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Effects Of Plasma-Assisted Acid Heat Treatment On The Structure And Physicochemical Properties Of Waxy Maize Starch

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Abstract:
Background: *Waxy maize starch exhibits strong hydrophilic ability, high swelling power and viscosity, and difficult to retrogradation, due to its high amylopectin content, holding great potentials in food application. The acid heat treatment is commonly employed to produce modified starch with high resistance towards hydrolysis, during which new glucoside bonds are formed, such as α-1,2, β-1,2 and α-1,3, β-1,3 and other glucoside bonds. Cold plasma had been emerged as a surface modification technology and has been drawn considerable interests in starch modification over years. The combined effects of cold plasma and acid-heat treatment on waxy maize starch had not been investigated.*
Materials and Methods: *In this study, waxy maize starch was selected as raw material. Dielectric barrier discharge (DBD) plasma was applied as pretreatment method, followed by the acid heat method, to obtain modified starch under different treatment conditions.*
Results: *The chromaticity results showed that the brightness of modified starch after treatment was weakened. The solubility of modified starch was greatly improved, while the swelling power was significantly decreased. The pasting property measured by RVA showed that the viscosity of treated starches was significantly lower than that of native starch, displaying no typical pasting profiles. DSC results indicated that the endothermic peaks gradually decreased with the increase of plasma pretreatment intensity. X-ray diffraction patterns were not significantly changed after dual modification. However, the relative crystallinity decreased after treatment. FTIR spectroscopy showed the R1047/1022 ratio of dual treated starches was significantly lower than native starch, indicated that the plasma and acid heat treatment destroyed the short-range ordered structure on the surface of starch granules. The digestion extents of dual modified starch were significantly lower than that of starch without DBD plasma pretreatment. With the increase of plasma pretreatment intensity, the resistant starch (RS) content generally increased. The reduced digestibility could be mainly attributed to the higher amounts of pyrodextrin that formed during following acid heat treatment.*
Conclusion: *This study could provide a new strategy for the dual modification of waxy maize starch, and provide a theoretical basis for expanding the application of plasma technology in the field of starch modification.*

Key Word: *Cold plasma; Acid heat treatment; Waxy maize starch; Physicochemical properties*

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I. Introduction

The amylopectin of waxy maize starch (WMS) accounted for more than 95% of the total starch content. WMS exhibits strong hydrophilic ability, high swelling power and viscosity, and difficult to retrogradation, due to its high amylopectin content, holding great potentials in food application [1]. The acid heat treatment process will produce resistance, and the preparation process will produce a large number of new glucoside bonds, such as α-1,2, β-1,2 and α-1,3, β-1,3 and other glucoside bonds as well as glucan, β glucoside bond structure, in addition to contain some irregular structures [2], these structures cannot be degraded by human digestive enzymes. Therefore, the treated waxy maize starch has the characteristic of "anti-digestion". Therefore, its products can inhibit the rapid rise of postprandial blood glucose level, regulate serum cholesterol and triglyceride levels, reduce the content of low and medium density fat in the viscera, and are widely used in health care products, functional drinks, dairy [3] products, flour products [4], meal replacement foods, slimming products, special food, etc.

At present, natural starch has the disadvantages of poor water solubility, easy regeneration and instability to temperature, pH and shear power, so its application is limited to some extent [5]. Plasma technology is a new non-thermal physical modification technology, which has the advantages of safety, high efficiency, environmental protection and no waste generation [6], and has great potential in the starch modification process. Plasma is the fourth state of matter, the system contains electrons, ions, free radicals, photons and other active particles [7], and these particles carry higher energy, so as to modify the surface of the material. The previous research results for starch modification showed that plasma treatment could effectively promote the dissolution of starch, inducing cracks on the surface of starch granules, increasing the number of surface and internal holes, which can provide a larger specific surface area for subsequent acid heating treatment. In this study, dielectric barrier discharge (DBD)plasma technology and acid-heat method were used to dually modify starch, and the influence of plasma-assisted treatment on waxy maize starch was studied. This study could provide a new strategy for the dual modification of waxy maize starch, and provide a theoretical basis for expanding the application of plasma technology in the field of dual modification on waxy maize starch.

II. Material And Methods

Materials

Waxy maize starch (food grade, Shanghai Yiluan Food Ingredients Co., LTD.); anhydrous ethanol, glacial acetic acid, calcium chloride, sodium acetate (Analytically pure, Tianjin Hengxing Chemical Reagent Manufacturing Co., LTD.); hydrochloric acid (Analytically pure, Tianjin Fengchuan Chemical Reagent Technology Co., LTD.).

Instruments and equipment

Model ME204/02 electronic analytical balance (accuracy 0.01g, Mettler Toledo LTD., Switzerland); pHS-3C Thunder magnetic pH meter (Shanghai Precision Scientific Instrument Co., LTD.); CTF-2000R Dielectric barrier plasma generator (Suman Plasma Technology Co., LTD.); RVA-Tecmaster Rapid Viscosity Analyzer (Perten Instruments, Sweden); Nicolet 5700 Fourier Infrared Spectrometer (Thermo isher Scientific, USA); D8 Advance X-ray diffractometer (Bruker, Germany); Q2000 Differential scanning calorimeter (TA Corporation, USA); UV-2102PCS ultraviolet-visible spectrophotometer (Shanghai Uniko Instrument Co., LTD.).

Plasma-assisted acid heat treatment

Waxy maize starch was firstly treated by dielectric barrier discharge plasma in air environment. The dielectric diameter of the upper and lower circular quartz plates is 5 cm, and the discharge spacing is 8 mm to ensure uniform discharge. The input voltage was set to 110 V, and the frequency was adjusted to obtain the input current at 0.8 A, 1.0 A and 1.2 A, respectively. The exposure duration was 30 s, 60 s and 90 s, respectively. The treated samples were collected and stored in sealed bags for subsequent testing.

After plasma treatment, 10 g of plasma modified starch (dry basis) was weighed into flasks, 5 mL of 0.2% hydrochloric acid solution by volume was added to make the acid concentration reach 0.10% (w/w) of the starch dry basis, and stir thoroughly. Then, the flasks containing starch mixture was placed into a 50°C oven for pre-drying to obtain its moisture content to less than 5%. All pre-dried starch was placed into an oven that has been heated to 120°C and heated for 60 min. Afterward, the starch samples were cooled to room temperature. Grind it with a mortar and sieve it through a 100-mesh screen, and collect it for subsequent testing. The samples were named in sequence as blank control (without plasma treatment), WMS-P0.8-30, WMS-P0.8-60, WMS-P0.8-90, WMS-P1.0-30, WMS-P1.0-60, WMS-P1.0-90, WMS-P1.2-30, WMS-P1.2-60 and WMS-P1.2-90.

Chromaticity

The values of L*, a*, b * were measured by color difference meter. Certain amounts of samples were weighed and stacked them to one side the transparent tape, so that the powder was evenly covered, then both ends of the transparent tape were folded in half and sealed. Specific measurement method was as follows: firstly, zero position correction, blackboard and whiteboard correction respectively, select 3 tests for each sample, write the number, make records, and take the average value. The total color difference (ΔE) and color intensity (ΔC) of starch are calculated by the following formula:

Where L* represents brightness, a* represents red (+) and green (-), and b* represents yellow (+) and blue (-).

Swelling power and solubility

Weigh 0.24 g of sample and place it in a 5 mL centrifuge tube, add 3 mL of distilled water to prepare 8% (w/w) suspension [8], and heat it in a water bath at 50, 60, 70, 80 and 90 for 30 min. during this period, take it out regularly for vortex mixing. After heating, take out and cool to room temperature, centrifuge at 6000 R/min for 10 min, and separate the precipitation from the supernatant. Take the supernatant in a dish, and then put it in an oven to dry to constant weight. The weighed dry weight of the supernatant is recorded as A1, the precipitation in the centrifuge tube is recorded as A2, and the dry weight of the original sample is recorded as w. Solubility and swelling power are calculated according to the following formula:

Where S stands for solubility; SP stands for swelling power; A_1 indicates the weight of the supernatant after drying, g; A_2 represents the precipitation in the centrifuge tube, g.

Pasting properties

Weigh 3.0 g of sample (dry basis) into the RVA aluminum barrel, and then add distilled water until the overall weight is 28.0 g. Using standard program 1, the pasting viscosity curve, peak viscosity (PV), valley viscosity (TV), disintegration viscosity (BV), final viscosity (FV), rebound viscosity (sb) and pasting temperature (PT) were obtained by Thermoline 3.0 software.

Thermal properties

The thermodynamic properties of the samples were determined by differential scanning calorimetry (DSC). Weigh about 3.00 mg (dry basis) of the sample into a pure aluminum crucible, add distilled water in the ratio of 1:3 (w/v) of sample: water, and test after equilibrating at room temperature for 12 h. Using an empty aluminum plate as a reference, heat from 20 to 110 at a heating rate of 10 /min. TA universal analysis software was used to calculate and analyze the heat absorbed by starch during gelatinization (enthalpy change ΔH) and the corresponding gelatinization transition temperature (onset temperature To, peak temperature Tp, end temperature Tc).

Structural Characterization

X-ray diffraction was used to study the crystallization characteristics, Fourier transform infrared spectroscopy was used to study the changes of molecular chemical groups, and the effect of different plasma treatment conditions on the structure of samples was studied with starch without plasma pretreatment as the control.

X-ray diffraction

The crystallization characteristics of the samples were determined by an X-ray diffraction (XRD). The sample was placed in a closed container containing saturated sodium chloride solution for water balance for 3 days. Using Cu K α radiation (λ=0.154 nm) at 40 kV and 40 mA, scanning range 4~40° (2θ) with scanning rate of 5 °(2θ)/min. MDI jade 6.5 software was used to analyze the diffraction patterns and calculate the relative crystallinity (RC).

Fourier transform infrared (FT-IR) spectroscopy

The sample was mixed with potassium bromide and fully ground and pressed, the scanning range was 500 ~ 4 000 cm^{-1}, the resolution was 4 cm^{-1}, and the scanning times was 64 times. With the help of OMNIC software, baseline correction and deconvolution were performed on the 800 ~ 1200 cm^{-1} spectrum, and the absorbance ratio of the sample at 1047 cm^{-1}/1022 cm^{-1} was calculated.

In vitro digestibility

100 mg (dry basis) sample was accurately weighed and dissolved it in 4 mL 0.1M sodium acetate buffer (pH=5.2); Freshly prepared α-amylase solution of 1 mL was add to the mixture, and then add 125 μL starch to glucosidase. The enzyme and starch were mixed by shock and placed in a magnetic stirring water bath at 37 , and incubated at 260 r/min for 2 h. At 20, 40, 60, 80, 100 and 120 min, 0.10 mL starch digestible solution was taken and placed in 95% ethanol solution added with 0.90 mL, the digestion reaction was terminated, and the supernatant was absorbed after centrifugation at 6000 r/m for 6 min. Absorb 1 mL of the supernatant and put it in a centrifuge tube, add 0.5mL of DNS color developing solution, mix it well and heat it in a 95 water bath for 5min, cool it to room temperature and set the volume to 10 mL. The absorbance of each sample was measured by spectrophotometer, and the hydrolysis rate of starch in each digestion period was obtained by conversion formula.

The hydrolysis rate of starch was calculated by the glucose content in different digestion periods, and the relationship between the digestibility of starch and time was drawn. The relative proportions of RDS, SDS and RS in starch samples were calculated. The formula is as follows:

$RDS(\%) = (G20-FG)\times0.9\times100$

$SDS(\%) = (G120-G20)\times0.9\times100$

$RS(\%)=(TS-RDS-SDS)/TS\times100$

Where 0.9 is the conversion coefficient of glucose content to starch content; FG is the content of free glucose; G20 and G120 are the amount of glucose released after 20 min and 120 min, respectively; TS is the original dry base mass of each sample.

Statistical analysis

All experiments in this study were repeated at least 3 times, and the data were presented in the form of mean ± standard variance. Significance analysis was conducted using SPSS 22.0 software ($P < 0.05$).

III. Result

Chromaticity

Table 1 showed the chromaticity L* a*、b*、ΔE、ΔC. L* represents brightness, a* represents red value (+) and green value (-), b* represents yellow value (+) and blue value (-), ΔE represents the total color difference of starch, and ΔC represents the strength of starch. It can be seen from Table 1 that with the increase of discharge power, the brightness (L*) of WMS shows a downward trend, which might be due to the color deepening caused by oxidation reaction or scorching on the surface of starch granules. At the same time, the proportion of red (a*) and yellow (b*) increased, while the proportion of blue (-a*) and green (-b*) decreased, indicating that the overall color of WMS changed to yellow. ΔE is a measure of color difference and has a negative correlation with discharge power, which might be the higher discharge power led to more oxidation reactions, which affected the color of starch granules.

With the increase of current, the brightness of treated samples decreased further. Possible explanation could be that the increase of current intensified the oxidation degree of starch granules, which affected the color performance. A similar color change trend was observed with the increase of treatment time, indicating that the extension of treatment time also promoted the oxidation reaction of starch granules. The increase of b* value should be paid special attention because it is usually related to the oxidation degree of starch. This oxidation might be due to the hydrolysis of α-1,4 glycosidic bonds and α-1,6 glycosidic bonds in starch molecules under high temperature and acidic conditions. The breaking of these bonds might lead to the formation of hemiacetal groups, which then react with the -OH groups of glucose units at random positions in the starch molecule to form new glycosidic bonds, such as α-1,2 and α-1,3 glycosidic bonds [9].

Table 1 The chromaticity values of starch samples

Samples	L*	a*	b*	Δ E	Δ C
Blank control	98.88	0.00	3.00	98.92	3.00
WMS - P0.8-30	98.44	-0.5	3.13	98.49	3.16
WMS - P0.8-60	98.39	-0.26	3.64	98.45	3.64
WMS - P0.8-90	98.25	-0.23	3.76	98.32	3.76
WMS - P1.0-30	98.22	-0.2	3.83	98.29	3.83
WMS - P1.0-60	98.12	-0.19	3.83	98.19	3.83
WMS - P1.0-90	98.09	-0.18	3.87	98.16	3.87
WMS - P1.2-30	97.99	-0.14	3.95	98.06	3.95
WMS - P1.2-60	97.16	-0.08	4.23	97.25	4.23
WMS - P1.2-90	97.09	-0.04	6.01	97.27	6.01

Swelling power and solubility

Fig. 1 showed the changes of solubility and swelling power of modified starches. It was obvious that the solubility of plasma-assisted acid-heat treated starch was significantly higher than that of starch without DBD plasma pretreatment (blank control), while the swelling power was generally lower than that of starch without DBD plasma treatment. The increase in solubility might be due to the impact of high-energy particles on the WMS molecular chain during discharge, resulting in the breakage or depolymerization of some starch molecules into smaller soluble starch fragments, and the acid heat treatment destroyed the amorphous and crystalline regions of starch granules, resulting in a large number of soluble small molecular substances [10]. With the increase of discharge intensity, the swelling power decreased with the increase of DBD power. This might be because the plasma destroyed the amylose structure, which greatly reduced its water holding capacity and expansion ability. Moreover, the high-energy bombardment of the plasma might lead to the decrease of the binding ability of amylopectin molecules with water, thus reducing the swelling power of WMS. Sifuentes-nieves et al. [11] reported that under the action of plasma, the binding ability of amylopectin molecules with water decreased, thus reducing the swelling power. Lizerun et al [12] also found that the swelling power of plasma-treated wheat starch was significantly lower than that of native starch, and decreased with the increase of plasma discharge power. The solubility of WMS was improved after plasma treatment. During the acid heating period, the solubility of WMS was improved after plasma treatment, which indicated that the dispersion of WMS in water is increased, which would also contribute to the application of starch in food processing.

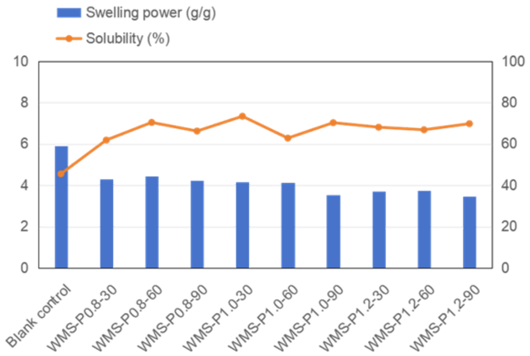

Fig.1 Swelling power and solubility of treated starch samples

Pasting properties

Fig. 2 showed the pasting characteristics of starch under different treatment conditions. The viscosity of plasma-assisted acid-heat treated starch was significantly higher than that of without DBD plasma treatment. The parameters indicating starch gelatinization process include the following aspects: peak viscosity (PV), trough viscosity (TV), final viscosity (FV), breakdown viscosity (BV), setback viscosity (SB), peak temperature (PT). Setback viscosity is usually an indicator to measure the gelatinization energy or retrogradation capacity of starch [13]. It could be seen from Fig. 2 that acid-heat treatment significantly changed the viscosity of WMS. Commonly, native starch exhibited typical pasting curves with sharply elevated viscosity under the heating and stirring. However, compared with the viscosity of native starch (not given), the peak viscosity of starch decreased significantly after plasma treatment and acid heat treatment. The viscosity of treated starches was significantly lower than that of native starch, displaying no typical pasting profiles, which might be because the acid heat treatment (with or without plasma pretreatment) led to the cleavage of molecular chains and the formation of a large number of starch fragments and amylose [14], resulting in the reduction of the interaction between components in the gel system, thus reducing the viscosity of starch paste. With the increase of treatment intensity, the peak viscosity of each treated sample showed no differences. This might be due to the reduced fluidity of the amorphous region in starch granules, and the reduction of gelatinized starch granules due to the formation of new groups by intermolecular crosslinking. The trough viscosity of starch samples gradually decreased when the plasma discharge current was stronger and the treatment duration of plasma increased. This result showed that the swelling property of starch granules was destroyed, which was consistent with the previous results. In addition, the pasting time of starch was slightly prolonged, which might be due to the aggregation of starch granules during plasma treatment, resulting in the weakening of the binding power between water molecules and starch granules [15].

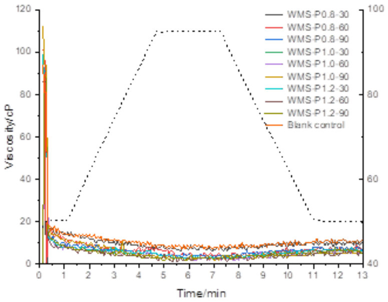

Fig. 2 RVA pasting curves of treated starch samples

Thermal properties

The thermodynamic curves of dual modified starch samples were shown in Fig. 3, and the specific thermodynamic phase transition parameters were shown in Table 2. The endothermic peak gradually decreased with the increase of treatment intensity. This might be because the increase of treatment strength led to the destruction of starch structure, which reduced its crystallinity. Commonly for native WMS, there is a relatively obvious endothermic peak at around 50-70 . This endothermic peak reflects the gelatinization phase transition of starch. In this process, the structure of starch changed, resulting in endothermic effect. With the increase of plasma discharge current, the gelatinization enthalpy decreased significantly. The lowest gelatinization enthalpy was observed for starch pretreated with plasma at 1.0A for 90s. DSC results were generally consistent with the XRD results, indicating that the plasma and acid heat treatment destroyed the crystal structure of the native starch, resulting in the loss of double helix packing orders. In addition, T_o, T_p and T_c of the dual-treated starches did not differ significantly with treatment intensity, which possibly indicated that dual treatment only affected the crystallinity number of waxy starch, without affecting the integrity of the crystals. The high energic plasma particles were reported to induce etching changes on the granule surfaces, making it easier for water molecules to ingress the interior of starch, thus reducing the resistance of gelatinization. These effects were suggested to further favor the following acid heat treatment.

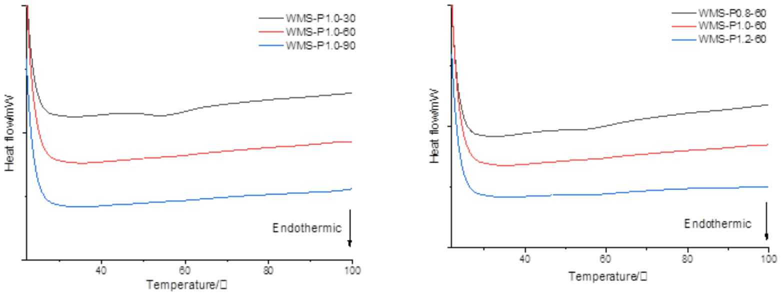

Fig. 3 DSC curves of treated starch samples

Table2 Gelatinization phase transition parameters of treated starch samples

Samples	T_o ( )	T_p ( )	T_c ( )	ΔH (J/g)
WMS - P0.8-60	48.51	54.53	77.42	0.52
WMS - P1.0-60	48.56	55.33	67.72	0.86
WMS - P1.2-60	50.76	57.63	71.79	0.19
WMS - P1.0-30	51.65	58.76	66.53	0.13
WMS - P1.0-90	55.43	60.37	69.18	0.13

Notes: T_o, T_p, T_c and △H represents the onset, peak, conclusion temperature and enthalpies, respectively.

Crystallinity

Fig. 4 showed the X-ray diffraction patterns and the corresponding relative crystallinity of dual treated starches under different conditions. Commonly, WMS showed a typical A-type diffraction pattern, with peaks at 15°, 17°, 18° and 23° (2θ), respectively. After dual treatment, the X-ray diffraction patterns were not significantly changed. However, the relative crystallinity (RC) of WMS decreased after treatment. It has been reported that high-energy bombardment of the crystallization region and destruction of the branched chain structure were induced by the active substances induced by the plasma exposure, resulting in the decrease of the crystallinity. At the fixed plasma discharge current of 1.0 A, the dual treated starch showed gradually reduced RC, from 43.92% to 41.85%, when the plasma treatment duration increased (30~90 s). In addition, under the fixed plasma treatment duration of 60 s, the dual treated starch showed gradually reduced RC, from 43.64% to 42.19%, when the plasma discharge current increased (0.8~1.2 A).

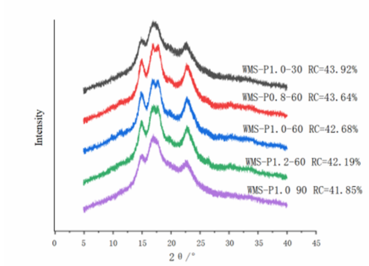

Fig. 4 XRD patterns of treated starch samples

FTIR spectroscopy

The infrared spectrum of WMS under different DBD processing conditions in Fig.5. The corresponding infrared ratio of the deconvolution spectrum was shown in Table 3. In the spectrum, 1022 cm^{-1} was mainly corresponded to the amorphous region of starch, and 1047 cm^{-1} and 995 cm^{-1} corresponded to the crystalline region of starch. The IR spectrum showed similar peaks, indicating the plasma and acid heat treatment did not generate new chemical groups. It was worth noting that the peaks around wavenumber 2900 cm^{-1}, which was assigned to -OH groups, was enhanced, with the plasma treatment intensity (discharge current and treatment duration), compared to the sample WMS-P0.8-60. It was suggested that the dual treatment enhanced higher hydrogen bonding within the starch chain. Meanwhile, the $R_{1047/1022}$ ratio value of dual treated starches was significantly lower than native starch, indicated that the plasma and acid heat treatment destroyed the short-range ordered structure on the surface of starch granules. It has been reported that the high energy action of plasma could induce the destruction of the ordered structure on the surface of starch granules. However, despite the increased treatment intensity, the short-range order did not decline greatly, which might because plasma treatment did not significantly affect the internal structure of starch.

Table 3 Infrared ratio calculated based on deconvoluted infrared spectrum

Samples	$R_{1047/R1022}$
WMS - P0.8-60	0.953
WMS - P1.0-60	0.968
WMS - P1.2-60	0.934
WMS - P1.0-30	0.938
WMS - P1.0-90	0.935

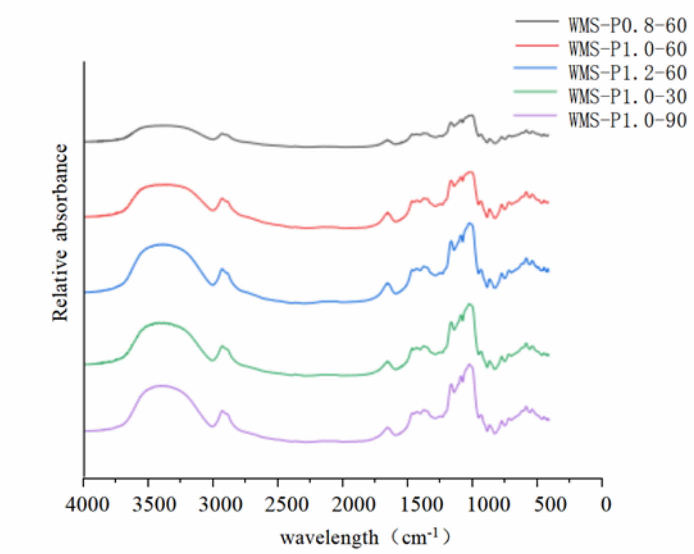

Fig. 5 FTIR spectra of WMS pretreated under different DBD plasma treatment conditions

In vitro digestibility

Fig. 6 showed the in vitro digestibility curves of WMS under different treatment condition, and the content of starch nutritional fractions were shown in Table 4. The digestion extents of dual treated starch were significantly lower than that of starch without DBD plasma pretreatment (blank control), indicating that the following acid heat treatment further generated resistance towards hydrolysis. However, no significant differences were observed between different plasma discharge current or treatment durations. The reduced digestibility could be mainly attributed to the following acid heat treatment due to the generated indigestible glucoside bonds. Previous studies had been reported that DBD plasma modification could induce depolymerization of starch chains, thus resulting in more small fractions. It was suggested that the plasma treatment exert an activation role during the following acid heat treatment because the breakage of glucoside bonds could favor the molecular rearrangement reactions which could form pyrodextrin. In addition, the resistant starch (RS) was rather lower than the other counterparts, showing only 27.10%, while the dual treated samples exhibited much higher RS content, ranging from 43% to 47%. With the increase of plasma pretreatment intensity, the RS contents generally increased and the RDS +

SDS content generally decreased. The increased RS content was suggested to be attributed to the higher amounts of pyrodextrin that formed during following acid heat treatment.

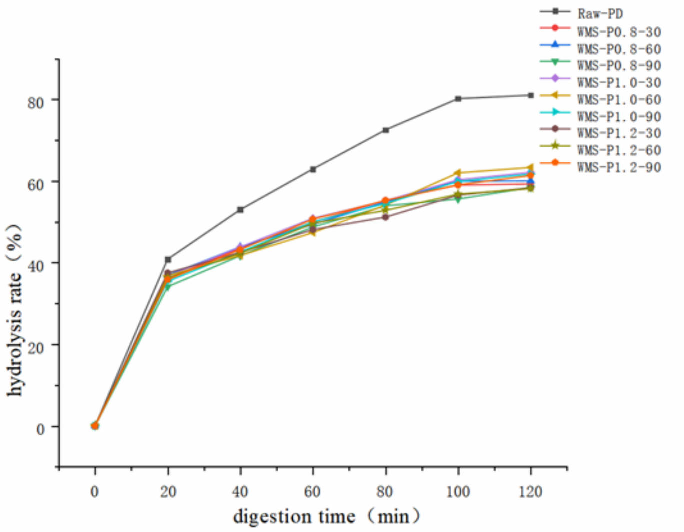

Fig. 6 In vitro starch digestion curves of native and treated starch samples

Table 4 Content of starch nutritional fractions

Samples	RDS (%)	SDS (%)	RS (%)
Blank control	36.72	36.17	27.10
WMS - P0.8-30	32.51	20.83	46.65
WMS - P0.8-60	33.20	20.83	45.95
WMS - P0.8-90	30.66	21.88	47.44
WMS - P1.0-30	32.99	22.92	44.08
WMS - P1.0-60	33.11	23.87	43.02
WMS - P1.0-90	31.86	23.67	44.47
WMS - P1.2-30	33.73	18.76	47.50
WMS - P1.2-60	32.62	19.70	47.66
WMS - P1.2-90	32.24	22.95	44.81

IV. Conclusion

In this study, WMS was subjected to dual modifications combined with DBD plasma and acid heat treatment. The effects of plasma-assisted acid heat treatment on starch structure and physicochemical properties were investigated under different plasma processing conditions.

The chromaticity results showed that the brightness of modified starch after treatment was weakened. The solubility of modified starch was greatly improved, while the swelling power was significantly decreased. The pasting property measured by RVA showed that the viscosity of treated starches was significantly lower than that of native starch, displaying no typical pasting profiles, which might be because the acid heat treatment (with or without plasma pretreatment). DSC results indicated that the endothermic peaks gradually decreased with the increase of plasma pretreatment intensity, indicating the dual modifications resulted in the loss of double helix packing orders. The gelatinization transition temperature showed that the thermal stability of modified starch was improved as onset temperature was delayed, possibly suggesting the plasma pretreatment destroyed the amorphous region of starch particle and retained the crystals with more stable structure. X-ray diffraction patterns were not significantly changed after dual modification. However, the relative crystallinity decreased after treatment. FTIR spectroscopy showed the $R_{1047/1022}$ ratio of dual treated starches was significantly lower than native starch, indicated that the plasma and acid heat treatment destroyed the short-range ordered structure on the surface of starch granules. The digestion extents of dual modified starch were significantly lower than that of starch without DBD plasma pretreatment (blank control). With the increase of plasma pretreatment intensity, the RS contents generally increased and the RDS + SDS content generally decreased. The reduced digestibility could be mainly attributed to the higher amounts of pyrodextrin that formed during following acid heat treatment. This study could provide a new strategy for the dual modification on waxy maize starch, and provide a theoretical basis for expanding the application of cold plasma technology in the field of starch modification.

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