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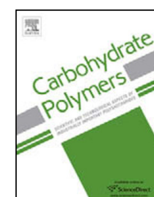

Crystallization and chain reorganization of debranched rice starches in relation to resistant starch formation

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ABSTRACT

The effects of chain distribution, concentration, temperature and hydrothermal treatments on the recrystallization behavior and formation of resistant starch (RS) were investigated. Waxy and normal rice starches were debranched at 10 and 21% w/w solid concentrations, incubated at 25 or 50 °C, and further subjected to annealing or heat moisture treatment (HMT) to enhance RS formation. The crystallization at 25 °C favored the formation of the B-type structure, whereas crystallization at 50 °C led to the A-type structure with a higher melting temperature (100-120 °C) and a higher RS content (52%). All incubated samples showed an increase in RS content after subsequent hydrothermal treatments. The sample incubated at a high temperature contained the highest RS content (74.5%) after HMT with larger/perfect crystallites. These results suggested that the RS formation could be manipulated by crystallization conditions and improved by hydrothermal treatments which are dependent on the initial crystalline perfection.

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1. Introduction

Crystallization of starchy materials into resistant starch (RS) is a result of the re-association of amylose chains in the form of double helices that are loosely arranged into a partially crystalline system that resists the diffusion and binding of hydrolytic enzymes (Eerlingen & Delcour, 1995). Resistant starch (RS) is desirable for the human diet because of its prebiotic effects and associated health benefits for the colon (Topping & Clifton, 2001). It is also considered to be beneficial for the dietary management of metabolic and lifestyle disorders, including obesity, type-II diabetes and hyperlipidemia (Kim, Chung, Kang, Kim, & Park, 2003).

Enzymatic debranching using pullulanase or isoamylase has been applied to produce linear starch chains, providing for more mobility of chains and ordered alignment; thus, the chains aggregate into perfectly crystalline structures (Cai, Shi, Rong, & Hsiao, 2010; Ozturk, Koksel, Kahraman, & Ng, 2009). The properties of debranched products are dependent on the chain length distribution, the degree of debranching and the debranching conditions. Crystallized debranched products from amylose-containing starch generally have better thermal stability than those from waxy rice starch; however, the broad chain length distribution of debranched products containing amylose inhibits the formation of products with low crystallinity (Birkett, Cui, Shi, & Thatcher, 2006). High concentration, high temperature, and short chains are known to induce A-type crystallization, whereas low concentration, low temperature and long chains favor the formation of B-type crystals (Buléon, Véronèse, & Putaux, 2007; Cai & Shi, 2014). Consequently, a variety of ordered structures are formed, depending on the predominant crystallization process, the molecular conformation, intermolecular associations or a combination of these factors, which, in turn, impact the thermal stability and the enzyme susceptibility of the RS (Cai & Shi, 2010, 2014).

Post-crystallization treatments to modify the crystalline structure into a more perfect structure have been well documented for hydrothermal treatments, i.e., autoclaving-cooling cycles and temperature cycling (Kim et al., 2010; Ozturk et al., 2009). In addition to those treatments, heat moisture treatment (HMT) and annealing are two types of hydrothermal treatment that are often used to modify the physicochemical properties and digestibility

Abbreviations: DWRS, debranched waxy rice starch; DNRS, debranched normal rice starch; RS, resistant starch; Xc, crystallinity; To, onset temperature; Tp, main peak temperature; TMi, minor transition temperature; ΔH_p, enthalpy of main endotherm; ΔH_{Mi}, enthalpy of minor endotherm; ΔH_{total}, enthalpy of total endotherms; LT, low temperature; HT, high temperature; HMT, heat moisture treatment.

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of starch granules. Both treatments involve incubation of starch granules at low or high moisture contents and temperature above the glass transition temperature (T_g) but below the melting temperature (T_m) (Jacobs & Delcour, 1998). An increase in the chain mobility around the crystals, increasing their size and perfection, decreases enzyme accessibility. Previous investigations of the effects of hydrothermal treatments on the structural and physicochemical properties of starch focused on native starch, but few studies have been conducted on retrograded starch (Mutungi et al., 2011; Mutungi, Rost, Onyango, Jaros, & Rohm, 2009). In addition, limited information is available regarding structural properties and starch digestibility deriving from the combined effects of crystallization conditions. The objective of this study was to investigate the effect of the crystallization conditions which were chain length distribution, solid concentration and temperature, and subsequent post-hydrothermal treatments on the crystalline structure, thermal stability and enzyme resistance in debranched rice starches.

2. Materials and methods

2.1. Materials

Waxy (RD6 variety) and normal rice grains (Phitsanulok 1 variety, 12.6% amylose) were obtained from the Bureau of Rice Research and Development (BRRD), Thailand. Rice starch was extracted from rice flour using a sodium chloride, ethanol and sodium hydroxide solution according to a method described elsewhere (Ju, Hettiarachchy & Rath, 2001). Isoamylase (EC 3.2.1.68, E-ISAMY) and a resistant starch assay kit were purchased from Megazyme (Megazyme International Ireland Ltd., Bray, Ireland). The isoamylase activity was 1.2×10^3 isoamylase activity units (IAU)/mL at 50 °C and pH 4.5.

2.2. Debranching and incubation

Starches (15 g, dry basis, db) were mixed with sodium acetate buffer (0.05 M, pH 4.5) to obtain 10 and 21% (w/w) solid concentrations. The slurries were gelatinized in a shaking water bath using a multi-step process: heating at 60 °C for 10 min, 85 °C for 20 min and at 99 °C for 1 h. The pastes were cooled to 50 °C, and isoamylase (5 IAU/g of dry starch) was added and maintained at 50 °C for 24 h with glass bead shaking. After 24 h of debranching, samples (40 mL) were taken and freeze-dried for analysis. The remaining samples were incubated at either low temperature (LT, 25 °C for 3 days) or high temperature (HT, 50 °C for 6 days). The LT-incubated samples were air dried overnight at room temperature (25 ± 2 °C), while the HT-incubated samples were dried at 50 °C overnight.

2.3. Annealing

The incubated samples (1 g, db) were mixed with 2.33 mL of water in tightly closed tubes and subjected to nitrogen bubbling for 10 min. Annealing was performed at 15 and 7 °C below the main peak temperature (T_p) for 16 h in a hot air oven. After 16 h of annealing, the samples were filtered over a glass filter and dried at 40 °C overnight.

2.4. Heat–moisture treatment

The incubated samples (1 g, db) were weighed into tightly closed tubes and mixed with 0.43 mL of water to obtain 70% solid content. The oxygen in the air space was removed by purging the air space with nitrogen for 5 min. The sample tubes were placed in a hot air oven at 130 °C for 2 and 4 h. Finally, the samples were dried at 40 °C overnight.

2.5. High-pressure size exclusion chromatography with multiple angle laser light scattering detection (HPSEC/MALSS) analysis

The freeze-dried debranched starches (50 mg) were solubilized in 1 M KOH (500 μL) at 4 °C for 2 days under gentle magnetic stirring and subsequently diluted with 4.5 mL of deionized water. The resulting solution was neutralized and then filtered through a 0.45-μm filter. Then, an aliquot was injected into HPSEC/MALLS. The equipment was the same as previously described (Pohu, Planchot, Putaux, Colonna, & Buleon, 2004). The SEC columns used were three HemaBio (1000, 100 and 40) (250 mm × 8 mm) from Sopares (Gentilly, France) coupled to a HemaBio guard column (Sopares, Gentilly, France. The two-online detectors were a Dawn DSP-F MALLS instrument fitted with a K5 flow cell and a He-Ne laser (λ = 658 nm) (Wyatt Technology Corporation, Santa Barbara, CA) and an ERC-7515A refractometer (Erma, Tokyo, Japan). The eluting solvent was 0.1 N KOH, and the flow rate was 0.4 mL min^{-1}. The column oven temperature was controlled at 40 °C.

2.6. Resistant starch content

The RS was analyzed according to the official AOAC method 2002.02.(McCleary & Monaghan, 2002). In short, the samples (100 mg) were mixed with 4 mL of an enzyme mixture of pancreatic α-amylase (10 mg/mL) and amyloglucosidase (3 U/mL) and then incubated at 37 °C for 16 h with agitation. After incubation, unhydrolyzed starches were collected by ethanol precipitation and centrifugation. The pellets were treated with 2 mL of 2 M KOH to solubilize the RS. The RS solution was adjusted to pH 4.75 with 8 mL of 1.2 M acetate buffer, and then amyloglucosidase (3300 U/mL) was added, and the solution was incubated at 50 °C for 30 min. The samples were centrifuged at 3000×*g* for 10 min. The liberated glucose of the supernatant was measured by reacting with glucose oxidase-peroxidase reagent at 50 °C for 20 min, and then the absorbance was measured at 510 nm.

2.7. Differential scanning calorimetry (DSC)

DSC was conducted using a DSC Q100 (TA Instruments Inc., Eschborn, Germany) calibrated with indium. Duplicate samples (9 mg) were weighed into hermetic aluminum pans, and 40 μL of DI water was added. The pans were hermitically sealed and allowed to equilibrate overnight at ambient temperature. DSC runs were performed from 10 to 200 °C at a heating rate of 3 °C min^{-1}. Forty microliters of water was used as the reference. The data were analyzed using Universal Analysis 2000 V4.4 software (TA Instruments–Waters LLC).

2.8. Wide-angle X-ray diffraction (WAXD)

The moisture of all samples was adjusted to about 20% by water phase sorption for 10 days in desiccators under partial vacuum at 90% relative humidity. Approximately 20 mg of sample was sealed between two tape foils to prevent any significant change in the water content during measurement. The diffractograms were recorded on a BRUKER™ (Karlsruhe, Germany) D8 Discover diffractometer with Cu Kα_1 radiation (λ = 0.15405 nm). The diffracted beam was collected with a two-dimensional GADDS detector, and the recording time was 600 s. The distance from the sample to the detector was 100 mm. X-ray spectral data were visualized and normalized using KaleidaGraph software. The spectra were baseline corrected, and peaks were assigned and integrated using Origin Pro 8 (OriginLab Corporation, Northampton, USA). Pearson VII functions were used to fit the individual crystalline peaks (Lopez-Rubio, Flanagan, Gilbert, & Gidley, 2008), whereas a Gaussian function was used to fit an amorphous peak at $2\theta = 19°$. The relative crystallinity

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