Quality Assurance and Safety of Crops & Foods, 2020; 12 (2): 89–99

Microstructure, thermodynamics and rheological properties of different types of red adzuki bean starch

J. Zhang[1] and A. Zhai[1,2]*

[1]*College of Food, Heilongjiang Bayi Agricultural University, Xinfeng Lu 5, Daqing 163319, China P.R.;* [2]*Key Laboratory of Agro-Products Processing and Quality Safety of Heilongjiang Province, Daqing 163319, China P.R.*

Corresponding Author: A. Zhai, 420680832@qq.com

Received: 19 February 2020 / Accepted: 20 April 2020 / Published: 7 June 2020

RESEARCH ARTICLE

Abstract

Starches were isolated from three cultivars of red adzuki beans, including Da Hongpao (DHP), Bao Qinghong (BQH) and Zhen Zhuhong (ZZH), and their morphological, structural and physicochemical properties were studied. Statistical analysis of the physicochemical and functional properties data revealed a significant ($P < 0.05$) difference among the three starch types. Starch of DHP cultivar showed low amylose content, smooth and round particle morphology, with obvious polarised crosses. The average particle size of the three adzuki bean types was in the range of 35.58–43.29 μm, with that of DHP being the smallest, 35.58 μm. The X-ray diffraction patterns showed that all the starches were type A with reflections (2θ) at 15.0°, 17.03° and 23.3°. The bands of Fourier transforms infrared spectra of the three starches revealed their carbohydrate properties, and the intensity of the Fourier spectral absorption band of starch from DHP was weaker than that of the other cultivars. Further, the relative crystallinity of the three starches ranged from 22.7 to 29.4%, and DHP showed the highest crystallinity of 29.4%. Additionally, starch of the DHP cultivar revealed high gelatinisation, peak viscosity and enthalpy as compared to those from the other two adzuki bean cultivars. The shear viscosity of the three starch types decreased with increasing shear rate; when the shear rate was 10 s^{-1}, the shear viscosity of the DHP-derived starch significantly decreased. Moreover, both the modulus (G') and the loss modulus (G") increased with increasing dynamic frequency, and the DHP-derived starch showed the lowest G' and G" values. In summary, this work provides data that may help in promoting the application of starches isolated from red adzuki bean in the food industry.

Keywords: adzuki bean, crystallinity, gelatinisation temperature, shear viscosity

1. Introduction

Adzuki bean (*Vigna angularis* L.), a member of the Fabaceae family, is widely distributed in north-eastern China. It has been widely used in traditional Chinese herbal medicine for thousands of years (Luo *et al.*, 2016). The annual planting area of adzuki beans is approximately 800,000 hectares, and the total annual output of China is approximately 300,000 tons. Numerous studies have reported that extracts from adzuki bean have diverse physiological functions, including antioxidant, anti-inflammation, atherosclerosis, anti-cancer and cardiovascular effects (Blazek and Copeland, 2008). Although it has a high starch content, most of the research on adzuki bean starch mainly focuses on the basic physical and chemical properties and gelatinisation characteristics of adzuki bean starch (Das *et al.*, 2015). In addition, there are also scholars comparing the properties of red adzuki beans and other legume starches (Yuliana *et al.*, 2012). In order to improve the utilisation rate of adzuki bean resources in the food industry, it is essential to select high-quality adzuki bean varieties through in-depth research on the structural characteristics of adzuki bean starch. Scanning electron microscopes, polarising microscopes, laser particle size analysers, X-ray diffractometers and Fourier infrared spectrometers are precision instruments useful for studying the microstructure and characteristics of starch (Wang *et al.*, 2011). These approaches can be used to evaluate starch particle morphology, molecular particle size, crystal structure and molecular functional groups to optimise the adzuki bean processing (Reddy *et al*., 2016). In addition, rheological analysis can reveal important physicochemical properties of starch. Thus, rheological analysis is an important approach for determining the texture of foods such as adzuki bean starch. Several studies have been performed to characterise the properties of the native and processed starches such as adzuki bean starch (Li *et al*., 2015), rice starch (Shunjing *et al*., 2017), corn starch (Chen *et al*., 2018) and resistant starch (Zhang *et al*., 2018). However, properties of starch from different red adzuki bean cultivars are not fully characterised and understood. Therefore, the aim of this study was to comprehensively investigate the morphological, structural and physicochemical properties of starches isolated from three red adzuki bean cultivars.

2. Materials and methods

Materials

Adzuki bean (*V. angularis* L.) was purchased from Clay Farm (Daqing City, Heilongjiang Province, China). Samples of the three types of red adzuki bean, Da Hongpao (DHP), Bao Qinghong (BQH) and Zhen Zhuhong (ZZH), were collected during the harvest season, November 2019. All chemicals and reagents used in this study were of analytical grade and purchased from Tianjin Technology Co., Ltd. (Shanghai, China).

Isolation of red adzuki bean starch

Starch was extracted from the adzuki beans as described by Wang *et al*. (2016) with minor modifications. The seeds (100 g) were immersed in 500 mL of 0.3% sodium sulphite solution at room temperature for 24 h. The seed coats were removed by manual abrasion and then the cotyledons were washed with distilled water and crushed in a laboratory blender for 5 min. The slurry was sieved through 100 and 200-mesh sieves. The filtrate was suspended in distilled water (1:5 ratio) and allowed to stand for 12 h at room temperature. The supernatant was drained off, the starch layer was dissolved in 400 mL of 0.02% NaOH and allowed to settle for 2 h at 4 °C, and the supernatant was decanted. Precipitated starch was washed with distilled water until a neutral pH was obtained, followed by centrifugation at 2054.325 ×*g* for 15 min and then dried at 40 °C for 24 h in an oven. The dried starch was ground and screened through a 100-mesh sieve and then stored in screw-capped containers until use.

Chemical composition analysis of starch isolates

The compositions of isolated starches were determined following the official methods of the Association of Official Analytical Chemists (Horwitz, 1990). Moisture content was evaluated by gravimetric analysis. The samples were dried in a hot air oven at 105 °C until a constant weight was achieved, and the ash quantity was analysed using a muffle furnace temperature at 550 °C. Crude protein content was determined by the standard Kjeldahl method using 6.25×N as the conversion factor. The lipid contents of starches were analysed using the solvent extraction technique (Morrison and Laignelet, 1983). The amylose content of isolated starches was evaluated as described previously (Li *et al*., 2015).

Scanning electron microscopy analysis

The morphology of starch granules was examined by scanning electron microscopy (SEM, S-3400N, Hitachi, Tokyo, Japan) with 20 kV potential accelerator. For SEM, the starch sample was directly applied onto double-sided sticky tape placed on metal stubs and coated with carbon, observed and photographed (Wang *et al*., 2010).

Polarised microscopy analysis

The morphology of starch granules was evaluated by microscopy (Microscope, NP-800TRF, Ningbo, China) with a polarised cross. Starch samples were prepared in a 1% starch suspension and mixed to ensure that the starch particles were fully dispersed. After placing one drop on a clean glass slide, polarising microscopy was performed, and images were acquired.

Granule size distribution

The particle size distribution of the separated starch was analysed with a laser scattering-based particle size analyser (Mastersizer, Malvern Instruments, Malvern, UK). The specific setting parameters were as follows: sample concentration 34%, medium refractive index 1 + 0.00i and sample refractive index 1.51+0.01i. First, the circulating feed pump introduces absolute ethanol into the sample well to perform background measurement of the dispersant, ambient scattered light and electronic noise. After subtracting the background, the sample was stirred and an appropriate amount of sample was added, and then the sample pump and stirrer were adjusted in order to reduce the speed of the turntable by half for sample testing (Sukhija *et al*., 2016).

X-ray diffraction and relative crystallinity

An X-ray diffractometer (D X'Pert PRO X, Malvern Instruments, Malvern, UK) was used to record the X-ray diffraction (XRD) and crystallinity of the separated starch, with a CuKα value of 1.54 radiation, power of 1,600 W and step number of 1.5 rad/min with a 2θ range between 3 and 35, with a voltage of 40 kV and filament current of 30 mA (Nara and Komiya, 1983).

Fourier transforms infrared (FT-IR) spectroscopy analysis

An infrared spectrum of the separated starch was obtained using a spectrophotometer (Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA) at room temperature. Before the measurement, 0.5–2 mg of red adzuki bean starch was mixed with 100–200 mg of finely dried KBr powder and ground until the sample was uniform. The sample was measured with a Fourier infrared spectrometer beam for full-band scanning. The scanning range was 4,000–400 cm^{-1}, and the resolution was 4 cm^{-1} (Chen *et al.*, 2016).

Thermal properties analysis

The gelatinisation temperature and enthalpy of the separated starch were evaluated using a differential scanning calorimeter (TA-Q20 DSC, TA Instruments, New Castle, DE, USA) as described by Reddy et al. 2015b. First, 3.5 mg (dry basis) starch was mixed with 7 μL of distilled water. The starch slurry was added to the differential scanning calorimeter (DSC) sample holder. The protective gas was nitrogen, flow rate was 50 mL/min, scanning temperature range was 20–120 °C and heating rate was 10 °C/min.

Pasting properties analysis

The gelatinisation characteristics of the extracted starch were examined using a Rapid Visco Analyser (RVA 4500, Perten Instruments, Hägersten, Sweden) as described by Reddy et al. 2015b. The sample (3.0 g, dry basis) was directly mixed with distilled water (25 mL) to prepare a starch suspension and dispersed in an Rapid Visco Analyser (RVA) tank and homogenised manually using a plastic paddle to prevent clumping. The dispersion was then incubated at 35 °C for 3 min, heated to 95 °C at a rate of 6 °C/min, incubated at 95 °C for 2.5 min and then cooled at a rate of 6 °C/min to 50 °C. This temperature was maintained for 2 min while stirring at 960 r/min in the first 10 s followed by a rest time of 160 r/min (Gałkowska and Juszczak, 2019).

Static rheological properties analysis

Using an advanced rotary rheometer (AR-G2, TA Instruments, New Castle, USA), the correlation between the shear viscosity and shear rate of starch at room temperature was examined. Before measurement, three starch samples were incubated at 25 °C for 6 min. The samples were exposed to a shear stress range of 0.1–1,000 Pa and a shear rate range of 0.01–100 s^{-1}, with the stress scan test performed at a constant angular frequency of 1 rad/s (Teng *et al.*, 2013).

Dynamic rheological properties analysis

Using an advanced rotary rheometer (AR-G2, TA Instruments, New Castle, USA), the relationship between the storage modulus (G’) and loss modulus (G”) of the system and frequency at 25 °C was determined. The frequency scan range was 0.1–40 Hz, fixed frequency was 1 Hz, stress value was 1%, temperature scanning range was 25–100 °C and heating rate was 5 °C/min (Singh *et al.*, 2003).

Statistical analysis

All data are reported as averages of triplicate observations and expressed as the mean ± standard deviation of the mean. Statistical analysis was performed using SPSS 20 software (SPSS, Inc., Chicago, IL, USA) and Excel (Microsoft, Redmond, WA, USA). Data were analysed by one-way analysis of variance. When significant differences were observed ($P < 0.05$), the data were compared using the Duncan multi-range test.

3. Results and discussion

Chemical composition of starch isolates

The findings of the physical and chemical composition of the starches isolated from three types of adzuki bean

Table 1. Physicochemical properties of starches from red adzuki bean.

Samples	Moisture(%)	Mass fraction of starch (%)	Protein (%)	Fat (%)	Amylose (%)
ZZH	8.58 ± 1.3^{c}	74.29 ± 0.6^{a}	0.35 ± 0.03^{a}	0.05 ± 0.004^{ab}	35.43 ± 0.18^{a}
BQH	10.56 ± 0.9^{ab}	73.54 ± 0.8^{b}	0.39 ± 0.02^{b}	0.07 ± 0.003^{a}	31.29 ± 0.20^{b}
DHP	11.04 ± 0.5^{a}	75.16 ± 0.5^{bc}	0.28 ± 0.04^{c}	0.03 ± 0.001^{bc}	28.35 ± 0.13^{c}

[a]Values expressed are mean ± standard deviation. Values with the same superscripts in a row did not differ significantly ($P < 0.05$).
[b]Different superscript letters in the same column indicate significant differences ($P < 0.05$).
BQH, Bao Qinghong; DHP, Da Hongpao; ZZH, Zhen Zhuhong.

including DHP, BQH and ZZH are shown in Table 1. The moisture content of red adzuki bean starch exhibited significant ($P < 0.05$) differences, with a value ranging from 8.58 to 11.04%. This may be because similar extraction techniques and similar times and drying temperatures were used for the isolated starches. Thus, the moisture content of the starches isolated from the three types of adzuki bean was within the accepted range for powdered dry products (<15%) (Ozcan and Jackson, 2002). The mass fraction of red adzuki bean starch exhibited significant ($P < 0.05$) differences, and the values ranged from 73.54 to 75.16%. The results of protein and fat contents exhibited significant difference ($P < 0.05$) among DHP, BQH and ZZH. The values of protein and fat contents of starches isolated from the three types of adzuki bean ranged from 0.28 to 0.35% and from 0.03 to 0.07%, respectively. This is consistent with the low protein and fat contents commonly found in the starch granules of legumes (Zhang *et al*., 2015). The low protein and fat contents may reflect the effectiveness of the isolation process for purifying the starches. Further, the chemical composition of starches could be affected by botanical source as well as climatic and agronomic conditions, and by the process of harvesting and isolation. The amylose content of starches extracted from the three types of adzuki bean is summarised in Table 1. Generally, the content of amylose has an impact on the nutritional, functional and quality characteristics of starch products, since the amorphous region of starches is mainly composed of amylose. Amylose contents of extracted starches exhibited significant ($P < 0.05$) differences, and the values were 28.35 to 35.43% for starches isolated from DHP, BQH and ZZH, respectively. The difference in amylose content of isolated starches could be due to genotype as well as soil and climatic conditions (Abegunde *et al*., 2013). Moreover, amylose is synthesised after the formation of the crystalline matrix, and the amylose is deposited in the available space in the starch granule, which defines its distribution inside the starch granule and, consequently, the physicochemical features of the starch (Tang et al., 2002).

Morphological characteristics

Granules morphology

SEM was performed to observe the micro-surface structures of the three types of red adzuki bean starch (magnification 1,000×). As shown in Figure 1, the three types of red adzuki bean starch particles show irregular shapes. Most particles of ZZH had irregular oval shapes, different sizes and a few slightly convex surfaces (Figure 1A). The surface of BQH was relatively smooth and approximately regular oval (Figure 1B). The large DHP had a full and spherical shape with a smooth surface (Figure 1C). The starch granules showed different morphologies because the amylose content of DHP was significantly higher than those of the other two types (Reddy *et al*., 2017), making the starch appear more full-grained. These results agree with findings of Reddy *et al*. (2017) and Wang *et al*. (2017) who found that starch granules of adzuki bean are smooth, round, oval to kidney or irregular shaped. Also, Gong *et al*. (2017) and Xu *et al*. (2018) found that the native red adzuki bean starch shows round or oval shapes with few fissures on the surface.

Polarised cross analysis

Starch exhibits birefringence properties; thus, under a polarisation microscope, the density and refractive index differences in the crystalline and amorphous structures

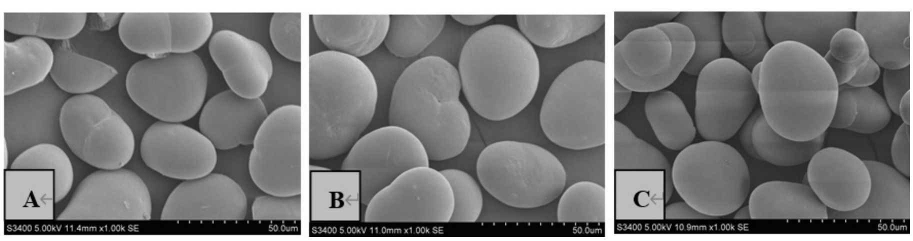

Figure 1. Scanning electron micrographs (SEM) of starch from adzuki beans (1,000×).

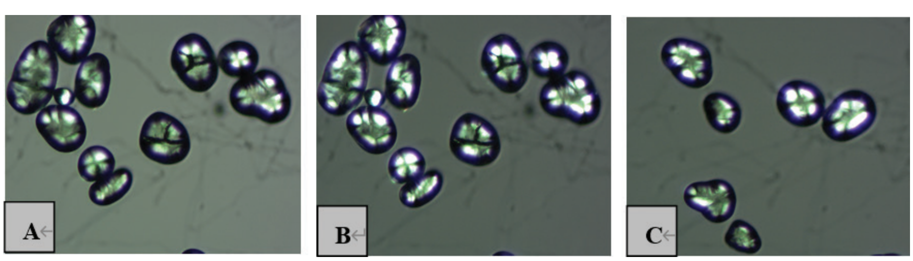

Figure 2. Polarised cross of starch from adzuki beans.

inside cause the starch particles to cross polarise. The polarised crosses of the three types of red adzuki bean starch are shown in Figure 2. The polarised crosses of starch from ZZH (Figure 2A) were less obvious than those of the starch from DHP (Figure 2B) and BQH (Figure 2C). Changes in the polarised cross of starch particles can be used to qualitatively characterise the differences in the crystal structure of the particles. If the crystal structure of the ordered arrangement of starch molecular chains within the starch particles significantly differs, the polarised cross will also differ (Atrous *et al*., 2015), consistent with the findings of this study. Wang *et al*. (2017) found that the native adzuki bean starch showed typical Maltese crosses, reflecting the arrangement of starch crystallites within the granules.

Granule size distribution

The particle size distribution is the ratio of the number of particles with different size ranges to the total number of particles. This index affects the use of starch and product quality. The particle size and distribution of different red adzuki bean starch particles are shown in Table 2 and Figure 3. The average particle diameter and surface area of the three types of starch particles of red adzuki bean showed significant differences. The particle size of ZZH was 43.29 μm, which is significantly higher than the values determined for the other two types. The average particle size of DHP was 35.58 μm, which is significantly lower than those of the other two types. BQH showed a surface area of 15.52 μm, which is significantly larger than those of the other two types. ZZH was found to have a surface area of 8.3 μm, which was significantly lower than those of the other two types. When the starch particle size is large, the amylopectin content is low. Interactions among thermal energy, water absorption and swelling cause the α-1,6 glycosidic bond structure in the amorphous region of the starch to loosen, and small-molecule starch cross links with other chains to form a larger particle structure (Wang *et al*., 2015). This causes the starch to show a lower gelatinisation temperature during the heating process and decreases the taste quality; therefore, DHP, which showed a higher amylopectin content and relatively small particle size, would have a soft mouthfeel after processing.

Table 2. Particle size of starches from red adzuki bean.

Samples	Volume average particle size(μm)	D_{10}/μm	D_{50}/μm	D_{90}/μm	Surface area average particle size (m_2/g)
ZZH	43.29 ± 1.3^a	29.13 ± 0.6^a	45.12 ± 0.43^a	59.87 ± 0.18^a	8.39 ± 0.24^a
BQH	39.04 ± 0.9^b	26.98 ± 0.8^b	42.16 ± 0.39^b	57.90 ± 0.20^b	15.52 ± 0.6^c
DHP	35.58 ± 0.5^c	25.16 ± 0.5^{bc}	40.92 ± 0.25^c	55.28 ± 0.13^c	11.37 ± 0.41^{ab}

[a]D10, D50 and D90 indicate that particles with a particle size smaller than the particle size account for 10, 50, and 90%.
[b]Values expressed are mean ± standard deviation. Values with the same superscripts in a row did not differ significantly (P < 0.05).
[c]Different superscript letters in the same column indicate significant differences (P <0.05).
BQH, Bao Qinghong; DHP, Da Hongpao; ZZH, Zhen Zhuhong.

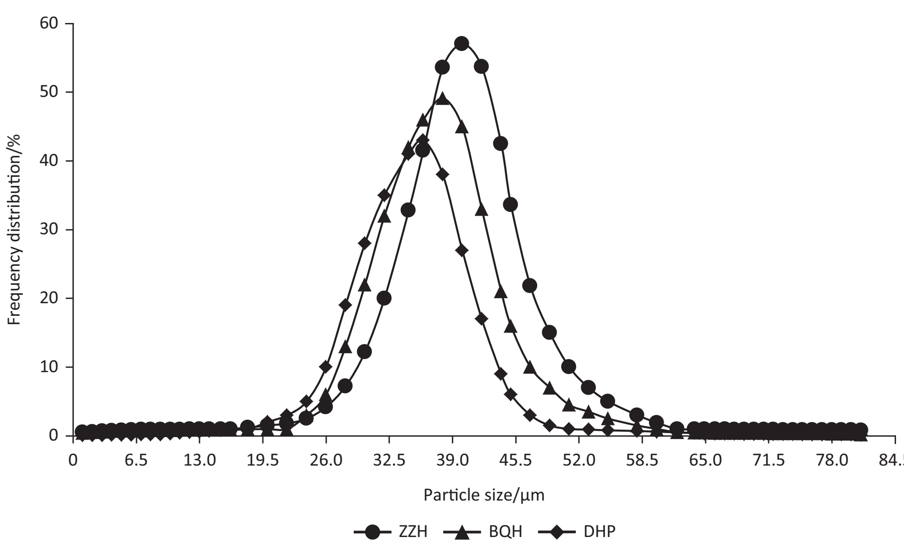

Figure 3. Particle distribution of starches from three types of red adzuki beans.

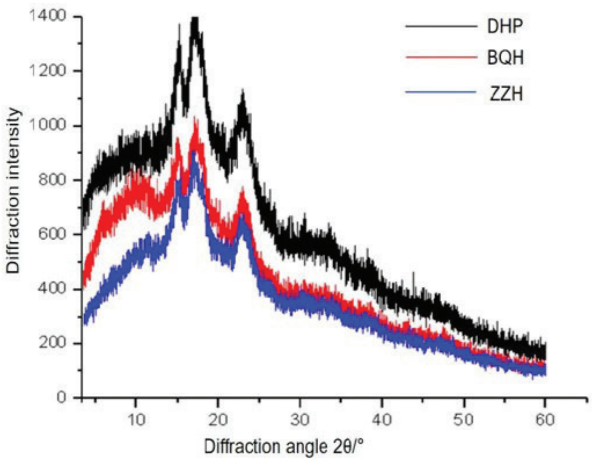

Figure 4. X-diffraction pattern of starches from three types of red adzuki beans.

Table 3. Relative crystallinity (%) of starches from red adzuki bean.

Samples	Relative crystallinity (%)
ZZH	22.7 ± 0.18[c]
BQH	26.1 ± 0.20[b]
DHP	29.4 ± 0.13[a]

[a]Values expressed are mean ± standard deviation. Values with the same superscripts in a row did not differ significantly (*P* < 0.05).
[b]Different superscript letters in the same column indicate significant differences (*P* < 0.05).
BQH, Bao Qinghong; DHP, Da Hongpao; ZZH, Zhen Zhuhong.

These results indicate that DHP is suitable for producing instant red adzuki bean paste and other products. Reddy *et al.* (2017) found that starches from adzuki bean showed a unimodal size distribution, with an average diameter value of 45.65 μm, ranging between 25 and 60 μm.

X-ray diffraction and relative crystallinity

The crystal structure and relative crystallinity of the three types of adzuki bean starch are shown in Figure 4 and Table 3. The three types of adzuki bean starch showed strong diffraction peaks at diffraction angles (2θ) of 15°, 17° and 23°, indicating typical A-type crystal structures. The relative crystallinity ranged from 22.7 to 29.4% ($P < 0.05$), with DHP showing the highest value. As the crystallinity of starch is mainly related to accumulation of the amylopectin double helix, DHP starch also had the highest amylopectin content. Exposure to heat and water weakens the ability of amylopectin to form hydrogen bonds with water molecules compared to this ability of amylose; the binding force with water is also lower than that of amylose. Similar XRD patterns were reported for the red adzuki bean starch by Reddy *et al.* (2017). However, Wang *et al.* (2017), Gong *et al.* (2017) and Xu *et al.* (2018) found that the native red adzuki bean starch exhibited a C-type crystalline structure, that is, a mixture of A- and B-type crystalline structures.

FT-IR spectra

The results of FT-IR spectroscopy of the three types of red adzuki bean starch are shown in Figure 5. The wide frequency band near 2,934–3,001 cm^{-1} indicates complex vibrational stretching of the intermolecular and intramolecular hydroxyl groups; the peak at 2,007–2,395 cm^{-1}

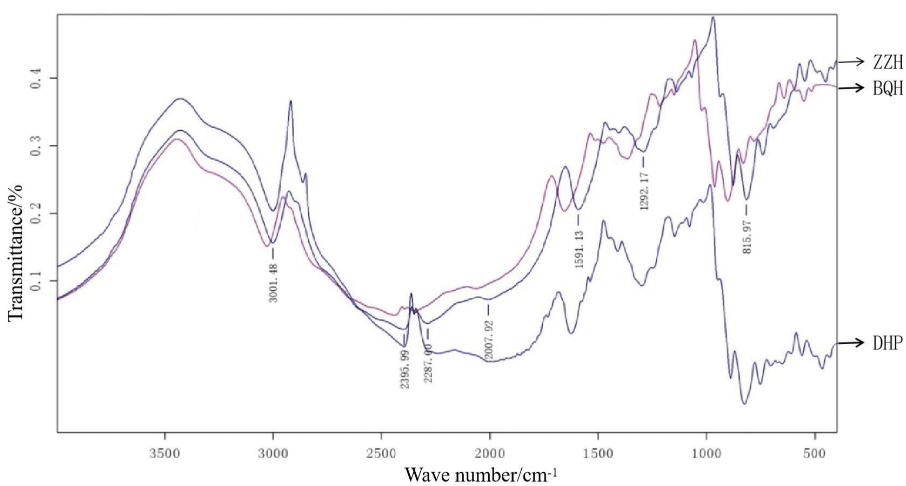

Figure 5. Fourier transforms infrared (FT-IR) map of starches from three types of red adzuki beans.

Table 4. Thermal properties of starches from red adzuki bean.

Samples	T_o (°C)	T_c (°C)	T_p (°C)	ΔH_{gel} (J/g)
BQH	60.38 ± 0.25[b]	68.02 ± 0.02[b]	77.87 ± 0.11[c]	7.34 ± 0.19[ab]
ZZH	59.75 ± 0.55[bc]	67.9 ± 0.23[c]	89.73 ± 0.31[a]	6.55 ± 0.30[c]
DHP	62.92 ± 0.16[a]	71.98 ± 0.08[a]	84.8 ± 0.24[b]	7.47 ± 0.46[a]

[a]Values expressed are mean ± standard deviation. Values with the same superscripts in a row did not differ significantly ($P < 0.05$).
[b]Different superscript letters in the same column indicate significant differences ($P < 0.05$).
BQH, Bao Qinghong; DHP, Da Hongpao; ZZH, Zhen Zhuhong.

Table 5. Pasting properties of starches from red adzuki bean (cP).

Samples	Peak viscosity (cP)	Trough viscosity (cP)	Breakdown viscosity (cP)	Final viscosity (cP)	Setback viscosity (cP)
DHP	11,461 ± 1.2[a]	5,023 ± 2.7[c]	6,438 ± 1.5[a]	6,170 ± 1.8[c]	1,147 ± 0.5[a]
ZZH	8,614 ± 0.4[c]	6,329 ± 1.1[a]	2,285 ± 0.8[c]	6,863 ± 2.6[a]	534 ± 3.5[c]
BQH	8,632 ± 1.3[b]	6,020 ± 3.0[b]	2,612 ± 1.9[b]	6,595 ± 0.4[b]	575 ± 1.8[b]

[a]Values expressed are mean ± standard deviation. Values with the same superscripts in a row did not differ significantly ($P < 0.05$).
[b]Different superscript letters in the same column indicate significant differences ($P < 0.05$).
BQH, Bao Qinghong; DHP, Da Hongpao; ZZH, Zhen Zhuhong.

corresponds to the ring -CH extension related to the methine hydrogen atom; the peak at 1,292–1,591 cm^{-1} corresponds to coupling of CO stretching and COH bending in the starch molecule; the peaks observed at 766–996 cm^{-1} are caused by the skeleton mode vibration of α-1,4 glycosidic bonds. The absorption peak intensities of the three types of red adzuki starch showed some differences. The order of intensity was: ZZH > BQH > DHP. The absorption peak intensity is positively correlated with the amylose content. Therefore, the absorption peak intensity of ZZH was strong because of its high amylose content (Correia *et al.*, 2012). These results agree with FT-IR spectra of red adzuki bean reported in previous investigations (Gong *et al.*, 2017; Reddy *et al.*, 2017; Xu *et al.*, 2018).

Determination of thermodynamic properties

Thermal properties

Table 4 shows the pasting properties of the three types of red adzuki bean starch measured by DSC, which showed significant differences ($P < 0.05$). The onset temperature of gelatinisation (T_o) was 59.75–62.92 °C, with the starting temperature of DHP showing the highest value. The enthalpy of gelatinisation (ΔH_{gel}) indicates the loss of molecular order within starch granules, which arises in the starches during gelatinisation. The enthalpy values of DHP, BQH and ZZH were 7.47, 6.55 and 7.34 J/g, respectively, revealing significant differences ($P < 0.05$). Because the enthalpy value is related to the bonding force and number of double helix structures in the crystalline region of starch granules, the lower enthalpy value observed for ZZH indicated fewer double helix chains, which is related to the crystalline region of starch granules. Adjacent amylopectin double helix interactions in ZZH are weak, and the molecular arrangement of starch particles is disordered, enabling the starch to more easily gelatinise and show a lower starting temperature. In contrast, DHP starch showed a higher enthalpy value and starting temperature; thus, it is more suitable for producing red adzuki bean instant food that requires heating. The gelatinisation temperatures of starches are influenced by different factors such as ratio of amylose and amylopectin, molecular structure, degree of crystallinity, and size and shape of starch granules. The thermal properties agree with those reported for the adzuki bean starch in previous studies (Gong *et al.*, 2017; Reddy *et al.*, 2017; Wang *et al.*, 2017; Xu *et al.*, 2018).

Pasting properties

The RVA properties of the three types of red adzuki bean starch significantly differed, as shown in Table 5 ($P < 0.05$). The peak viscosity of the three starches ranged from 8,614 to 11,461 cP, with DHP showing the highest peak viscosity. In addition, the final viscosity of the three starches was 6,170–6,863 cP, with ZZH showing the highest final viscosity. Table 5 shows that ZZH exhibited

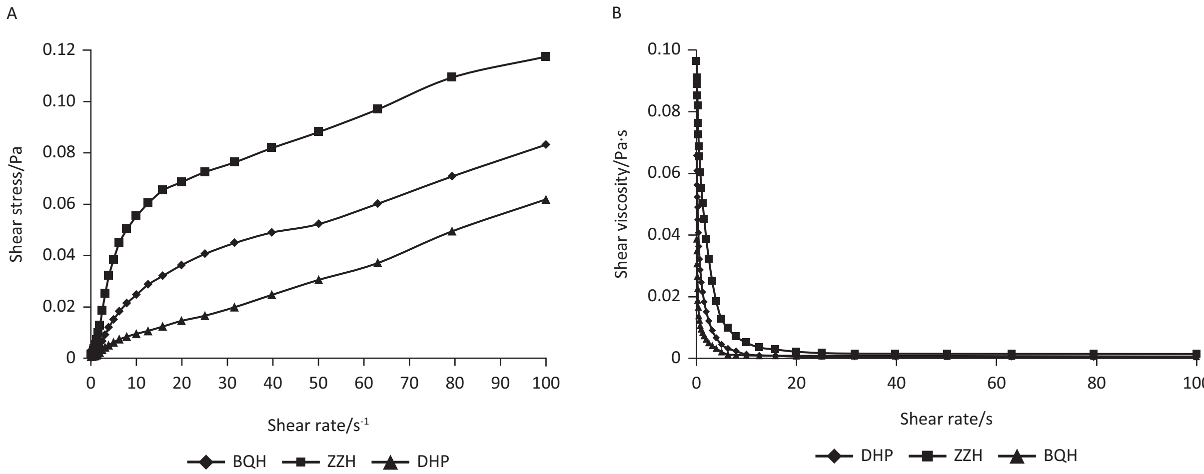

Figure 6. The shear stress (A) and shear viscosity (B) are functions of shear rate.

a sharp decrease, beginning at the attenuation value. The viscosity change during cooking indicates the stability of starch in the paste (Hanjun *et al.*, 2002). ZZH becomes hard and brittle after cooling during food processing, and its gel's water retention capacity gradually deteriorates, and poor sensory qualities develop. In contrast, DHP showed a higher attenuation value; its heat resistance during continuous cooking was low and it showed a high viscoelasticity after cooling. Therefore, the texture and taste of DHP will likely remain soft and elastic during continuous processing. It was reported that starch granules with high amylose content would display low peak viscosity due to controlled swelling of starch granules (Reddy *et al.*, 2017). However, it is well known that pasting properties of a starch are influenced by several factors such as amylose content, crystallinity, swelling power, and size and shape of starch granules. The pasting properties of adzuki bean starch agree with the findings of Gong *et al.* (2017), Wang *et al.* (2017) and Xu *et al.* (2018).

Rheological properties

Static rheological properties

Figure 6 shows a static rheology diagram of the three types of red adzuki bean starch. The shear stress of the three starches increased with an increasing shear rate, and the starches exhibited characteristics of a pseudoplastic fluid (Figure 6A). As the viscosity increased with shear rate, all three curves bended towards the shear stress axis to varying degrees (Figure 6B). These fluids were all non-Newtonian based on the rheological properties of the starches. As the shear rate increased, the shear viscosity of the starch paste decreased. When the shear rate was 10 s^{-1}, viscosity sharply decreased, with DHP showing the most obvious decline and a strong shear thinning phenomenon (Teng *et al.*, 2011). Because the amylopectin content of DHP starch is high, amylopectin molecules become entangled under low flow rates or at rest, exhibiting a sticky phenomenon. As the flow rate is increased, the scattered chains show a lower tendency to interact. Therefore, the resistance of mechanical shearing of DHP during continuous processing is lower, making this starch suitable for processing into repeatedly heatable foods, such as instant red beans or functional drinks.

Dynamic rheological properties

The dynamic modulus includes the storage modulus (G') and loss modulus (G"). A larger storage modulus indicates a stronger ability of a material to recover its shape. A larger loss modulus reflects the material's ability to resist flow. The dynamic rheological properties of the three types of red adzuki bean starch are shown in Figure 7; G' (Figure 7A) and G" (Figure 7B) both increased with increasing dynamic frequency, showing a typical weak gel dynamic rheology spectrum. Among them, DHP showed the lowest G' and G" values because of its high amylopectin content, and its macromolecular chains moved freely. The flow of starch paste is affected by external forces, which alter the conformation (Varavinit *et al.*, 2000). The ability of starch to restore its original shape and resist flow is weak after deformation, indicating good fluidity. Thus, DHP remains soft when processed into bean paste, fillings or other cakes.

4. Conclusion

In this study, starches from three red adzuki beans (DHP, BQH and ZZH) were isolated and characterised. These isolated starches showed different structural and physicochemical properties. We compared and analysed different varieties of red adzuki bean to determine the differences

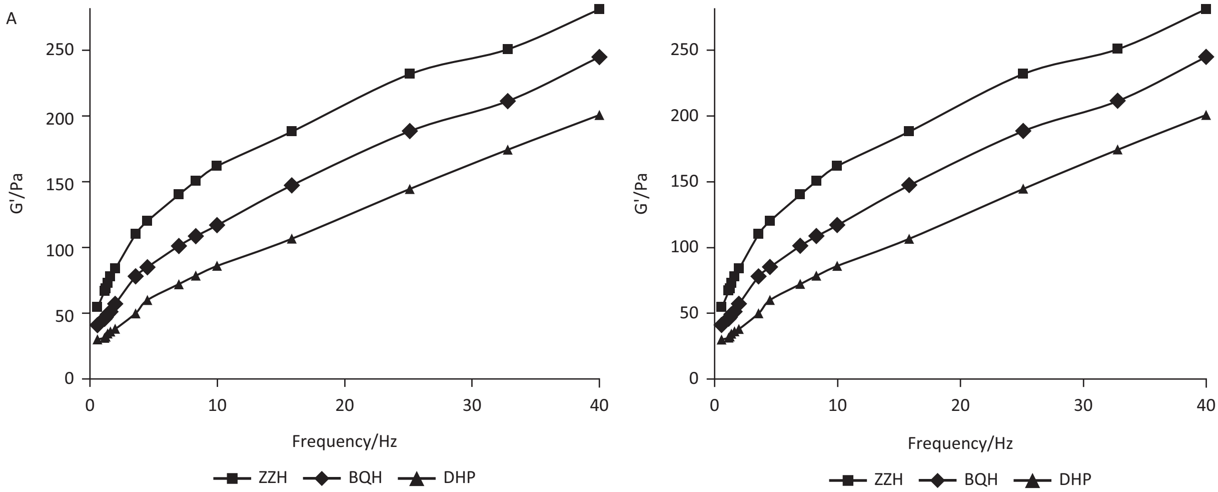

Figure 7. The storage modulus (A) and loss modulus (B) are functions of dynamic frequency.

in the starch microstructure, thermodynamics and rheology properties. The results show that compared with BQH and ZZH, DHP granules had lower amylose contents, smooth and round particle morphology, as well as obvious polarised crosses, higher gelatinisation starting temperatures, peak viscosity, enthalpy values, and breakdown viscosity, and lower trough viscosity, final viscosity, shear stress, storage modulus (G') and loss modulus (G") values. In addition, the content of amylopectin in DHP was high, resulting in a smaller particle size, higher crystallinity and lower Fourier spectral absorption peak intensity. DHP has suitable microstructure, thermodynamic and rheological properties for applications in the food industry. Finally, this study provides knowledge for the utilisation of starches isolated from adzuki bean seeds that would be relevant for both domestic and industrial applications.

Acknowledgements

This project is jointly supported by a grant from Heilongjiang Bayi Agricultural University (grant number: YJSCX2018-Y54) and a research grant from Key Laboratory of Agro-Products Processing and Quality Safety of Heilongjiang Province (grant number: 2031011027).

Conflict of interest

The authors declare that they have no conflicts of interest with respect to research, authorship and/or publication of this article.

Compliance with ethical standards

This article does not contain any studies with human participants or animals performed by any of the authors. Informed consent was obtained from all individual participants included in the study.

Funding

This research received no specific grant from any funding agency in the public, commercial or not-for-profit sectors.

References

Abegunde, O.K., Mu, T.H., Chen, J.W. and Deng, F.M., 2013. Physicochemical characterization of sweet potato starches popularly used in Chinese starch industry. Food Hydrocolloids 33(2): 169–177. https://doi.org/10.1016/j.foodhyd.2013.03.005

Atrous, H., Benbettaieb, N., Hosni, F., Danthine, S., Blecker, C., Attia, H. and Ghorbel D., 2015. Effect of γ-radiation on free radicals formation, structural changes and functional properties of wheat starch. International Journal of Biological Macromolecules 80: 64–76. https://doi.org/10.1016/j.ijbiomac.2015.06.014

Blazek, J. and Copeland, L., 2008. Pasting and swelling properties of wheat flour and starch in relation to amylose content. Carbohydrate Polymers 71(3): 380–387. https://doi.org/10.1016/j.carbpol.2007.06.010

Chen, B., Guo, Z., Zeng, S., Tian, Y., Miao, S. and Zheng, B., 2018. Paste structure and rheological properties of lotus seed starch–glycerin monostearate complexes formed by high-pressure homogenization. Food Research International 103: 380. https://doi.org/10.1016/j.foodres.2017.10.069

Chen, Y.J., Cai, W.X. and Xu, B.J., 2016. Phytochemical profiles of Edible Kudzu (*Pueraria thomsonii Benth*) grown in China as affected by thermal processing. Journal of Food Processing and Preservation 41(1): e12754. https://doi.org/10.1007/s13197-015-1809-0

Correia, P., Cruz-Lopes, L. and Beirao-Da-Costa, L., 2012. Morphology and structure of chestnut starch isolated by alkali and enzymatic methods. Food Hydrocolloids 28(2): 313–319. https://doi.org/10.1016/j.foodhyd.2011.12.013

Das, D., Jha, S. and Kumar, K.J., 2015. Isolation and release characteristics of starch from the rhizome of Indian palo.

International Journal of Biological Macromolecules 72: 341–346. https://doi.org/10.1016/j.ijbiomac.2014.08.009

Gałkowska, D. and Juszczak, L., 2019. Effects of amino acids on gelatinization, pasting and rheological properties of modified potato starches. Food Hydrocolloids 92: 143–154. https://doi.org/10.1016/j.foodhyd.2019.01.063

Gong, B., Xu, M., Li, B., Wu, H., Liu, Y. and Zhang, G., 2017. Repeated heat-moisture treatment exhibits superiorities in modification of structural, physicochemical and digestibility properties of red adzuki bean starch compared to continuous heat-moisture way. Food Research International 102: 776–784. https://doi.org/10.1016/j.foodres.2017.09.078

Tang, H., Watanabe, K. and Mitsunaga, T., 2002. Characterization of storage starches from quinoa, barley and adzuki seeds. Carbohydrate Polymers 49(1): 13–22. https://doi.org/10.1016/S0144-8617(01)00292-2

Horwitz, W., Albert, R., Deutsch, M.J. and Thompson, J.N., 1990. Precision parameters of methods of analysis required for nutrition labeling. part i. major nutrients. Journal Association of Official Analytical Chemists 73(5): 661–680.

Li, W., Tian, X., Liu, L., Wang, P., Wu, G., Zheng, J., Ouyang, S., Luo, Q. and Zhang, G., 2015. High pressure induced gelatinization of red adzuki bean starch and its effects on starch physicochemical and structural properties. Food Hydrocolloids 45: 132–139. https://doi.org/10.1016/j.foodhyd.2014.11.013

Luo, J., Cai, W., Wu, T. and Xu, B., 2016. Phytochemical distribution in hull and cotyledon of adzuki bean (*Vigna angularis* L.) and mung bean (*Vigna radiate* L.), and their contribution to antioxidant, anti-inflammatory and anti-diabetic activities. Food Chemistry 201: 350–360. https://doi.org/10.1016/j.foodchem.2016.01.101

Morrison, W. R and Laignelet, B., 1983. An improved colorimetric procedure for determining apparent and total amylose in cereal and other starches. Journal of Cereal Science 1(1): 9–20. https://doi.org/10.1016/S0733-5210(83)80004-6

Nara, S. and Komiya, T., 1983. Studies on the relationship between water-saturated state and crystallinity by the diffraction method for moistened potato starch. Starch-Stärke 35(12): 407–410. https://doi.org/10.1002/star.19830351202

Ozcan, S. and Jackson, D.S., 2002. The impact of thermal events on amylose-fatty acid complexes. Starch-Stärke 54(12): 593–602. https://doi.org/10.1002/1521-379x(200212)54:12<593::aid-star593>3.0.co;2-2

Reddy, C.K., Haripriya, S. and Vidya, P.V., 2015a. Morphology, physico-chemical and functional characteristics of starches from different banana cultivars. Journal of Food Science and Technology 52(11): 7289–7296. https://doi.org/10.1007/s13197-015-1809-0

Reddy, C.K., Pramila, S. and Haripriya, S., 2015b. Pasting, textural and thermal properties of resistant starch prepared from potato (*Solanum tuberosum*) starch using pullulanase enzyme. Journal of Food Science and Technology 52(3): 1594–1601. https://doi.org/10.1007/s13197-013-1151-3

Reddy, C.K., Kimi, L. and Haripriya, S., 2016. Variety difference in molecular structure, functional properties, phytochemical content and antioxidant capacity of pigmented rice. Journal of Food Measurement and Characterization 10(3): 605–613. https://doi.org/10.1007/s11694-016-9344-x

Reddy, C.K., Luan, F. and Xu, B., 2017. Morphology, crystallinity, pasting, thermal and quality characteristics of starches from adzuki bean (*Vigna angularis* L.) and edible kudzu (*Pueraria thomsonii* Benth). International Journal of Biological Macromolecules 105: 354–362. https://doi.org/10.1016/j.ijbiomac.2017.07.052

Singh, N., Singh, J., Kaur, L., Sodhi, N.S. and Gill, B.S., 2003. Morphological, thermal and rheological properties of starches from different botanical sources. Food Chemistry 81(2): 219–231. https://doi.org/10.1016/S0308-8146(02)00416-8

Sukhija,S., Singh, S. and Riar, C.S., 2016. Physicochemical, crystalline, morphological, pasting and thermal properties of modified lotus rhizome (*Nelumbo nucifera*) starch. Food Hydrocolloids 60: 50–58. https://doi.org/10.1016/j.foodhyd.2016.03.013

Shunjing, L., Yan, L.I., Rong, Y., Xiuting, H.U., Yunfei, L. and Chengmei, L., 2017. Effects of amino acids on pasting and rheological properties of rice starch. Food Science 15: 190–194. https://doi.org/10.7506/spkx1002-6630-201715029

Tang, H., Watanabe, K. and Mitsunaga, T., 2002. Characterization of storage starches from quinoa, barley and adzuki seed. Carbohydrate Polymers. https://doi.org/10.1016/S0144-8617(01)00292-2

Teng, L.Y., Chin, N.Y. and Yusof, Y.A., 2011. Rheological and textural studies of fresh and freeze-thawed native sago starch-sugar gels. I. Optimisation using response surface methodology. Food Hydrocolloids 25(6): 1530–1537. https://doi.org/10.1016/j.foodhyd.2011.02.005

Teng, L.Y., Chin, N.L. and Yusof, Y.A., 2013. Rheological and textural studies of fresh and freeze-thawed native sago starch–sugar gels. II. Comparisons with other starch sources and reheating effects. Food Hydrocolloids 31(2): 156–165. https://doi.org/10.1016/j.foodhyd.2012.11.002

Varavinit, S., Anuntavuttikul, S. and Shobsngob, S., 2000. Influence of freezing and thawing techniques on stability of sago and tapioca starch pastes. Starch-Starke 52(6–7): 214–217. https://doi.org/10.1002/1521-379X(200007)52:6/73.0.CO;2-3

Wang, H., Wang, Z., Li, X., Chen, L. and Zhang, B., 2017. Multi-scale structure, pasting and digestibility of heat moisture treated red adzuki bean starch. International Journal of Biological Macromolecules 102: 162–169. https://doi.org/10.1016/j.ijbiomac.2017.03.144

Wang, J.Y., Yang, S.Y., Huang, Y.L., Tien, H.W., Chin, W.K. and Ma, C.C.M., 2011. Preparation and properties of graphene oxide/polyimide composite films with low dielectric constant and ultrahigh strength via in situ polymerization. Journal of Materials Chemistry 21(35): 13569. https://doi.org/10.1039/C1JM11766A

Wang, L., Xie, B., Shi, J., Xue, S., Deng, Q., Wei, Y. and Tian B., 2010. Physicochemical properties and structure of starches from Chinese rice cultivars. Food Hydrocolloids 24(2–3): 208–216. https://doi.org/10.1016/j.foodhyd.2009.09.007

Wang, S. and Copeland, L., 2015. Effect of acid hydrolysis on starch structure and functionality: a review. Critical Reviews in Food Science and Nutrition 55(8): 1081–1097. https://doi.org/10.1080/10408398.2012.684551

Wang, S., Liu, C., Wang, S., 2016. Drying methods used in starch isolation change properties of C-type chestnut (*Castanea mollissima*) starches. LWT—Food Science and Technology 73: 663–669. https://doi.org/10.1016/j.lwt.2016.07.012

Xu, M., Saleh, A.S.M., Liu, Y., Jing, L., Zhao, K., Wu, H., Zhang G., Yang, S.O. and Li, W., 2018. The Changes in Structural, Physicochemical, and Digestive Properties of Red Adzuki Bean Starch after Repeated and Continuous Annealing Treatments. Starch – Stärke 70(9–10). https://doi.org/10.1002/star.201700322

Yuliana, M., Huynh, L.H., Ho, Q.P., Truong, C.T. and Ju, Y.H., 2012. Defatted cashew nut shell starch as renewable polymeric material: isolation and characterization. Carbohydrate Polymers 87(4): 2576–2581. https://doi.org/10.1016/j.carbpol.2011.11.044

Zhang, D., Mu, T. and Sun, H., 2018. Effects of starch from five different botanical sources on the rheological and structural properties of starch–gluten model doughs. Food Research International 103: 156–162. https://doi.org/10.1016/j.foodres.2017.10.023

Zhang, L., Sun, B., Xie, P., Li, H., Su, H., Sha, K., Huang, C., Lei, Y., Liu, X. and Wang, H., 2015. Using near infrared spectroscopy to predict the physical traits of Bos grunniens meat. LWT—Food Science and Technology 64(2): 602–608. https://doi.org/10.1016/j.lwt.2015.06.022