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Structure and digestibility of debranched and repeatedly crystallized waxy rice starch

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ABSTRACT

Debranched waxy rice starch was subjected to repeated crystallization (RC) treatment, and its physicochemical properties and digestion pattern were investigated. The A-type crystalline pattern of native starch was crystallized to a complex of B- and V-type patterns by debranching and RC treatment. Among the treated starches, the relative crystallinity of debranched starch reached its maximum (29.6%) after eight repetitions of crystallization. Changes in weight-average molar mass among treated starch samples were not significantly different. The repeated-crystallized starches showed higher thermal transition temperatures and melting enthalpy than that of debranched starch. As a result, slowly digestible starch (SDS) content of repeated-crystallized starches reached a very high level (57.8%). Results showed that RC treatment induced structural changes of waxy rice starch result in a great amount of SDS.

1. Introduction

Starch is the principal carbohydrate in cereal grains and an important source of nourishment for humans. From a nutritional point of view, starch is generally classified as rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) based on the rate and extent of its digestibility (Englyst, Kingman, & Cummings, 1992). RDS causes an increase in blood glucose level immediately after ingestion, leading to a series of health complications such as diabetes and cardiovascular diseases in long term (Brennan, 2005). RS is not digested in the small intestine but fermented in the large bowel into short-chain fatty acids that provide additional energy to the body along with a high proportion of butyrate that is beneficial to colonic health (Cummings, Beatty, Kingman, Bingham, & Englyst, 1996; Zhang & Hamaker, 2009). SDS is digested slowly throughout the small intestine to provide a slow and prolonged release of glucose, and it may help control and prevent hyperglycaemia-related diseases. Consequently, food and starch ingredients with high levels of SDS and RS can be advantageous to satiety, glucose tolerance improvement, physical performance, as well as blood lipid level reduction in both healthy individuals and those with hyperlipidemia (Ells, Seal, Kettlitz, Bal, & Mathers, 2005; Jenkins et al., 2002). Recently, SDS received much attention as a new functional food component or ingredient in novel food product development (Miao, Jiang, & Zhang, 2009).

Recently, substantial efforts have been made to modify the starch to reduce its digestibility, including temperature-cycled crystallization (Park, Baik, & Lim, 2009; Tian et al., 2012; Xie, Hu, Jin, Xu, & Chen, 2014a; Zeng et al., 2014; Zhang, Hu, Xu, Jin, & Tian, 2011), enzymatic modification (Casarrubias-Castillo, Hamaker, Rodriguez-Ambriz, & Bello-Pérez, 2012; Miao et al., 2009; Shin, Choi, Park, & Moon, 2010; Shin et al., 2004), hydrothermal treatment (Chung, Liu, & Hoover, 2010; Lee, Kim, Choi, & Moon, 2012; Lee, Shin, Kim, Choi, & Moon, 2011; Zeng, Ma, Kong, Gao, & Yu, 2015), retrogradation treatment (Chung, Lim, & Lim, 2006; Hu, Xie, Jin, Xu, & Chen, 2014; Tian et al., 2013; Xie, Hu, Jin, Xu, & Chen, 2014b), chemical modification (Güzel & Sayar, 2010; Han & BeMiller, 2007), acid modification (Shin et al., 2007, 2009) and functional starch resources. Among these techniques, pullulanase debranching and crystallization treatment are cost-effective, safe and more suitable for commercial use.

Enzymatic methods by debranching treatments have been applied to prepare slowly digestible starch (Miao et al., 2009; Shin et al., 2004). Previous studies have been focused on the effect of debranching and crystallization on the physicochemical

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properties and digestibility of various starches (Cai & Shi, 2010, 2013; Cai, Shi, Rong, & Hsiao, 2010; Miao et al., 2009; Zeng et al., 2014). The above studies have shown that debranching and different crystallization conditions resulted in structural changes within the starch molecule, which in turn is influenced by gelatinization parameters, molecular structure, crystalline structure and susceptibility towards enzyme. Another effective method for the preparation of SDS is retrogradation of gelatinized starch. Tian et al. (2013) reported a dual-retrogradation treatment of rice starch (29.3% amylose) and showed that a maximum SDS yield of 56.7% was observed with the time interval of 36 h. Moreover, Hu et al. (2014) investigated the effects of single-, dual- and triple-retrogradation treatments on digestibility and structural characteristics of waxy wheat starch. As a result, the yield of SDS in a dual-retrogradation-treated starch with retrogradation time interval of 48 h reached a maximum of 44.41%. In addition, Xie et al. (2014b) investigated the repeated retrogradation treatment of waxy potato starch and suggested that a maximum SDS content (40.41%) was obtained by dual cycling with the time interval of 48 h. These studies suggest that structural changes of starches by cycled retrogradation treatment significantly affect the digestibility, which can be used for preparing SDS product.

Rice starch is used as an additive in various foods, industrial products, desserts, bakery products and as a fat mimetic in foods such as ice cream, yoghurt and salad dressings. Because of its wide-ranging food and industrial applications, waxy rice starch has been extensively studied. Debranching and heating–cooling cycles mainly concentrated on the temperature cycles of the crystallization process, which provide the environment for the nucleation and propagation of crystallites (Park et al., 2009; Tian et al., 2012; Xie et al., 2014a; Zeng et al., 2014; Zhang et al., 2011). This research is focused on the repeated gelatinization and crystallization of short linear chain aggregates. The gelatinization process results in the breakage of hydrogen bond of double helix, while the crystallization process leads to the reassociation of short linear chains through hydrogen bonding and to the formation of new crystallites. In our knowledge, no further report was found studying the combination of debranching and repeated gelatinization-crystallization treatment on the physicochemical properties and digestibility of waxy rice starch. Thus, the objective of this study was to investigate to what extent changes to molecular weight, crystalline structure, gelatinization properties and nutritional fractions of waxy rice starch during debranching and repeated gelatinization-crystallization are influenced by molecular structure.

2. Materials and methods

2.1. Materials

Waxy rice starch (0% amylose) was obtained from Jiangsu Baobao Group (Nantong, China). Porcine pancreas α-amylase (EC3.2.1.1, 16 U/mg) type-B and amyloglucosidase (EC 3.2.1.3, 300 U/mL) from *Aspergillus niger* were purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). Megazyme glucose assay kit (GOPOD method) was bought from Megazyme International Ireland Ltd. (Wicklow, Ireland). Other chemicals and solvents were all of analytical grade.

2.2. Preparation of debranched starch (DS)

Waxy rice starch (15 g, dry basis) slurry (10% w/v in diluted pH 5.2 buffer solution containing 0.2 M sodium acetate and 0.2 M acetic acid) was boiled with continuous stirred for 30 min. The temperature of cooked starch was adjusted to 58 °C and debranched by pullulanase at 60 ASPU/g of starch for 12 h. The debranched starch gels were proved to be linear (Cai & Shi, 2010). Immediately after the reaction, the starch gel was exposed to a deactivated enzyme reaction at 100 °C for 30 min and cooled to room temperature. The starch gel was stored at 4 °C for 4 days. After that, the precipitated specimen was centrifuged, washed 3 times with distilled water and air-dried then milled to pass through a 100-mesh sieve for the further experiment. The pullulanase debranched starch (DS) was designated as 1 time of gelatinization–crystallization.

2.3. Repeated crystallization (RC) treatment

The initial moisture content of the DS was approximately 12%. The moisture content of the DS was adjusted to 80% by adding appropriate amounts of distilled water and transferred into the glass containers. Specimens were sealed and boiled with continuous magnetic stirred for 30 min. The glass containers were allowed to stand 48 h at 4 °C for recrystallization. The boil and recrystallization treatment was repeated a series of 2, 4, 6 and up to 8 times. Afterwards the containers were opened, and the starch samples were air-dried then milled to pass through a 100-mesh sieve.

2.4. X-ray diffraction and relative crystallinity

X-ray diffraction analysis was performed with an X-ray diffractometer (D8 ADVANCE, Bruker, Germany) operated at 40 kV and 40 mA producing Cu Kα radiation of 1.5418 Å wavelength, scanning through the 2θ range from 3° to 35° at a rate of 2°/min. The moisture of a specimen was regulated to about 15% by storage in a sealed desiccator over water at 25 °C. Relative crystallinity was calculated according to the method of Nara and Komiya (1983) using MDI Jade 5.0 software (Material Date, Inc. Livermore, California, USA).

2.5. High-performance size-exclusion chromatography (HPSEC) and multi-angle laser-light scattering (MALLS) with refractive index (RI) detector

Starch sample (12.5 mg) was stirred in 25 mL of dimethyl sulfoxide (DMSO) contain 50 mM LiBr and heated in a boiling water bath for 30 min. After that, the liquid system was stirred for 24 h at room temperature. The solutions were then filtered through a nylon filter (0.22 μm type membrane, Millipore, USA) before injection into the MALLS system (Wyatt Technology, Santa Babara, CA, USA) consisting of a pump (P2000, Spectra System, San Hose, CA), an injector valve with a 1 mL loop, SEC column (P8514-806, Showa Denko, Tokyo, Japan), a MALLS (Dawn DSP-F, Wyatt Technology) fitted with an argon laser (488 nm), and an Optilab 903 RI detector (Wyatt Technology). The sample (1 mL) was injected into the system and ran at a flow rate of 0.3 mL/min. The mobile phase was DMSO and degassed under vacuum. The column oven temperature was controlled at 40 °C. The molecular weights were calculated using the ASTRA 6.1 software program (Wyatt Technology).

2.6. Differential scanning calorimetry

The thermal transitions of starches were investigated with the use of a differential scanning calorimetry (DSC 8000, Perkin Elmer Inc., Norwalk, USA). A starch sample (3 mg) was weighed in a stainless steel pan and the excess water was added to obtain a starch/water with a ratio of 3:7. The pans were then sealed, equilibrated for 4 h at room temperature, then heated from 30 to 130 °C at the rate of 10 °C/min. Gelatinization onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c),