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Debranching and temperature-cycled crystallization of waxy rice starch and their digestibility

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ABSTRACT

Slowly digestible starch (SDS) was obtained through debranched waxy rice starch and subsequent crystallization under isothermal and temperature-cycled conditions. Temperature-cycled crystallization of dual 4/−20 °C produced a higher yield of SDS product than isotherm crystallization. Crystal structure of SDS products changed from A-type to a mixture of B and V-type X-ray diffraction patterns. The relative crystallinity was higher in the temperature-cycled samples than that of isotherm. Attenuated total reflectance Fourier transform infrared spectroscopy suggested that the peripheral regions of isothermal storage starch were better organized than temperature-cycles. Temperature cycling induced higher onset temperature for melting of crystals than isothermal storage under a differential scanning calorimeter. The cycled temperature storage induced a greater amount of SDS than the isothermal storage.

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 digestion (Englyst, Kingman, & Cummings, 1992). RDS causes an increase in blood glucose level immediately after ingestion and SDS is digested completely in the small intestine but this process is slow. RS is not digested in the small intestine but fermented in the large bowel into short-chain fatty acids (Cummings, Beatty, Kingman, Bingham, & Englyst, 1996). SDS offers the advantage of a slow increase of postprandial blood glucose level and sustains blood glucose level over time which is helpful in controlling and preventing the hyperglycemia related diseases. Foods containing a substantial amount of SDS could be advantageous to satiety, physical performance, improve the glucose tolerance and reduce blood lipid levels in both healthy individuals and those with hyperlipidemia (Jenkins et al., 2002).

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; Zhang, Hu, Xu, Jin, & Tian, 2011), enzymatic modification by debranching (Miao, Jiang, & Zhang, 2009; Shin et al., 2004), hydrothermal treatment (Chung, Liu, & Hoover, 2010; Lee, Kim, Choi, & Moon, 2012; Lee, Shin, Kim, Choi, & Moon, 2011), retrogradation treatment (Chung, Lim, & Lim, 2006; Tian et al., 2013), chemical modification (Güzel & Sayar, 2010; Han & BeMiller, 2007), acid modification (Shin et al., 2007, 2009; Zhang, Huang, Luo, & Fu, 2012) and functional starch resources. Among the enzymatic methods, pullulanase debranching and crystallization treatment are cost-effective, safe and more suitable for commercial use (Miao et al., 2009; Shin et al., 2004).

Enzymatic modification by debranching generates short linear α-1,4-linked glucans, resulting from reforming of double helix structure by low temperature crystallization. A process for making SDS products by using debranching waxy rice starch, waxy maize starch and waxy sorghum have been reported (Guraya, James, & Champagne, 2001; Miao et al., 2009; Shin et al., 2004). A few authors have reported the impact of temperature-cycle on the formation of SDS in waxy rice starch (Tian et al., 2012; Zhang et al., 2011) and waxy maize starch (Park et al., 2009). A temperature near the glass transition temperature favors nucleation, whereas a higher temperature up to the melting temperature favors propagation (Baik,

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Kim, Cheon, Ha, & Kim, 1997; Durrani & Donald, 1995; Silverio, Fredriksson, Andersson, Eliasson, & Åman, 2000). When the storage temperature of gelatinized starch was cycled between the temperature for nucleation and the temperature for propagation, the rate of recrystallization could be accelerated (Bemiller, 2007; Slade, Oltzik, Altomare, & Medcalf, 1987). Temperature cycling induces a stepwise nucleation and propagation, promoting the growth of crystalline regions and perfection of crystallites (Silverio et al., 2000). These processes depend on the storage temperature, cycled interval and storage time.

Because of its wide-ranging food and industrial applications, waxy rice starch has been extensively studied. In our knowledge, no further report was found using a combination of pullulanase debranching and subsequent temperature-cycled crystallization treatment to produce SDS. It is important to understand its digestibility so that novel methods can be developed to produce SDS that has practical applications in the food industry. Englyst's method, which can be used to determine the portions of starch and starch degradation products, was developed to imitate the physiological conditions of starch digestion. The primary objective of this study is to investigate the digestibility and physicochemical properties of starch prepared by pullulanase debranching and subsequent temperature-cycled crystallization treatment.

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). Pullulanase (EC 3.2.1.41, 2800 ASPU/g) from *Bacillus licheniformis* was attained from Guangzhou Yulibao Biotechnology Co., Ltd. (Guangzhou, China). 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 the SDS products

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 cooked at 100 °C with continuous stirring for 30 min. The temperature of cooked starch gels was adjusted to 58 °C and debranched by pullulanse 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 gels were heated at 100 °C for 30 min to deactivate the enzyme and cooled to room temperature. The gels were subjected to isothermal and temperature-cycled crystallization with different temperature cycles at the time intervals of 24 h for four days. The temperature cycles were designed as described in Table 1. The four days isothermal crystallization was describered as 4/4 4/4 °C. Temperature-cycled crystallization of 4/−20 4/−20 °C, 4/30 4/30 °C and 4/40 4/40 °C was describered as dual 4/−20 °C, dual 4/30 °C and dual 4/40 °C, respectively.

Table 1
The different temperature cycles used during four days of crystallization.

Temperature cycles	Storage temperature (°C)			
	Day 1	Day 2	Day 3	Day 4
4/4 4/4 °C	4	4	4	4
4/−20 4/−20 °C	4	−20	4	−20
4/30 4/30 °C	4	30	4	30
4/40 4/40 °C	4	40	4	40

Specimens were subjected to water bath (thawing dual 4/−20 °C samples) treatment at 45 °C after dual cycles. The precipitate was centrifuged, washed three times with distilled water and dried at 40 °C overnight then gently ground by a mortar and pestle to pass through a 100-mesh sieve.

2.3. ATR-FTIR analysis

ATR-FTIR analysis of starches was obtained with an FT-IR spectrometer (TENSOR27, BRUCK, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector using an attenuated total reflectance (ATR) mode. For each spectrum, 16 scans were recorded at a resolution of 4 cm^{-1} at room temperature. Spectra were baseline-corrected and then deconvoluted over the range of 1200–800 cm^{-1}. A half- width of 22 cm^{-1} and a resolution enhancement factor of 2.2 were used. The amplitudes of absorbance for each spectrum at 1022 and 1047 cm^{-1} were noted and the ratio of amplitudes of absorbance at 1047 cm^{-1} and at 1022 cm^{-1} was calculated per sample to estimate the degree of order of the starch at the surface (Sevenou, Hill, Farhat, & Mitchell, 2002).

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 by the ratio of the crystalline area to the total diffractogram area (Nara & Komiya, 1983).

2.5. 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 DSC pan and the excess water was added to obtain a starch/water 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), gelatinization range (ΔT) and enthalpy values (ΔH) were measured to characterize the thermal properties of starch.

2.6. 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) which contain 50 mM LiBr and heated it 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, USA), an injector valve with a 1 mL loop, SEC column (P8514-806, Showa Denko, Tokyo, Japan), a MALLS fitted with an argon laser (488 nm), and an Optilab 903 refractive index detector (Wyatt Technology, Santa Barbara, CA, USA). 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). Each sample was analyzed in duplicate.