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Modification in Physicochemical, Structural and Digestive Properties of Potato Starch During Heat-Moisture Treatment Combined with Microwave Pre- and Post-Treatment

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Key words: heat-moisture treatment, microwave treatment, physicochemical properties, structural properties, digestibility, potato starch

The objective of this study was to investigate the effects of modification by heat-moisture treatment (HMT) combined with microwave pre- and post-treatment (MW) on the physicochemical, structural and digestive properties of potato starch. The light microscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) were used to determine the structural properties of starch. FT-IR and XRD spectra implied that MW and HMT destroyed the double helices and crystalline structure of potato starch. The relative crystallinity of modified starch granules (15.17–18.17%) was lower than that of native starch (19.39%). In the case of physicochemical properties, the modified starches had higher pasting temperature (68.8–93.0°C) and setback viscosity (807–3168 cP), but lower peak viscosity (1315–3662 cP) and breakdown viscosity (17.3–78.3 cP) than that of native potato starch, which were 68.5°C, 496 cP, 6598 cP and 2526 cP, respectively. The HMT and MW modifications significantly increased the content of slowly digestible starch and resistant starch. The resistant starch content of starch obtained by HMT combined with MW post-treatment was significantly higher than that of starch obtained by HMT combined with MW pre-treatment and single HMT. These results may promote good understanding of the effects of HMT combined with MW pre- and post-treatment on physicochemical properties and digestibility of potato starch, and wide utilization of microwave and heat-moisture techniques in starch modification.

INTRODUCTION

As the fourth largest crop in world production after corn, rice and wheat, potato is the largest non-cereal food crop widely cultivated around the world, containing about 75% starch by dry weight [Santos *et al.*, 2016; Zhang *et al.*, 2017]. Potato starch has larger particle size, higher swelling capacity, transparency and viscosity than rice starch or maize starch [Cao & Gao, 2020; Singh *et al.*, 2016], and it is widely used as food thickener, stabilizer or carrier for bioactive compounds in food and industrial products [Singh *et al.*, 2003].

However, the properties of low shear, heat sensitivity and easy retrogradation of native potato starch limit its use in some industrial fields [Singh *et al.*, 2004]. Therefore, in order to overcome the shortcomings and achieve desired properties, starch can be modified by physical, chemical and enzymatic methods [Colussia *et al.*, 2020; Gałkowska & Juszczak, 2019; Zhang *et al.*, 2019]. Heat-moisture treatment (HMT) is currently the most studied physical modification method of starch, in which starch granules are treated at high temperature (90–120°C) with certain moisture content (10–35%) for certain time (15 min–16 h) [Wang *et al.*, 2016; Zavareze & Dias, 2011]. Samples are stored in an airtight container before HMT to keep moisture at a constant level. The increased pressure of the sealed environment generated by heating is conducive to increase thermal energy, which is constantly transformed into kinetic energy through the motion of water molecules. This leads to massive segmental movements and the glassy state of amorphous regions of starch can be shifted to a more flexible state, thus HMT makes it possible to control the movement of molecules at high temperatures, monitoring the water concentration [Schafranski *et al.*, 2021; Wang *et al.*, 2021]. HMT alters the interactions of polymer chains in starch by destroying crystalline and helical structures. The structure of starch chains within the amorphous and crystalline granules is reorganized during heat-moisture treatment, resulting in expansion of starch granules, changes in crystallinity, leaching of amylose, and changes in other properties such as gelatinization, retrogradation and thermal stability [Arns *et al.*, 2015; Chung *et al.*, 2010; Tan *et al.*, 2017]. HMT also could partially convert rapidly digested starch (RDS) into slowly digested starch (SDS) and/or resistant starch (RS), resulting in increased content of SDS and/or RS [Uzizerimana *et al.*, 2021]. SDS and RS could interfere with suppressing metabolic diseases due to relatively low glycemic response, thus SDS and RS consumption could

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present health benefits [Wang *et al.*, 2017]. Starch modified by HMT can be used in sauces, candies, canned food, pasta and other foods, as well as an ingredient to increase SDS and RS content [Kaur & Singh, 2019].

Microwave is an electromagnetic radiation in the frequency ranging from 300 MHz to 300 GHz. During microwave treatment (MW), electromagnetic energy is converted into heat energy by triggering high-frequency movement of molecules [Singh *et al.*, 2012]. MW becomes another appealing physical modification method of starch for its uniform heating, high heating rates and environmental protection [Braşoveanu & Nemţanu, 2014]. Many investigations have evidenced that microwave irradiation can change morphology, alter molecular structure, rearrange the structural order and crystalline regions of starch, which consequently affects its physicochemical properties, such as absorption ability, swelling power, gelatinization, retrogradation and digestability [Chen *et al.*, 2021a; Kumar *et al.*, 2020; Wang *et al.*, 2019].

The effects of single HMT and MW on functionalities and structural properties of starch have been investigated by many researchers as reviewed by Schafranski *et al.* [2021] and Oyeyinka *et al.* [2021]. However, the mechanism of dual modification combined with HMT and MW is far from being fully understood. Therefore, the purpose of this research was to evaluate the effects of HMT assisted by MW pre- and post--treatment on the morphological, physicochemical and *in vitro* digestion properties of potato starch. This research presented a comprehensive understanding of the effects of HMT and MW bi-directional modifications on functional and digestibility properties of starch, as well as the related mechanism, which would provide a useful theoretical basis for further studies on improving the application of microwave technology in starch modification.

MATERIALS AND METHODS

Potato starch extraction

Potato tubers of Favorita variety sold locally in Hezhou city (Guangxi, China) were selected as raw materials, and native potato starch was extracted according to the procedure described by Deka & Sit [2016]. Potato tubers were washed, peeled and cut into cubes before being ground by a high--speed laboratory blender (Joyoung, JYL-C19V, Joyoung Company Limited, Jinan, Shandong, China) for 3 min. The slurry was mixed with distilled water (1:10, *v/v*), and then was filtered with multiple-layer absorbent gauze. The filtered slurry was kept for 4–5 h for sedimentation, then the liquid was poured off, distilled water was added to wash the sediment, and the above process was repeated several times until the liquid was clarified. The final sediment was laid flat in a tray and dried in a hot-air oven (DH411C, Yamato, Tokyo, Japan) at 45°C for 24 h. The dried starch was pulverized with a universal pulverizer (FW100, Tianjin City Taisite Instrument Co., Ltd., Tianjin, China) and passed through an 80-mesh sieve to obtain native potato starch. Native potato starch was kept in airtight polyethylene bags for further analysis. The composition of potato starch was determined as following: total starch 82.38±0.87 g/100 g dry matter (d.m.), lipid 0.12±0.07 g/100 g d.m., protein 0.35±0.10 g/100 g d.m., moisture 10.83±0.18 g/100 g. Total starch was determined using the Megazyme starch assay kit based on AOAC International 996.11 method [AOAC, 2005]. The GB 5009.6–2016, GB 5009.5–2016 and GB 5009.3–2016 methods of China National Standard for Food Safety [China National Standard for Food Safety, 2016] were used to determine content of lipid, protein and moisture, respectively.

Heat-moisture treatment of starch

The heat-moisture treatment (HMT) of native potato starch was carried out according to the procedure described by Deng *et al*. [2021a, b]. The moisture content of native potato starch was measured before HMT. Then, 70 g of four parallel native potato starch samples were weighed into different 500-mL Duran laboratory bottles, and a certain amount of ultrapure water was added into each bottle to adjust the moisture content to 25 g/100 g. The mixtures were equilibrated at 25°C for 24 h to achieve moisture balance. When equilibration had finished, the samples were subjected to HMT at 90°C for 1.5 h, 4 h, 8 h and 12 h, respectively, in a DH411C hot-air oven. After HMT, the treated starch samples were dried at 45°C for 24 h using the same hot-air oven, so that the starch moisture was less than 12 g/100 g. The dried potato starch was intermittently pulverized for 50 s (pulverized for 5 s, stopped for 5 s to avoid too high temperature of starch caused by pulverization) using an FW100 pulverizer (Tianjin City Taisite Instrument Co., Ltd.). The pulverized starch was sieved through an 80-mesh sieve, then hermetically packaged in polyethylene bags, and stored in a glass desiccator for further studies. According to the duration of HMT, the prepared dry starch powder samples were named as HMT1.5, HMT4, HMT8 and HMT12, respectively.

Microwave treatment of starch

The moisture content of native potato starch was adjusted to 25 g/100 g as described above and the starch mixture was equilibrated at 25°C for 24 h. So prepared starch was subjected to MW according to the previous research method described by Deng *et al*. [2021b]. Briefly, the moisture-balanced starch was placed flat into a lab dish (18 cm in diameter), covered with microwave-specific plastic wrap, and 10 holes were evenly pierced with toothpicks. Then, the lab dish with starch was placed in a microwave oven (G80F20CN2L-B8(RO), Guangdong Galanz Microwave Appliance Manufacturing Co., LTD, Foshan, Guangdong, China) for 5 min at 400 W power (increasing the power or time of microwave heating will cause the starch granules to burn). The treated starch samples were dried and stored according to the method mentioned above in single HMT. The prepared starches were named MWS.

Dual modification of starch

Potato starch modifications by HMT in combination with microwave pre-treatment (MW-HMT) and by HMT in combination with microwave post-treatment (HMT-MW) were performed [Deng *et al*., 2021b]. Briefly, the moisture-balanced MWS samples (25 g/100 g) were subjected to HMT at 90°C for 1.5 h, 4 h, 8 h and 12 h, next, dried and stored according to the procedure described above for single HMT. The prepared

starches were named as MW-HMT1.5, MW-HMT4, MW--HMT8 and MW-HMT12, respectively. To obtain HMT--MW starches, the moisture content of HMT1.5, HMT4, HMT8 and HMT12 samples was adjusted to 25 g/100 g. After equilibration at 25°C for 24 h, the starch mixtures were subjected to MW according to the description above for single MW. The starch samples were dried and named as HMT1.5-MW, HMT4-MW, HMT8-MW and HMT12-MW, respectively.

Scanning electron microscopy (SEM)

An SU8100 scanning electron microscope (Hitachi Ltd., Tokyo, Japan) was used at an acceleration voltage of 2.0 KV to observe the microstructure of starch granules. The dried starch samples were deposited on the specimen holder by using double-sided adhesive tape and sputter-coated with gold.

Light microscopy

A small amount of each starch sample was placed on a microscope slide with 1–2 drops of glycerol with a distilled water mixture (1:1, *v/v*) to disperse the starch evenly, then the starch was covered with coverslip and placed on the objective table of the microscope (BX53, Olympus Corporation, Tokyo, Japan). The normal light microscopic images and polarized light microscopic images of starch samples were observed and captured under normal light mode and polarized light mode, respectively, with the magnification of ×400.

Determination of pasting properties

A rapid visco-analyzer (RVA Starch Master2, Perten Instruments, Stockholm, Sweden) was used to evaluate the pasting and paste properties of the starch according to the methods described by Sui *et al*. [2015] with slight modifications. A 2.5-g portion of each starch (corrected to moisture content of 14 g/100 g) was mixed with 25 mL of distilled water and kept in the test slot of the equipment. The temperature gradient was as follows: equalization at 50°C for 1 min, increased from 50°C to 95°C within 3.75 min and maintaining at 95°C for 2.5 min, and then decreased to 50°C in 3.75 min and maintaining at 50°C for 2 min.

Determination of swelling power and solubility

Swelling power and solubility of starch samples were determined in triplicate according to the method of Guo *et al.* [2015]. A 0.60 g portion (dry basis) of starch sample was placed into a pre-weighed 50-mL centrifuge tube with 30 mL of distilled water. The starch was completely dispersed in the distilled water by oscillating with a turbine mixer (XW-80A, Haimen Kylin-Bell Lab Instruments Co., Ltd., Haimen, Jiangsu, China) for 5 s. After that, all the centrifuge tubes with starch samples were placed in a water bath oscillator with the speed of 200 rpm for 30 min at 55, 65, 75, 85, and 95°C. The samples were cooled to room temperature before being centrifuged at 2150×*g* for 20 min with an L550 centrifuge (Hunan Xiangyi Laboratory Instrument Development Ltd. Co., Changsha, Hunan, China). The supernatants were poured into pre-weighed aluminum specimen boxes and dried to a constant weight in a DH411C hot-air oven at 105°C, while sediments were immediately weighed. The swelling power (SP, g/g, on dry weight basis) and solubility (S, %) were calculated as follows:

$$Solubility\ (S) = \frac{Weight\ of\ dried\ supernatant}{Weight\ of\ dried\ starch\ sample} \times 100 \quad (1)$$

$$Swelling\ power\ (SP) = = \frac{Weight\ of\ sediment}{Weight\ of\ dried\ starch\ sample\left(1 - {Solubility}/{100}\right)} \quad (2)$$

Fourier transform infrared spectroscopy (FT-IR) analysis

The starch samples were placed directly on to sampling unit of an FT-IR spectrophotometer (Spectrum, Perkin Elmer, Waltham, MA, USA) to determine the FT-IR spectra with a scanning spectral range from 4000 cm^{-1} to 400 cm^{-1} at 25°C.

X-Ray diffraction analysis

X-Ray diffraction (XRD) analysis of starch samples was carried out by an X-ray diffractometer (Rigaku Ultima IV, Ultima IVTM, Tokyo, Japan) equipped with a goniometer at 40 kV (target voltage) and 40 mA (tube current). The measurement diffraction angle (2θ) ranged from 4° to 40° at a scanning rate of 4°/min with a step size of 0.02°. MDI Jade 6 software was used to calculate the relative crystallinity (%) of each starch sample according to the following equation:

$$Relative\ crystallinity = = \frac{Area\ of\ crystalline\ peaks}{Total\ area\ of\ crystalline\ and\ amorphous\ peaks} \times 100 \quad (3)$$

***In vitro* digestibility analysis**

The contents of rapidly digested starch (RDS, starch which was digested within the first 20 min), slowly digested starch (SDS, starch which was digested between 20 and 120 min) and resistant starch (RS, the residual starch which was digested after 120 min) in native potato starch and treated starch were determined according to the method previously described by Han *et al.* [2021] with some modifications. In brief, 200 mg of starch samples with 10 mL of a sodium acetate buffer solution (0.1 M, pH 5.2) were added to a flask and heated in boiling water for 30 min to completely gelatinize starch. Afterwards, tubes were cooled in a water bath at 37°C and incubated for 30 min with 160 rpm shaking. Then, the enzyme solution of 5 mL of α-amylase from porcine pancreas (300 U/mL, Shanghai Yuanye Bio-Technology Co., Ltd, Shanghai, China) and 2 mL of amyloglucosidase from *Aspergillus niger* (225 U/mL, Shanghai Yuanye Bio-Technology Co., Ltd) were added to each sample tube, and incubation was continued in a water bath at 37°C with 190 rpm shaking. Then, 1 mL of the digestion solution was pipetted into a test tube with 20 mL of anhydrous alcohol to stop the enzyme reaction at intervals of 20 and 120 min, and then centrifuged at 2810×*g* for 10 min in an L550 centrifuge. The released glucose concentration in the supernatant was measured with the glucose oxidase/peroxidase (GOPOD) assay kit (Megazyme, International Ltd. Co., Wicklow, Ireland). The glucose content multiplied by a factor of 0.9 was used to calculate the percentage of hydrolyzed starch and the following formulas were used to calculate the contents of RDS (%), SDS (%), and RS (%):

$$RDS = G20 \times 0.9/TS \quad (4)$$

$$SDS = (G120 - G20) \times 0.9/TS \quad (5)$$

$$RS = 100 - RDS - SDS \quad (6)$$

where: G20 and G120 are the glucose contents after 20 min and 120 min of hydrolysis, respectively; TS is the total starch content of each sample.

Statistical analysis

All the measurements were performed three times unless otherwise stated, and the data were recorded as means ± standard deviation (SD). One-way analysis of variance (one-way ANOVA) with post-hoc Duncan's test was performed by Data Processing System (7.05 for Windows, Hangzhou Ruifeng Info-technology Co., Hangzhou, Zhejiang, China). Differences were considered significant at $p < 0.05$. Microsoft Office Excel 365 (Microsoft Corp., Redmond, WA, USA) and Origin Pro 8 (OriginLab Corp., Northampton, MA, USA) were used to report the data.

RESULTS AND DISCUSSION

Morphological properties

The surface structural characteristics of native potato starch and modified potato starch samples observed by SEM are presented in Figure 1. The native potato starch granules showed oval or spherical-like shape with no obvious fissures and grooves on the smooth surface. This result was consistent with previous findings reported by Xu *et al*. [2018]. Although there were no noteworthy changes in the structure of starch after the MW, HMT and dual MW and HMT, the surface of treated starch granules became rougher with a different degree of pitting and indentation compared with native starch (Figure 1). Similar results were obtained for millet starch and rice starch modified by MW and HMT, respectively [Li *et al*., 2019a; Wang *et al.*, 2018]. Dual MW and HMT modification made the surface of starch granules rougher with more serious depressions or scallops than single MW or HMT modification, especially in the case of the double modified starch granules *via* HMT assisted by MW pre-treatment (Figure 1).

For HMT-treated starch, the changes on starch granules surface can be attributed to the partial gelatinization caused by pressure and thermal energy, consequently leading to inconsistent swelling and/or aggregation/fusion of starch particles and rough surface, or even to concavities on the granules surface [Wang *et al*., 2018]. For MW-treated starch, the surface roughness and deformation were mainly related to the penetration of microwave energy. When the microwave energy was high enough, the molecular chains that constituted the starch granule structure would break, enventually resulting in pore formation and possible collapse in starch granules [Chen *et al.*, 2021b].

Light microscopy

The micrographs of native potato starch and modified potato starch granules observed under normal light microscopy are shown in Figure 2 and the micrographs of all the starch samples observed under polarized light microscopy are shown in Figure 3. The normal light microscopy image of native starch (Figure 2) exhibited hilum structure with smooth surface, while all treated starch granules showed obvious hollow structure at hilum. The hilum is located in the amorphous zone with relatively fragile structure [Li *et al.*, 2020]. Due to this fragile structure, coupled with partial swelling and disruption of starch granules caused by the MW, HMT and dual modification, the large hollow structure appeared at the umbilicus section of starch granules (Figure 2). Because of the penetration of microwave irradiation, single MW modification had greater effects on hollow structure at the hilum of starch granules than single HMT. Compared with single modified starch, this phenomenon was more obvious in double modified starch, especially in the HMT starch pretreated by MW.

Although the polarized light microscopy of native potato starch granules (Figure 3) and all the modified starches showed a typical Maltese cross with black polarization cross or birefringence, the contour of the Maltese cross of all the modified starches became distorted and fuzzy after MW, HMT and dual modification, and the black zone in the center of the cross became relatively larger than that of native potato starch. These results were similar to those from the previous research of HMT

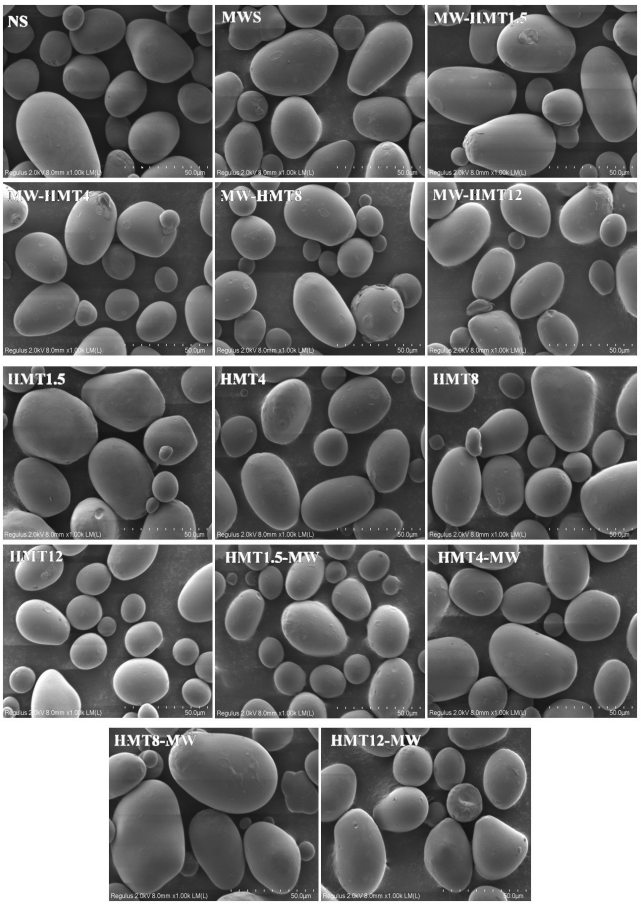

FIGURE 1. Scanning electron microscopy (SEM) micrographs (×1000) of native (NS) and modified potato starches: MWS: single microwave treatment; MW-HMT: heat-moisture treatment combined with microwave pre-treatment; HMT-MW: heat-moisture treatment combined with microwave post-treatment; 1.5, 4, 8, 12 mean the heating duration of HMT (h).

lily starch [Li *et al.*, 2020]. Thermal and microwave energy generated by HMT and MW might induce changes in radial orientation of double helices and amylopectin chains, and eventually changed intensity of birefringence [Ji & Yu, 2018].

Pasting properties

The pasting properties of native and modified potato starch are listed in Table 1 and the rapid viscosity analysis (RVA) pasting profiles are illustrated in Figure 4. The RVA pasting profiles and the pasting properties of potato starch were significantly changed by single MW, single HMT and HMT combined with MW pre- and post-treatment. The peak viscosity of native potato starch was 6598 cP, which was higher than that of all the treated starch samples. The pasting temperature of native potato starch was 68.5°C, which was significantly increased to 73.5–93.0°C after MW and HMT except for the MWS (68.8°C) and the HMT1.5 (71.0°C). Higher pasting temperature indicated interactions between starch chains enhanced by MW and HMT, and more energy was required to destroy the enhanced starch structure during gelatinization process. All the MW-treated starch samples and HMT-treated starch samples showed lower peak viscosity, holding viscosity and breakdown viscosity than that of native potato starch. Similar results were reported for HMT mango kernel starch and MW millet starch [Bharti *et al.*, 2019; Li *et al.*, 2019a]. The decrease in peak viscosity of the sample may be attributed to the recombination and rearrangement in starch granules after MW, HMT, MW-HMT and HMT-MW, which limited the leaching of starch components from granules into the medium, consequently resulting in a decreased peak viscosity. Reduction in holding viscosity representing starch degradation upon application of high temperature and shear, indicated a decrease in peak viscosity [Kaur & Singh, 2019; Li *et al.*, 2019a]. The low breakdown viscosity indicated high thermal stability, resistance development against shear exerted from heating and lower deterioration tendency [Kumar *et al.*, 2020]. Compared with native potato starch setback viscosity (496 cP), all the treated starch samples had higher setback viscosity ranging from 807 to 3168 cP, with the highest values noted for HMT1.5-MW and HMT1.5, and the lowest one for MW-HMT12 (Table 1). Additionally, the duration of HMT affected the pasting properties. The peak viscosity, hold viscosity and final viscosity of HMT modified starch decreased successively with the extension of HMT duration. Moreover, HMT combined with MW pre- and post-treatment resulted in lower peak viscosity than that of starch modified by single MW or

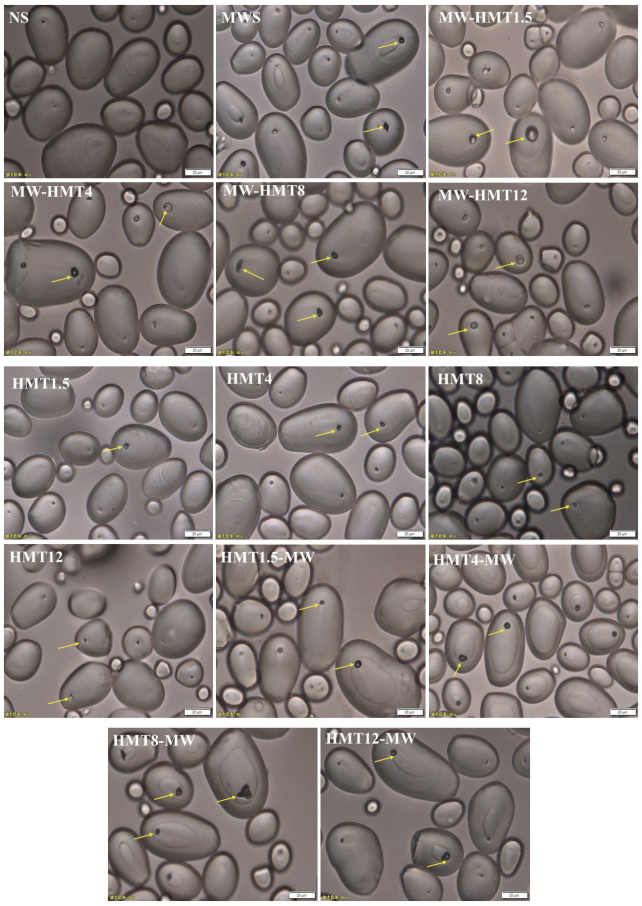

FIGURE 2. Normal light micrographs (×400) of native (NS) and modified potato starches: MWS: single microwave treatment; MW-HMT: heat-moisture treatment combined with microwave pre-treatment; HMT--MW: heat-moisture treatment combined with microwave post-treatment; 1.5, 4, 8, 12 mean the heating duration of HMT (h). The arrows illustrate the treated starch granules showing obvious hollow structure at hilum.

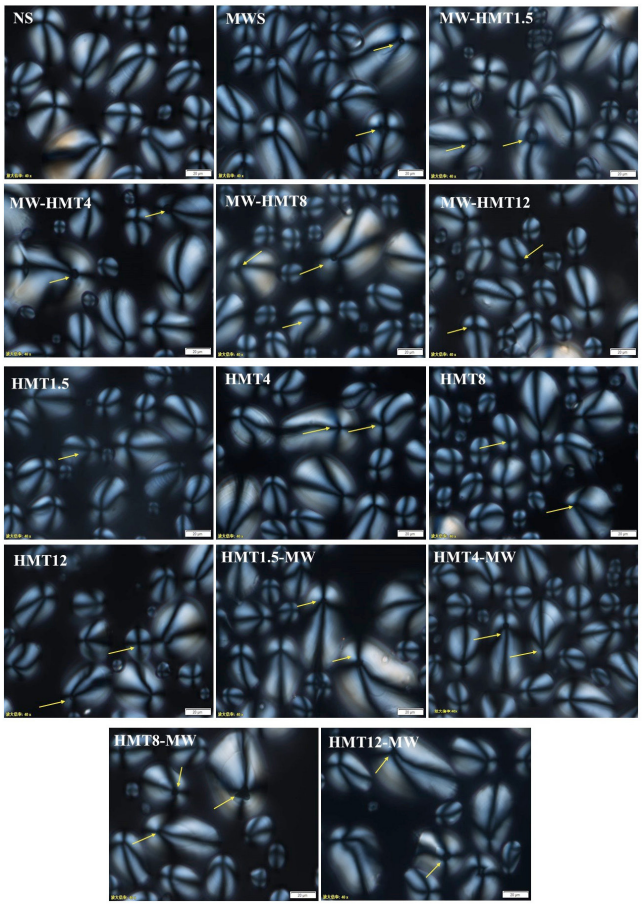

FIGURE 3. Polarized light micrographs (×400) of native (NS) and modified potato starches: MWS: single microwave treatment; MW-HMT: heat-moisture treatment combined with microwave pre-treatment; HMT--MW: heat-moisture treatment combined with microwave post-treatment; 1.5, 4, 8, 12 mean the heating duration of HMT (h). The arrows illustrate the treated starch granules showing obvious hollow structure at hilum.

TABLE 1. Pasting properties of native and modified potato starches.

Starch	Pasting temperature (°C)	Peak viscosity (cP)	Hold viscosity (cP)	Final viscosity (cP)	Breakdown viscosity (cP)	Setback viscosity (cP)
NS	68.5±0.2^{f}	6598±73^{a}	4072±25^{a}	4567±37^{c}	2526±47^{a}	496±12^{j}
MWS	68.8±0.1^{f}	3662±27^{b}	3597±31^{b}	6644±13^{a}	65.7±3.5^{bc}	3047±42^{b}
MW-HMT1.5	80.8±1.5^{bc}	2145±9^{e}	2090±9^{e}	4559±88^{c}	54.3±1.5^{bcde}	2439±39^{c}
MW-HMT4	88.50±1.0^{a}	1591±22^{g}	1548±18^{g}	3027±56^{e}	42.3±3.8^{cdef}	1479±40^{e}
MW-HMT8	92.9±2.0^{a}	1339±6^{jk}	1309±2^{k}	2290±26^{h}	30.3±6.4^{ef}	985±50^{h}
MW-HMT12	93.0±0.6^{a}	1315±18^{k}	1256±19^{l}	2064±18^{i}	58.3±1.5^{bcd}	807±4^{i}
HMT1.5	71.0±0.4^{ef}	3522±8^{c}	3443±11^{c}	6553±88^{a}	78.3±3.5^{b}	3110±79^{ab}
HMT4	80.5±5.6^{bc}	2173±58^{e}	2111±56^{e}	4528±150^{c}	61.7±2.1^{bcd}	2417±98^{c}
HMT8	76.5±1.5^{cd}	1582±21^{g}	1545±18^{g}	3019±14^{e}	38.0±5.6^{def}	1474±17^{e}
HMT12	76.8±0.4^{cd}	1433±2^{hi}	1416±16^{i}	2573± 23^{g}	17.3±14.6^{f}	1157±27^{g}
HMT1.5-MW	73.5±2.7^{de}	2591±24^{d}	2516±23^{d}	5684±91^{b}	75.3±2.1^{b}	3168±102^{a}
HMT4-MW	81.9±5.3^{b}	1854±16^{f}	1799±15^{f}	3696±48^{d}	55.0±2.0^{bcde}	1936±50^{d}
HMT8-MW	75.5±2.0^{de}	1475±58^{h}	1457±36^{g}	28033±97^{f}	55.0±8.9^{bcde}	1345±67^{f}
HMT12-MW	82.4±3.7^{b}	1392±8^{ij}	1373±13^{j}	2465±9^{g}	18.7±11.6^{f}	1092±22^{g}

All values are the mean of triplicate determinations± standard deviation. The means within the same column with different letters are significantly different ($p<0.05$). NS: native potato starch; MWS: single microwave treatment; HMT: heat-moisture treatment; MW: microwave treatment; MW-HMT: heat-moisture treatment combined with microwave pre-treatment; HMT-MW: heat-moisture treatment combined with microwave post-treatment; 1.5, 4, 8, 12 mean the heating duration of HMT (h).

single HMT. Starch modified by HMT combined with MW pre-treatment had lower peak viscosity, hold viscosity and final viscosity than the starch modified by HMT combined with MW post-treatment or the starch modified by single HMT, indicating that MW-HMT starch had lower resistance to heat and shear than HMT-MW starch or HMT starch.

Swelling power and solubility

Differences in cohesive force within starch granules can be characterized by differences in swelling and solubility. The swelling power of native and modified potato starches is shown in Table 2 and the solubility of native and modified potato starches is shown in Table 3. With an increase in test temperature, the swelling power of native starch and modified starches increased. The modified starch showed lower swelling power than native starch when the test temperature was 65°C, 75°C and 85°C, while opposite results were obtained at 95°C, and the MWS sample showed the highest swelling power (21.58%) at 95°C. MWS had the higher swelling power than MW-HMT modified starch at the same test temperature;

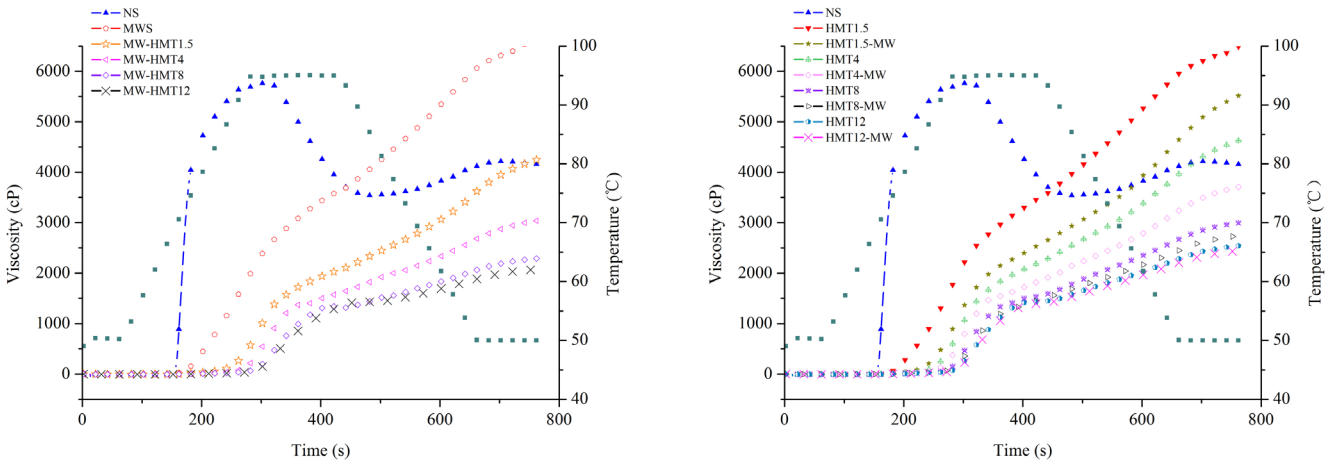

FIGURE 4. Rapid viscosity analysis pasting profiles of native (NS) and modified potato starches: MWS: single microwave treatment; MW-HMT: heat-moisture treatment combined with microwave pre-treatment; HMT-MW: heat-moisture treatment combined with microwave post-treatment; 1.5, 4, 8, 12 mean the heating duration of HMT (h).

TABLE 2. Swelling power of the native and modified potato starches.

Starch	Swelling power (%)				
	55°C	65°C	75°C	85°C	95°C
NS	2.28±0.03^{h}	12.13±0.79^{a}	14.14±0.16^{a}	17.10±0.12^{a}	13.29±0.57^{f}
MWS	4.02±0.23^{a}	12.94±0.19^{b}	12.59±0.20^{c}	15.74±0.26^{b}	21.58±0.04^{a}
MW-HMT1.5	3.05±0.01^{b}	11.20±0.17^{c}	12.31±0.32^{cd}	12.92±0.11d^{ef}	16.37±0.14^{c}
MW-HMT4	2.84±0.05^{c}	9.58±0.19^{ef}	11.65±0.55^{e}	12.90±0.09^{def}	14.27±0.14^{e}
MW-HMT8	2.63±0.07^{ef}	9.04±0.24^{fgh}	10.56±0.16^{fgh}	11.27±0.23^{g}	14.12±0.83^{e}
MW-HMT12	2.52±0.02^{fg}	8.69±0.23^{h}	10.70±0.02^{fg}	11.19±0.12^{g}	14.35±0.38^{e}
HMT1.5	2.46±0.10^{g}	11.13±0.39^{cd}	13.28±0.64^{b}	13.76±0.70^{c}	18.27±0.31^{b}
HMT4	2.48±0.06^{g}	10.00±0.03^{e}	12.36±0.19^{cd}	13.35±0.16^{cd}	16.36±0.09^{b}
HMT8	2.47±0.04^{g}	9.18±0.15^{fgh}	11.56±0.03^{e}	13.16±0.25^{de}	15.53±0.25^{d}
HMT12	2.47±0.02^{g}	8.85±0.30^{h}	10.89±0.30^{f}	12.58±0.08^{f}	15.20±0.18^{d}
HMT1.5-MW	2.79±0.00^{cd}	10.61±0.25^{d}	11.84±0.31^{de}	13.08±0.01^{def}	18.34±0.03^{b}
HMT4-MW	2.69±0.04^{de}	9.95±0.11^{e}	10.25±0.33^{gh}	12.85±0.20^{def}	16.39±0.06^{c}
HMT8-MW	2.42±0.02^{g}	9.45±0.11^{efg}	10.04±0.13^{h}	12.73±0.11^{ef}	16.81±0.40^{c}
HMT12-MW	2.41±0.08^{g}	8.99±0.32^{gh}	9..95±0.09^{i}	12.56±0.16^{f}	16.56±0.20^{c}

All values are the mean of triplicate determinations± standard deviation. The means within the same column with different letters are significantly different ($p<0.05$). NS: native potato starch; MWS: single microwave treatment; HMT: heat-moisture treatment; MW: microwave treatment; MW-HMT: heat-moisture treatment combined with microwave pre-treatment; HMT-MW: heat-moisture treatment combined with microwave post-treatment; 1.5, 4, 8, 12 mean the heating duration of HMT (h).

TABLE 3. Solubility of native and modified potato starches.

Starch	Solubility (%)				
	55°C	65°C	75°C	85°C	95°C
NS	4.29±0.44^{a}	4.69±0.31^{a}	2.11±0.17^{j}	2.70±0.17^{i}	7.70±0.31^{g}
MWS	3.59±0.47^{b}	3.24±0.21^{b}	2.77±0.27^{i}	5.64±0.63^{f}	7.27±0.13^{g}
MW-HMT1.5	0.77±0.06^{g}	3.29±0.07^{b}	2.73±0.07^{i}	5.94±0.33^{f}	8.70±0.30^{f}
MW-HMT4	1.53±0.15^{f}	3.18±0.11^{b}	2.98±0.03^{i}	6.70±0.24^{e}	9.94±0.37^{e}
MW-HMT8	2.37±0.02^{de}	3.09±0.06^{bc}	3.51±0.31^{h}	7.29±0.19^{d}	11.36±0.46^{b}
MW-HMT12	2.29±0.04^{e}	3.02±0.04^{bc}	2.32±0.13^{j}	7.18±0.05^{de}	13.54±0.02^{b}
HMT1.5	2.40±0.08^{de}	2.80±0.14^{cd}	5.63±0.15^{f}	4.59±0.11^{g}	7.35±0.30^{g}
HMT4	2.32±0.00^{e}	3.08±0.18^{bc}	6.91±0.25^{d}	4.70±0.15^{g}	11.28±0.31^{b}
HMT8	2.38±0.07^{de}	2.65±0.11^{d}	8.35±0.08^{b}	5.86±0.09^{f}	14.05±0.18^{b}
HMT12	2.66±0.11^{cd}	2.70±0.15^{d}	6.14±0.31^{e}	3.57±0.30^{h}	8.69±0.28^{f}
HMT1.5-MW	3.75±0.17^{b}	3.11±0.07^{bc}	3.01±0.13^{i}	7.14±0.47^{de}	8.43±0.39^{f}
HMT4-MW	2.94±0.06^{c}	3.09±0.08^{bc}	4.42±0.12^{g}	8.09±0.13^{c}	10.53±0.36^{d}
HMT8-MW	1.63±0.12^{f}	4.68±0.14^{a}	7.64±0.21^{c}	15.28±0.13^{b}	13.69±0.14^{b}
HMT12-MW	1.37±0.10^{f}	4.94±0.34^{a}	15.66±0.39^{a}	34.83±0.33^{a}	15.65±0.18^{a}

All values are the mean of triplicate determinations± standard deviation. The means within the same column with different letters are significantly different ($p<0.05$). NS: native potato starch; MWS: single microwave treatment; HMT: heat-moisture treatment; MW: microwave treatment; MW-HMT: heat-moisture treatment combined with microwave pre-treatment; HMT-MW: heat-moisture treatment combined with microwave post-treatment; 1.5, 4, 8, 12 mean the heating duration of HMT (h).

moreover, the swelling power of HMT modified starch (HMT, MW-HMT and HMT-MW) generally decreased with the treatment time when test temperature was the same. The decrease in starch swelling power can be attributed to the enhancement of molecular interactions between amylose and amylopectin, and the amylose-lipid complexes formed during MW and HMT [Han *et al.*, 2021]. Moreover, the swelling power of starch granules can also be affected by starch granules physical destruction, starch molecule rearrangement or/and starch chains re-associations induced by MW and HMT [Li *et al.*, 2019a].

The leaching of soluble molecules of starch granules, such as amylose, sugars can be characterized by solubility. Modified potato starch showed generally higher solubility than native starch when the test temperature was >75°C, and the solubility of starch samples increased respectively with the increase in test temperature from 75°C to 95°C (Table 3). This indicates that temperature increase could induce the leaching of amylose or sugars from starch granules. MW, HMT, HMT combined with MW pre- and post-treatment could cause depolymerization of starch molecules, resulting in a higher ratio of short chains which had greater tendency to hydration than native starch molecules [Han *et al.*, 2021]. At the same test temperature, the solubility of HMT and HMT-MW starch increased with the length of heating time, which indicated that long time heat-moisture treatment could enhance the molecular depolymerization of starch. The MW, HMT and HMT combined with MW pre- and post-treatment can cause the weathering of starch granules, which consequently leads to the improvement of solubility [Deka & Sit, 2016]. However, high gelatinization temperature of modified starch could lead to low solubility at low test temperature. The modified starch had not been gelatinized at low temperature, and the soluble substances cannot be leached out from the starch granules, resulting in low solubility.

FT-IR analysis

FT-IR is used to monitor the appearance, type and the strength of hydrogen bonds, which reflect the changes in starch molecule structure [Li *et al.*, 2021]. The ratio of crystalline regions to amorphous regions of starch granules can be indicated by the absorbance ratio of 1047/1022 cm^{-1}, while the short-range order can be indicated by the absorbance ratio of 1047/1035 cm^{-1} [Zhang *et al.*, 2021]. A higher absorbance ratio of 1047/1022 cm^{-1} indicates larger crystalline region and a higher absorbance ratio of 1047/1035 cm^{-1} indicates a higher short-range order of starch. The FT-IR spectra of native potato starch and modified potato starch are shown in Figure 5 and their corresponding absorbance ratios of 1047/1022 cm^{-1} and 1047/1035 cm^{-1} are summarized in Table 4. As shown in Figure 5, absorption peaks of characteristic groups of all starch granules had similar position and shape, indicating that there was no new absorption peak observed in the spectra, which indicated that any of the modification treatments (single MW, single HMT and HMT combined with MW pre- and post-treatment) neither created new functional groups nor altered the primary structure of the potato starch.

All modified starch granules had lower absorbance ratios of 1047/1022 cm^{-1} than that of native starch, and HMT combined with MW pre- and post-treatment had stronger effects on the decrease in the absorbance ratios than single MW or single HMT. What is more, with the increase in HMT duration, the ratios of 1047/1022 cm^{-1} of single HMT starch samples and HMT starch samples post-treated by MW decreased to different extents, while opposite results were observed for HMT starch samples pre-treated by MW. The ratios of 1047/1035 cm^{-1} of all the starch samples had the same variation trend as that of 1047/1022 cm^{-1}. These results indicated that microwave irradiation and heat-moisture treatment might have destroyed the double helix structure and crystal region of starch granules [Li *et al.*, 2019b]. Under different treatment conditions, the changing trend of the ratios of 1047/1022 cm^{-1} and 1047/1035 cm^{-1} was consistent with the changing trend of relative crystallinity analyzed by XRD (Table 4), which further confirmed that single MW, single HMT and HMT combined with MW pre- and post- treatment destroyed the crystal structure of potato starch.

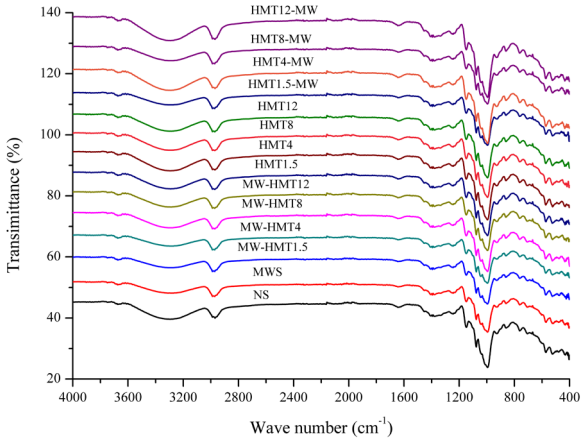

FIGURE 5. Fourier transform infrared spectroscopy spectra of native (NS) and modified starches: MWS: single microwave treatment; MW-HMT: heat-moisture treatment combined with microwave pre--treatment; HMT-MW: heat-moisture treatment combined with microwave post-treatment; 1.5, 4, 8, 12 mean the heating duration of HMT (h).

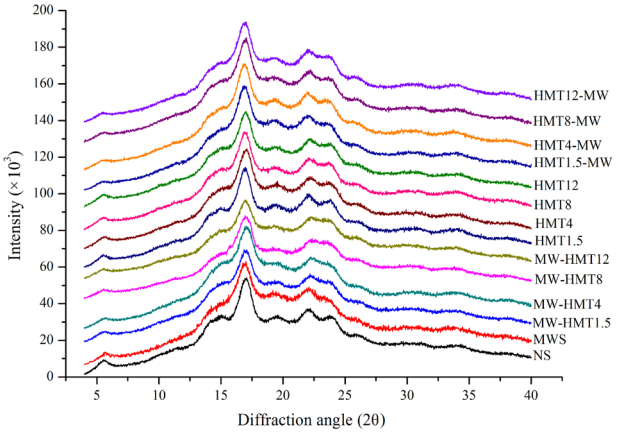

FIGURE 6. X-ray diffraction pattern of native (NS) and modified potato starches. MWS: single microwave treatment; MW-HMT: heat-moisture treatment combined with microwave pre-treatment; HMT-MW: heat--moisture treatment combined with microwave post-treatment; 1.5, 4, 8, 12 mean the heating duration of HMT (h).

TABLE 4. Fourier transform infrared spectroscopy intensity ratios, relative crystallinity and digestibility properties of the native and modified potato starches.

Starch	1047/1022 cm^{-1}	1047/1035 cm^{-1}	Relative crystallinity (%)	Digestibility properties		
				RDS (%)	SDS (%)	RS (%)
NS	1.0361±0.0001^{a}	1.0083±0.0001^{a}	19.39±0.04^{a}	31.14±0.10^{a}	55.17±0.17^{bc}	13.69±0.10^{h}
MWS	1.0150±0.0001^{h}	0.9992±0.0000^{e}	15.35±0.07^{h}	29.14±0.10^{de}	55.90±0.37^{b}	14.97±0.43^{fg}
MW-HMT1.5	1.0099±0.0001^{k}	0.9965±0.0001^{i}	15.55±0.00^{fg}	28.91±0.10^{ef}	55.23±0.34^{bc}	15.86±0.38^{f}
MW-HMT4	1.0100±0.0002^{k}	0.9957±0.0000^{j}	15.65±0.02^{e}	28.43±0.10^{gh}	52.17±0.09^{d}	19.40±0.16^{c}
MW-HMT8	1.0180±0.0001^{f}	0.9980±0.0002^{f}	15.74±0.01^{d}	27.66±0.60^{i}	50.05±1.02^{f}	22.29±0.53^{c}
MW-HMT12	1.0176±0.0000^{g}	0.9978±0.0001^{g}	15.83±0.01^{c}	28.54±0.10^{fg}	57.25±0.68^{a}	14.21±0.78^{gh}
HMT1.5	1.0268±0.0000^{b}	1.0008±0.0000^{c}	18.17±0.04^{b}	28.11±0.31^{h}	57.87±0.35^{a}	14.02±0.38^{gh}
HMT4	1.0232±0.0002^{c}	1.0002±0.0002^{d}	15.80±0.06^{cd}	29.41±0.10^{d}	54.57±0.44^{c}	16.02±0.42^{f}
HMT8	1.0217±0.0000^{d}	0.9992±0.0001^{e}	15.60±0.02^{ef}	29.80±0.20^{c}	47.36±0.93^{g}	22.85±0.72^{c}
HMT12	1.0206±0.0000^{e}	0.9981±0.0001^{f}	15.17±0.04^{i}	30.23±0.10^{b}	47.33±1.20^{g}	22.44±1.10^{c}
HMT1.5-MW	1.0235±0.0000^{c}	1.0042±0.0000^{b}	15.64±0.03^{e}	29.52±0.10^{cd}	51.43±0.01^{de}	19.05±0.09^{e}
HMT4-MW	1.0205±0.0003^{e}	1.0003±0.0000^{d}	15.50±0.01^{g}	28.16±0.10^{gh}	50.75±1.37^{ef}	21.09±1.47^{d}
HMT8-MW	1.0135±0.0000^{i}	0.9969±0.0000^{h}	15.39±0.03^{h}	28.88±0.26^{ef}	43.29±0.32^{h}	27.83±0.47^{a}
HMT12-MW	1.0130±0.0005^{j}	0.9957±0.0000^{j}	15.35±0.04^{h}	29.12±0.10^{de}	46.37±0.33^{g}	24.50±0.37^{b}

All values are the mean of triplicate determinations± standard deviation. The means within the same column with different letters are significantly different ($p<0.05$). RDS: rapidly-digestible starch; SDS: slowly-digestible starch; RS: resistant starch; NS: native potato starch; MWS: single microwave treatment; HMT: heat-moisture treatment; MW: microwave treatment; MW-HMT: heat-moisture treatment combined with microwave pre-treatment; HMT-MW: heat-moisture treatment combined with microwave post-treatment; 1.5, 4, 8, 12 mean the heating duration of HMT (h).

X-Ray diffraction analysis

X-Ray diffraction (XRD) analysis is an important technique used to evaluate changes in starch structure. The patterns of native starch and modified starch analyzed by XRD are shown in Figure 6 and the corresponding relative crystallinity was listed in Table 4. Native potato starch exhibited a B-type of X-ray diffraction pattern, which was characterized with a small peak at 5.6° 2θ, a peak at 17° 2θ, and a doublet at 22° 2θ and 24° 2θ [Juansang *et al*., 2017; Li *et al.*, 2020]. There were some significant changes in the intensities of peaks between native potato starch and modified potato starch. Similar reduction in peak intensities of taro starch after HMT and MW was observed by Deka & Sit [2016]. Significant changes in the XRD patterns of all the modified starches were observed (Figure 6). The diffraction peak at 15° 2θ of all the MW-HMT starch and MWS became smooth, the diffraction peaks at 19.5° 2θ gradually disappeared and the double peaks at 22° 2θ and 24° 2θ merged into a broad peak. Similar changes were observed between HMT and HMT-MW starch, the diffraction peak at 19.5° 2θ, and the double peaks at 22° 2θ and 24° 2θ gradually became smooth with the prolongation of heat-moisture treatment time. These results indicate that the X-ray diffraction of potato starch could be changed from B-type to a mixture of A+B type after HMT or/and MW modification. Similar results were obtained by Li *et al.* [2020] regarding lily starch modification by HMT. Thirty six water molecules in a central channel of the B-unit cell vaporized during the modification process of MW, HMT, MW-HMT and HMT-MW, and then a pair of double helices moved into the central channel which was originally occupied by the vaporized water molecules, leading to the change of crystalline orientation and destruction of crystalline regions, which eventually induced changes in the XRD pattern of potato starch (B→A+B) [Gunaratne & Hoover, 2002; Li *et al.*, 2020].

All modified potato starch granules had lower relative crystallinity than that of native starch, which was 19.39% (Table 4). The relative crystallinity of MWS, MW-HMT1.5, MW-HMT4, MW-HMT8, MW-HMT12 was 15.35%, 15.55%, 15.65%, 15.74% and 15.83% respectively, which indicated that the relative crystallinity of MW-HMT starch increased with the prolongation of heat-moisture treatment time. Moreover, HMT-MW starch had lower relative crystallinity than that of the single HMT starch at the same heat moisture treatment condition. The reduction of relative crystallinity of microwave-irradiated millet starch was also observed by Li *et al*. [2019a]. The source of starch and HMT conditions affected the changes observed in starch crystallinity. The results of this research showed that the effect of HMT on potato starch relative crystallinity was consistent with the previous study on the effect of HMT on that of normal maize starch and waxy maize starch [Sui *et al.*, 2015]. HMT disrupted the amylopectin crystallites and induced the instability of the lamellar arrangement of starch granules, which made the relative crystallinity of HMT starch lower than that of native potato starch [Colussia *et al.*, 2020]. The decrease in crystallinity of the MW starch attributed to the vibrational motion of the polar molecules induced by the microwave radiation directly impacted the crystalline

lamellae inside the granule and destroyed their radial crystalline structure [Palav & Seetharaman, 2006; Mollekopf *et al.*, 2011]. What is more, under the combined effect of thermal energy, microwave radiation and moisture, irreversible damage occurred in crystalline regions of starch granules, inducing the growth of the amorphous or semi-crystalline regions, and consequently reducing the relative crystallinity of starch [Khunae *et al.*, 2007].

In vitro digestibility

Based on the rate and degree of *in vitro* digestion, starch is commonly classified into three categories: RDS, SDS and RS, among which SDS and RS are considered to be beneficial to human health [Xu *et al.*, 2019]. The contents of RDS, SDS and RS in native potato starch were 32.14%, 55.17% and 13.69%, respectively (Table 4), which were inconsistent with the results of previous research reported by Wang *et al.* [2019] showing RDS, SDS and RS contents in native potato starch at 22.5%, 12.8% and 64.7% respectively. The unusual results of RDS, SDS and RS contents in native potato starch might be attributed to the method of *in vitro* digestion. Gelatinized and non-gelatinized starch samples showed different *in vitro* digestibility, which was confirmed by Ji & Yu [2018] and by Piecyk & Domian [2021], while the results of Chen's [2020] research directly indicated that gelatinized and non-gelatinized potato starch showed different contents of RDS, SDS and RS. The gelatinized starch showed higher RDS content than non-gelatinized starch for their granular structure had been already disrupted during the cooking process and thus became more susceptible to enzymatic hydrolysis [Li *et al.*, 2020].

The RDS content of all modified potato starches was significantly ($p<0.5$) lower than that of native potato starch, while the RS content was generally higher (Table 4). When the heating time of HMT was less than 12 h, the RS content increased successively with the prolongation of heat-moisture treatment time. Previous studies have reported that HMT could increase the content of RS and the total content of SDS and RS in maize starch [Sui *et al.*, 2015] and sweet potato starch [Trung *et al.*, 2017], while MW also increased the content of RS and the total content of SDS and RS in *Canna edulis* Ker starch [Zhang *et al.*, 2010] and debranched mung-bean starch [Huong *et al.*, 2021]. Amylopectin in starch was partly degraded, the hydrogen bonds between starch molecules were broken, and the molecular chains in starch granules were separated by microwave heating, all these resulting in swelling and gelatinization of starch particles. HMT further rearranged the molecular structures, transformed some RDS fractions into SDS and/or RS fractions and increased the resistance of starch to enzymatic hydrolysis [Li *et al.*, 2018; Liu *et al.*, 2019]. Furthermore, dual modification of HMT and MW increased the total content of SDS and RS but decreased the content of RDS in potato starch (Table 4). It was worth mentioning that under the same HMT heating time, the RS content of HMT-MW starch was higher than that of HMT starch, *e.g.*, the RS content of HMT1.5-MW (19.05%) was higher than that of HMT1.5 (14.02%). Additionally, HMT-MW starch also had a higher RS content than that of MW-HMT starch under the same HMT heating time, *e.g.*, the RS content of HMT1.5-MW (19.05%) was higher than that of MW-HMT1.5 (15.86%). All these results indicated that dual starch modification *via* HMT and MW had greater effects on starch digestion than single MW or HMT, and the sequence of dual modification also affected starch digestibility.

CONCLUSIONS

HMT, MW and HMT combined with MW pre- and post-treatment had significant effects on the microstructure, crystalline and structural properties and digestibility of potato starch. As can be observed from the scanning electron microscopy, normal light and polarized light microscopy, some depressions or potholes appeared on the surface of starch granules after modification, and the center of polarized cross structure slowly expanded. Dual starch modification *via* MW and HMT made the surface of its granules rougher and caused more serious depressions or scallops than single modification with MW or HMT, especially in the case of HMT-MW. All the treatments increased the pasting temperature and setback viscosity but decreased peak viscosity and breakdown viscosity of starch. Modified starch showed lower swelling power than that of native starch when the test temperature was 65–85°C, while opposite results were obtained at 95°C. Modified starch samples showed higher solubility than that of native starch when test temperature was 75–95°C. The FT-IR and XRD spectra implied that HMT and MW destroyed the double helices and crystalline structure of potato starch. All treatments increased the content of RS but reduced the content RDS of potato starch. Under the same HMT heating duration, the RS content of starch modified by HMT combined by with MW post-treatment was significantly higher than that of starch modified by HMT combined by MW pre-treatment and single HMT. The information obtained in this paper might be beneficial to the industrial applications of microwave and heat-moisture techniques deployed to modify starch and eventually produce new starch materials satisfying the potential consumer requirements.

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CONFLICT OF INTERESTS

Authors declare no conflict of interests.

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