A review on the physicochemical properties of starches modified by microwave alone and in combination with other methods

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Highlights

- Microwave heat treatment is a promising starch modification method
- Microwaving presumably affect amylopectin chain resulting in a less ordered starch
- Combination of microwaving with other methods improves starch functionality
- Microwaving strengthens starch bonds and increases amylose-amylose interactions
- Microwaved starches in food systems needs to be considered in future applications

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Contents

Abstract

Native starches are unsuitable for most industrial applications. Therefore, they are modified to improve their application in the industry. Starch may be modified using enzymatic, genetic, chemical, and physical methods. Due to the demand for safe foods by consumers, researchers are focusing on the use of cheap, safe and environmentally friendly methods such as the use of physical means for starch modification. Microwave heating of starch is a promising physical method for starch modification due to its advantages such as homogeneous operation throughout the whole sample volume, shorter processing time, greater penetration depth and better product quality. More recently, the use of synergistic methods for starch modification is being encouraged because they confer better functionality on starch than single methods. This review summarizes the present knowledge on the structure and physicochemical properties of starches from different botanical origins modified using microwave heating alone and in combination with other starch modification methods.

Keywords: Microwave heating; Synergy; Physicochemical properties

1. Introduction

Starch is available as a reserve carbohydrate in many plant parts including roots, tubers, cereals and seeds [1]. It is composed of mainly amylose and amylopectin in different ratios. According to Tester et al. [2], these two starch components account for approximately 98 to 99% of starch on the dry weight basis. Starch functional and physicochemical properties are greatly influenced by the ratio of these starch components [3], their chain length distribution [4, 5] and the presence of minor components such as lipids [6]. In the native form, starches have limited applications due to their poor resistance to extreme processing conditions such as high temperature and shear that are frequently encountered in the industry. Starches are therefore modified to overcome these shortcomings and to increase their usefulness for various industrial applications [7]. Starch modification may be achieved by enzymatic, genetic, chemical and physical methods or a combination of some of these methods [3, 7].

The use of single modification methods has been widely studied for starch from different botanical origin. Although single modification methods have been largely successful, dual modification methods seem to be promising to create starches with novel functionality that could meet various industrial needs. As an example, Bambara groundnut starch, modified using a combination of physical and chemical methods reportedly gave better functional properties such as reduced syneresis rate compared to the use of either a physical or chemical method [8]. Babu et al. [9] also found that foxtail millet starch modified by a combination of ultrasonication and annealing had better shear stability compared to the native starch or starch modified by ultrasonication or annealing alone. The application of microwave heating alone in the modification of starch has been widely studied [10-16] and more recently, a combination of microwave heating with other methods is now being investigated [17-24], for better functionality, compared to what is obtainable with single modification methods, thus expanding starch application in different areas [25]. Table 1 summarises the dual modification method (mostly chemical in combination with microwave heating) which have been reported for various starch sources. This review summarizes the present knowledge on the physicochemical properties of starch modified using microwave heating in combination with other modification methods.

2. Mechanism of microwave heating of starch

Microwaving heating of starch involves the application of electromagnetic wave within the frequency range of 300 GHz and 300 MHz [42]. Polar materials, like starch, are capable of absorbing microwave energy, consequently aligning themselves with its electric field [43]. Braşoveanu and Nemtanu [42] classified the mechanism governing the changes in starch structure during microwave heating into four stages. The first stage involves the dielectric relaxation phenomenon of water molecule, which is responsible for the initial heating of starch. This is followed by a rapid increase in temperature which is accompanied by loss of moisture from the starch granule interior. The moisture loss presumably creates a high pressure inside the granules and further causes granule expansion which occurs from the centre. The last stage involves clear evidence of starch granule degradation. From the mechanism described, it is clear that heat provided by the electromagnetic radiation can result in significant changes in starch functionality even at a very short microwaving time (< 1 min) [16]. Although the physicochemical changes observed in microwaved starches are similar to those reported for traditional physical modification methods such as annealing and heat-moisture treatment, microwaving seems to be a more convenient method for starch modification [13]. This is because the heating process involves high penetrating power of microwave energy, rapid and uniform heating of the starch samples. Contrary to the principle in conductive heating which involves the transfer of heat between low internal temperature and high external temperature regions, microwave heating operates based on molecular friction that results from the interaction between molecules of the material and the oscillating electromagnetic field having a frequency in the microwave regions. Therefore, in the latter, there is an internal generation of heat, as well as bulk heating, throughout the sample, hence heating occurs comparatively faster [41, 43]. Two properties which determine microwave heating are dielectric constant (how molecules couple with microwave energy) and dielectric loss factor (the ability of a material to absorb microwave energy and transform it to heat) [44]. According to Braşoveanu and Nemtanu [42], the most important property in microwave heating is the dielectric dissipation factor, i.e., the ratio of dielectric loss factor to dielectric constant. The heat generated during microwaving of starch has been reported to produce free radicals which are capable of depolymerizing large starch molecules into smaller ones through the cleavage of glycosidic bonds [45]. It is speculated that during microwaving of starch, the branched-chain part of amylopectin is partly affected resulting in a less ordered structure and this change in structure has been suggested to depend largely on the microwaving power and time [10, 11, 16]. Zhong et al. [23] reported that microwaving may result in an intense movement of the molecular chain in a short time without destroying the starch granules. But some authors found that even at a microwaving time of less than 60 s, there were significant changes in starch structure and functional properties [11, 16]. Majority of the studies on starch modification using microwave and other methods took advantage of the rapid heating involved during microwaving and the improvements in interactions with chemicals or additives added. Propagation of microwave energy through a material depends on the dielectric and magnetic properties of a medium. However, starch does not have a magnetic component but responds only to the electric field of an electromagnetic field. This makes the relative complex permittivity of starch, vis-à-vis its absorption, reflection, and transmission of microwave energy, a key electric property in microwave heating [46]. Lewicka et al. [47] explained that there is a strong heating of the moisture contained in the material while being microwaved, and this is due to a swift re-orientation of dipoles, as well as the removal of hydrogen bonds. As a result, structural changes occur in the material.

3.0 Synergistic modification of starch using microwave and other methods

Recent trends of starch modification are now exploring a combination of physical and chemical methods in improving starch physicochemical properties. Synergistic modifications of microwave heating in combination with other physical and chemical methods have been reported to improve the physicochemical properties of starches from different botanical origins [17-20, 22, 37, 38]. This section will describe the effect of microwave heating in improving interactions of chemicals and starch during modification, and also document the synergy of both microwave and the chemicals on granule morphology, structure, swelling, pasting, gelatinization and digestibility.

3.1 Degree of substitution

Chemical modifications of starch using methods such as acetylation, carboxymethylation, hydroxypropylation, methylation and succinylation have been found to require longer reaction time with low degree of substitution compared to using microwave-assisted methods. An earlier study by Singh and Tiwari [28] reported a novel microwave-accelerated method for methylating soluble starch within a very short reaction time under milder conditions. According to Yang et al. [10], microwave heating destroys starch crystal structure and increases the contact area between the reagents and the starch particles. Generally, microwave heating has been reported to improve the degree of substitution (DS) of chemicals with starch [22, 29, 37]. Lin et al. [29] studied the effect of different microwave powers (150-400 W) and times (0-12 min) on the DS of hydroxypropyl corn starch using propylene oxide at 8%. Both microwaving power and time increased the DS but this plateaued at a microwaving power of 300 W, and began to decline after reaching a maximum of 6 min. Liu et al. [37] also found that microwave heating at 300 W in combination with carboxymethylation reduced the time required for carboxymethylation of potato starch by 83% compared to when a conventional method was used at the same DS. It seems that the effectiveness of microwave heating with chemical methods can be hampered at a higher microwaving power. High power (>300 W) reportedly caused gelatinization and agglomeration of starch molecules which presumably resulted from an increase in the temperature of the reaction system during microwave heating, especially at a longer exposure time [29, 37]. However, pre-treating starch with microwave heating even at a relatively high microwave power of 600 W and at a very short time (30 s) before acetylation gave higher DS in potato starch [22]. These authors reported almost double the DS of acetylated potato starch which was pre-treated with microwave compared to potato starch without microwave heating at the same acetyl content. The increase in DS was attributed to the microwave heating step which produced porous starch with cavities that enhanced the contact area between the esterifying agent and the starch granules, and possibly facilitated the entry of the agent into the starch granule interior [22]. The differing DS between microwave-assisted and conventional starch modification processes have been associated with different energy distribution [48]. While the authors found similarities when the DS of microwaved (120 min) and conventionally (water bath) heated (300 min) starch samples were compared, it was observed that the effect was more in the former. Future studies may be required to determine the effect of microwave heating before and after chemical modification such as acetylation and carboxymethylation to ascertain when microwave heating will be more preferred. Besides, optimization of reaction conditions such as chemical agent concentration, microwave heating time and power, the influence of amylose content on the physicochemical properties of starches modified with microwave heating and other methods may also require future investigation. This is particularly important because a high microwaving power may also lead to decomposition of chemicals, as well as starch gelatinization before the interaction between the starch molecule and the modifying agent.

3.2 Granule morphology

Studies have demonstrated various effects of microwave heating on the granule size, shape and birefringence of starches. An example is available in the research conducted by Gonzalez and Perez [49] to investigate the effect of microwave irradiation on some of the properties of lentil starches. It was reported that, although there was no considerable morphological alteration, boat-shaped granules of the starches were affected by microwave treatment, becoming surface-roughened. Similarly, there was no significant modification in the granular morphology of microwaved rice starches when compared to its native form, but the granules were more aggregated in the former [50]. Xie et al. [11] gave a more comprehensive description of the morphological response of potato starch granules to time-varied microwaving heating. The researchers observed that the level of alteration was dependent on the period of exposure to microwave energy. Scanning electron microscopy (SEM) analysis showed that the native potato starch which was clear, regular elliptical shaped, with smooth surfaces exhibited different levels of deformation at 5 s (rare flaws or fractures on surfaces of some of the granules), 10 s (noticeable flaws of fractures but intact granule integrity), 15 s (rough and crimpy granular surface with loss of integrity), and 20 s (heavily deformed, fractured, and collapsed starch granules) of microwave heating.

Differences have been found between the granule morphology of starch modified with microwave heating and other methods (Fig. 1). While acetylation alone resulted in rough surfaces of potato starch granules (20% moisture), microwave heating at 600 W for 30 s before acetylation showed apparent pores and greater roughness after acetylation [22]. Sun et al. [38] reported that normal corn (5% moisture) and waxy corn (5% moisture) starches modified with xanthan gum and microwave heating (600 W for 4-6 mins) had granules with rough surfaces after xanthan addition. However, the granules formed lumps following microwave heating, indicating better interaction of xanthan gum with the starches under microwave heating [38]. The change in granule morphology, including the presence of pores on granule surface, therefore, will depend on several factors such as, when microwave heating was done (i.e. before or after other modification methods). For example, microwave-assisted carboxymethylation of potato starch showed a greater collapse in the granule structure compared to carboxymethylation without microwave heating [37]. Other factors that may play a role in influencing granule morphology is the starch moisture content. High moisture content seems to facilitate greater penetration of the microwave energy resulting in pore formation and possible collapse in granule structure depending on the power and exposure time.

3.3 Swelling

Starch swelling involves interaction between the crystalline and amorphous regions of starch [51, 52]. Thus, changes in starch swelling and solubility may be attributed to alterations in the crystalline and amorphous regions. Microwave heating of starch has generally been found to result in a significant reduction in starch swelling [15, 16]. The reduction in starch swelling after microwave heating presumably results from rearrangement of crystalline regions within the starch granules, which might become more randomly distributed within the starch granule [15].

Reported data on the swelling power of starch modified using synergistic modification methods of microwave heating and other methods generally showed a greater reduction in swelling when dual methods were used, compared to when microwave heating or other methods were used alone [22, 24]. Zhao et al. [22] reported that microwave-pre-treated starch before esterification showed a greater reduction in swelling power compared to un-microwaved starch that was subsequently esterified. Esterification increased the swelling power of the starches but microwaving before esterification substantially reduced the swelling power of potato starch [22]. According to the authors, microwave-pre-treated starches exhibited approximately 53% reduction in swelling power compared to un-pre-treated samples at 90 °C at the same esterification level (12 mL/100 g).

Microwave heating of starch before complexation with stearic acid or microwaving lipid-complexed starch resulted in a greater reduction in swelling of starch than when microwaving was used alone [24]. It was suggested that microwaving further enhanced the interaction between starch and the lipids. The reduction in swelling power of native starch modified with lipids has been attributed to the interaction of lipids with amylose in the hydrophobic tube, which prevents starch granule hydration and swelling [53] and also the covering of starch granule surface by the lipid molecule [54]. Hence, the greater reduction in swelling power further suggests that microwaving creates an enabling environment for the interaction of starch with lipids, perhaps by creating pores which would facilitate the movement of lipids into the starch granules. Several studies reportedly showed obvious pores on starch granule surface after microwave heating [11, 16, 55]. Furthermore, since starches with a higher proportion of longer amylopectin chains are responsible for high swelling power, it is also possible that the lower swelling power of the modified starch resulted from damaged granule structure due to microwave heating [22]. This presumably caused gelatinization and strengthened the interaction of amylose and amylopectin chains, which makes it difficult for water molecules to enter into the starch granule interior. The functional properties of starch including swelling and solubility have been found to vary with the degree of cross-linking attained. For instance, Xiao et al. [56], using epichlorohydrin, reported that a low degree of cross-linking resulted in an increased swelling power and solubility while a higher degree of crosslinking resulted in the opposite. Cross-linking is one of the widely used starch chemical modification methods that is believed to reinforce hydrogen bonds in starch granules with chemical bonds which act as a bridge between molecules [26, 57]. The degree of cross-linking, however, may be enhanced using microwave heating. Synergistic modification of cassava starch using cross-linking agents (sodium tripolyphosphate) and microwave heating was found to increase the degree of cross-linking and the increase was with an increase in microwave heating time [27]. Another study on microwave-assisted cross-linking of banana starch using phosphoryl chloride also found a decrease in swelling power and retrogradation tendencies [26].

3.4 Crystallinity patterns

X-ray diffraction (XRD) study is an important technique used to assess changes in starch structure. By the use of XRD, starch has been shown to display four types of crystalline pattern (A, B, C or V polymorphs). The A and B crystalline patterns are differentiated based on the packing arrangement of double helices within amylopectin and the level of hydration [58]. The A-type is less hydrated since the double helices are closely packed, while the B-type has a more hydrated helical core [58, 59]. The majority of the studies on microwaved starch revealed that the crystalline pattern remained unchanged after microwave heating [10, 12, 13, 15, 16]. Other reports found a change from B-type crystallinity to the A-type for potato starch [12] and *Canna* *edulis Ker* tuber starch [14] or a change from B to a mixture of A and B in amylomaize starch [15]. Some other studies have also reported a decrease [10, 13, 16] or an increase [14] in the degree of crystallinity of microwave-treated starch. Variation in the XRD results may be attributed to differences in the heating time as well as moisture content of the treated starches.

Differences have been observed in the crystalline pattern of starch and the degree of crystallinity after modification of starch using microwave and other methods. A study by Lin et al. [29] found that neither microwaving nor microwaving in combination with hydroxypropylation changed the crystalline pattern of corn starch. The crystalline pattern of normal rice and waxy rice starches also remained unchanged after a combined modification of microwave heating and heat-moisture treatment (15 and 35% moisture levels), but the degree of crystallinity reduced especially at a higher moisture content of 35% [36]. Sun et al. [38] also found that the XRD pattern of normal corn and waxy corn starches modified with microwave heating and xanthan gums did not change. However, their intensities and the degree of crystallinity of the reflections of the crystal unit cells decreased, indicating changes in the lattice structures [38]. The crystalline pattern of potato starch modified with microwave heating and esterification changed from the B-type polymorph to the C-type [22]. These changes appear to depend on the type of starch (normal or waxy), moisture content and the modification method used in combination with microwave heating. Future studies may be required to also determine the influence of microwave heating and other methods on starch with varying amylose contents.

3.5 Pasting properties

Pasting refers to changes in the starch structure after gelatinization [60, 61]. In general, breakdown, trough, final and setback viscosities reportedly decreased after microwave heating of starch [10, 13, 55]. The extent of decrease in these pasting properties was found to depend on the microwave heating time [10, 55]. A higher microwave heating time was found to result in a greater decrease in the pasting properties of starch [10, 16, 55]. However, different results have been observed in the pasting temperature of microwave-treated starches. Colman et al. [55] observed a slight but significant decrease in the pasting temperature of microwave-treated cassava starch. The pasting temperature decreased with increasing microwave heating time [55]. Other researchers, however, found that the pasting temperature increased after microwave heating of waxy maize starch [10], and wheat and corn starches [13]. According to the report of Yang et al. [10], the higher pasting temperature of microwave-treated waxy maize starch indicates that the starch had a high resistance effect on rupture and swelling. The resistance presumably resulted from the reorganisation of the starch granules due to the strengthening of bonds between the starch granules.

Different results have been observed in the pasting properties of starch when microwave heating was combined with other methods. The pasting temperature of potato starch did not change significantly when potato starch was modified with microwave heating and minerals [39, 40]. According to the authors, the enrichment of potato starch with magnesium or copper ions resulted in a greater reduction in all pasting properties. These authors also found that the microwave heating power also played a significant role in the modification process, even in the presence of different mineral additives (potassium, magnesium, copper, or iron). For example, a combination of microwaving at a higher power of 800 W and addition of minerals gave a higher reduction in the peak, breakdown, setback and final viscosities of potato starch compared to when the starch was microwaved at 440 W [39]. The mechanism of interaction between starch and mineral elements seems to be very similar to those found when other ligands such as lipids are added to starch, except that radicals are formed in starch when mineral elements are used. The formation of radicals has not been reported in starch-lipid complexes, to the best of our knowledge, however, paramagnetic ions such as Fe (III) and Cu (II) have been reported to interact with the starch matrix, forming starch-metal complexes and these ions undergo a change in their oxidation state during microwave or thermal treatment influencing the mechanism of radical generation [39, 62, 63]. Furthermore, variation in ion radius size is suggested to be the main factor differentiating the radical formation process during complexation with starch. Potassium ions are larger (about two-fold) than magnesium ions and this difference in size can damage starch structure during its incorporation, facilitating a more radical formation [39].

Villanueva et al. [33] reported that the modification of rice starch with microwave and protein both significantly decreased the peak viscosity. A greater reduction in peak viscosity was found when native rice starch was modified with proteins than when a combination of microwaving and protein addition was used. The reduction was associated with a reduction in starch fraction due to replacement with proteins [64]. The possibility of starch-protein interaction cannot be ruled out since proteins can also form complexes with starch and may contribute to starch gel-matrix weakening [65]. Furthermore, proteins can also retain water, or compete for it with starch granules, consequently reducing the initial swelling of starch granule [33]. Zhao et al. [22] further showed that microwave heating can further change the pasting properties of starch before esterification. These authors found a substantial reduction in the pasting properties of potato starch modified with microwave heating and esterification compared to native starch that was esterified, but the changes were highly dependent on the level of esterification [22]. The viscosity of starch has been found to increase rather than decrease in the presence of gum and microwave heating [38]. Although gums are well-known to contribute to starch viscosity, it seems that starch composition also plays a significant role in increased viscosity of starch. Microwave-assisted dry heating with xanthan gum increased the peak viscosity of normal corn starch by approximately 47% relative to when waxy corn starch (56%) was used [38]. The difference observed, including a higher setback viscosity, with normal corn starch rather than waxy starch was associated with the variation in amylose contents. This seems plausible since amylopectin is known to significantly contribute to swelling, while amylose acts as a diluent restricting starch swelling. A study on microwave irradiation of waxy and non-waxy hull-less barley starch found that amylose played a significant role in the properties of isolated and in-kernel starches during microwave treatment [66]. Hence, the effect of microwave heating in combination with other methods on starch pasting properties also depend largely on the starch composition among other factors which have been discussed earlier. Another important factor worthy of mention that plays a significant role in the pasting properties of starch modified with microwave treatment and other methods is the sequence or order of modification, with regards to which modification is done first. For example, cassava starch modified with lipids and subsequent microwave heating reportedly had higher reduction (approx. 19%) in peak viscosity compared with the starch modified with microwave treatment followed by modification with stearic acid (approx. 9%) and the native starch alone modified with added stearic acid (approx. 7%) [24]. As further noted in this study, the higher reduction in peak viscosity of cassava starch containing stearic acid with subsequent microwave treatment indicates that microwave heating enhances better interaction of lipids and starch and favoured the formation of more starch-lipid complexes [24]. This observation is in agreement with an earlier study, which noted that microwave heating accelerates reaction processes when used in combination with chemical modification methods like oxidation and esterification, resulting in a significant improvement in yield [47].

3.6 Gelatinization properties

Gelatinization properties of starch are commonly determined by differential scanning calorimeter (DSC) where the starch-water mixture is heated in a tightly sealed aluminium pan

[67]. Gelatinization involves hydration and swelling of starch granules [3] and the process leads to a phase change of starch granules from an ordered to a disordered state [61, 68]. The phase transition occurs in the presence of excess water and over a temperature range which is specific for starch from different botanical origins [3]. Gelatinization properties such as onset gelatinization temperature (T_o), peak gelatinization temperature (T_p), conclusion gelatinization temperature (T_c) and the enthalpy of gelatinization (ΔH_{gel}) are influenced by several factors including amylose content and chain length distribution of amylopectin. In general, starches with low amylose content have been found to display high gelatinization temperature [69-72]. However, Noda et al. [73] found that the starches with abundant short amylopectin chains would exhibit low T_o, T_p, T_c and ΔH_{gel}. Except for ΔH_{gel}, the T_o, T_p and T_c of starches generally increased after microwave heating [10, 13-16]. The increase in T_o, T_p and T_c may be attributed to better hydration of amorphous regions [14]. It has been suggested that gelatinization involves the uncoiling and melting of double helices composed of external chains of amylopectin and partial amylose [74]. Furthermore, the melting of double helix during gelatinization is assisted by hydration of amorphous regions, which imparts stress on crystalline regions, thereby stripping polymer chains from the surface of starch crystallites [74].

Modification of cassava starch with microwave heating in combination with stearic acid reportedly shifted the T_p to a higher endotherm (92.04-101.85^oC) while the native starch displayed a T_p of 65.10^oC [24]. Synergistic modification of cassava starch using microwaved starch and stearic acid or microwaving cassava starch that has been complexed with stearic acid both enhanced the degree of complexation than when native starch was complexed with stearic acid [24]. Gelatinization temperatures are associated with the molecular architecture of the crystalline regions, which corresponds to the distribution of amylopectin short chains [22]. Microwaved starch that was further modified with esterification and native starch that was esterified both showed reduction in T_o, T_p, T_c and ΔH_{gel}, but the reduction reportedly increased with levels of esters from 4 to 12 mL/100 g [22]. The reduction in gelatinization temperatures was associated with the incorporation of acetyl groups which inhibited the interaction among starch granules and reduced the chance of starch crystallization production [75]. Sun et al. [38] also found that microwave heat treatment in combination with xanthan gum similarly reduced the T_o, T_p, and T_c of normal corn and waxy corn starch. Waxy starch reportedly showed a higher reduction in the gelatinization temperatures compared with the normal corn starch. With the growing interest in the production of more thermally stable starches for use in the food industry, future studies on synergistic modification methods including those involving microwaving should provide information on the gelatinization properties of the modified starches.

3.7 Digestibility

In terms of digestibility, starch can be classified into rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) according to the rate of glucose release and its absorption in the gastrointestinal tracts [76]. RDS is the fraction of starch that causes a sudden rise in blood glucose level after ingestion, and SDS is the fraction that is digested completely in the small intestine at a lower rate as compared to RDS [61]. RS cannot be digested in the small intestine but is fermented by microbes in the large intestine to form short-chain fatty acids [61] and this process is known to significantly contribute to intestinal health and gives functionality to the human system [77, 78]. Many factors may influence the digestibility of starch. These include, but are not limited to, starch botanical source [79], amylose content [80], amylose chain length [81], degree of crystallinity [82, 83], and molecular structure of amylopectin [84].

The type of modification can also greatly affect starch digestibility. Microwave heating reportedly decreased the rate of digestibility in *Canna edulis Ker* tuber starch [14]. These authors found that starch moisture content, microwave power, as well as microwave heating time influenced the rate of starch digestibility after microwave treatment. An increase in moisture content from 20 to 35% decreased starch digestibility, but starch digestibility increased slightly when the moisture content reached 40% [14]. Moisture content seems to play a very critical role on the impact of microwave heating on starch digestibility. Li et al. [85] studied the effect of microwave heating and varying moisture contents of 30%, 35%, 40%, 45%, and 50%. According to their report, starch digestibility increased with increasing moisture content, and a greater effect was observed at above 40%. The cracks and pores on starch granules after microwave heating (Fig. 1) may explain the increase in the digestibility of modified starches. These pores and cavities on the starch surface could facilitate the access of hydrolyzing enzymes into the granule interior and this perhaps is enhanced in the presence of a greater amount of moisture. More recently, microwave-treated rice starch was found to show stronger molecular reassembly during digestion compared to native starch [21]. The microwaved starch samples exhibited slowly digestible features resulting in increased SDS fraction and a slower digestion rate [21]. A combination of microwave heating and retrogradation was shown to decrease starch digestibility due to the recrystallization that occurs during retrogradation [31]. The retrogradation step seemed to have enhanced the development of a compact starch structure that is usually more resistant to enzymatic hydrolysis [86, 87]. It is important to also note that the botanical source of the starch and composition as earlier stated also plays a vital role in the digestibility properties of starch after modification. For example, while the RDS in corn starch reduced by approximately 19% after a combined microwave heating and retrogradation, the RDS component of chestnut and potato starches reduced by approximately 7 and 13%, respectively [31]. The RS and SDS fractions reportedly increased in varying amounts, which was associated with the difference in amylose content and the crystal structure of the starches. The increase in SDS fractions of the modified starch indicates that the starch could be used in the formulation of diets for the management of diabetes since the SDS fraction is more beneficial for the controlled release of glucose in the body. Microwave heating also enhanced canna starch esterification with citric acid and enhanced the formation of RS, which according to the authors was thermally stable [30].

4 Current and potential applications of microwave modified starch

To the best of authors' knowledge, there are no current food applications of microwaved starches in the industry, but several researchers have reported that starches modified with microwave heating alone or in combination with other methods have enormous potentials for various food and pharmaceutical applications. For example, Sriamornsak et al. [88] demonstrated that microwave modified starch displayed excellent properties as hydrophilic matrix excipients for sustained release tablets compared to their unmodified counterpart. The potential applications of microwave-modified starches and starches modified using microwave heating and other modification methods in food systems are highlighted below:

(i) Use in the reduction of staling tendencies in bread due to a reduction in setback viscosity after modification.

(ii) Owing to improved thermal stability, they could be useful for applications requiring high temperature, such as in extruded and baked products.

(iii) Concerning reduced digestibility, their roles in the production of low-calorie foods including foods developed for the management of diabetes is suggestive.

(iv) Incorporation into wheat dough or other flour composites for producing noodles with reduced cooking time. This is because microwave heating has been found to result in partial gelatinization of starch resulting in a faster rate of water uptake than in ungelatinized (non-treated) noodles [89].

5 Conclusions and recommendation

The effect of microwave heating alone on starch has been well researched, but the impact of microwaving in combination with other modification methods seems to be at the rudimentary stage. More studies are required to further confirm the advantages of using microwave heating in synergistic mode with other modification methods and their impact on starch functionality should be further documented. Generally, the impact of combining microwave heating with other methods is greater than when either microwave heating or the other method was used alone. Thus, future studies using synergistic modification method should be encouraged. Due to the effect of starch source on physicochemical properties of microwave heated starches, future studies may need to also focus on starches extracted from legumes since there are only a few studies on legume starches. Majority of the studies reported in the literature focused primarily on the influence of microwave treatment on the functionality of corn and potato starches with very limited research on legume starches. Hence, future studies may be important to understand the impact of microwave heating on other promising starch sources. It is important to emphasize that the majority of studies in literature only suggest the possible use of modified starches in foods. Future studies would therefore be required to investigate their application in model food systems. Also, the use of sophisticated techniques such as the use of confocal laser scanning microscopy, nuclear magnetic resonance and atomic force microscopy should be explored in future research.

Authors declare no conflict of interest

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Credit Authors Statement

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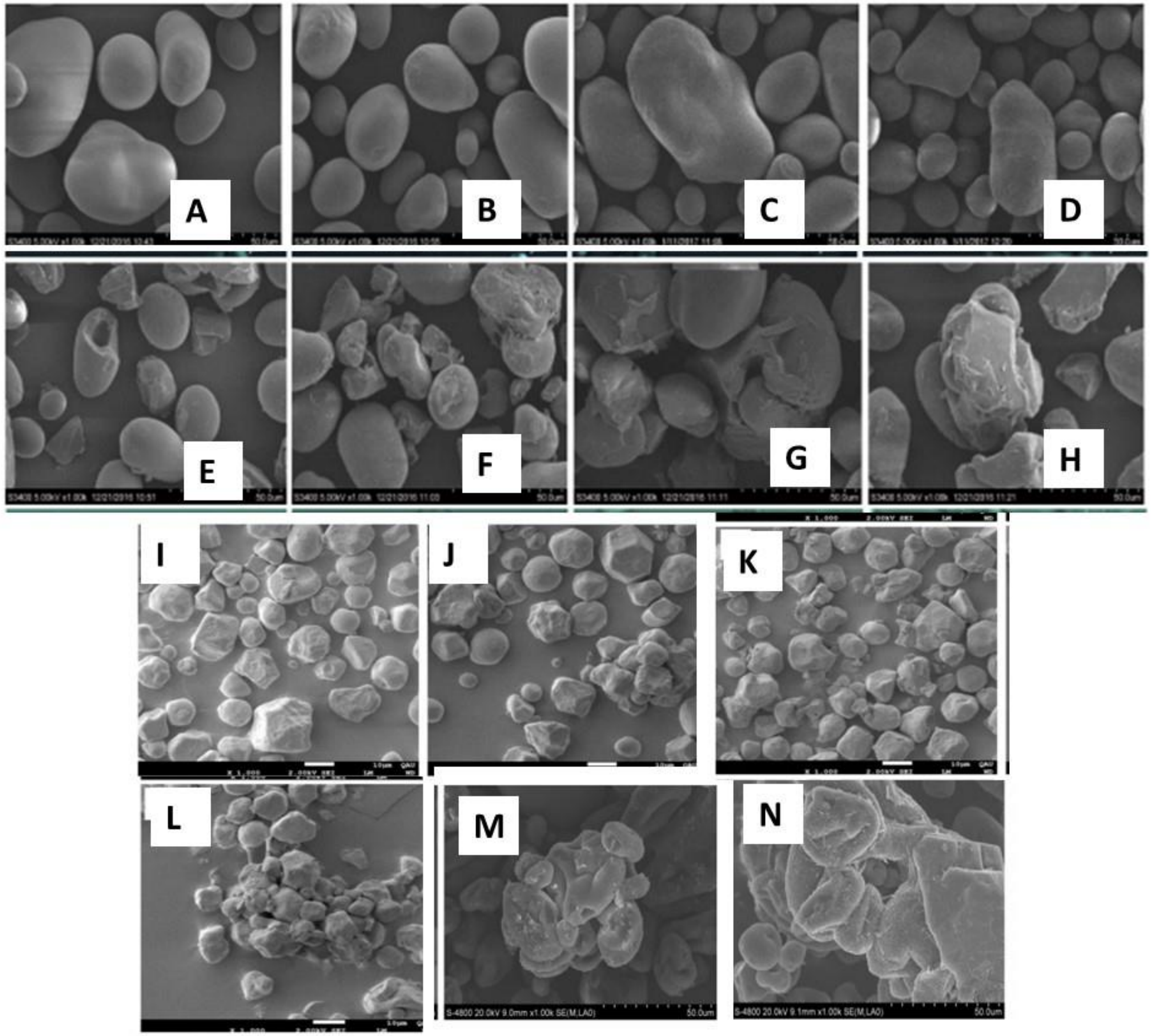

Fig. 1: Micrographs of starches modified with microwave heating and other methods (Reproduced with permission from Elsevier)

A: Native potato starch without acetylation or microwave heating

B: Acetylated potato starch without microwave heating at acetylation level of 4 mL/100 g, starch, db

C: Acetylated potato starch without microwave heating at acetylation level of 8 mL/100 g, starch, db

D: Acetylated potato starch without microwave heating at acetylation level of 12 mL/100 g, starch, db

E: Microwaved pre-treated potato starch without acetylation

F: Microwaved pre-treated potato starch at acetylation level of 4 mL/100 g, starch, db

G: Microwaved pre-treated potato starch at acetylation level of 8 mL/100 g, starch, db

H: Microwaved pre-treated potato starch at acetylation level of 12 mL/100 g, starch, db

I: Native corn starch without microwave heating and xanthan gum

J: Native corn starch with xanthan gum and microwave heating

K: Waxy corn starch without microwave heating and xanthan gum

L: Waxy corn starch with xanthan gum and microwave heating

M: Carboxymethyl potato starch prepared without microwave heating

N: Carboxymethyl potato starch prepared with microwave heating

Figure 1A-H [22]; Figure 1I-L [38]; Figure 1M&N [37]

Table 1

Summary of methods used for dual starch modification and various starch sources

Starch type	Dual modification method		Reference
Banana	Microwave heating	Crosslinking	[26, 27]
Corn	Microwave heating	Methylation	[28]
Corn	Microwave heating	hydroxypropylation	[29]
Cassava	Microwave heating	Lipids	[24]
Canna	Microwave heating	Citric acid esterification	[30]
	Microwave heating	Retrogradation	[31]
Potato	Microwave heating	Methylation	[32]
Potato	Microwave heating	Protein	[33]
Potato	Microwave heating	silicic acid	[34]
Potato	Microwave heating	Zinc	[35]
	Microwave heating	Heat moisture treatment	[36]
Potato	Microwave heating	Acetylation	[22]
Potato	Microwave heating	Carboxymethylation	[37]
	Microwave heating	Xanthan gums	[38]
Potato	Microwave heating	Minerals	[39, 40]
Rice	Microwave heating	Protein	[33]
Wheat	Microwave heating	Conductive heating	[41]