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REVIEW

Current Status and Perspectives of Starch Powders Modified by Cold Plasma: A Review

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Abstract
Starch is an important part of the human diet; however, this macromolecule has undesired physicochemical properties associated with its limited water solubility, low viscosity, and poor thermal stability, limiting its food applications. Cold plasma (CP) is an emerging and nonthermal technology used in recent years to modify the physicochemical properties of starch powders. This paper comprehensively reviewed the application of CP in starches, including information about reactors and gases used to modify starches with CP, the application in starch granules, and the combination with other treatments such as hydration, dry heat, chemical and enzymatic treatments, extrusion, ultra-high-pressure, and microwave. Modified starch granules by atmospheric CP showed depolymerization of starch molecules, impacting the amylose content, crystalline structure, water solubility, and thermal properties. Certain gases used in CP, such as hexamethyldisiloxane and helium, can induce cross-linking in starch granules, increasing thermal and mechanical properties. CP associated with physicochemical treatments is more efficient in inducing starch depolymerization, improving the modification of the physicochemical properties of this macromolecule. CP is a useful tool for modifying the properties of starch granules; however, further research and development are necessary to elucidate its industrial application.

Keywords Cold plasma · Digestibility · Nonthermal treatment · Physicochemical properties · Native starches · Modified starches

Introduction

Starch is a natural polymer that exists as semicrystalline granules and is composed of two polymers, i.e., amylose, a linear biopolymer of α-D-glucose units linked by α-1,4-glycosidic bonds, and amylopectin, a highly branched biopolymer in which the α-D-glucose units are linked via α-1,4- and α-1,6-glycosidic bonds [1]. Starch is an important ingredient in the food industry due to its bulking, thickener, gelling, and water-holding properties. However, native starches have many disadvantages associated with poor water solubility and shear and thermal stability, presenting insufficient physical and functional properties [2].

Enzymatic, chemical, and physical modifications have been used to widen the applicability of starch. The use of enzymes to modify starch granules is expensive, reducing its application at an industrial scale. Although chemical methods have high efficiency, some factors such as cost, chemical residues, time consumption, and waste management have negatively impacted their use [3]. Nowadays, physical modifications are preferred in food ingredients due to safer, simpler, and low-cost processes that prevent chemical residues [2]. Among the physical modifications, nonthermal technologies such as irradiation, high-pressure processing, and pulsed electric field have gained more interest since they can be used to modify ingredients and foods sensitives to heat [4].

Cold plasma (CP) is an emerging nonthermal technology used in recent years as a physical method to modify proteins, carbohydrates, and natural pigments, to inactivate and

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reduce microbial growth, eliminate mycotoxins and food contaminants, and improve the adhesion of food packaging materials [5–12].

In recent years, CP has been proposed as an alternative to modifying starch granules, improving their food applications [13–16]. Previously, Okyere et al. [17] reviewed the types of reactors used to produce CP and their food applications, including some application in starch granules. In the review of Zhu et al. [18] was concluded that cold plasma modifies the crystallinity degree in starch granules by attacking the amorphous region, as well as inducing surface corrosion and channel disintegration of starch granules. It should, however, be noted that CP can be used alone or combined with physicochemical treatments to modify starch granules. To date, no review paper has comprehensively analyzed and reviewed the different physicochemical treatments which can be coupled with CP to modify starch granules. Therefore, the novelty and objective of this review article are to present the state of the art concerning the main alternatives coupled to CP and used to modify starch granules.

The current review was based on research studies developed over the last six years using six databases: Web of Science, Science Direct, Scopus, PubMed, Scielo, and Google Scholar. The search term "starch AND cold plasma" on the research studies' title, abstract, and keywords were used to select the literature to be analyzed in the current review.

Types of Cold Plasma Systems Used to Modify Starches

Plasma consists of completely or partially ionized gas that results from applying sufficient energy – mainly from electromagnetic field sources – to a neutral gas, forming reactive species [19]. This gaseous phase comprises free electrons, free radicals, ions (positive and negative), atoms and molecules (excited and neutral), and emitted UV–Vis radiation. Plasma is classified into two types: thermal and nonthermal. Thermal plasma has a local equilibrium between gas and electron temperature. In nonthermal plasma – or cold plasma (CP) – the temperature is near to room, the electrons (lighter particles) are at a very high temperature, and the other gas particles (heavy particles) are at room temperature; this creates a no-local equilibrium [4]. The non-equilibrium is maintained because the energy transfer from the applied electric field is much faster and more efficiently transferred to the electrons than by the collisions between electrons and heavy particles, keeping the gas at low temperatures [20].

CP is an emergent technology widely used in research to change the characteristics of raw materials, such as starch. CP can be used at low pressures to atmospheric pressures, applying different gases and flow rates; however, atmospheric pressure and air as ionizing gas are preferred due to low cost and availability. The CP can be generated by several reactors configurations, and the most applied for starch modification is dielectric barrier discharge (DBD) [21–24], followed by plasma jet (PJ) [25, 26], and radio frequency (RF) [27, 28].

Typically, DBD consists of a powered and a grounded electrode arranged in parallel with a dielectric barrier (polymer, glass, quartz) between them to limit and distribute the energy and prevent the formation of sparks [4, 20]. The material to be treated is placed between the electrodes directly receiving the plasma. DBD is the most used CP type due to low costs, scalability, versatility, enabling different electrode configurations, and using different materials (Fig. 1a) [4].

PJ has the same principle as DBD; however, the reactor is cylindrical, containing two electrodes and a dielectric barrier [20]. The gas to be ionized – usually a noble gas or a known gas mixture – flows through the center of the cylinder under a high flow rate, being blown out of the plasma formation region, resulting in a jet rich in plasma reactive species in the open environment. Thus, the material is placed at the system outlet to be in contact with the jet (Fig. 1b).

Different systems can generate plasma through RF. Inductively coupled plasma (ICP) and capacitively coupled plasma (CCP) are the most common. In ICP, RF voltage is applied across two parallel electrodes, and the sample is placed between the electrodes (Fig. 1c). In CCP, RF current circulates in coils or antennas, and the plasma is conducted to a dielectric chamber where the sample is placed [4, 29]. Other reactors have been to a lesser extent to modify the surface of materials by CP. The scientific literature about the use of CP to modify the physicochemical properties of starch granules reports that almost 2/3 of the studies used a DBD reactor (63%), followed by RF (14%) and glow discharge (11%). Other reactor types, such as PJ, corona discharge, and pin-to-plate, have been less used (Fig. 2a) to treat the starch granules directly. Glow discharge CP is generated when a power source is used in radio or microwave frequency coupled to electrodes or an induction coil, while pin-to-plate and corona discharge systems are similar to DBD, using two electrodes, but pins form the upper high-voltage electrode instead of an upper plate. Most information about CP and reactor types can be found in the specialized literature [4, 19, 29].

Starches have been CP treated mostly using atmospheric air (51%) (Fig. 2b). Specials gases such as CO_2, hexamethyldisiloxane, N_2, Ar, and He also have been used to modify starches by CP (Fig. 2b). Unfortunately, around 10% of the studies did not inform the type of gas used (Fig. 2b), which does not guarantee reproducibility. Atmospheric CP and CP

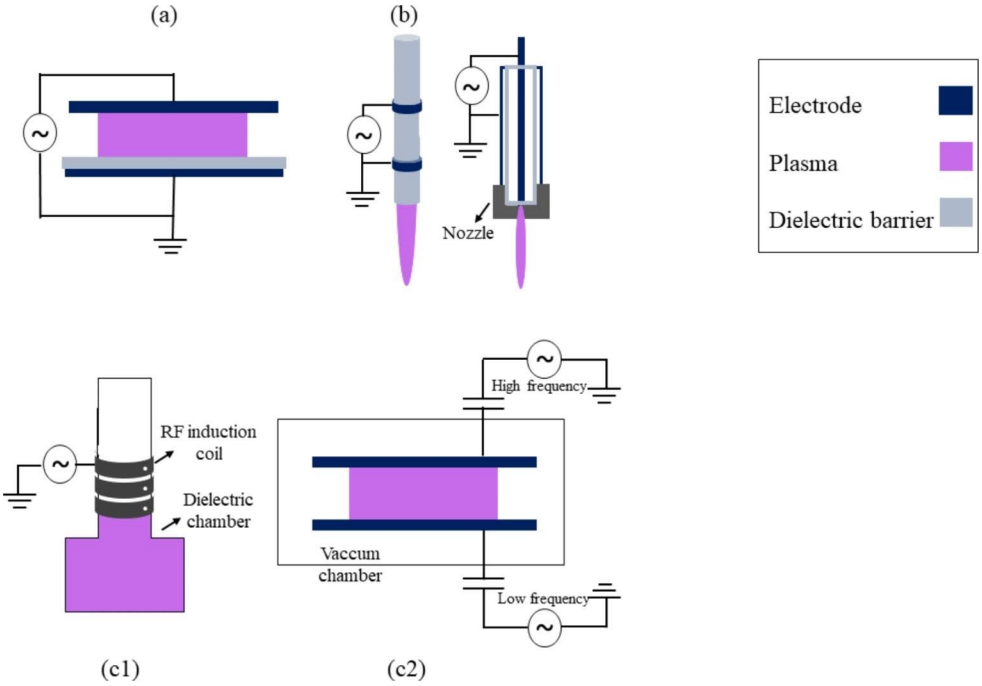

Fig. 1 Schematic configurations of main cold plasma systems reported by the literature for treating starch: **(a)** Atmospheric pressure dielectric barrier discharges; **(b)** Atmospheric pressure plasma jet, (c1) Inductively coupled plasma (ICP), and (c2) Capacitively coupled plasmas (CCP). Adapted with permission from Laroque et al. [4]

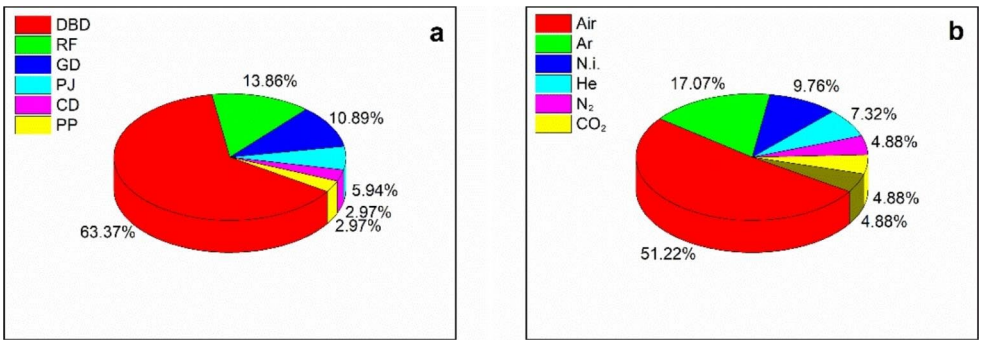

Fig. 2 Reactor **(a)** and gas **(b)** types used to modify starch granules with cold plasma. DBD (dielectric barrier discharge), RF (radio frequency), PP (pin-to-plate), PJ (plasma jet), GD (glow discharge), CD (corona discharge), HDMSO (hexamethyldisiloxane), N.i. (not informed)

using special gases have been used to modify starch granules (dry) and starch granules dispersed in water. In recent years, studies using air as generation gas at atmospheric pressure have increased because it facilitates the use of CP since it does not require the supply of special gases nor vacuum pumps and chambers, reducing the treatment costs.

Starch Granules Modified by Cold Atmospheric Plasma

Cold atmospheric plasma – i.e., cold plasma obtained from the air at atmospheric pressure – was used to modify different starch sources. For instance, tartary buckwheat, sorghum, wheat, and quinoa starches were DBD CP-treated at 20 kV and 1 kHz for 30 s and, in general, CP induced the depolymerization of starch granules, generating short length chains, which altered powders' physicochemical, pasting, and thermal properties (Fig. 3) [14]. Samples were similarly affected by the plasma reactive species, although the treatment was more effective depending on the starch source and property analyzed. For example, the amylose content of all sources was reduced after treatment, but a significant difference was observed between samples, ranging from 62 to 80% reduction. A solubility enhancement was observed after the treatment; wheat and tartary buckwheat starches showed a more pronounced result when compared to sorghum and quinoa sources [14]. The samples' viscosity was greatly reduced regarding pasting properties, with no swelling or gelatinization observed during RVA (rapid visco-analyzer) testing, except for treated tartary buckwheat starch [3]. A reduction of viscosity was also reported for DBD CP-treated corn starch by Bie et al. [1], with this effect being enhanced by longer treatments (> 5 min). The gelatinization temperatures of all samples were increased, and their gelatinization peaks broadened, though the only sample with a significant increase in gelatinization enthalpy was tartary buckwheat starch.

Regarding the digestibility of tartary buckwheat, sorghum, wheat, and quinoa starches no significant difference

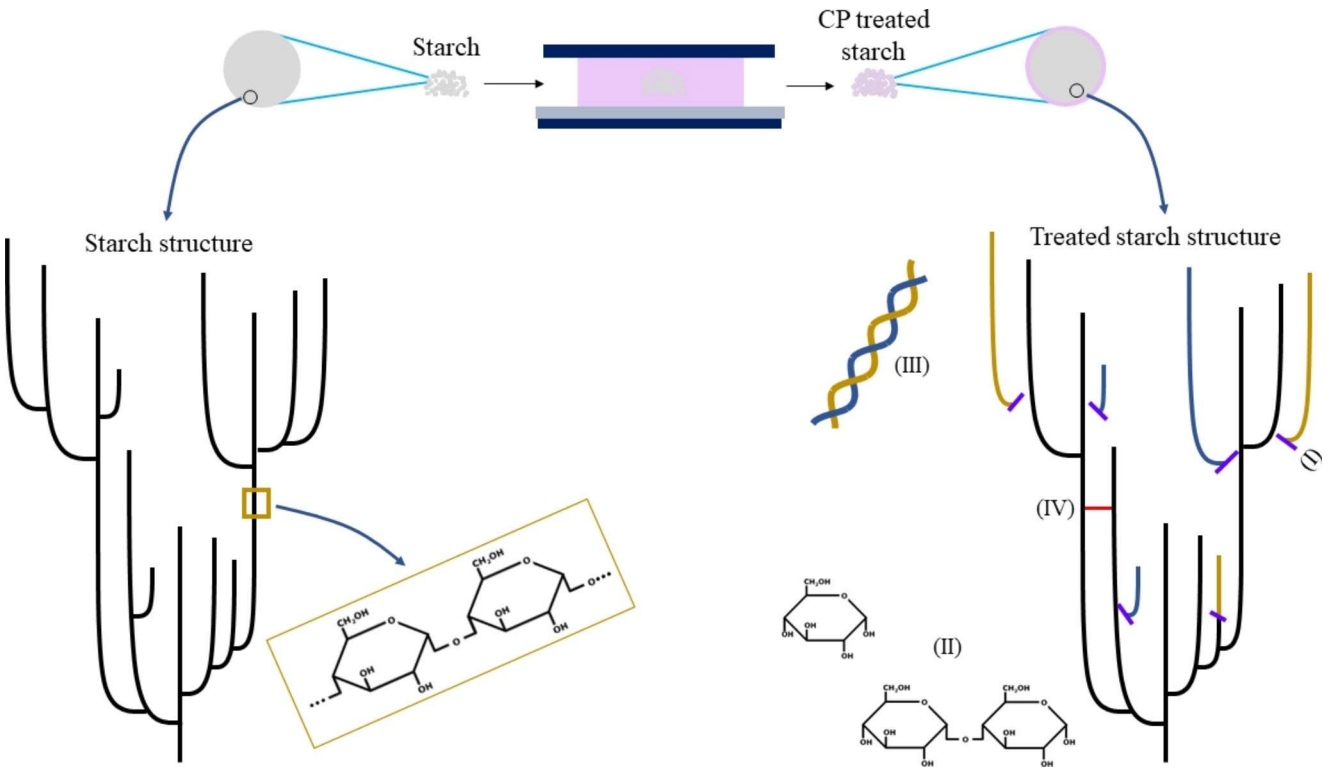

Fig. 3 Schematic representation of the effect of cold plasma (CP) on the starch structure: **(I)** depolymerization of starch chains resulting in **(II)** the formation of oligomers and simple sugars, and **(III)** double helices; **(IV)** cross-linking between starch chains promoted by CP reactive species

was observed for rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS), except for the RDS of sorghum starch, which increased 48%, and the RS of wheat starch, which decreased 36% [3]. Furthermore, CP parameters may also affect the treatment results. Native tartary buckwheat starch has an amylose content of roughly 30%, which was reduced depending on the CP treatment parameters. DBD CP at 15 kV and 1 kHz for 20 s reduced amylose content in tartary buckwheat starch to 21%, whereas a stronger and longer treatment with 20 kV and 1 kHz for 40 s reduced it to 7%. Typically, higher voltages ($\geq$20 kV) and longer treatments ($\geq$40 s) enhance the effects of CP treatment. For tartary buckwheat starch, stronger treatments resulted in lower pasting properties, higher thermal properties, solubility, and relative crystallinity. It may also reduce RS in tartary buckwheat starch and improve SDS and RDS, making it more available for enzymatic hydrolysis [14].

However, increasing the voltage and residence time of cold plasma starch treatment does not guarantee improvements in their properties, as Carvalho et al. [21] demonstrated when treating aria starch with DBD CP. The authors used voltage ranging from 7 to 20 kV with a fixed frequency of 200 Hz for 15 min and observed that optimum results were achieved at 14 kV. A trend in amylose content reduction was observed until 14 kV, with an increase when 20 kV was applied. It was attributed to the complexation of starch molecules due to new bounds generation favored by the higher voltage [21]. In contrast to Gao et al. [3], CP-treated aria starch remained viscous during RVA analyses, and their viscosity was higher when compared to native starch. The non-monotonous behavior can be attributed to the different starch sources, electrical frequency, and treatment duration [3, 21]. A similar increase in viscosity was also reported by Zhang et al. [30] when treating tapioca starch with DBD CP, though low pressure was applied. Moreover, a trend in reducing gelatinization temperature and enthalpy with increasing the voltage was observed.

DBD CP treatment influenced in vitro digestibility of aria starch. RDS was increased when voltages up to 14 kV were used, with a simultaneous reduction of SDS. The treatment did not affect RS in all tested voltages. Treatment voltage from 14 to 20 kV resulted in a slight reduction of RDS with no significant modification of SDS or RS [21].

Even though DBD is the most used method for generating CP for starch treatment (Sect. 2), other CP sources show promising results using air as the generation gas. RF CP was applied to rice starch at 0.15 mbar with 40 and 60 W of applied power for 5 and 10 min [31]. A reduction in the amylose content of rice starch was reported (from 29.93 to 22.83%), which was more pronounced when higher power or residence time was used, similar to the treatments with DBD CP aforementioned [3, 21, 31]. The treated starch

had higher values of water absorption index (from 8.9 to 11.5 g/g), solubility (from 5.1 to 6.7%), swelling power (from 9.6 to 12.3 g/g), and peak viscosity during RVA test (from 3113 to 4533 cP). No significant difference was observed in gelatinization temperature, and gelatinization enthalpy was lowered when 60 W was applied for 10 min. The rice starch properties may have increased due to the depolymerization of starch molecules, amylose/amylopectin ratio modifications, and the leaching out of amylose caused by CP reactive species [31]. Depolymerization of CS was also reported by Bie et al. [1], where particles of lower molecular weight were observed after CP treatment. Longer exposure times (10 and 20 min) were later tested with corn and tapioca starches. Contrary to rice starch, the amylose content of tapioca starch increased (from 17.21 to 20.06 g/100 g). with higher power and residence time. Also, an increased in gelatinization temperature and enthalpy was observed for tapioca starch, while only a reduction in gelatinization enthalpy was reported for CS. This reinforces that the effects of CP treatments may vary depending on the starch source [2]. In both cases, the greater the power and time applied, the bigger the difference observed. Finally, both tapioca and corn starches had higher pasting properties after RF CP treatment when compared to control samples [2], which was also observed by Zhang et al. [30] after CP treatment of tapioca starch.

Another type of CP investigated for starch treatment is the pin-to-plate configuration, which treated mango sed kernel starch at 170 and 230 V for 15 and 30 min [16]. Apart from reducing the amylose content, the treatment increased the water absorption index, water solubility, and swelling power at any voltage and treatment time tested. The higher the CP parameter, the higher the properties values found. Samples treated for 30 min at 230 V had similar water absorption index, water solubility, and swelling power at 70 °C to those of control samples at 80 °C. Therefore, CP treated mango sed kernel starch requires less energy to achieve similar hydration properties compared to untreated mango sed kernel starch. Furthermore, a significant increase in freeze-thaw syneresis was reported, increasing from 25 to 58%. These changes were attributed to the depolymerization of glycosidic linkages and an increase in hydroxyl groups. Regarding pasting properties, all pin-to-plate treatments increased the viscosity of mango sed kernel starch solutions, though no significant difference was observed between different treatment conditions [16]. Arrowroot starch was also CP-treated using a pin-to-plate system (190 to 230 V and 1100 Hz for 5 to 15 min). Swelling power and water absorption index of arrowroot starch were improved in any conditions applied and required less energy to achieve similar values when compared to untreated arrowroot starch, similar to CP-treated mango sed kernel starch [16, 32]. This is achieved by higher presence of hydrophilic groups, surface etching, and cross-linking after CP-treatment, augmenting the attachment of water molecules on starch chains, improving surface area and starch integrity due to cross-linked chains. Moreover, all pasting properties, crystallinity, and gelatinization temperature and enthalpy were enhanced after treatment [32].

Regardless of the CP system, the treatments may change amylose content, water absorption index, water solubility, swelling power, pasting properties, relative crystallinity, gelatinization temperature and enthalpy, freeze-thaw syneresis, and digestibility of the starches. They are consequences of depolymerizing starch molecules, changes in the amylose/amylopectin ratio, formation of small sugars (maltose and glucose), cross-linking between starch chains, increased surface roughness, and increased hydroxyl groups within the starch chains due to interactions with CP reactive species. The degree of effectiveness of each treatment will depend on the starch source and CP parameters voltage, treatment length, electrical frequency, and pressure. DBD CP studies modified starch granules using voltage, treatment length, electrical frequency, and pressure of 60 V to 30 kV, 30 s to 30 min, 200 Hz to 1 kHz, and 20 to 50 Pa, respectively [3, 14, 21, 31]. However, the broad range of operating parameters and a lack of cause-consequence relationships indicate that more systematic studies are necessary to understand and predict the physicochemical properties of starch granules treated by each CP.

Starch Granules Modified by Cold Plasma Using Special Gases

Although using air as generation gas for CP would be easier and cheaper, studies verified the possible differences in CP-treated starch when using special gases, such as hexamethyldisiloxane, He, Ar, and N_2. The effect of using hexamethyldisiloxane in CP treatment for corn starch was investigated by Sifuentes-Nieves et al. [28]. The authors conducted the RF CP treatments at 0.45 mbar using 90 W of power for 30 min, which significantly reduced the relative crystallinity of corn starch (up to 48% reduction) and increased its thermal stability. The low pressure applied during the plasma bombardment increased the compactness of the starch structure due to water removal, allowing CP reactive species to interact more easily with amylose. Moreover, an increase in C–C interactions while a reduction of C–OH bounds was observed, suggesting an increase in the cross-linking of starch molecules (Fig. 3). Therefore, hexamethyldisiloxane plasma treatment can be used as an alternative to granular starch modification similarly to conventional chemical methods [28]. In another study, RF CP

treatment using hexamethyldisiloxane (vacuum (pressure not informed), 90 W for 10 min) was compared to DBD CP treatment using a mixture of Ar and hexamethyldisiloxane (1 atm, 12 kV and 25 kHz for 10 min) in corn starches containing 30 to 70% amylose content. Starch samples with 70% amylose content underwent the highest modification, with significant differences between CP types. Both types increased the gelatinization temperature and enthalpy of high amylose content samples, though RF CP increased the most. DBD CP treatment formed a thin coat on the surface of starch granules due to hexamethyldisiloxane polymerization, with vibration modes observed in FTIR spectra, which was not observed in RF CP treatment. DBD also generated a higher electronic density of reactive species, although RF CP was able to penetrate deeper into the starch granules by promoting higher degree of fissures on the starch granules surface. As a result, a more ordered structure and possibly higher removal of amorphous regions from the granules are in RF-treated samples compared to DBD and control samples. Moreover, corn starch with 70% of amylose content had higher gelatinization temperature and enthalpy when compared to DBD CP-treated and untreated corn starch, which indicates a more aligned structure – or higher degree of crystallinity – in with higher thermal stability RF CP-treated samples [33].

For Ar CP, studies verified its effect on talipot palm starch [34], tapioca starch [30], waxy maize starch, waxy potato starch, and waxy rice starch [27]. Talipot palm starch was treated using low-pressure glow discharge CP (0.5 mbar, 7.5 and 15 W for 30 and 60 min), and it was observed a decrease in relative crystallinity after CP treatment. Moreover, a significant decrease in pasting properties was also observed for all treatments. Thus, the greater the power and residence time applied, the higher the effect. However, a slight significant reduction in pasting temperature was observed after treatments. Changes in gelatinization temperature were reported. Treatments with 7.5 W were similar to control samples. On the other hand, 15 W significantly reduced onset, gelatinization, and conclusion temperatures. All treatments reduced the enthalpy of gelatinization of talipot palm starch; however, power had a more significant effect when compared to time. The authors concluded that those changes were due to depolymerization, amylose/amylopectin ratio modifications, and molecular degradation [34]. Contrarily to talipot palm starch, tapioca starch pasting properties were enhanced after DBD CP treatment (0.05 atm, 30 kV, and 43.5 kHz for 20 and 30 min), and no significant difference was observed in different residence times. Also, treatments did not alter the pasting temperature of tapioca starch [30]. Waxy maize starch, waxy potato starch, and waxy rice starch were all treated using RF CP (vacuum (pressure not informed), 120 W for 1 h) with a mixture of CO_2 and Ar (25:15 cm^3/min of CO_2:Ar). After treatment, the peak viscosity of waxy maize starch and waxy rice starch decreased, while waxy potato starch viscosity increased. This difference was attributed to the possible oxidation of lipids in the starch-lipid complexes of waxy rice starch and waxy maize starch and the higher capacity of swelling of waxy potato starch, increasing the viscosity due to starch leaching out. Moreover, waxy potato starch displayed an increased breakdown viscosity after treatment; however, a decrease was observed for waxy rice starch and waxy maize starch, which could indicate a lower degree of cross-linking in waxy potato starch, reducing paste stability. A slight reduction in onset temperature for all samples was observed, indicating a reduction in thermal stability, while an increase in gelatinization enthalpy may be due to induced cross-linking and a higher presence of double helices. All three starches evaluated had a significant increase in RS after treatment, possibly due to the cross-linking induced by reactive plasma species, removing OH groups from glucosyl units, and promoting cross-linking by ether linkage [27].

Tapioca starch was also treated using DBD CP (0.5 atm, 30 kV, and 43.5 kHz for 20 and 30 min) with CO_2 and He as generation gases [30]. Peak, trough, breakdown and final viscosities were enhanced after CP-treatment when compared to control samples. Higher values were observed for tapioca starch treated with He compared to CO_2, with exception of breakdown viscosity, probably due to the higher degree of cross-linking promoted by He CP. Still, modifications to pasting properties were generally similar among treatments using CO_2, He, air, or Ar for 20 and 30 min. It can be inferred that He CP-treatment produces tapioca starch with higher peak and trough viscosities when applied for 30 min compared to CO_2, Ar, and air CP treated samples, as well as control tapioca starch. The authors attributed this to a higher capacity of He CP in promoting cross-linking in tapioca starch by cleaving the reducing ends of the polymeric chain (C–OH) and forming ether linkages (C–O–C). This enhanced cross-linking could be observed in the FTIR spectra of treated samples, with He exhibiting the highest peaks for C–O–C, CH, and CH_2. Moreover, it was concluded that air was the weakest in promoting cross-linking [30]. Zhang et al. [35] also analyzed the modifications induced on potato starch using glow plasma (2000 Pa, 245 V, and 1.1 A for 30, 45, and 60 min) with He and N_2 as generation gases. Treatments resulted in starch with reduced gelatinization temperature and enthalpy, pasting properties, and relative crystallinity with enhanced effect in longer residence times. The authors concluded that these modifications were caused by inducing chemical reactions and disorganizing the supramolecular structure of amylose and amylopectin. Furthermore, He was able to generate more reactive species when

compared to N_2, therefore displaying an increased effect on the analyzed properties [35].

Cold Plasma Enhanced by Physicochemical Treatments

Hydration and Dry Heat Treatments

Current combinations of technologies have been reported in the literature, such as drying, chemical, and enzymatic treatments, extrusion, ultra-high-pressure, and microwaves, to intensify starch modification. Hydration and dry heat treatments have been coupled with CP to modify the structure and physicochemical properties of native starches. In the hydration treatment, starch is dispersed in an aqueous medium prior to heating, whereas in the dry heat treatment, high temperatures are applied directly to the powder. Recently, Yan et al. [36] studied the effect of CP using a DBD system on modifying banana starch dispersed in distilled water (Table 1). Starch treated with CP did not reveal surface modifications. However, relative crystallinity in starch granules decreased from 21.8 to 17.1% as the treatment intensity increased from 60 to 100 W. It may be due to depolymerization and decomposition of starch chains during CP treatment, resulting in a poorly arrangement of the damaged starch chains (Fig. 4). Starches modified this way presented a much higher water solubility at 55 ºC (15.5 g/100 g) when compared to untreated banana starch (1.35 g/100 g). Also, a peak viscosity reduction was observed from 5242 cP (unmodified starch) to 153 cP (modified starches). In contrast, Wu et al. [37] observed an increase in the relative crystallinity (from 20.4 to 24.6%) and gelatinization temperature (from 64.7 ºC to 66.5 ºC) in banana starch dispersed in water and treated with CP using a corona electrical discharge (Table 1). The authors correlated the increase in relative crystallinity with the dehydroxylation of the starch amorphous region through condensation and ether bond formation, rearranging starch chains in a more orderly crystalline structure. Unfortunately, the presence of these chemical groups was not confirmed, and the standard deviation values of relative crystallinity and gelatinization temperature were not reported in this research. Finally, Wu et al. [37] also observed a reduction in the viscosity behavior of treated banana starches dispersed in water; hence, peak viscosity decreased from 100.4 RVU (untreated starch) to 44.4 RVU (treated starch). Viscosity results agree with those informed by Yan et al. [36] for similar starch. These authors concluded that CP did not alter banana starch's resistant fraction and amylose levels. Further studies could investigate the digestibility of this starch dispersed in water and treated with CP.

Dry heat has been used as a pretreatment of starches to be modified by CP (Fig. 4). Ge et al. [38] treated red adzuki bean starch at 130 ºC for 1, 3, and 9 h, followed by CP treatment using a DBD reactor (Table 1). Furthermore, the effects of dry heat and CP were investigated separately. The authors observed that dry heat reduced the amylose content from 24.3 to 16.9% (9 h), whereas similar amylose content reduction was obtained in starches treated for 10 min with CP (16.2% of amylose content). Combined dry heat for 9 h and CP for 10 min reduced the amylose content to 10.4%. Also, relative crystallinity decreased from 28.6 to 25.1% (CP, 10 min), and 26.4% (dry heat = 9 h) while starches treated with both dry heat for 9 hand CP for 10 min presented relative crystallinity of 21.3%. These authors correlated the starch modification with depolymerization of amylose chains and degradation of the crystalline regions in starch granules. Also, they observed an increase in the solubility in water of red adzuki bean starch. It doubled at 90 ºC from 16.3 to 33.6% after 9 h of dry heat followed by 10 min of CP. The same combined treatments reduced the peak viscosity from 4271 cP (untreated starch) to 933 cP, increased the gelatinization temperature from 55 to 61 °C and decrease the gelatinization enthalpy from 13.5 to 10.6 J/g. Combined treatments also had effect on digestibility properties. Rapidly digestible starch was reduced from 63.6 to 61.4% when only dry heat for 9 h was applied and further reduced to 51.5% when coupled with CP for 10 min. Slowly digestible starch increased from 23.5 to 28.0% with 9 h of dry heat and further increased to 42.3% when combined with 5 min of CP. For resistant starch, a reduction to 9.8 from 12.9% can be achieved using only dry heat for 3 h, whereas a further increase to 13.2% can be reached combining dry heat for 1 h and CP for 1 min. Interestingly, the resistant starch can also be lowered to 6.2% with the use of dry heat for 9 h and CP for 3 min [38]. The same authors observed that starches treated with dry heat and CP increased in slow digestion starch (SDS) and resistant starch (RS) because the treated granules had amylose/amylopectin depolymerization, low molecular weight, and low degree of polymerization. These small components resist enzymatic hydrolysis by forming double helices and separating amylose-amylose. Based on results informed by Ge et al. [38], it is possible to conclude that dry heat coupled with CP can impart physicochemical modifications in starch granules, which was not observed when using these techniques separately.

Chemical and Enzymatic Treatments

Chemical and biochemical (enzymatically catalyzed) reactions have been used to induce starch modifications before or after CP treatment (Fig. 4), aiming, among others, the starch cross-linking to increase the presence of RS. In this

Table 1 Reactor type, operating parameters and physicochemical properties of starch after cold plasma treatment

Starch type and sample preparation	Reactor configuration and specifications	Operating parameters	Gas composition	Solubility	Swelling Power	Relative Crystallinity	Viscosity	Gelatinization		Reference
								T_p	ΔH	
Banana starch dispersed in distilled water (1:9 w/w)	DBD Parallel electrodes (Ø = 50 mm), dielectric quartz layers, and discharge gap of 8 mm	Current intensity: 2 A Voltage: 30, 35, 40, 45, and 50 V, Time = 3 min	N.i.	↑ Enhanced from 1.35– 10.30 to 15.05–55.92 g/100 g at 55–95 °C with 100 W.	↓ Reduced from 3.0–15.0 to 2.8–3.5 g/g at 55–95 °C with 100 W.	↓ From 21.82 to 17.15% with 100 W.	↓ Peak viscosity reduced from 5242.0 to 153.0 cP with 100 W.	N.i.	N.i.	[36]
Banana starch dispersed in distilled water (1:3 w/w)	CED N.i.	Current intensity: 60 A Voltage: 30, 40, and 50 kV/cm Time = 3 min	N.i.	N.i.	N.i.	↑ From 20.4 to 24.6% with 50 kV/cm.	↓ Peak viscosity reduced from 100.4 to 44.4 RVU with 50 kV/cm.	↑ From 64.7 to 66.5 °C with 50 kV/cm.	↓ From 4.7 to 2.9 J/g with 50 kV/cm.	[37]
Red adzuki bean starch (powder)	DBD Discharge gap: 2 mm	Current intensity: 2 A Voltage: 40 V Time = 1, 5, and 10 min	Air	↑ Enhanced from 1.77–16.3 to 3.45–22.67% at 50–90 °C with 10 min treatment.	↓ Reduced from 3.21–31.90 to 2.28–19.97 g/g at 50–90 °C with 10 min treatment.	↓ From 28.59 to 25.13% with 5 min treatment.	↓ Peak viscosity reduced from 4271 to 450 cP with 10 min treatment.	↑ From 55.01 to 61.82 °C with 10 min treatment.	↓ From 13.52 to 12.12 J/g with 10 min treatment.	[38]
Corn starch (powder)	DBD Parallel electrodes (Ø = 55 mm), dielectric quartz layers, and discharge gap N.i.	Current intensity: 1 A Voltage: 40 V Time = 1, 3, and 9 min	Air	↑ Enhanced from 0.46–11.58 to 1.92–20.47% at 50–90 °C with 9 min treatment.	↓ Reduced from 1.82–16.85 to 1.49–8.86 g/g at 50–90 °C with 9 min treatment.	↓ From 41.77 to 38.01% with 9 min treatment.	↓ Peak viscosity reduced from 3205 to 711 cP with 9 min treatment.	↑ From 68.99 to 70.12 °C with 9 min treatment.	↓ From 11.22 to 10.01 J/g with 9 min treatment.	[22]
Modified rice starch (powder)	DBD Parallel electrodes (Ø = 90–100 mm), quartz cuvette, and discharge gap of 13 mm	Current intensity: 1 A Voltage: 40 V Time = 1, 3, 6, and 9 min	Air	↑ Enhanced from 29.38–51 to 51.57–88% at 25–90 °C with 9 min treatment.	↑ Enhanced from 4.2–33.8 to 7.4–62.8 g/100 g at 25–90 with 9 min treatment.	↓ From 27.54 to 20.69% with 9 min treatment.	↑ Peak viscosity increased from 888 to 1729 cP with 9 min treatment.	N.i.	N.i.	[39]

Table 1 (continued)

Starch type and sample preparation	Reactor configuration and specifications	Operating parameters	Gas composition	Solubility	Swelling Power	Relative Crystallinity	Viscosity	Gelatinization		Reference
								T_p	ΔH	
Corn starch (powder)	RF Rotatory (20 RPM) cylindrical glass reactor (0.5 L)	Frequency: 13.56 MHz, Pressure: 0.45 mbar Gas flux: 0.35 cm^3/min Power: 90 W Time = 30 min	HMDSO	N.i.	N.i.	↓ Reduction of 12, 43 and 18% for starch with 30, 50 and 70% amylose, respectively.	N.i.	↑ Only 70% amylose starch was affected. Increased from 82.54 to 90.25 °C.	↑ Only 70% amylose starch was affected. Increased from 7.84 to 12.27 J/g.	[28]
Corn starch (powder) with 30, 50 and 70% amylose content	RF Rotatory (20 RPM) cylindrical glass reactor (0.5 L)	Frequency: 13.56 MHz, Gas flux: 0.35 cm^3/min Power: 90 W Time = 10 min	HMDSO	N.i.	N.i.	N.i.	N.i.	↑ Only 70% amylose starch was affected. Increased from 82.40 to 91.96 °C.	↑ Only 70% amylose starch was affected. Increased from 8.57 to 10.29 J/g.	[33]
	DBD Coaxial electrodes, dielectric quartz tube	Frequency: 25 kHz Voltage: 12 kV Time = 10 min	Ar/HDMSO	N.i.	N.i.	N.i.	N.i.	↑ Only 70% amylose starch was affected. Increased from 82.40 to 88.95 °C.	↑ Only 70% amylose starch was affected. Increased from 8.57 to 9.89 J/g.	
Modified proso millet starch	DBD Discharge gap of 12 mm	Current intensity: 0.8 A Voltage: 40 V Time = 1, 3, and 5 min	Air	N.i.	N.i.	↓ From 31.52 to 25.47% with 5 min treatment.	↓ Peak viscosity decreased from 3247 to 405 cP with 5 min treatment.	N.i.	N.i.	[40]
Naked barley starch (powder)	DBD Discharge gap of 13 mm	Current intensity: 0.8 A Voltage: 40 V Time = 1, 5, and 10 min	Air	↑ Enhanced from 0.23–12.25 to 0.76–32.68% at 50–90 °C with 10 min treatment.	= No significant changes were observed at 50–90 °C range.	↓ From 39.57 to 34.43% with 10 min treatment.	↓ Peak viscosity decreased from 2522.0 to 917 cP with 10 min treatment.	↑ From 61.26 to 62.35 °C with 10 min treatment.	↓ From 8.45 to 6.50 J/g with 1 min treatment.	[41]

Table 1 (continued)

Starch type and sample preparation	Reactor configuration and specifications	Operating parameters	Gas composition	Solubility	Swelling Power	Relative Crystallinity	Viscosity	Gelatinization		Reference
								T_p	ΔH	
Sweet potato starch (powder)	DBD Parallel electrodes (Ø = 55 mm), dielectric quartz layers, and discharge gap of 13 mm	Current intensity: 1 A Voltage: 40 V Time = 1, 3, and 9 min	Air	↑ Enhanced from 0.57–10.84 to 1.16–15.94% at 50–90 °C with 9 min treatment.	↓ Reduced from 2.11–30.56 to 1.96–22.05 g/g at 50–90 °C with 9 min treatment.	↓ From 33.76 to 30.86% with 9 min treatment.	↓ Peak viscosity decreased from 5270 to 1302 cP with 9 min treatment.	↑ From 64.19 to 70.80 °C with 9 min treatment.	↑ From 10.54 to 14.81 J/g with 9 min treatment.	[42]
Wheat starch (powder)	DBD Parallel electrodes (Ø = N.i.), dielectric quartz layers	Current intensity: 1 A Voltage: 40 V Time = 2, 6, and 10 min	Air	N.i.	↓ Reduced from 2.41–13.85 to 2.31–11.56 g/g at 50–90 °C with 10 min treatment.	= No significant changes were observed.	↓ Peak viscosity decreased from 2503 to 631 cP with 10 min treatment.	↑ From 62.39 to 62.94 °C with 10 min treatment.	↑ From 9.82 to 11.76 J/g with 10 min treatment.	[24]

DBD: dielectric barrier discharge; CED: Corona electrical discharge; RF: Radio frequency; HMDSO: Hexamethyldisiloxane; N.i: Not informed

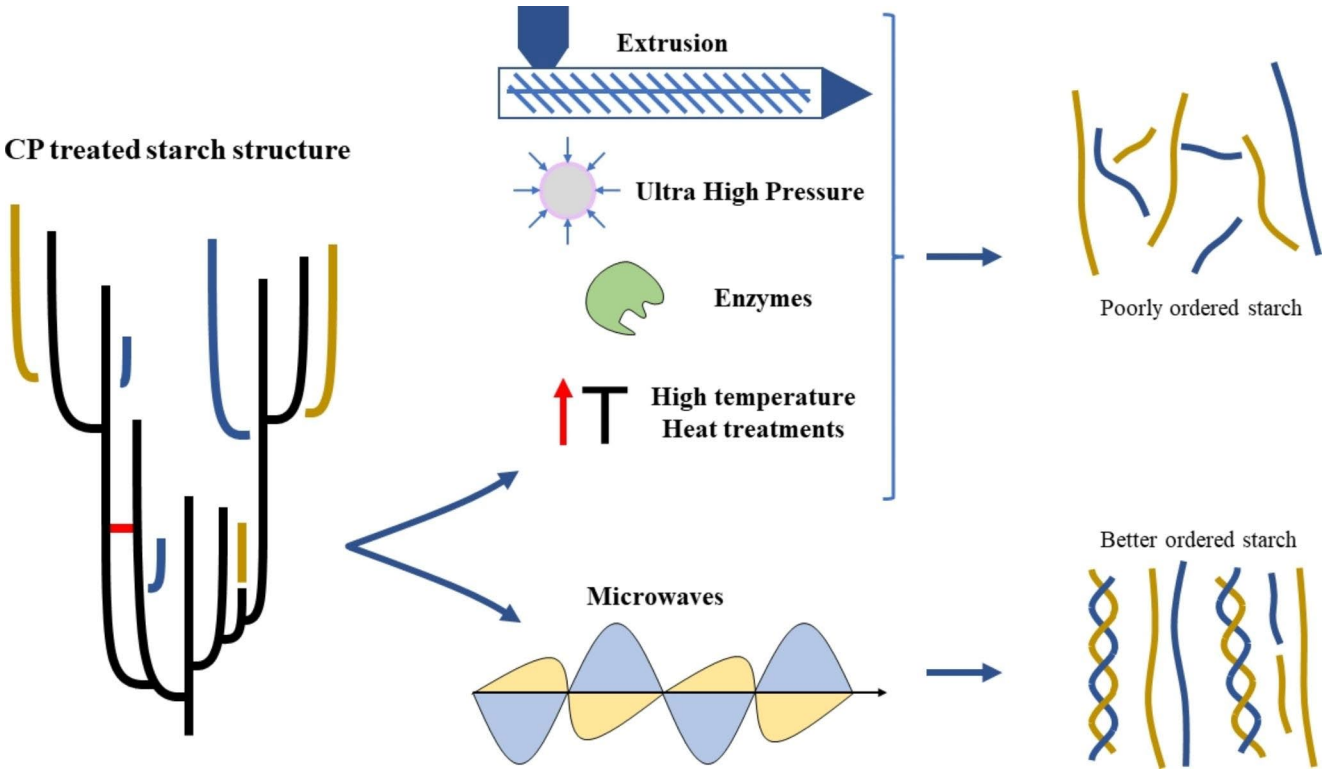

Fig. 4 Schematic representation of the effect of dual starch modifications on the starch structure: Cold plasma (CP) and physicochemical treatments (extrusion, ultra-high pressure, high temperature, heat treatments (drying), and microwaves

context, corn starch powder was treated with CP (Table 1) for 1, 3, and 9 min, followed by sodium trimetaphosphate/sodium tripolyphosphate treatment [22]. The authors observed increased phosphorus content, substitution degree in starch granules, presence of short-starch chains, and chain rearrangements, improving the number of chemical bonds at this cross-linking process. The starch granules after CP-treatment for 9 min and cross-linking with 10% trimetaphosphate/sodium tripolyphosphate had higher RS (65.2%) when compared to untreated corn starch (11.4%), starch only CP-treated for 9 min (20.6%), and starch only cross-linked with 10% trimetaphosphate/sodium tripolyphosphate (23.2%). Moreover, the combined treatment in these condition increased the gelatinization temperature and decreased the gelatinization enthalpy when compared to untreated and starch single treated starch [22]. In another study, rice starch was modified chemically with alcohol, NaOH, and HCl to produce water-soluble rice starch, which was then modified with CP. The authors concluded that CP resulted in a decrease in amylose content, RC, and short-range order, improving solubility, swelling power, and flowing capacity. Furthermore, the enzymatic hydrolysis in dually modified starches was higher (72%) when compared with water-soluble rice starch (22%). The same authors speculated that water-soluble rice starch treated with CP could be used to manufacture instant and functional foods [39].

Esterification of starch by citric acid was improved by CP pretreatment [41]. Etching and pores caused by CP on the surface of starch granules improve its surface area, thus augmenting the citric acid capability of accessing and reacting with the starch structure, resulting in a higher degree of substitution. Also, CP treatment enhances the amylose content of citrate starch when up to 30% in mass (w:w, citric acid:starch) was added. These results were attributed to the depolymerization of amylopectin caused by CP and the formation of reactive groups, which facilitated citric acid penetration and reduced starch molecular weight. Starch relative crystallinity decreased as a depolymerization side effect since it creates short chain fractions that can interfere with the crystalline structure, which is more pronounced after citric acid esterification. On native starch, these smaller short-chain fractions enhance the RDS and RS while decreasing the SDS and may form double helices, resisting enzyme hydrolysis. In the case of citrate starch, SDS and RS increased, and RS reduced due to the substitution of hydroxyl groups by citric anhydride, forming cross-linked citrate starch and reducing the effectiveness of digestive enzymes. Therefore, CP pretreatment could increase the esterification of starch granules and produce foods with high RS content [41].

Enzymes have been used to modify starch granules as an energy-efficient method compared to classical thermal treatments. A pretreatment with CP could enhance the effectiveness of enzymatic treatments on starch granules by augmenting starch chain mobility. In this context, Ge et al. [42] studied the effects of CP (Table 1) pretreatment on sweet potato starch modification by pullulanase. The authors found that the co-treatment enhanced the amylose content, solubility, and thermal properties while lowering the molecular weight, degree of polymerization, and swelling power. Similarly to Shen et al. [41], pretreating starch with CP increased RS and SDS while decreasing rapidly digestible starch. The authors attributed that to reduced deep crystalline regions and the production of defective regions after co-treatment. The same authors concluded that CP is a promising technique for producing starch-based foods with lowered digestibility [42]. These results were also close to the ones obtained when the modification of wheat starch was performed by α-amylase followed by CP (Table 1) [24]. RS and RDS contents were improved, and SDS content was decreased. Nevertheless, the study also concluded that a co-treatment of enzymes and CP could produce foods with increased RS content [24].

Extrusion, Ultra-High-Pressure, and Microwave

Extrusion is another option to modify starch granules before treating them with CP (Fig. 4). Recently, Sun et al. [43] compared the physicochemical properties of potato starch and extruded potato starch, both treated with CP for 1, 5, and 9 min (Table 1). Potato starch treated with CP revealed an increase of water solubility at 90 ºC from 7.9% (native starch) to 71.5%, whereas dually treated potato starch (dually treatment: extrusion followed by CP) had solubility in water values around 80%. In the same study, dually treated potato starches revealed high RDS and low RS values compared to starches treated only with CP [43]. This study suggests that the combination between twin-screw extrusion and CP had more profound modifications than the single treatment. However, the increase in RDS and reduction in RS values could reduce the application of these modified starches in food formulations since starches having low RDS and high RS are desired in the food industry [43]. In another study, the same research group treated proso millet starch with ultra-high pressure followed by CP and concluded that dually modified starches enhanced the resistance to high temperature and shearing, as well as improved the pasting stability of proso millet starch. In addition, dually treated starches slightly increased the SDS content from 7% in starches treated with ultra-high pressure to 10.7% in starches dually treated [40]. RDS also increased in dual treatments (from 41.2 to 49.1%), indicating an increase in the percentage of starch that would be quickly digested in the human gastrointestinal tract.

Generally, starches dually modified by extrusion or ultra-high pressure combined with CP have shown less ordered double-helices (Fig. 4) [40, 43]. In contrast, the treatment of starch granules with microwave followed by CP can produce modified starches with higher RS since microwave can promote ordered short-range double helices and increase the short-range order of the starch (Fig. 4). Hence, an increase of 28% of RS was observed in rice starch treated with microwave followed by CP [44].

Conclusions and Future Aspects

Cold Plasma has been demonstrated as a useful technique for significantly modifying starch granules' physicochemical properties. Among the many existing CP systems, starch granules have been mostly treated with atmospheric-air CP in the dielectric barrier discharge (DBD) configuration. It has been demonstrated that CP induces the depolymerization of starch granules. Thus, CP reduces the length of chains, amylose content, crystallinity, and viscosity; and increases water solubility index and swelling. In general, CP-treated starch granules are more available for enzymatic hydrolysis. However, contradictory results were observed due to different CP operational parameters.

CP treatment using special gases has been evaluated little. He and hexamethyldisiloxane demonstrated great potential for inducing cross-linking in starch granules. However, other gases and different CP configurations may be used to explore other possibilities. In the same way, few studies have been done with coupled CP and other (pre-) treatments. The hydration, dry heat, chemical/biochemical reactions, extrusion, and ultra-high pressure presented a synergistic effect, improving the depolymerization and digestibility of starch granules. In contrast, combining CP and microwave can promote the ordered short-range double helices, increasing the resistant starch content desired in functional foods due to reduced digestibility.

CP has shown an important impact on starch granules and their properties. However, more systematic studies are needed since many did not use comparable operating parameters during CP treatment. Also, it is clear that there are many combining possibilities among starch origins, CP parameters and configurations, and various other coupled treatments that would lead to different and unique results. Furthermore, future research studies must be carried out to treat starch granules by CP at an industrial scale, analyzing the economic and environmental factors of this emerging technique alone or in combination with other physicochemical treatments. Treated starch granules with CP must be compared with starches granules modified by conventional physicochemical treatments and then applied in product formulations to prove their applicability.

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Declarations

Conflict of Interest The authors declare no conflict of interest.

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