Food Chemistry 271 (2019) 102–108

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Hierarchical structure and physicochemical properties of highland barley starch following heat moisture treatment

Kun Liu[a,1], Binjia Zhang[a,b,1], Ling Chen[a,*], Xiaoxi Li[a], Bo Zheng[a,*]

[a] Ministry of Education Engineering Research Center of Starch & Protein Processing, Guangdong Province Key Laboratory for Green Processing of Natural Products and Product Safety, School of Food Science and Engineering, South China University of Technology, Guangzhou 510640, China
[b] Key Laboratory of Environment Correlative Dietology (Ministry of Education), College of Food Science and Technology, Huazhong Agricultural University, Wuhan 430070, China

ARTICLE INFO

Keywords:
Highland barley starch
Heat moisture treatment
Hierarchical structure
Digestibility
Pasting properties

ABSTRACT

Herein, we concern the multi-scale structure and properties (digestibility and pasting) of highland barley starch following heat moisture treatment (HMT). With the moisture content (MC) rose, HMT reduced the molecular weight (molar mass) but increased the amylose content and the V-type polymorph. When the MC was lower than 25%, a higher MC resulted in increases in the long- (crystallites) and short-range orders (double helices, *etc.*); nonetheless, a further elevated MC (*i.e.*, 30%) tended to reduce the amounts of these ordered structures. Also, the SAXS results reveal that the lamellar structure could be gradually vanished by the increased MC. These structural changes on multiple scales transformed part of rapidly digestible starch into the slowly digestible and/or resistant forms, accompanied by higher pasting temperature and lower paste viscosity. Hence, highland barley starch following HMT can serve as a food ingredient with reduced digestion rate and paste viscosity.

1. Introduction

Highland barley, a unique plateau crop, has gained enormous attention in the development of foods (e.g., breakfast cereals, and noodles) with better nutritional values (Cheng et al., 2016; Gong, Jin, Wu, Wu, & Zhang, 2012; Shen et al., 2016). Particularly, highland barley often contains more protein, dietary fiber, vitamin and unsaturated fat acids than common cereals; the cereal lysine, phytosterols and β-glucans endow highland barley with excellent health benefits. Starch, the main component of highland barley, is crucial in governing the application-related performance of highland barley products (Asare et al., 2011). For instance, the pasting properties of starch are closely related to food thickening/gelling behaviors; the digestibility of starch ingredient often links to the nutritional features of foods (*e.g.*, glycemic index).

In fact, there are two major starch biopolymers, including amylose and amylopectin. The chains of these two polymers assemble on different scales in the starch granule to form a hierarchical structural system, mainly involving the granule, the growth rings, the blocklets, the lamellae and the crystallites (Copeland, Blazek, Salman, & Tang, 2009; Pu, Chen, Li, & Li, 2013). The multi-scale structural characteristics (*e.g.*, amount of molecular orders, and degree of lamellar ordering) have been shown capable of determining the physicochemical properties of starch, such as digestibility, thermal features and pasting properties (Blazek & Gilbert, 2010; Liu, Xie, Yu, Chen, & Li, 2009; Lopezrubio, Flanagan, Shrestha, Gidley, & Gilbert, 2008; Tan et al., 2015; Tao et al., 2018; Xie, Halley, & Averous, 2012). Again, the tightly assembled molecular chains within starch hierarchical structure could suppress the enzyme diffusion and hydrolysis, and thus make the digestion rate for unmodified starch several times lower than that for cooked starch (Bertoft & Manelius, 1992; Noda et al., 2008). Hence, using specific treatments to modulate the multi-scale structure of starch is an effective way for production of starch products with tailored physicochemical properties.

Heat moisture treatment (HMT) is widely used for starch modifications due to its advantages regarding high product safety and low waste generation (Zavareze & Dias, 2011). HMT is a typical physical process, in which the starch is treated at a low moisture level (< 35%) for 15 min to 16 h); the temperature ranges from 84 to 120 °C (Hoover, 2010; Pratiwi, Faridah, & Lioe, 2018; Zavareze & Dias, 2011). It is shown that HMT alters the structural features, *e.g.*, molecular weight, helices, crystallinity and granule, and thus affect the digestion and pasting properties for different starches such as rice, breadfruit, red adzuki bean and potato starch (Tan et al., 2017; Wang, Wang, Li, Chen,

* Corresponding authors.
E-mail addresses: felchen@scut.edu.cn (L. Chen), 201710104198@mail.scut.edu.cn (B. Zheng).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.foodchem.2018.07.193
Received 19 April 2018; Received in revised form 26 June 2018; Accepted 25 July 2018
Available online 26 July 2018
0308-8146/

& Zhang, 2017; Wang, Zhang, Chen, & Li, 2016). Moreover, HMT promotes the interactions of starch chains by disrupting the crystalline and helical structures, followed by reassociation of the disrupted crystals and the mobility of amorphous regions that favors ordering of double helices (Pratiwi et al., 2018; Zavareze & Dias, 2011; Zheng et al., 2018). Interestingly, HMT can transform rapidly digestible and resistant starch fractions into the slowly digestible forms (Tan et al., 2017; Zeng, Ma, Kong, Gao, & Yu, 2015). Yet, to date, how HMT affects the physicochemical features (digestion, pasting behaviors, *etc*.) of highland barley starch has not been wholly revealed especially from a view point of hierarchical structure. The lack of this understanding hinders the rational development of highland barley starch following HMT with desirable pasting and digestion properties.

In this study, highland barley was used to isolate starch material, which was subject to HMT at varied moisture levels (15–30%). Then, we used combined techniques to investigate the multi-level structures (*i.e*., molecular weight, helices, crystallites, lamellae and granule) of highland barley starch as well as its pasting behaviors and digestibility. Thereafter, the structure-property relationship of HMT treated highland barley starch was discussed.

2. Materials and methods

2.1. Materials

Highland barley starch was extracted from highland barley (harvested from Xining district of Qinghai province, China) according to a previously described method (Wang et al., 2017). Porcine pancreatic α-amylase (Cat. No. P7545, activity 8 × USP, USA), and amyloglucosidase (Cat. No. A3306, activity 318 U/mL, USA) were obtained from Sigma-Aldrich Co., Ltd. The glucose oxidase-peroxidase assay kit (GOPOD, K-GLUC) was purchased from Megazyme (Wicklow, Ireland). Amylose (A0512) and amylopectin (A8515) were purchased from Sigma-Aldrich (Saint Louis, USA). Chromatographically pure dimethyl sulfoxide (DMSO) was purchased from Sigma-Aldrich Co., Ltd. All other chemicals used in this study were of analytical grade. Distilled water was used throughout as well.

2.2. Heat-moisture treatment (HMT)

The total moisture content of highland barley starch was adjusted to a desired value (15%, 20%, 25% or 30%) by adding a necessary amount of distilled water in a self-sealed bag, and then each starch sample was equilibrated at 4 °C for 24 h before HMT. Then, 100 g (dry basis) of each starch sample with adjusted moisture content was placed in a 500 mL screw-capped steel cylinder which was then heated with rotation in the oil at 110 °C for 2 h, followed by cooling to room temperature. Afterward, the starches were removed from the containers and dried at 45 °C for 12 h. The samples were smashed and sieved using a 100-mesh sieve. In the following, codes as “HMT-15” will be used, in which “HMT” represents heat moisture treatment and “15” indicates the moisture content for HMT.

2.3. Scanning electron microscope (SEM)

A scanning electron microscope (Zeiss EVO18, Jena, Germany), under an accelerating voltage of 10.0 kV, was applied to examine the granular morphology of starch at 1000× magnification. Before measurements, native and HMT treated starch samples were spread onto circular metal stubs covered with double-sided adhesive carbon tapes and then sputtered with a layer of gold in a sputter coater.

2.4. Gel permeation chromatography coupled with multi-angle light scattering (GPC-MALS)

A GPC system (Waters, USA) equipped with a MALS detector (Wyatt Technology Co., Santa Barbara, USA) and a refractive index detector was used to measure the weight-average molecular weight (M_w, indicated by molar mass) and the molar mass distribution of starch samples. Two GPC columns (Styragel HMW 7 DMF 7.8 mm × 300 mm, Styragel HMW 6E DMF 8 mm × 300 mm) (whose temperature was controlled at 50 °C) and a wavelength of 658 nm were applied in the experiment. DMSO with LiBr (50 mmol/L), as the mobile phase, was firstly filtered through a 0.22 μm PTFE filter and then degassed with ultrasound treatment. 5 mg (dry basis) of each starch sample was suspended in 10 mL of the mobile phase, heated in boiling water for 1 h, and then shaken at 60 °C for 12 h to fully dissolve starch in the mobile phase. All solutions used in this experiment were filtered through a 5 μm PTFE filter film (Millipore Co., Billerica, USA). The flow rate and total injected volume were 1.0 mL/min and 0.1 mL, respectively. Astra V software was used to calculate M_w with Zimm model (Pu et al., 2013).

2.5. Amylose content (AC)

Amylose contents for the starches were determined using a previous method with minor modification (Herrero-Martínez, Schoenmakers, & Kok, 2004; Lim et al., 2015; McGrance, Cornell, & Rix, 1998). Firstly, starch (100 mg, dry basis) was dispersed in 1 mol/L NaOH, and diluted to 1 mg/mL solution with distilled water. Then, I_2/KI solutions (0.0025 mol/L I_2 and 0.0065 mol/L KI) were used to complex with starch helices. The Vis absorbance of the complex was measured through a spectrophotometer (Evolution 201 UV–Visible Spectrophotometer, Thermo Scientific Inc., Waltham, USA) at 620 nm. Finally, amylose content values of starch were calculated using a standard curve based on mixture solutions of amylose and amylopectin.

2.6. Attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR analyses of the starch samples were carried out on a Nicolet iS50 infrared spectrometer (Thermo Fisher, Waltham, USA) equipped with an ATR single-reflectance cell following the method of Mutungi (Mutungi et al., 2011). The spectra, recorded against an empty cell as the background, were acquired between 800 and 1200 cm^{-1} with 4 cm^{-1} resolution. All spectra, the averages of 64 scans, were baseline corrected and normalized. With deconvoluted spectra, the ratio of peak intensity at *ca*. 1047 cm^{-1} to that at 1022 cm^{-1} was calculated for each sample. The moisture content of all the samples was kept at about 10% before the analysis.

2.7. CP/MAS ^{13}C nuclear magnetic resonance (NMR) spectroscopy

A Bruker Advance III HD 400 spectrometer (Bruker, Germany) was used to perform the solid-state CP/MAS ^{13}C NMR measurements at a ^{13}C frequency of 100.6 MHz (Tan, Flanagan, Halley, Whittaker, & Gidley, 2007). Before the measurements, starch samples (*ca*. 200–300 mg, dry basis) were packed in cylindrical and PSZ (partially stabilized zirconium oxide) rotors with 4 mm diameter. ^{13}C spectra were recorded with at least 3000 scans and a recycle delay of 2 s. Also, amorphous starch standards were prepared by heating the suspensions at 1% starch concentration at 95 °C for 30 min, and then the gelatinized starches were lyophilized. The dried gelatinized starch sample was crushed to obtain amorphous starch powders. Such amorphous starches were measured under the same testing conditions to acquire amorphous starch NMR spectra. The ordered and amorphous phases of starch samples were calculated from the total spectra that were deconvoluted by subtracting a scaled amorphous starch spectrum until zero intensity was attained at 84 ppm according to previous method (Tan et al., 2007).