



Effect of heat-moisture treatment on physicochemical properties of chickpea starch

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Abstract

Chickpea starch was modified by heat-moisture treatment (HMT). The effect of heat-moisture treatment on the amylose content of chickpea starch was studied, and the physicochemical properties, gelatinization properties, texture properties and digestion properties of modified chickpea starch were compared and analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR). After HMT, the amylose content of chickpea starch increased. Compared with the natural starch, the morphology of starch granule was changed and destroyed under the condition of higher water content (30%). It was found that the crystalline morphology had no obvious change, and the structure was still C-type. In FT-IR spectra, the position of characteristic absorption peak had no obvious change, and the internal structure and main components of chickpea starch had no obvious change. The solubility, swelling power, transparency, freeze-thaw stability and gelation ability of chickpea starch treated with HMT decreased, while the thermal stability increased and the anti-digestibility enhanced.

Keywords: chickpea starch; heat-moisture treatment; physicochemical properties.

Practical Application: First, the physicochemical properties of HMT starch were analyzed, which provided a theoretical basis for further processing of chickpea starch. Addition, after HMT, the starch solubility and swelling power decreased, the starch can be used in foods that need to limit swelling, such as noodles, vermicelli, rice noodle, etc. Finally, according to its anti-digestibility, it can be used in health food.

1 Introduction

The chickpea is a kind of Fabaceae, belongs to the leguminous plant. At present, there are more than 40 countries in the world to cultivate chickpea. Because of its tolerance to barren, drought and high yield, it has been cultivated for more than 2500 years in Xinjiang (Kaur & Prasad, 2021). Studies have found that chickpeas are good for your health and have many benefits, including lowering cholesterol, protecting your skin, strengthening your immune system and regulating blood sugar (Ullah et al., 2020). In recent years, the nutritional characteristics of legumes have aroused people's attention. Chickpeas contain a variety of nutrients, such as protein, dietary fiber, starch and unsaturated fat. In particular, the content of starch is as high as 40% ~ 60%, however, the utilization of chickpea is not high, resulting in the waste of chickpea resources.

Starch is a kind of macromolecule polymer, which is considered as an important commercial raw material in many processed foods, and it was widely used in foods because of its gel and gelatinization properties (Garcia-Santos et al., 2019; Mesa et al., 2019). In addition, starch can also be used as food packaging raw materials (Costa et al., 2021). However, in most cases, the properties of natural starch are not ideal, because of high viscosity, low solubility, thermal decomposition and poor stability, and other factors, its use is limited (Ariyantoro et al., 2021). For example, in long-term heating, acidic environment or high shear, gelatinization stability is poor, leading to the

breakdown of the starch gel network (Acevedo et al., 2022). In addition, in the frozen, starch has a strong retrograde ability, easily lead to dehydration. Therefore, it should be modified by physical or chemical methods to enhance its (natural starch) functional properties to adapt to different industrial uses (Deng et al., 2022).

Hygrothermal treatment is a kind of physical modification, which is usually carried out at high temperature (90-120 °C) and limited water content (10%-30%). HMT can change the structure and physicochemical properties of starch, it includes starch granule structure, starch gelatinization property, retrogradation property, gel texture, rheological property, heat stability, amylose content and crystallinity of starch granule (Fonseca et al., 2021; Li et al., 2021). These changes have attractive to the food, pharmaceutical and cosmetic industries. HMT does not involve the use of chemicals or enzymes, it is a cheaper, greener way to modify starch, it mainly includes the advantages of easy to obtain, large production, low cost and no chemical residue (Wang et al., 2022), therefore this modification method is widely used (Ji et al., 2022; Zhang et al., 2023).

In this study, chickpea starch was studied by HMT under different moisture content, the changes of physicochemical properties (solubility, swelling power, transparency, freeze-thaw stability), particle morphology, crystal morphology, gelatinization

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properties, gel texture properties and in vitro digestibility before and after HMT were determined, which provided theoretical guidance for developing new chickpea starch products in the future.

2 Materials and methods

2.1 Materials

Chickpea starch (Self-made by dilute alkali method in laboratory, the purity is 95 DW%), potato amylose and amylopectin, porcine pancreatic alpha-amylase and glycosidase were purchased from Yuanye Biotechnology Co.Ltd (Shanghai, China). Anhydrous glucose, Potassium sodium tartrate, 3,5 dinitrosalicylic acid, Glacial acetic acid, Glycosidase, Anhydrous ethanol, Potassium bromide were purchased from Sinopharm Chemical Reagent Co.Ltd. All other chemicals used were of analytical grade, unless otherwise stated. Double distilled water was used for the preparation of all solutions.

2.2 Heat-moisture treatment of chickpea starch

The heat-moisture treatment was performed according to the method of Dewi et al. (2022) with minor modifications. The chickpea starch with measured moisture content is put into a closed container with high temperature resistance, the water content of starch was controlled by adding different quality distilled water to reach 15%, 20%, 25% and 30%, respectively. Then the bottle cap was screwed tightly and put it in 4 °C to balance water for 24 h. The balanced chickpea starch was placed in a 110 °C oven, heated for 4 hours, removed and placed in a 40 °C oven, and dried for 24 hours. The treated chickpea starch was named HMT-15, HMT-20, HMT-25, HMT-30 according to the moisture content of the chickpea starch.

2.3 Determination of amylose

The amylose content was determined by using the iodine binding colorimetric method (Han et al., 2021c). Potato amylose and amylopectin were used as standard samples for establishing the standard curves. The standard curve equation is $y = 1.0081x - 0.0016$, $R^2 = 0.9992$. The iodine affinity of starches was determined using a UV/visible Spectrophotometer (UV-2102PC, Unico Instrument Co., Ltd., Shanghai, China).

2.4 The morphology of starch granules

The scanning electron microscope (Apero S, Lecht instruments and Equipment Co., Ltd. Shenzhen, China) was used to observe the surface morphology of chickpea starch granules. Samples were mounted on SEM stubs with double-sided adhesive tape, coated with gold, and micrographs were taken at 3000× magnification (Jia et al., 2022).

2.5 Determination of solubility and swelling power

The dried starch samples were recorded as M and it were mixed with water to 1% starch suspension. The temperature was set at 55, 65, 75, 85, 95 °C for 30 min. After the slurry was cooled and centrifuge at 4000 r/min for 10 min. The supernatant was

pour into the weighing bottle, then dry at 100 °C to constant weight and weigh it (label as A). The precipitate call as P, the solubility (S) and swelling power (B) of starch were calculated by the Equations 1-2 (Kunyanee & Luangsakul, 2022).

$$S(\%) = \frac{A}{M} \times 100\% \quad (1)$$

$$B(\%) = \frac{P}{M \times (1 - S)} \times 100\% \quad (2)$$

2.6 Determination of transparency

Take the dried starch sample and mixed it with water to form a 1% starch suspension. Put it in a boiling water bath and stirring for 30 minutes. Take it out to be cooled and use distilled water as a blank, the absorbance A was determined at 620 nm, and the transparency of starch was calculated by the Equation 3:

$$T = \frac{1}{10^A} \quad (3)$$

2.7 Determination of freeze-thaw stability of starch paste

According to the method (Marboh & Mahanta, 2021), 6% starch suspension was stirred in a boiling water bath for 30 minutes, and the starch gel was refrigerated at 4 °C for 24 h then put into a centrifuge tube and weighed (m_1). Then freezing at -18 °C for 24 h, thawing at room temperature and centrifuge at 3000 r/min for 20 min, discard the supernatant and called the sediment as m_2 , calculate the precipitation rate according to the Equation 4, and cycled the above steps 5 times.

$$I = \frac{(m_1 - m_2)}{m_1} \times 100\% \quad (4)$$

2.8 X-ray Diffraction (XRD)

An X-ray diffractometer (LP-XRD, Kirshida Electronic Technology Co., Ltd. Shenzhen, China) was used to examine the crystalline patterns of the starch samples. The measurement was operated at 40 kV and 40 mA with the angle of diffraction scanning from 5° to 40° with a step length of 0.02° and scanning speed of 2°/min (Rodboontheng et al., 2022).

2.9 Fourier Transform Infrared (FT-IR) spectroscopy

The FTIR spectra of starch sample were recorded on a FTIR spectrophotometer (LP-FTIR-300, Shimadzu Co., Ltd. Japan). The starch powder was blended with KBr powder and pressed into tablet before measurement. The wavelength range was 4000 cm^{-1} to 400 cm^{-1} at a resolution of 4 cm^{-1} (Zhang et al., 2020).

2.10 Determination of starch gelatinization curve (RVA)

The gelatinization properties of starch samples were detected by rapid viscosity analyzer (RVA0524, Huishi Instrument Equipment Co., Ltd. Shanghai, China). The 3.0 g starch sample was mixed with 25 mL of water, starch slurry was equilibrated at 50 °C for 1 min, then heated from 50 °C to 95 °C at a rate of 12 °C/min. The temperature was held at 95 °C for 2.7 min, and the mixture was reduced to 50 °C for 1 min. The peak, trough

peak, final, breakdown value, setback viscosities and pasting temp were recorded (Yassaroh et al., 2021).

2.11 Determination of gel texture of starch

The 12% starch suspension was gelatinized by heating in a boiling water bath, cooled to room temperature, sealed and then placed at 4 °C for 24 hours, then the gel properties of the samples were measured by a texture analyzer. TPA compression mode was used. The velocities were 2 mm/s, 5 mm/s, 5 mm/s respectively. The compression rate was 50%. The probe was P/0.5 R (Uzizerimana et al., 2021).

2.12 Determination of digestibility of starch in vitro

A sample of 200 mg of starch was mixed with 15 mL of sodium acetate buffer solution (pH 5.2) at a concentration of 0.2 mol/L, place in a boiling water bath for 30 min and remove for cooling. When the temperature reach to 37 °C, put it into a 37 °C constant temperature oscillating water bath for 5 min. Quickly add 15 U of glycosidase (1 mL) and 290 U of porcine pancreatic alpha-amylase (4 mL), and immediately shake in a water bath at 37 °C. At 20 min and 120 min, 0.5 mL hydrolysate was taken out respectively, after adding anhydrous ethanol to kill the enzyme. The content of glucose in supernatant was calculated by DNS method, and the RDS, SDS and RS were calculated by Equations 5-7 (Li et al., 2020).

$$RDS = \frac{(G_{20} - FG) \times 0.9}{TS} \times 100\% \quad (5)$$

$$SDS = \frac{(G_{120} - G_{20}) \times 0.9}{TS} \times 100\% \quad (6)$$

$$RS = \frac{[TS - (RDS + SDS)]}{TS} \times 100\% \quad (7)$$

3 Results and analysis

3.1 Changes in amylose content

The amylose content of natural starch (NS) changed significantly after HMT as shown in Table 1. The amylose content of chickpea starch increased with the increase of water content after HMT. When the water content increased from 15% to 30%, the amylose content of HMT starch increased from 37.20 ± 0.20% to 39.33 ± 0.17% ($p < 0.05$). When the moisture content of HMT reached 30%, the amylose content increased by 2.13% compared with the native starch, which indicated that the properties of chickpea starch changed during HMT. The main reason is that the structure of starch molecular chain has been changed, and the structure change of starch molecular chain is caused by the interaction of amylose-amylose, amylose-amylopectin and amylopectin-amylopectin (Asranudin et al., 2021). The amylose molecular structure is destroyed under the action of high temperature and high humidity, which causes the amylose to break and form more short amylose, some long amylopectin forms amylose with the

transformation of its structure, which may lead to the increase of amylose content (Han et al., 2021a).

3.2 The change of particle morphology

After HMT of chickpea starch with different moisture content, some changes occurred among the starch granules. As shown in Figure 1, the granule morphology of natural starch is mostly elliptical forms (Miranda et al., 2019). After HMT, the granule morphology of chickpea starch did not change greatly when the moisture content was 15%, 20% and 25%, but some surface damage could be seen. When the moisture content was 30%, the starch granules were depressed and seriously deformed. The results showed that the morphology of starch granules did not change at low moisture content, but changed with the increase of HMT moisture content. This may be because during heat-moisture treatment, excess water molecules enter the amorphous region of the starch, expanding at 110 °C and contracting as they are removed and cooled, as a result, the surface is partially sunken (Na et al., 2020). There are some hallows appeared on the chickpea starch surface after HMT. This effect may be due to the weaker tissue structure which determined a compact form and dents formation under pressure and heating (Schafranski et al., 2021).

3.3 Changes in solubility and swelling power

As shown in Figures 2-3, chickpea starch after HMT was significantly different from natural starch ($p < 0.05$). When the heating temperature was raised from 55 °C to 95 °C, the solubility and swelling power of natural starch and HMT starch increased with the increase of temperature. The solubility and swelling power of HMT chickpea starch were lower than that of natural starch at all temperature, and decreased with the increase of HMT moisture content. At 95 °C, the solubility and swelling power of natural starch were 15.2% and 16.6% respectively, and those of HMT-30 were 8.8% and 9.2% respectively.

The decrease of starch solubility and swelling power in chickpea was closely related to the water content added during HMT. This may be due to the partial degradation of amylopectin after HMT, the formation of more amylose, and cause the internal structure of starch rearrangement. The interaction between amylose-amylose and amylose-amylopectin makes the internal bond energy of starch molecule stronger, the double helix structure more compact, and the starch molecule inside the granule is not easy to dissolve. The solubility and swelling power of starch are reduced by reducing the ability of starch particles to bind with water (Han et al., 2021b). This is consistent with the finding that increased amylose content leads to decreased solubility and swelling power (Uzizerimana et al., 2021).

3.4 Changes in transparency

Compared with the natural starch, the transparency of chickpea starch after HMT decreased significantly, and the

Table 1. Amylose content of chickpea starch and HMT starch.

Species	NS	HMT-15	HMT-20	HMT-25	HMT-30
Content %	37.20 ± 0.20 ^a	37.74 ± 0.16 ^d	38.27 ± 0.27 ^c	38.82 ± 0.25 ^b	39.33 ± 0.17 ^a

Different letters in the same column indicate significant difference ($P < 0.05$).

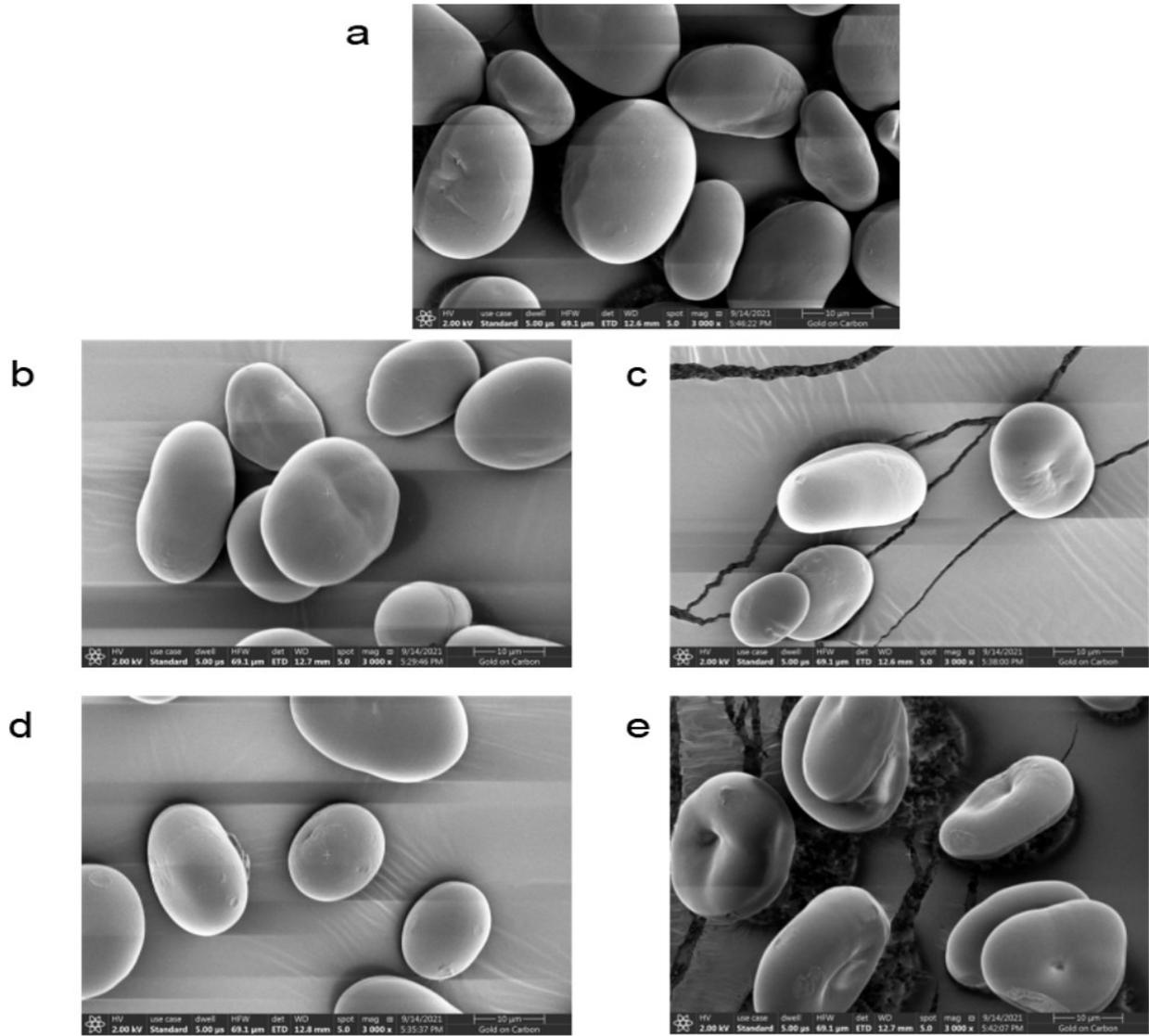


Figure 1. SEM of NS (a) and HMT starch (b HMT-15, c HMT-20, d HMT-25, e HMT-30).

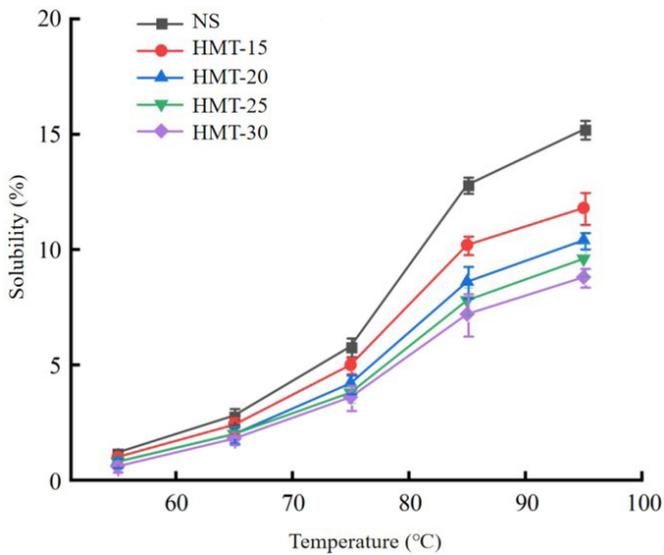


Figure 2. The solubility of starch in chickpea treated with HMT.

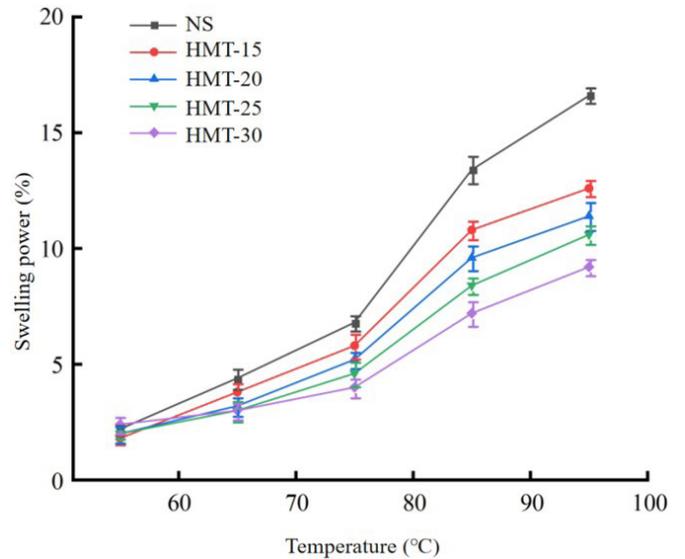


Figure 3. The swelling power of starch in chickpea treated with HMT.

transparency of chickpea starch decreased with the increase of HMT moisture content. The transparency of HMT starch and natural starch is shown in Figure 4. When the moisture content of HMT was 30%, the transparency of starch was 7.08%, which was 3.09% lower than that of natural starch. The transparency depends on the swelling size of starch granules and the content of amylopectin after gelatinization. The higher the content of amylopectin will cause the stronger transmittance of light and the higher transparency (Das & Sit, 2021). At high temperature and high humidity, some long branched starch molecules react physically with vaporized water, and some glycoside bonds are broken, which leads to the increase of short amylose in HMT process, the content of amylose in chickpea starch was increased indirectly (Han et al., 2021c). The other reason maybe is that amylose reacts with liposome to form lipid-complex, which limits the expansion of starch, the transparency of starch was reduced, the transparency of HMT starch paste was lower than that of natural starch paste. This is consistent with before studies, which HMT reduced the transparency of starch (Das & Sit, 2021).

3.5 The change of syneresis rate

The freeze-thaw stability of starch is usually expressed by syneresis rate. During the storage of frozen foods, repeated freezing and thawing were often required. If the stability of starch paste is not good, freezing and thawing alternately, the gel formed by starch is easy to be destroyed, resulting in free water precipitation. The syneresis rate of natural starch and HMT starch after 5 times freeze-thawing is shown in Figure 5. The syneresis rate increases with the increase of HMT water content. The syneresis rate of natural starch was 36.8% after one times freeze-thawing, while HMT-30 starch was 48.8%. When natural starch reached to 46.3% after five times freeze-thawing, while HMT-30 starch reached to 59.8%. It can be seen that the precipitation rate of natural starch and HMT starch increased with the increase of freezing-thawing times. HMT increased the

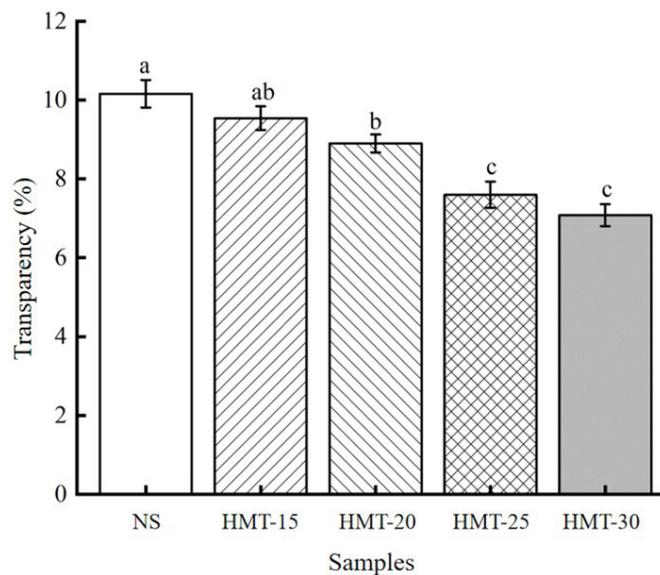


Figure 4. Transparency of starch paste treated by HMT. Note: different letters in the same column indicate significant difference ($P < 0.05$).

precipitation rate of starch, which indicated that HMT reduced the freeze-thaw stability. HMT makes amylopectin degradation, so that amylose increased. Because of the strong hydrogen bonding ability of amylose, the water in the gel was squeezed out, and HMT restricted the swelling of starch particles, which resulted in the increase of water precipitation rate (Gebremedhin & Admassu, 2022). Therefore, the freeze-thaw stability of HMT starch could not be improved.

3.6 Analysis of X-ray diffraction

Starch granule is not a simple starch molecule, it is a polymer composed of many amylose and amylopectin molecules. This polymer is composed of two parts, the ordered crystalline region and the disordered amorphous region. The relative crystallinity index can be obtained by X-ray diffraction analysis. As shown in Figure 6, the characteristic diffraction peaks of chickpea starch after HMT appeared at 5.6°, 15°, 17°, 18°, 23°, respectively, and

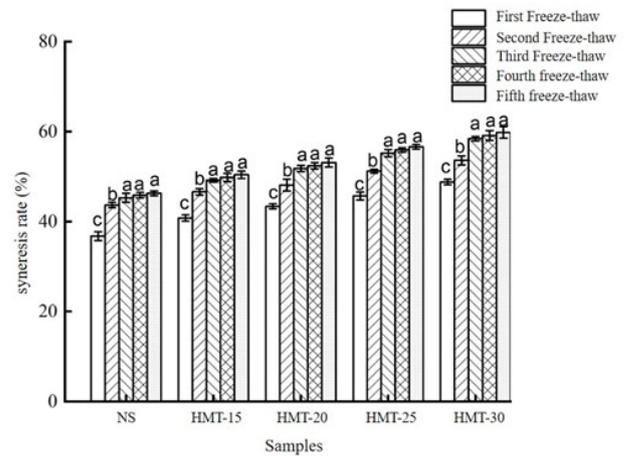


Figure 5. Effect of heat-moisture treatment on frozen-thaw stability. Note: different letters in the same column indicate significant difference ($P < 0.05$).

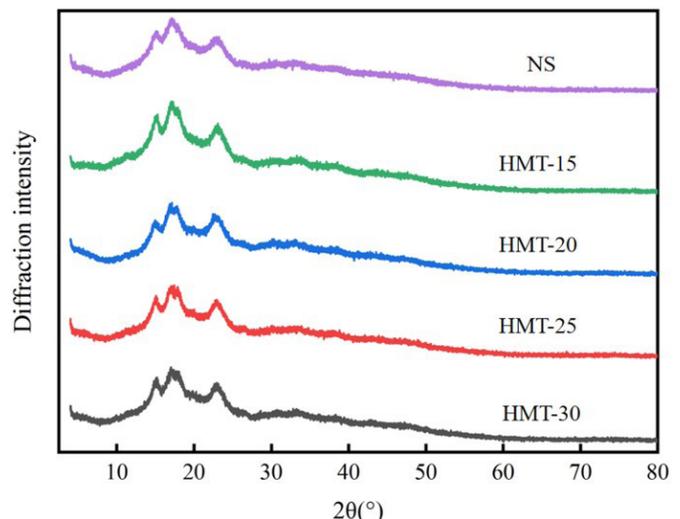


Figure 6. Effect of HMT on X-ray diffraction pattern of chickpea starch.

the double shoulder peaks appeared at 18° . It can be found that chickpea starch after HMT, its crystalline morphology did not change, that is, it is still C-type crystal structure. As shown in Table 2, the original crystalline structure was destroyed after HMT, this resulted in a decrease in its crystallinity. When the moisture content of HMT was 30%, the lowest crystallinity was 19.59%, and compared with natural starch, the crystallinity was reduced by 11.45%. Firstly, it may be that the hydrogen bond is broken and the crystallinity decreases during the treatment. Secondly, the continuous destruction of starch microcrystals and the rearrangement of starch molecules (recrystallization), which is caused by the increase of HMT water content, will also make the relative crystallinity of starch decrease (Yang et al., 2022). The crystallinity of starch was calculated by Jade software. It was found that the characteristic diffraction peak intensity of starch changed and decreased with the increase of moisture content of HMT, compared with that of natural starch, the degree of crystallization also decreases, so it can be seen that the change trend of crystallinity is the same as that of characteristic diffraction peak.

3.7 Analysis of the Fourier transform infrared spectrum

Figure 7 shows the FTIR spectra of natural starch and HMT starch at different moisture contents. The changes of IR spectra are closely related to the molecular structure and chemical bonds of starch samples. Compared with natural starch, HMT starch showed no significant changes in the position of the characteristic absorption peaks in the infrared spectra, and no new absorption peaks appeared. The internal structure of HMT starch had no obvious change.

There are four obvious absorption peaks in the natural starch spectrum, among which the stretching vibration absorption peaks of C-O-H are at 1022 cm^{-1} , which is usually used to describe the amorphous region of starch. There are several sharp absorption peaks (929 cm^{-1} , 857 cm^{-1} , 763 cm^{-1} , 576 cm^{-1}) in the range of $500\text{--}1000\text{ cm}^{-1}$, which are the absorption peaks of the stretching vibration of the whole sugar ring. C-C and C-O stretching vibration absorption peaks were found at 1154 cm^{-1} . The peak observed at 1643 cm^{-1} belongs to the absorption peak formed by the two -OH clipping of water molecule, which mainly comes from the water molecule absorbed by starch. The asymmetric stretching vibration absorption peak of -CH₂- appears at 2929 cm^{-1} . The stretching vibration peak of -OH was observed at 3385 cm^{-1} . Compared with natural starch, the absorption peaks of HMT starch and natural starch were not different, and no new absorption peaks were found. After HMT, chickpea starch still retained its original skeleton shape. Siwatch et al. (2022) and Wu et al. (2021) have carried out experiments on amaranth starch and rice starch, and their results confirm the same conclusion.

3.8 Changes of viscosity properties

The gelatinization properties of natural starches and HMT starches were determined by rapid viscosity analyzer. As shown in Figure 8, there was a significant difference between the gelatinization properties of natural starch and HMT starch ($p < 0.05$). All gelatinization parameters were significantly reduced except gelatinization temperature. According to Table 3,

the disintegration and regeneration values of chickpea starch decreased with the increase of HMT moisture content. Compared with natural starch, the disintegration value of HMT-30 decreased by 959 cP, and the lower disintegration value will have the better thermal stability of starch. The retrogradation value decreased by 2691 cP. The lower retrogradation value means that starch was more resistant to aging. With the increase of gelatinization temperature, the highest gelatinization temperature was 90.55°C when the moisture content was 30%, which indicated that HMT gradually increased the heat resistance of chickpea starch. The results showed that HMT could improve the gelatinization properties of chickpea starch. HMT increased the short-range ordered structure of starch granules, decreased the swelling

Table 2. Relative crystallinity of chickpea starch and HMT starch.

Species	NS	HMT-15	HMT-20	HMT-25	HMT-30
Relative crystallinity (%)	31.04	26.02	25.14	22.30	19.59

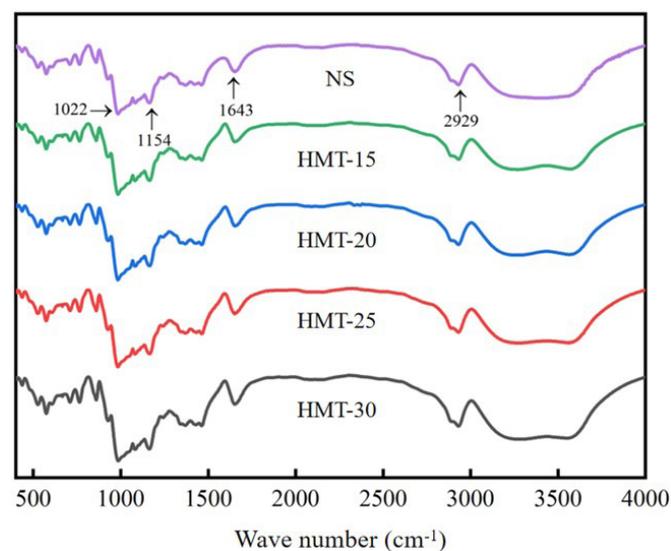


Figure 7. Infrared spectra of natural and HMT chickpea starch.

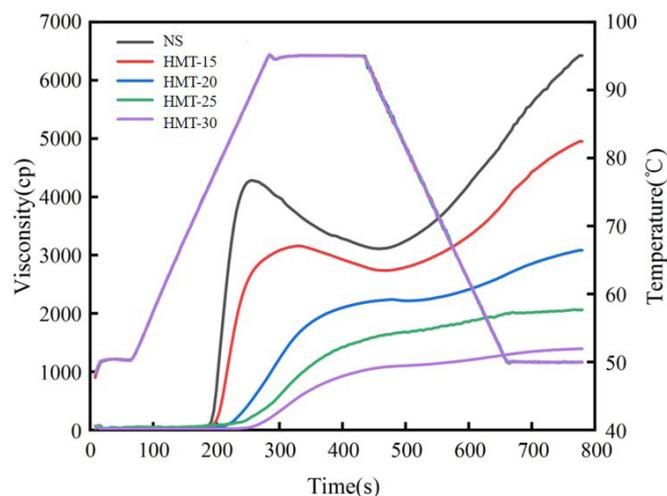


Figure 8. Viscosity characteristic curves of native starch and HMT starch.

power of starch granules, decreased the viscosity of starch granules, and increased the gelatinization temperature of starch granules (Ariyantoro et al., 2021). The water-binding capacity and thickening ability of starch granules were characterized by peak viscosity. When the moisture content of HMT was 30%, the peak viscosity (985 cp) was significantly lower than that of natural starch (4284 cp). It may be that with the increase of water content and heating temperature, the amylose content in chickpea starch increases continuously, and its heat resistance also increases, and the gelatinization temperature increases gradually, so these reduced viscosity value.

3.9 Changes in gel properties of starch

Texture properties are usually determined by amylose content and amylopectin chain length distribution. As shown in Table 4, the gel properties of natural starch and HMT starch changed significantly ($p < 0.05$). Compared with natural starch, the gel parameters of HMT starch decreased. When the moisture content was 30%, the hardness, cohesion, elasticity, adhesion and chewiness of HMT starch decreased by 15.67 g, 0.46 N, 1.64 mm, 14.02 N and 73 mj, respectively. This is due to in high temperature and humidity, water molecules and heat energy acting on starch, which resulting in amylose's breaks and the formation of more short amylose (Sindhu et al., 2021). In addition, the change of molecular chain structure will change the gel network structure

of gelatinized chickpea starch, which resulted in the decrease of gel texture value of chickpea starch.

3.10 Changes of digestion in vitro

As shown in Table 5, the contents of RDS, SDS and RS in chickpea starch changed significantly after HMT ($p < 0.05$). From the table, it can be found that the content of RDS decreases with the increase of HMT moisture content, but the content of SDS and RS increases before the moisture content of HMT reaches 25%. The change of starch digestibility usually depends on many factors, including amylose content, starch source, starch solubility and granule size. The decrease of RDS in HMT starch may be due to a relatively tight particle structure inside starch granules was formed, which led to the inability of some enzymes to quickly enter the starch granules (Brahma & Sit, 2020). However, when the moisture content increased to 30%, the RDS of HMT starches began to increase, while the SDS and RS contents began to decrease. This may be because chickpea starch in high temperature, high humidity environment, chickpea starch and vaporized water physical reaction, resulting in more serious damage to the amylopectin chain, the ability of amylase to hydrolyze starch was enhanced, so RDS content in starch began to rise, SDS and RS began to decline. HMT could increase the content of SDS and RS in starch gelation. Therefore, HMT starch is more beneficial to health (Sandhu et al., 2020).

Table 3. Paste viscosity parameters of native starch and HMT starch (unit: cP).

Species	Peakviscosity	Valley viscosity	Collapse value	Final viscosity	The regenerated value	Gelatinization temperature (°C)
NS	4284 ± 31 ^a	3110 ± 13.6 ^a	1174 ± 36.7 ^a	6424 ± 62 ^a	3314 ± 57.4 ^a	75.05 ± 0.4 ^a
HMT-15	3158 ± 35.2 ^b	2736 ± 46.2 ^b	422 ± 42.3 ^b	4952 ± 69 ^b	2216 ± 68.2 ^b	75.8 ± 0.6 ^a
HMT-20	2225 ± 39.8 ^c	2006 ± 45.5 ^c	281 ± 10.7 ^c	3302 ± 109.1 ^c	1296 ± 78.8 ^c	80.75 ± 0.5 ^b
HMT-25	1496 ± 102.4 ^d	1215 ± 100.3 ^d	219 ± 11.6 ^c	2059 ± 121.5 ^d	844 ± 22.2 ^d	87.15 ± 0.9 ^c
HMT-30	985 ± 11.6 ^e	770 ± 11.0 ^e	215 ± 6.8 ^c	1393 ± 18.2 ^e	623 ± 7.6 ^e	90.55 ± 0.4 ^c

Different letters in the same column indicate significant difference ($P < 0.05$).

Table 4. Gel texture parameters of natural starch and HMT starch.

Species	Hardness/g	Cohesion/N	Elasticity/mm	Adhesion/N	Chewiness/mj
NS	29.79 ± 0.58 ^a	0.76 ± 0.01 ^a	5.62 ± 0.15 ^a	19.88 ± 0.4 ^a	102 ± 5.03 ^a
HMT-15	19.86 ± 0.99 ^b	0.70 ± 0.03 ^a	5.13 ± 0.19 ^{ab}	12.22 ± 0.53 ^b	63.3 ± 2.34 ^b
HMT-20	18.67 ± 0.97 ^b	0.54 ± 0.04 ^b	4.95 ± 0.42 ^{bc}	8.57 ± 0.16 ^c	34.1 ± 2.29 ^c
HMT-25	15.97 ± 0.57 ^c	0.43 ± 0.04 ^c	4.47 ± 0.21 ^{cd}	7.58 ± 0.29 ^d	33.9 ± 1.92 ^c
HMT-30	14.12 ± 0.68 ^d	0.3 ± 0.01 ^d	3.98 ± 0.31 ^d	5.86 ± 0.38 ^e	29 ± 1.8 ^c

Different letters in the same column indicate significant difference ($P < 0.05$).

Table 5. Contents of RDS, SDS and RS in chickpea starch.

Species	RDS/%	SDS/%	RS/%
NS	83.29 ± 1.6 ^a	10.44 ± 0.4 ^d	6.27 ± 0.4 ^b
HMT-15	78.48 ± 1.2 ^b	12.6 ± 0.6 ^c	8.92 ± 0.3 ^d
HMT-20	73.08 ± 1.5 ^c	14.76 ± 0.3 ^b	12.16 ± 0.2 ^c
HMT-25	69.39 ± 2.0 ^d	16.29 ± 0.4 ^a	14.32 ± 0.3 ^a
HMT-30	71.37 ± 0.9 ^{cd}	15.3 ± 0.2 ^b	13.33 ± 0.4 ^b

Different letters in the same column indicate significant difference ($P < 0.05$). RDS: rapidly digestible starch; SDS: slowly digestible starch; RS: resistant starch.

4 Conclusion

In this paper, the effect of hydrothermal modification on the chickpea starch was studied and characterized by SEM, XRD and FT-IR, the physicochemical properties, gelatinization properties, texture properties and digestion properties of modified chickpea starch were compared and analyzed. After HMT, the amylose content of chickpea starch changed significantly, showing an upward trend. Compared with natural starch, the shape of HMT starch granule changed little, but under the condition of high water content (30%), the shape of HMT starch granule was destroyed, appeared depression and changed. It was found by XRD that after HMT, the crystalline morphology had no obvious change, and the structure was still C-type. In FT-IR spectra, the position of characteristic absorption peak had no obvious change, which indicated that the internal structure and main components of chickpea starch had no obvious change.

Compared with natural starch, the solubility, swelling power and transparency of HMT starch were decreased. The syneresis rate of chickpea starch increased with the increase of HMT moisture content. When the moisture content of HMT starch was 30%, and after five freeze-thaw experiments, the syneresis rate of starch reached the maximum value of $59.8 \pm 1.3\%$, compared with natural starches, HMT starches increased the syneresis rate of chickpea starches by 13.5%. It indicated that HMT decreased the freeze-thaw stability of chickpea starches.

The gel texture property decreased and the viscosity decreased with the increase of HMT moisture content, the gelatinization temperature increased gradually, which indicated that HMT could improve the thermal stability of chickpea starch. The RDS content of HMT starch decreased, SDS and RS content increased, which indicated that HMT enhanced the anti-digestibility of chickpea starch.

Hydrothermal treatment is a kind of physical modification, there is safe and no chemical reagent residue. After HMT, the starch solubility and swelling power decreased, it can be used in foods that need to limit swelling, such as noodles, vermicelli, rice noodle, etc. According to its anti-digestibility, the resistant starch can be prepared by studying its treatment time, temperature and so on. In this paper, the physicochemical properties of HMT starch were analyzed, which provided a theoretical basis for further processing of chickpea starch.

Ethical approval

This study does not contain any studies with human participants or animals performed by any of the authors.

References

- Acevedo, B. A., Villanueva, M., Chaves, M. G., Avanza, M. V., & Ronda, F. (2022). Modification of structural and physicochemical properties of cowpea (*Vigna unguiculata*) starch by hydrothermal and ultrasound treatments. *Food Hydrocolloids*, 124, 107266. <http://dx.doi.org/10.1016/j.foodhyd.2021.107266>.
- Ariyantoro, A. R., Affandi, D. R., Yulviatun, A., Ishartani, D., & Septiarani, A. (2021). Pasting properties of jack bean (*Canavalia ensiformis*) modified starch with heat moisture treatment. *IOP Conference Series. Earth and Environmental Science*, 905(1), 012092. <http://dx.doi.org/10.1088/1755-1315/905/1/012092>.
- Asranudin, Holilah, Syarifin, A. N. K., Purnomo, A. S., Ansharullah, & Fudholi, A. (2021). The effect of heat moisture treatment on crystallinity and physicochemical-digestibility properties of purple yam flour. *Food Hydrocolloids*, 120, 106889. <http://dx.doi.org/10.1016/j.foodhyd.2021.106889>.
- Brahma, B., & Sit, N. (2020). Physicochemical properties and digestibility of heat moisture-treated potato starches for different treatment conditions. *Potato Research*, 63(3), 367-383. <http://dx.doi.org/10.1007/s11540-019-09445-w>.
- Costa, L. A., Diógenes, I. C. N., Oliveira, M. A., Ribeiro, S. F., Furtado, R. F., Bastos, M. S. R., Silva, M. A. S., & Benevides, S. D. (2021). Smart film of jackfruit seed starch as a potential indicator of fish freshness. *Food Science and Technology*, 41(2), 489-496. <http://dx.doi.org/10.1590/fst.06420>.
- Das, A., & Sit, N. (2021). Modification of taro starch and starch nanoparticles by various physical methods and their characterization. *Stärke*, 73(5-6), 2000227. <http://dx.doi.org/10.1002/star.202000227>.
- Deng, C., Melnyk, O., & Luo, Y. (2022). Optimization of heat-moisture treatment on potato starch and study on its physicochemical properties. *Technology Audit and Production Reserves*, 3(65), 43-49. <http://dx.doi.org/10.15587/2706-5448.2022.260149>.
- Dewi, A. M. P., Santoso, U., Pranoto, Y., & Marseno, D. W. (2022). Dual modification of sago starch via heat moisture treatment and octenyl succinylation to improve starch hydrophobicity. *Polymers*, 14(6), 1086. <http://dx.doi.org/10.3390/polym14061086>. PMID:35335417.
- Fonseca, L. M., Halal, S. L. M. E., Dias, A. R. G., & Zavareze, E. D. R. (2021). Physical modification of starch by heat-moisture treatment and annealing and their applications: a review. *Carbohydrate Polymers*, 274, 118665. <http://dx.doi.org/10.1016/j.carbpol.2021.118665>. PMID:34702484.
- Garcia-Santos, M. D. S. L., Conceição, F. S., Villas Boas, F., Souza, B. M. S., & Barretto, A. C. D. S. (2019). Effect of the addition of resistant starch in sausage with fat reduction on the physicochemical and sensory properties. *Food Science and Technology*, 39(Suppl. 2), 491-497. <http://dx.doi.org/10.1590/fst.18918>.
- Gebremedhin, G., & Admassu, H. (2022). Effects of heat-moisture treatment and hydroxypropylation on the physical, physicochemical, thermal, and functional properties of anchote (*Coccinia abyssinica*) starch. *Journal of Food Measurement and Characterization*, 16(6), 4771-4787. <http://dx.doi.org/10.1007/s11694-022-01566-0>.
- Han, L., Cao, S., Yu, Y., Xu, X., Cao, X., & Chen, W. (2021a). Modification in physicochemical, structural and digestive properties of pea starch during heat-moisture process assisted by pre- and post-treatment of ultrasound. *Food Chemistry*, 360, 129929. <http://dx.doi.org/10.1016/j.foodchem.2021.129929>. PMID:33989884.
- Han, L., Wei, Q., Cao, S., Yu, Y., Cao, X., & Chen, W. (2021b). The assisting effects of ultrasound on the multiscale characteristics of heat-moisture treated starch from *Agriophyllum squarrosum* seeds. *International Journal of Biological Macromolecules*, 187, 471-480. <http://dx.doi.org/10.1016/j.ijbiomac.2021.07.123>. PMID:34324904.
- Han, M., Dang, K., Wang, J., Gao, L., Wang, H., Ivanistau, A., Yang, Q. & Feng, B. (2021c). New type of food processing material: the crystal structure and functional properties of waxy and non-waxy proso millet resistant starches. *Molecules*, 26(14), 4283. <http://dx.doi.org/10.3390/molecules26144283>. PMID:34299557.
- Ji, X., Rong, L., Yu, Q., Chen, Y., Li, J., & Xie, J. (2022). Gallic acid and heat moisture treatment improve pasting, rheological, and microstructure properties of Chinese yam starch-chitosan gels: a comparative study. *International Journal of Biological Macromolecules*,

- 222(Pt A), 114-120. <http://dx.doi.org/10.1016/j.ijbiomac.2022.09.090>. PMID:36113602.
- Jia, R., McClements, D. J., Dai, L., He, X., Li, Y., Ji, N., Qin, Y., Xiong, L., & Sun, Q. (2022). Improvement of pasting and gelling properties of potato starch using a direct vapor-heat moisture treatment. *International Journal of Biological Macromolecules*, 219, 1197-1207. <http://dx.doi.org/10.1016/j.ijbiomac.2022.08.178>. PMID:36057295.
- Kaur, R., & Prasad, K. (2021). Technological, processing and nutritional aspects of chickpea (*Cicer arietinum*) - a review. *Trends in Food Science & Technology*, 109, 448-463. <http://dx.doi.org/10.1016/j.tifs.2021.01.044>.
- Kunyanee, K., & Luangsakul, N. (2022). The impact of heat moisture treatment on the physicochemical properties and in vitro glycemic index of rice flour with different amylose contents and associated effects on rice dumpling quality. *LWT*, 154, 112694. <http://dx.doi.org/10.1016/j.lwt.2021.112694>.
- Li, H., Wang, R., Liu, J., Zhang, Q., Li, G., Shan, Y., & Ding, S. (2020). Effects of heat-moisture and acid treatments on the structural, physicochemical, and in vitro digestibility properties of lily starch. *International Journal of Biological Macromolecules*, 148, 956-968. <http://dx.doi.org/10.1016/j.ijbiomac.2020.01.181>. PMID:31972200.
- Li, Z., Guo, D., Li, X., Tang, Z., Ling, X., Zhou, T., & Zhang, B. (2021). Heat-moisture treatment further reduces in vitro digestibility and enhances resistant starch content of a high-resistant starch and low-glutelin rice. *Foods*, 10(11), 2562. <http://dx.doi.org/10.3390/foods10112562>. PMID:34828843.
- Marboh, V., & Mahanta, C. L. (2021). Physicochemical and rheological properties and in vitro digestibility of heat moisture treated and annealed starch of sohphlang (*Flemingia vestita*) tuber. *International Journal of Biological Macromolecules*, 168, 486-495. <http://dx.doi.org/10.1016/j.ijbiomac.2020.12.065>. PMID:33316343.
- Mesa, E., Manjarres-Pinzon, K., & Rodriguez-Sandoval, E. (2019). Gluten-free cheese bread from frozen dough: effect of modified cassava starch. *Food Science and Technology*, 39(Suppl. 2), 654-661. <http://dx.doi.org/10.1590/fst.30118>.
- Miranda, J. A. T. D., Carvalho, L. M. J. D., Vieira, A. C. D. M., & Castro, I. M. D. (2019). Scanning electron microscopy and crystallinity of starches granules from cowpea, black and carioca beans in raw and cooked forms. *Food Science and Technology*, 39(Suppl. 2), 718-724. <http://dx.doi.org/10.1590/fst.30718>.
- Na, J. H., Kim, H. R., Kim, Y., Lee, J. S., Park, H. J., Moon, T. W., & Lee, C. J. (2020). Structural characteristics of low-digestible sweet potato starch prepared by heat-moisture treatment. *International Journal of Biological Macromolecules*, 151, 1049-1057. <http://dx.doi.org/10.1016/j.ijbiomac.2019.10.146>. PMID:31739028.
- Rodboontheng, W., Uttapap, D., Wandee, Y., Udchumpisai, W., Kotatha, D., Puttanlek, C., & Rungsardthong, V. (2022). Simple thermal and freezing treatments to improve absorption capacity and alter digestibility of canna starch granules. *International Journal of Biological Macromolecules*, 194, 861-869. <http://dx.doi.org/10.1016/j.ijbiomac.2021.11.141>. PMID:34838854.
- Sandhu, K. S., Siroha, A. K., Punia, S., & Nehra, M. (2020). Effect of heat moisture treatment on rheological and in vitro digestibility properties of pearl millet starches. *Carbohydrate Polymer Technologies and Applications*, 1, 100002. <http://dx.doi.org/10.1016/j.carpta.2020.100002>.
- Schafanski, K., Ito, V. C., & Lacerda, L. G. (2021). Impacts and potential applications: a review of the modification of starches by heat-moisture treatment (HMT). *Food Hydrocolloids*, 117, 106690. <http://dx.doi.org/10.1016/j.foodhyd.2021.106690>.
- Sindhu, R., Devi, A., & Khatkar, B. S. (2021). Morphology, structure and functionality of acetylated, oxidized and heat moisture treated amaranth starches. *Food Hydrocolloids*, 118, 106800. <http://dx.doi.org/10.1016/j.foodhyd.2021.106800>.
- Siwath, M., Yadav, R. B., & Yadav, B. S. (2022). Annealing and heat-moisture treatment of amaranth starch: effect on structural, pasting, and rheological properties. *Journal of Food Measurement and Characterization*, 16(3), 2323-2334. <http://dx.doi.org/10.1007/s11694-022-01325-1>.
- Ullah, A., Farooq, M., Rehman, A., Hussain, M., & Siddique, K. H. M. (2020). Zinc nutrition in chickpea (*Cicer arietinum*): a review. *Crop & Pasture Science*, 71(3), 199. <http://dx.doi.org/10.1071/CP19357>.
- Uzizerimana, F., Dang, K., Yang, Q., Hossain, S., Gao, S., Bahati, P., Mugiraneza, N. G., Yang, P., & Feng, B. (2021). Physicochemical properties and in vitro digestibility of tartary buckwheat starch modified by heat moisture treatment: a comparative study. *NFS Journal*, 25, 12-20. <http://dx.doi.org/10.1016/j.nfs.2021.09.001>.
- Wang, Q., Li, L., Liu, C., & Zheng, X. (2022). Heat-moisture modified blue wheat starch: physicochemical properties modulated by its multi-scale structure. *Food Chemistry*, 386, 132771. <http://dx.doi.org/10.1016/j.foodchem.2022.132771>. PMID:35344719.
- Wu, C., Ji, G., Gao, F., Qian, J. Y., Zhang, L., Li, Q., & Zhang, C. (2021). Effect of heat-moisture treatment on the structural and physicochemical characteristics of sand rice (*Agriophyllum squarrosum*) starch. *Food Science & Nutrition*, 9(12), 6720-6727. <http://dx.doi.org/10.1002/fsn3.2622>. PMID:34925801.
- Yang, S., Dhital, S., Zhang, M., Wang, J., & Chen, Z. (2022). Structural, gelatinization, and rheological properties of heat-moisture treated potato starch with added salt and its application in potato starch noodles. *Food Hydrocolloids*, 131, 107802. <http://dx.doi.org/10.1016/j.foodhyd.2022.107802>.
- Yassaroh, Y., Woortman, A. J. J., & Loos, K. (2021). Physicochemical properties of heat-moisture treated, stearic acid complexed starch: the effect of complexation time and temperature. *International Journal of Biological Macromolecules*, 175, 98-107. <http://dx.doi.org/10.1016/j.ijbiomac.2021.01.124>. PMID:33508365.
- Zhang, B., Saleh, A. S. M., Su, C., Gong, B., Zhao, K., Zhang, G., Li, W., & Yan, W. (2020). The molecular structure, morphology, and physicochemical property and digestibility of potato starch after repeated and continuous heat-moisture treatment. *Journal of Food Science*, 85(12), 4215-4224. <http://dx.doi.org/10.1111/1750-3841.15528>. PMID:33190270.
- Zhang, Z., Zheng, B., Du, A., Chen, J., & Chen, L. (2023). Insight into the retardation of retrogradation of chestnut starch by heat-moisture treatment with flavonoids. *Food Chemistry*, 404(Pt A), 134587. <http://dx.doi.org/10.1016/j.foodchem.2022.134587>. PMID:36257264.