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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

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ABSTRACT

The effects of repeated heat-moisture treatment (RHMT) and continuous heat-moisture treatment (CHMT) on structural, physicochemical and digestibility properties of red adzuki bean starch have been investigated and compared. The results showed that the starch granules had many rupture and scallops and some of the polarization cross disappeared after CHMT and RHMT. The crystal type of CHMT and RHMT starches changed from C-type to A-type. The pasting temperatures and gelatinization transition temperatures of CHMT and RHMT starches increased, while the pasting viscosities (peak, trough, breakdown, final and setback viscosity), solubility and swelling power of CHMT and RHMT starches decreased compare to native starch. The RDS and SDS contents of starch samples were higher than native starch, which indicate that the digestibility was improved by CHMT and RHMT. On the whole, the RHMT measures have more advantages in the changes of starch structural, physicochemical and digestibility properties compared to CHMT ones.

1. Introduction

Red adzuki bean or small red bean (*Vigna angularis*) is widely consumed in many countries, it mainly cultivated in northeastern part of China, north Korea, Japan, Philippines and other southeast Asian countries. It is a good health promoting food and a good nutritional source, and they are rich in iron, calcium, phosphorus and other mineral elements (Durak, Baraniak, Jakubczyk, & Świeca, 2013). Red adzuki bean can be used as functional ingredients of various foods, such as dessert, drinks, pastry, and bean paste to improve the flavor, taste and viscosity of foods (Wang, Wang, Li, Chen, & Zhang, 2017). The red adzuki bean starch can prevent chronic diseases because of its relatively high granule stability, low insulin response and the high shear resistance of its paste (Rebello, Greenway, & Finley, 2014). However, as a kind of coarse legumes starch, the development and research of this starch dose not attract enough attention. It is necessary to expand the range of application and increase economic efficiency through modifying the properties of red adzuki bean starch. Starch properties could be modified by physical, chemical, biological and enzymatic means. And physical modification is deemed to be safe and no by-products of chemical reagents.

Heat-moisture treatment (HMT) is one of the physical modification, which heats starch granules at a low moisture level (< 35% w/w) and a

high temperature of 84–120 °C for a certain period of time from 15 min to 16 h (Hoover, 2010; Jacobs, Eerlingen, Spaepen, Grobet, & Delcour, 1998). Plentiful researches have indicated that HMT can influence the structure and physicochemical properties of tuber, cereal, and legume starches. The changes of HMT induced to the starch depended on the treatment conditions and starch source (Watcharatwinkul, Puttanlek, Rungsardthong, & Uttapap, 2009; Zavareze & Dias, 2011). Generally, HMT starches tended to have a higher thermal stability and gelatinization temperature, while the crystallinity, amylose leaching, viscosity, swelling power and solubility decreased after HMT (Gunaratne & Hoover, 2002; Hoover, 2010; Jacobs et al., 1998; Jayakody, Hoover, Liu, & Donner, 2007; Jiranuntakul, Puttanlek, Rungsardthong, Pancha-Arnon, & Uttapap, 2011; Zavareze & Dias, 2011). The crystalline structure could be transformed during HMT, which caused a transition from C_a-type to A-type for sweet potato starch (Huang, Zhou, Jin, Xu, & Chen, 2016), and a change from B- to A-type for potato starch and yam starch (Gunaratne & Hoover, 2002; Vermeylen, Goderis, & Delcour, 2006). However, the X-ray pattern of taro, cassava, normal corn starch, new cocoyam and rice starch could hardly be affected by HMT (Chung, Hoover & Liu, 2009; Gunaratne & Hoover, 2002; Jiranuntakul et al., 2011).

The HMT have been also reported to affect the starch digestibility with decreasing susceptibility to α -amylase for different starches. The

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slowly digestible starch (SDS) and resistant starch (RS) contents of corn, lentil and pea starches could be increased by HMT, and HMT could significantly increase the SDS content of sweet potato and waxy potato starch (Chung, Liu, & Hoover, 2009; Lee, Kim, Choi, & Moon, 2012; Shin, Kim, Ha, Lee, & Moon, 2005). Food rich in SDS is capable of prolonging the release of glucose and sustaining glucose levels, which may help control and prevent hyperglycemia-related diseases (Huang et al., 2016). Therefore, HMT has been widely used in the preparation of SDS products from various sources of starches at present.

Up to now, plentiful studies have stated the effects of continuous heat-moisture treatment (CHMT) on different sources of starches such as rice (Zavareze, Storck, Castro, Schirmer, & Dias, 2010), potato (Vermeulen et al., 2006), maize (Pukkahuta, Suwannawat, Shobsngob, & Varavinit, 2008), cassava (Gunaratne & Hoover, 2002), canna (Watcharatewinkul et al., 2009) and pinhão (Klein et al., 2013) at different treatment conditions (moisture, temperature and time). However, few researchers studied the effects of repeated heat-moisture treatment (RHMT) on digestibility, structural and physicochemical properties of starch. Thus, this study aimed to investigate the effects of RHMT and CHMT on the properties of red adzuki bean starch for the purpose of investigating the superiority of RHMT. We expect to expand the application of RHMT in food processing and provide theoretical basis for illustrating the mechanism of heat-moisture treatment on starch modification through the research.

2. Materials and methods

2.1. Materials

The red adzuki bean starch was provided by Henan Yichang Biotechnological Co., Ltd. (Henan, China), and the chemical component of starch on a dry basis were: 96.28% of starch (starch purity), 28.86% of amylose, 0.61% of protein, 0.27% of fat and 0.36% of ash, respectively. Pancreatin from porcine pancreas (USP grade) and amyloglucosidase from *Aspergillus niger* (100,000 u/ml) were bought at Aladdin Bio-chem Technology Co., LTD (Shanghai, China). α -Amylase (BR) was bought at Solarbio Science & Technology Co., LTD (Beijing, China). Other chemical reagents were of analytical grade (Sanli Chemical Reagent Co, Yangling, China).

2.2. Heat-moisture treatment of starch

100 g (dry basis) of red adzuki bean starch was exactly weighed and put into the Silk mouth bottles. Adding an appropriate amount of distilled water slowly with stirring to adjust the moisture content to be 30%, and then put the bottles at room temperature for 24 h in order to equilibrium moisture. For continuous heat-moisture treatment (CHMT), the bottles were put in a drying oven at 120 °C for 4, 6, 8, 10 and 12 h, respectively, and then dried in drying oven at 45 °C for 12 h. The resultant starches were milled and passed through a 100-mesh sieve, and the obtained samples were named as CHMT-4, CHMT-6, CHMT-8, CHMT-10 and CHMT-12, respectively.

For repeated heat-moisture treatment (RHMT), the bottles were put in a drying oven at 120 °C for 2 h, and cooled at room temperature for 60 min, then dried in drying oven at 45 °C for 12 h, milled and passed through a 100-mesh sieve and we can get one cycle of heat-moisture treatment (RHMT-1) starch sample. Two cycles of HMT starch sample (RHMT-2) was prepared by putting back into the first heat-moisture treated starch for another 2 h after it was cooled at room temperature for 60 min. According to the steps above, the starch samples were cycled six times of HMT. The cycling times of HMT of the starch samples ranging from 1 to 6 were designated as RHMT-1, RHMT-2, RHMT-3, RHMT-4, RHMT-5, and RHMT-6, respectively.

2.3. Microscopy observe

2.3.1. Light microscopy

Samples were weighted and prepared by dispersing into 50% glycerol-water solution, then transferring a drop to a glass slide. Samples were viewed through a coverslip for images viewed at 40 \times objective. Images were captured in a bright field light with SPOT Insight camera (Motic DMBA 400, Motic China Group Co., LTD.).

2.3.2. Scanning electron microscopy (SEM)

The surfaces of treated samples were observed by a SEM stub with a double-sided adhesive tape, coated with a thin gold, then placed in the SEM chamber. Scanning electron micrographs were captured using a SEM (JSM-6360LV, JEOL, Japan).

2.3.3. Confocal laser scanning microscopy (CLSM)

According to the method of Li et al. (2014), 4 μ l of freshly made APTS solution and 4 μ l of 1 M sodium cyanoborohydride were added to 2 mg of starch samples at 30 °C for 15 h, following were thoroughly washed 5 times with the appropriate amount of distilled water (1 ml) and suspended in 20 μ l of glycerol-water mixture (1:1, v/v). After staining with APTS the starch suspension was visualized using CLSM (Nikon Co., Ltd., Tokyo Japan) equipped with 100 \times plan apo/1.4011 oil UV.

2.4. X-ray diffraction (XRD)

Relative crystallinity degree and polymorphic composition were carried out using an X-ray diffractometer (Rigaku D/max-2551/PC, Rigaku Corporation, Tokyo, Japan). Operating procedures are as follows: all samples were scanned from 4 to 60° with the radiation source of Cu K α ; step size and step time were set 0.02 and 0.2 s, respectively.

2.5. Fourier transform-infrared spectroscopy (FT-IR)

The FT-IR spectra of native and treated samples were analyzed using a Vetex 70 (Bruker, Germany). The mixture of starch/KBr (1/100 mg/mg) were grounded finely, then were pressed into filmy tablets. The tablets were measured by transmission means. All samples were scanned from 4000 to 400 cm^{-1} at the speed of 4 cm^{-1} . The table of KBr was regarded as the background scanning.

2.6. Solubility and swelling power

Solubility (S) and swelling power (SP) were measured on the basis of the method described by Leach, McCowen, and Schoch (1959) with a slight of modification, which determined at 50, 60, 70, 80 and 90 °C, respectively. The indices were determined as follows: SP = weight of sediment \times 100 / weight of dry sample solids \times (100 – solubility); S = weight of dissolved solids in supernatant/weight of dry sample solids in the original sample \times 100.

2.7. Pasting properties

The pasting properties of starch samples were measured by the Rapid Visco Analyser (RVA-4500, Perten Instruments, Sweden). The starch samples were weighted 2.5 g (dry basis) and added to 25 ml distilled water. The paddle speed was 960 rpm for the first 10 s, and 160 rpm for the remainder of the experiment. The procedure was that the samples equilibrated at 50 °C for 1 min firstly, and then were heated from 50 °C to 95 °C at a rate of 12 °C/min, and held at 95 °C for 2.5 min, then cooled to 50 °C at 12 °C/min, and held at 50 °C for 2 min.

2.8. Differential scanning calorimetry

The thermal properties of starch samples were measured by

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