato	Pasting and gelling properties [88]. Production of potato starch film [89].
Tapioca/ Cassava	Increased quality gluten-free jasmine rice bread [90]. Thickener in fruit filling [91]. Enhancing soup product [92].
Rice	Emulsion stabiliser [93]. Improved gel properties with the addition of hydrocolloids [94].

Recent study reported that the knowledge of pasting properties in starch-based products is important in order to get required consistency [95]. Viscosity, gelling, digestibility and stability of frozen storage of heated starch suspensions were all depending on the starch chemical and structural characteristics together with different origins and botanical source [96]. Starch is the most important edible polysaccharide containing nutritionally high to low molecular weight sugars [97]. Food industry uses starch as a thickening, bulking agent, gelling and for water holding capacity making it as a treasured factor [98]. Recent study documented that fully digested starch in small intestine is known as digestible starch, the incompletely digested starch in small intestine is known as partially digested starch, while starch that totally forbids digestion in small intestine is known as resistant starch [99]. Table 3 shows a list of underutilised starch and its functions documented by previous studies. Underutilised source of plants remain undiscovered despite of its contribution to rising of world's food production [100].

Food industry favours starch which is stable, white in colour and odourless thus making (*Araucaria angustifolia*) seed as a perfect candidate by having 34% starch [101]. Recent study claimed that it is crucial to explore new and underutilised starch as it offers multiple functions in food and non-food industry [102]. Hairless Canary Seed (*Phalaris Canariensis* L.) and jackfruit seed were reported to act as a good gel stabiliser [103, 104]. Quinoa, on the other hand, is extremely stable and widely used in food grade pickering emulsion stabiliser specifically in (particle-stabilised emulsion) [105]. Carob is an excellent source for making gluten-free bread which suits people that are gluten intolerance [106]. Sweet potato, on the other hand, has been widely used in Chinese starch industry [107]. Another example is Chestnut (*Castanea sativa* Mill) which was claimed to have the same function as corn starch but when extracted by using low processing temperature [108]. Pinhão helps in β-carotene microencapsulation [109]. Jackfruit which is common to Southeast Asia and India was found to have seeds that able in increasing quality of chocolate aroma produced [110] and for encapsulation process of rice bran oil [111].

In addition, seeds of these *Artocarpus* genus were reported to function well in gelatinisation properties [112]. Flour was also one of the most common thing that can be obtained from jackfruit seed [113]. Thus, the jackfruit seed flour has ability of producing reduced calorie chocolate cake [113]. *Mangifera Indica* kernel, on the other hand, was documented in two previous studies to function well as a coating agent. In the first study, it was found to coat the almond kernel [114]. Starch extracted from mango seeds shows a superficial amount of starch which can be utilised in industry needing starch [114]. In the second study has reported that the mango kernel starch could help in retaining a longer shelf life of a tomato (*Solanum lycopersicum*) fruit [115]. From industrial by-products, mango kernel can be easily obtained and produced at low cost [116].

Besides that, soursop (*Anona muricata*) starch extracted from its white fleshy flesh has been used in bread production [117]. Tikhur (*Curcuma angustifolia*) was found to be able in having properties as tapioca sago starch [118], while moth bean (*Vigna Aconotifolia*) was claimed to be having good quality for food products requiring high thermal stability [119]. On the other hand, tamarind or in Malaysia is widely known as 'asam jawa' was reported by recent study that it contains high swelling power when tested in the range of 55 to 95 °C [120]. The unripe banana was found to have high ability in forming pasting properties [121]. Whereas, in another study comparing cooking banana and dessert banana, both have claimed to own potential in acting as an emulsifying agent [122]. Recent study stated that pea (*Pea sativum*) and *Bambara* groundnut (*Vigna subterranea*) is an underutilised food crops in Nigeria and currently explored of its potential in terms of starch isolation [123]. Lastly, litchi or is also known by Malaysian as lychee can be obtained in fresh form or canned in glucose syrup. Its kernel starch was reported to have good gel strength and elasticity [124]. Starch extracted from underutilised sources has numbers of unexploited applications. Therefore, it is important to do further research on potential source of starch either from indigenous fruits or botanical source, or it could be from industrial processing waste such as fruit peels and seeds.

Table 3 Underutilised starch and functions.

Starch source	Function
Hairless Canary Seed (*Phalaris Canariensis* L.)	Gel stabiliser [103, 104].
Quinoa	Food grade pickering emulsions stabiliser (particle-stabilised emulsions) [105].
Carob	Gluten-free bread production [106].
Sweet potato	Used in Chinese starch industry [107].
Chesnut (*Castanea sativa* Mill)	Substitute to cornstarch - lower processing temperature [108].
Pinhão	Microencapsulation of β- carotene [109].
Jackfruit seed	Chocolate aroma production [110]. Rice bran oil encapsulation [111]. Gelatinisation purposes [112]. Flour production [113]. Production of reduced calorie chocolate cake [113].
Mango kernel	Coating purpose – almonds (*Prunus dulcis*) kernels [114]. Edible coating for enhancing shelf- life of tomato (*Solanum lycopersicum*) fruit [115]. Composite film production [116].
Soursop (*Anona muricata*)	Bread production [117].
Tikhur (*Curcuma angustifolia*)	Mimic properties of Tapioca Sago [118].
Moth bean (*Vigna Aconitifolia*)	For food products requiring high thermal stability [119].
Tamarind (*Tamarindus indica* L.) kernel starch	For food products requiring high swelling power [120].
Banana	For food products requiring high pasting ability [121]. Emulsifying agent [122].
Litchi kernel starch	Good gel strength and elasticity [124].

3. Starch Modification

Starch is found in an ample amount and fall into second place compared to other carbohydrates and by applying some modification it can fit to various industrial demands [125]. Starch has broad applications in food industries. However, starch in native state is unable to attain specific industrial requirement. Thus, modifications can be made either physically or chemically [126]. In order to improve starch pasting properties and shelf life extension, modification of starch by using chemical is the most frequently used method [127]. Processing quality can be improved by altering pasting, gelatinizing and retrogradation properties of starch [128]. Commercialized starch such as corn and other type of cereals are normally underwent physical modification or simple chemical modification to enable them to be used by food or other industry [129]. Starch was modified physically or chemically in order to obtain heat stable or resistance towards heat product, stable during freeze-thaw process and easily dissolve either in hot or cold suspension [130].

One of the most common modification methods by using chemical is crosslinking [131]. Introducing intra and intermolecular bonds in starch molecule at random locations is known as cross-linking [132]. Thermal properties of starch can also be modified by applying cross-linking agent and not only changing physical characteristics however this is all depending on starch plant origin and botanical source [133]. Moreover, starch that has undergone chemical modifications is extensively used in food industry due to its better emulsion and pasting characteristics [134]. Native starch which is modified using acetylation and oxidation may be used as food additives [135]. The disadvantages of using chemical modification are easily causing chemical residue to be left after modifying starch and definitely not an eco-friendly even though it is a fast, simple, extensively used and efficient method [136].

Chemical modification of starch usually involves acid or base at high concentration to destroy hydrogen bond intermolecular interactions and crystallization areas [137]. Hydroxyl group presence in starch may cause chemical reaction by exposing one or more reactive groups on its surface and will be efficiently coupled to matrix [138]. Modifying starch by using ether agents resulted in amphiphilic side chains of product and hydrophobic character of starch modified product was fixed by the length of alkenyl groups [139]. Recent study on using chemically modified starch in replacing fat in yogurt based products, suggested a good effect in syneresis and good flow and better viscoelastic characteristics [140]. However, there are two major disadvantages of utilizing solely pure starch which first is high attraction towards water and second is extreme rigidity [141].

Moreover, chemically modified starch will be susceptible to amylolytic enzymes due to the presence of chemical substituents and additional bonds [142]. Maltodextrin is an example of enzymatically modified starch by using amylolytic enzymes [143]. An adequate amount of starch-stearic acid complexes can be formed by modifying pure starch using few methods such as acetylation, de-branching and using enzyme such as β-amylase [144]. Canned and frozen foods required starch with low viscosity, thus starch modification is crucial in order to get the required viscosity [145]. Modification of starch helps in enhancing industrial application. One of them is pharmaceutical. Modifying corn, cassava and sweet potato using acetylation helps in producing stronger paracetamol which is not easily crumble during transportation and storage until reaching consumer [146].

Table 4 and Table 5 show some of the chemical and physical method for starch modification done by previous studies. Table 4 shows examples of starch that has been chemically modified. According to [147], oxidation produces starch film with the most stable tensile strength. Cross-linking and oxidation of starch isolated from elephant foot yam (*Amorphophallus paeoniifolius*) help in improving paste clarity, solubility and thermal characteristics when tested using DSC without causing any effect on starch granules [148].

Starch with low paste viscosity is suitable for production of edible coatings and biodegradable films [149]. Maleic acid was used to modify jackfruit seed starch in India to produce starch with high solubility because acid tends to break down the amylopectin at 1,6 bonds [150]. On the other hand, ionic gums were used in a study of modifying water chestnut (*Trapa natans*) starch [151].

Table 4 Chemically modified starch.

Starch source	Modification
Lotus rhizome (*Nelumbo nucifera*)	Oxidation and cross-linked [149]
Elephant foot yam (*Amorphophallus paeoniifolius*)	Oxidation and cross-linked [148].
Jackfruit seeds (*Artocarpus heterophyllus* Lam)	Maleic acid [150]
Water chestnut (*Trapa natans*)	Ionic gums [151]
Tapioca	Acetylation [152] Acetylation – acetic anhydride [153] Esterification – Dodecenyl succinic anhydride [154]
Maize	Acetylated (Ac) [156] Cross-linked [157]
Acha (*Digitaria exilis*)	Cross-linked with citric acid [158]
Banana (green/unripe)	Hydrochloric acid [159]
Mango kernel (*Mangifera indica* L.)	Hydrochloric acid [160]
Rice (*Oryza sativa* L.)	Citric acid, lactic acid and acetic acid [161] Acetylation – acetic anhydride [162, 163] Cross linking – citric acid [166]
Sago	Acid hydrolysis and hydroxypropylation [167] Acetylation – acetic anhydride [168] Esterification - Octenyl succinic anhydride (OSA) [169]
Durian (*Durio zibethinus*) seed starch	Acetic acid [170] Cross-linking [171]
Avocado (*Persea americana*, Miller)	Acetic acid [172] Cross-linking [173]
Black eyed pea (*Vigna unguiculata*)	Acid hydrolysis – Concentrated hydrochloric acid (36% by weight) [174]
Carioca beans (*Phaseolus vulgaris* L.; cv. Pérola)	Oxidation – sodium hypochlorite [175]
White Sorghum (*Sorghum bicolor*)	Oxidation – sodium hypochlorite [176] Dual modification – acid hydrolysis and succinylation [177]
Potato (*Solanum tuberosum* L.)	Oxidation – sodium hypochlorite [178] Acetylation and oxidation [179] Oxidation [180] Cross-linked with acetic anhydride [181] Cross-linked with sodium trimetaphosphate (STMP) / sodium tripolyphosphate (STPP) [183]
Barley *(Hordeum vulgare*)	Acetylation – sodium hydroxide (NaOH) and oxidation (active chlorine) [184]
Yellow sorghum	Acetylation, benzylation and hydroxypropylation [185]
Red Zaragoza bean (Phaseoluslunatus) seeds	Acetylation – acetic anhydride [187]
Pinhão (*Araucaria angustifolia*) seeds	Acid hydrolysis – hydrochloric acid [188]
Musa AAB (Poovan banana)	Acetylation [190]

Tapioca starch has been used as an alternative source for products requiring encapsulation as it comes from inexpensive source and in this case it helps to slow down release of crucial bioactive compound such as chlorogenic acid due to its increasing in hydrophobicity after acetylation [152]. Chlorogenic acid (5-caffeoylquinic acid, CGA) was claimed to aid in sliming process and could be found in a plentiful amount present in green coffee beans mainly *Robusta* species [153].

Acetylation is a chemical modification process by introducing acetyl groups in starch chains and this process can be confirmed by Fourier transform infrared spectroscopy (FTIR) [154]. Recent study suggested that by adding acetyl groups to cassava starch, it enables to be part of stabiliser in emulsion and starch gel in frozen food products as it can function well at low temperature [155]. Besides, maize or corn starch was also modified using the same acetylated (Ac) method and cross-linked [156, 157]. Cross-linking of starch was reported in a study on acha (*Digitaria exilis*) starch by introducing citric acid [158].

Modified unripe banana using hydrochloric acid does not show any changes based on its pattern which has been proved by X-ray diffraction and based on its structure by scanning electron micrograph [159]. Structure and shape of starch granule isolated from mango kernel (*Mangifera indica* L.) and has been modified by using acid also do not show any changes [160].

Rice (*Oryza sativa* L.) was previously modified by using three types of organic acids which are lactic, citric and acetic acid. The citric acid has the best result in modifying rice starch as it increases starch solubility [161]. By inserting acetyl groups into native starch, it will cause amylose and amylopectin to reassociate its current order and leads to decreasing in gelatinization temperature. This is where the process will be beneficial to industry when acetylation helps in reducing temperature for starch to gelatinize and will cut industrial processing cost. Acetylation causes starch granules in low-amylose rice starch to breakdown in which producing end products containing relative stability during cooking and sensitive to high temperature [163].

In order to classify starch, there are two common classifications which are waxy and non-waxy starches. Waxy starch is made up of 100% amylopectin with low amylose or either contains no amylose, whereas non-waxy starch has 20 – 30% amylose and 70% amylopectin. Rheological and textural properties of waxy rice products depend on its structure and gelatinization temperature [164]. Previous study comparing two rice starch varieties available in Australia claimed that waxy rice or commonly known as glutinous rice starch loses its original shape when heat is applied due to the presence of air space between the starch granule. Besides, its endosperm is whiter and more opaque when compared with non-glutinous or non-waxy rice [165]. Native rice starch is extensively used as binding agent and thickener in sauce production, puddings, foods for baby and processed meats. However when modified using cross linking agent such as citric acid, result obtained showed a better application of rice starch in food industry as a dietary fibre [166].

By combining acid hydrolysis and hydroxypropylation, modified sago starch are less prone towards retrogradation and even at high concentration it is still able to solubilise in cold water [167]. On the other hand, sago starch in Papua has been modified using acetic anhydride in acetylation process in order to improve its thickening properties [168]. Esterification is one of the modifications listed under chemical modification. Modification of native sago starch using esterification process using octenyl succinic anhydride (OSA) cause it to have potential to be applied as thickener replacing Arabic gum, emulsifier and oil-water emulsion stabilizer [169].

Durian seed starch obtained from night market in Perlis and Kedah, Malaysia was modified by using acetic acid in realising idea of using durian waste in order to be an alternative source of starch replacing current dependence on petroleum-based plastics [170]. Starch extracted from durian seed not only applicable for food industry. Recent study reported that modified starch by cross-linking from durian seed was found to act as a natural flocculant in landfill sector as the modification treatment helps in improving starch interconnection [171].

Modification of starch by using lactic acid shows no changes in structure of avocado seed when analysed by using scanning electron micrograph (SEM) while it causes reduction in thermal stability and crystallinity [172]. In a recent study, modifying avocado seed starch was done by using cross-linking method (*Persea americana* Mill.). Results obtained suggested that starch isolated from avocado seed can be an alternative source towards current available commercial starch source as it helps in improving paste viscosity and stability for cream soup production. In addition, chain of starch is stronger than native starch due to the presence of phosphate group gained during cross-linking process [173].

By applying concentrated hydrochloric acid at 36% by weight, black eyed peas (*Vigna* *unguiculata*) starch was able to be modified successfully when it shows an increment in its solubility, freeze-thaw stability and clarity of paste [174]. Common bean starch was modified by oxidation process using sodium hypochlorite as oxidizing agent. Results obtained proposed that these modified starch might be an alternative source in coating food products and in dairy products. In addition, as the concentration of oxidizing agent increases, starch obtained shows whiter in colour which could be a substitute in paper manufacturing [175].

Previous study suggested that oxidation helps in improving solubility and paste clarity of white sorghum starch and could be an alternative source for food products requiring high solid contents without over-thickening [176]. Reported studies claimed that white sorghum starch modified by combined acid hydrolysis and succinylation resulting in lower paste viscosity, less gumminess and reduced in tendency towards retrogradation which suits in food products requiring these properties for example frozen pie filling, custards and puddings [177].

Several studies have suggested acetylation and oxidation mode of modification makes potato as a potential source of film which can withstand high water activity in its surrounding. First study claimed that oxidation using sodium hypochlorite caused potato starch to have low water solubility as compared to its native starch. This study suggested modified potato starch can be turned into film and use it in a higher water activity environment [178].

Oxidation of potato starch as reported in previous study using oxidizing agent caused hydroxyl group of starch to transform into carboxyl or carbonyl group which could be one of the reason increasing in hydrophobicity of modified potato starch [179]. Second study reported potato starch modified using acetylation shows greater reduction in water vapour absorbing capability as compared to modification using oxidation process [180]. Potato starch properties were reported unable to modify most efficient at temperature of 25°C or lower when using acid hydrolysis [181].

On the other hand, cross-linking suggested different methods of modification in potato starch. Present hydrogen bonds in potato starch will be strengthen during cross-linking using cross-linking agent for example acetic anhydride which in turns resulting in starch product that has high resistant towards heat, acid and increase in shearing properties as compared to native and unmodified starch [182]. Another study reported modifying potato starch using sodium trimetaphosphate (STMP) or sodium tripolyphosphate (STPP) as its cross-linking agent resulted in modified starch having desired properties to be applied in food industry such as binding agent, stabilizer and thickener [183].

Previous study found that by inserting acetyl group through acetylation and addition of carbonyl and carboxyl group by oxidation makes barley starch decreasing in its viscosity and in turns reducing possibility to retrograde which could be a potential source in making biodegradable films [184]. Yellow sorghum starch was subjected to acetylation, benzylation and hydroxypropylation resulting in food product having low tendency towards retrogradation which could be a good alternative source in sauces and bread production [185].

During heating of starch in excess availability of water, starch takes up water and swelling occur inside the granule. In this condition, amylose and amylopectin disappear. This is called as gelatinization process. When heating stops, amylose starts to form back and in a longer term amylopectin will follow the same condition. This is known as retrogradation [186]. Increasing degree of acetylation in zaragoza (P*haseoluslunatus*) bean seeds starch obtained from Colombia resulting in a good alternative source in cream manufacturing due to high viscosity level [187].

Modification of pinhão seed starch using hydrochloric acid shows end result having better solubility and more transparent which could be an alternative source in coating materials or film [188]. What is actually happening during hydrolysis of acid is acid for example hydrochloric acid was added to the suspension of starch in aqueous condition and controlled at certain desired temperature below gelatinization temperature for a fixed period of time [189]. Results obtained from this study reported that pasting properties of poovan banana from India rises after acetylation process compared to its native form [190].

Table 5 shows several examples on physically modified starch. Altering starch granules and molecular structure is practiced in physical modification of starch in order to obtain a stabilize starch granules, decreasing in retrogradation and enhancing in paste and gel properties when in use [191].

Table 5 Physically modified starch

Starch source	Modification
Corn	Ultrasound treatment [211] Heat moisture treatment [212]
Pinhão (*Araucaria angustifolia*) seeds	Annealing, heat-moisture, sonication [214] Ultrasound treatment [215] Heat moisture treatment [217]
Potato	Ultrasonic treatment [218, 219, 220] Annealing and ultra - high pressure (UHP) [221]
Rice	Annealing [222] Heat-moisture treatment [223] Improved Extrusion Cooking Technology (IECT) [224] Parboiling – steeping step [225] Ultrasound treatment [226]
Sweet Potato	Annealing [227] Heat-moisture treatment [239] Repeated heat moisture treatment (RHMT) [228] Steam explosion [229]
Wheat	Annealing and ultra - high pressure (UHP) [230] Ultrasound treatment [231]
Yam (*Dioscorea spp*.)	Annealing [229] Annealing and ultra - high pressure (UHP) [229] Heat moisture treatment [232]
Jackfruit seed	Microwave [233] Partial gelatinization [234]
Foxtail millet	Heat moisture treatment [235] Ultrasound treatment (UT) [236]
Sago	Heat moisture treatment [238]
Red adzuki beans	Continuous and repetition heat moisture treatment [240]
Taro	Microwave and heat moisture treatment [241]
Water chestnut	Microwave [242]
Acorn	Annealing and heat moisture treatment [243]
Lotus (*Nelumbo nucifera* Gaertn) seed	Microwave [248]
Tapioca	Ball – milling [249]
Bambara groundnut (*Vigna subterranea*)	Annealing [254]
Ensete/False banana (*Ensete ventricosum* Musaceae)	Annealing and heat moisture treatment [255]
Morado banana	Heat moisture treatment [256]
Banana (*Musa sapietum* and *Musa paradisiaca*)	Heat moisture treatment [258]
White Sorghum (*Sorghum bicolor*)	Annealing [259]
Arrowroot (*Marantha arundinacea* L)	Autoclave – cooling treatment [260]

Heat moisture treatment (HMT) helps in improving elasticity of dough made from wheat and barley flour [192]. Besides HMT, ultrasound is another method commonly used to modify starch physically. Recent study reported that ultrasound is gaining recognition due to its various benefits such as low cost, efficient and eco- friendly as no chemical usage involved as compared to other chemical modification method [193]. According to [194], larger bubbles can be formed if lower frequency of ultrasound used and cavitation process that occur during ultrasound causing both covalent and non- covalent bond inside polymer such as starch to be broken down. By applying ultrasound, starch component present in plant polymer can be modified physically [195].

If modifying starch by using either fully or partially gelatinization, it will be able to produce starch with cold water-swelling capacity and gel barrier properties [196]. Rice (*Oryza Sativa* L.) being the major nutrient and calories source of Asian people was found by recent study in reducing its glycaemic index by applying heat moisture treatment and annealing [197]. The usage of modified starch among them is to increase viscosity, shelf life of food products, textures, solubility, appearance and emulsification of food products [198]. Annealing is categorised under hydrothermal modification method of starch other than HMT. The process of annealing includes starch nurtured in an excess amount of water in a temperature range below gelatinisation temperature but higher than temperature of glass transition [199].

Starch has been modified in order to gain a better surface area and increase in pore volume due to its huge presence worldwide at low cost [200]. Moreover, according to [201], varieties of indigenous corn starches from different botanical sources have been well studied and reported by previous researchers regarding its physicochemical characteristics. Recent study reported that modified starch able to replace current available dietary fat [201]. Human beings and animals with simple single-chambered stomach like cats, rats and pigs unable to digest native starch granules well [202]. When comparing between maltodextrin, native and modified tapioca starch, it was found that modified tapioca starch had a broader distribution of particle size [203].

Three most common function of modified starch in food industry are as agent of gelling, stabilising and thickening [204]. According to [205] starch-modified physically for example using the most common treatment such as heat-moisture treatment and annealing can produce a safe raw material. On the other hand, starch modified by using the chemical for example sodium hypochlorite (NaOCl) produced end products that have high viscosity, stronger resistance to acid, heat, and shear, swelling decreases and not easily breakdown [206]. Starch paste properties can be easily modified expressively by applying several cross-links [207].

When people consuming starchy foods for example bread and rice, main supply of energy was actually supplied by physical and chemical properties of starch that act as main source of carbohydrate [208]. Increasing the starch paste stability and reducing pH, heat and shear properties of tapioca starch during food processing is the main focus of modifying starch by food scientist in Thailand [209]. As an example, by undergo dual modification process, sorghum starch was reported to be a new potential source replacing current available biodegradable films [210].

Corn starch was reported successfully modified by applying ultrasound treatment [211]. Pre-treated samples with ultrasound treatment helps in altering corn starch physicochemical properties [212]. In another study, corn starch was modified using heat moisture treatment and resulted in reduction of swelling power, percent solubility, gelatinization enthalpy and pasting viscosities when compared with untreated corn starch samples [213].

Pinhão (*Araucaria angustifolia*) which could be found in Brazil and was reported to be in high starch content and can be modified physically using process of annealing, heat-moisture treatment and sonication [214]. Physically modified pinhão seed shows better results in terms of syneresis whereas other parameters show no significant difference as compared to its native starch [215]. Pinhão seed obtained from pines trees that grow well in forests Southern part of Latin America and when applying HMT, molecular structure and its properties changes which suggested that it could be utilised as it is an underutilised source of starch and apply in food and non – food based application [216]. HMT is an example of physical modification which reported in previous study on pinhão seeds can provide strongest effect towards gelatinization and enthalpy if tested using differential scanning calorimeter machine [217].

Potato was also modified by using ultrasound treatment [218, 219, 220]. Basically ultrasound is a sound waves having a frequency which beyond human hearing capability [221]. On the other hand, for rice starch, several methods have been reported by previous studies. Annealing [222], HMT [223], improved extrusion cooking technology (IECT) [224] and ultrasound treatment [225]. Steeping is the first step in parboiling process followed by heating and drying of rice. Recent study reported that starch isolated from rice kernels is different from kernel itself in terms of its structure and properties [226]. Recent study suggested starch extracted from sweet potato modified by using steam explosion can be a good source for treating diabetic patients by encapsulating this starch into the medicine [227]. Sweet potatoes were claimed by previous research on applying annealing [228] and HMT [229].

Recent study claimed that by annealing wheat starch, stability increases as the interaction between the starch chains increases. Combining both method of annealing and HMT modification causes starch granules structure in yam and potato starches to change [231]. Yam (*Dioscorea spp*.) starch was physically modified by annealing process [229]. Annealing or also recognized as tempering has caused a rising in pasting temperature, peak time, setback and final viscosities of yam starch as compared to modification using acid hydrolysis, results obtained is vice versa [232].

Recent study in Vietnam had partially gelatinized jackfruit seed starch as a modification procedure and results showing highly soft and elastic starch gel [233]. Modification of starch by using microwave was found to be more efficient and time saving compared to modification by using acid in a study using starch isolated from jackfruit seed in India [234].

Previous study reported that by applying physical modification such as hydrothermal treatment, modified starch obtained will be more viscous, transparent, stable and swelling power will also increase when compared with native starch. In addition, this process is known as pre-gelatinisation which could be the initial step crucial before chemical modification [235]. Foxtail millet starch in previous study was reported can be modified by using HMT and ultrasound treatment (UT). Heat moisture treatment is an interesting and alternative way of modifying starch physico-chemical properties without disturbing starch structure of molecule [236]. Heat moisture treatment when combined with citric acid shows changes in sweet potato starch crystallinity type from B to C and reduced its peak viscosity which shows that by applying such treatment, a significant change can be observed. Besides, another study reported starch isolated from sweet potato starch were successfully modified using repeated heat moisture treatment (RHMT) when a significant changes were observed on X-ray diffraction pattern and its crystallinity, thermal and pasting properties when compared with native starch [237].

Better noodles in terms of elasticity and firmness were detected in noodles made up from sago starch that has undergone heat moisture treatment [238]. In addition, another study also claimed that HMT caused reduction in sweet potato starch viscosity but shows rising in swelling power and solubility as compared to native or modified starch using annealing process [239]. Reduction paste viscosities properties, swelling power and solubility is supported by another study using continuous and repeated heat moisture treatment towards red adzuki beans starch in Yangling, China [240].

Taro starch was modified using dual modification of microwave and HMT shows better results in terms of viscosity and freeze-thaw stability as compared to native taro starch [241]. By applying microwave heating, starch extracted from water chestnut shows increasing in pasting properties and enthalpy values. However, the swelling power and percent solubility decreases [242]. Main reason of utilising modified starch in food industry is due to its ability in rapidly dissolves in cold water [242].

Acorn is the fruits gained from oak tree categorised under genus Quercus, which has been modified by using annealing and HMT. The HMT gave more significant result in terms of altering starch properties compared to annealing [243]. Previous study stated that amylose and amylopectin are the main component of acorn starch though amylopectin composition was found higher than amylose [244]. In a study producing gluten free bread from acorn flour, substitution at 20% shows the most significant impact on volume of bread and its physical characteristics. However, beyond these 20% addition of acorn flour will reduce bread volume. In conjunction with previous statement, carbon dioxide presence in gluten network formation inside bread dough has been reduced due to gluten network deficiency which in turns resulting in bread with lowers loaf volume [245].

Recent study claimed that lotus is normally found in a dried form rather than fresh form due to its short life span in fresh condition which contributes by enzymatic browning, microbial growth and deterioration of quality [246]. Lotus seed starch (*Nelumbo nucifera* Gaertn) has been modified using microwave heating, which resulted in increment of its crytallinity, volume of pore and surface area, whereas yield of extraction and average size of starch particle decreases [247]. Another study reported using microwave radiation on lotus seed starch helps in producing starch with low glycaemic and hydrolysis index due to increasing in number of resistant and slowly digestible starch by amplifying microwave radiation [248].

In this study, three methods of tapioca starch modification has been combined which are through enzymatic, acid hydrolysis and physical modification using ball milling as it was claimed to change structure of starch from its native condition to smaller size of starch granule [249]. Tapioca starch in paste form contains no odour, high in paste clarity and stickiness make it extensively used in food and non-food industry in Thailand. However, like other starch in native condition, tapioca starch unable to perform well in industry as it produces unwanted characteristic of gel with weak structure, cannot withstand shear forces and reduction in stability of viscosity when heat applied [250].

In order to have a better quality of starch based product, many of starch source have different degree of gelatinization so it can fit many food formulations depending on product needs [251]. Recent study found that by adding physically modified starch to yogurt based product containing skimmed milk powder, it enhances consumer acceptance and yogurt become creamier and having consistent texture compared to non-added starch based yogurt [252]. Modification of native starch will not only result in reduction of retrogradation occurrence but will also benefit in many ways. For example, paste of modified starch will be more stable during cooling and freezing process, less prone towards formation of gel, less opaque and enriches gel texture [253].

Modification of Bambara groundnut (*Vigna subterranea*), an underutilised starch source from Nigeria using annealing process reported to have caused cracks and pores on starch surface based on image obtained from SEM [254]. In a study of modifying starch using both hydrothermal treatment which are annealing and HMT, results obtained showed false banana (*Ensete ventricosum* Musaceae) starch could be possibly used as functional ingredients in both food and pharmaceuticals industry [255]. In a study of modifying Morado banana starch using HMT, results gained indicated that it a good method of producing starch which could fit industrial needs in terms of added value product [256].

HMT was able to change the diffraction patterns based on X-ray diffraction results on two types of banana starch (*Musa sapietum* and *Musa paradisiaca*) in Nigeria from B to C type [257]. Recent study claimed that annealing is a greener way of modifying desired properties of starch and enhance final product quality [258]. White sorghum (*Sorghum bicolor*) starch was subjected to annealing in a reported study shown increasing in paste clarity. Thus, it could be a functional additive in a food product requiring starch with high clarity [259].

Arrowroot is popular among Indonesian as it is one of the carbohydrate sources and scientifically known as (*Marantha arundinacea* L) has been modified using autoclave and cooling treatment. Gel produced from physically modified arrowroot showed a softer texture and less rigid [260]. Annealing, HMT, ultrasound and sonication are widely used in physical modification of starch. However, there are also other methods to modify such physically such as parboiling, ball milling, microwave and gelatinization. Therefore, there are varieties of choices to modify starch physically.

Conclusion

In conclusion, starches are widely used in food industries. Thus, modifying starch to fulfill specific industrial needs can be done either using chemical or physical treatment. Numbers of starch in the future should be produced from unexplored source with further studies done. This is because rather than to reduce the waste, it is cheaper and easily available source. The underutilised starch should be transformed into a more useful product for future use.

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