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A comparative study of annealing of waxy, normal and high-amylose maize starches: The role of amylose molecules

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ABSTRACT

The effect of annealing on starch structure and functionality of three maize starches (waxy, normal and high-amylose) was investigated, with the aim of understanding the role of amylose molecules during starch annealing. Amylose content, granular morphology and crystallinity of maize starches were little affected by annealing treatment. Annealing treatment did not alter the swelling power of waxy maize starch, but reduced the swelling power of normal and high-amylose maize starches. The thermal transition temperatures were increased, and the temperature range was decreased, but the enthalpy change was not affected greatly. The pasting viscosities of normal and waxy maize starches were decreased significantly, with the pasting temperature being little affected. The *in vitro* digestibility of three maize starches was not affected significantly by annealing treatment. Our results demonstrated that amylose molecules play an important role in the structural reorganization of starch granules during annealing treatment.

1. Introduction

Native starch is the main storage carbohydrate of higher plants and a major source of energy in the human diet. Starch is widely utilised in many food systems, contributing to the control of moisture, texture, viscosity, mouth-feel and shelf-life, during processing and in the finished products (Wang & Copeland, 2013a, 2013b). Linear amylose and highly branched amylopectin together form starch granules. Despite its seemingly simple composition, the starch granule has a very complex hierarchical structure from a nanometre-sized lamella to a micrometre-sized granule (Pérez & Bertoft, 2010; Wang & Copeland, 2013a). Linear amylose molecules mainly locate at the amorphous centre of the granules, with some being dispersed radially among the peripheral amylopectin clusters (Pérez & Bertoft, 2010; Wang, Blazek, Gilbert, & Copeland, 2012; Wang & Copeland, 2013a). Differences in amylose content, amylopectin fine structure and the way they are organised within granules, give rise to substantial variability, between and within species, in structure and functionality of starch granules. The structural variability of native starch granules is reflected in differences in their functional properties, such as water absorption, swelling, pasting, gelatinization, retrogradation and susceptibility to enzyme attack, which are of great importance for food processing and human nutrition (Copeland, Blazek, Salman, & Tang, 2009; Wang & Copeland, 2013b).

Despite the wide range of botanical sources, native starch does not always have the functional properties suitable for various industrial applications. Therefore, native starch is often modified with physical, chemical and enzymatic methods to alter its functional properties relevant to industrial applications (BeMiller & Huber, 2010). From the food safety point of view, physical modification is considered to be a safe method since no chemicals or enzymes are left over in the final modified starches. Of the physical modification methods, annealing is important and promising to modify the properties of starch for generating food additives or ingredients with specific properties (Jayakody & Hoover, 2008; Tester & Debon, 2000; Zavareze & Dias, 2011). Although starch annealing has been studied extensively over the past 30 years, the results obtained have always been contradictory. The reasons for these discrepancies could be starch sources, starch structure, annealing conditions (such as water/starch ratio, annealing temperature, annealing time, the number of annealing step), and the methods used for the characterisation of its structure and function (Jacobs & Delcour, 1998; Jayakody & Hoover, 2008; Tester & Debon, 2000; Zavareze & Dias, 2011).

Amylose plays an important role in the structural stability of starch granules, with the radially dispersed amylose chains acting

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as reinforcing rods between the amylopectin molecules (Wang & Copeland, 2012a). Annealing is assumed to enhance the interaction of starch chains, but the way in which this interaction occurs is little known. In the present study, we aimed to provide an insight into the role of amylose molecules in the course of starch annealing, and its consequent effect on starch structure and functionality. To this end, the effect of annealing on structure and functionality of three maize starches (waxy, normal and high-amylose) was investigated. The changes in structural and functional properties were interpreted in terms of the role of amylose in the reinforcement of starch granules.

2. Materials and methods

2.1. Materials

Three maize starches (waxy starch-2% amylose content, normal starch-23% amylose content, and high-amylose starch-85% amylose content) were obtained from the National Starch and Chemical Company (Shanghai, China). The moisture content of the starches was about 12%. The starches were used without further purification.

2.2. Annealing

Starch annealing was conducted according to a method described elsewhere (Wang, Jin, & Yu, 2013). Starch samples (10 g) were weighed into 50 ml screw capped plastic tubes, to which 20 ml deionised water was added. The tube contents were mixed and incubated in a thermostatically controlled water bath at 45 °C for 24 h and 72 h. The annealing treatment temperature was set below the start temperature of thermal transition of native starch, as determined by DSC, to avoid any possible gelatinization. The treated samples were subsequently centrifuged (3000×g) for 15 min at 20 °C. The annealed starches were vacuum filtered, washed twice with distilled water and once with ethanol, and then air-dried at room temperature.

2.3. Apparent amylose content

The apparent amylose content was determined by the iodine binding colorimetric method (Williams, Kuzina, & Hlynka, 1970).

2.4. Field-emission scanning electron microscopy

Native and annealed starches were fixed on to the surface of double-sided, carbon-coated adhesive tape attached to an aluminium stub. The mounted starch samples were coated with gold prior to imaging in a field emission scanning electron microscope (Carl Zeiss ULTRA plus, Germany). The accelerating voltage was 1.01 kV.

2.5. Wide angle X-ray diffraction (WAXD)

The X-ray diffraction patterns of native and annealed starches were obtained using a Bruker D8 Focus X-ray diffractometer (Bruker AXS, Germany). The X-ray generator was equipped with a Cu-Kα source ($\lambda = 0.154$ nm) operating at 40 kW and 40 mA. The starch samples were kept at a constant humidity (75%) in a desiccator over a saturated solution of NaCl for one week before measurement. The diffraction intensity was measured from 4° to 50° as a function of 2θ, at a scanning speed of 0.5°/min and a step size of 0.04°. The relative crystallinity was quantitatively estimated according to a method described elsewhere (Wang, Yu, Zhu, Yu, & Jin, 2009), using the Origin software (Version 7.5, Microcal Inc., Northampton, MA, USA).

2.6. Swelling power

The swelling power of the native and annealed starches was determined in triplicate according to a method described elsewhere (Wang & Copeland, 2012b).

2.7. Differential scanning calorimetry

Measurements were made using a Modulated Differential Scanning Calorimeter MDSC 2920 instrument (TA Instruments Inc., Delaware, USA) equipped with a thermal analysis data station and data recording software. The operating conditions and definitions of thermal transition parameters were described elsewhere (Wang & Copeland, 2012c).

2.8. Pasting properties

The pasting profiles were measured using a Newport Scientific Rapid Visco Analyser 4 (RVA-4) (Newport Scientific, Australia). The starch concentration used in the present study was 6% (dry weight, 28 g total weight). The heating and cooling procedures were described elsewhere (Wang, Sharp, & Copeland, 2011).

2.9. In vitro starch digestibility

In vitro starch digestibility was determined by a modified Englyst, Kingman, and Cummings (1992) method, described elsewhere (Wang & Copeland, 2012a). Starch was classified into three components based on the rate of hydrolysis: rapidly digested starch (RDS, digested within 20 min), slowly digested starch (SDS, digested between 20 and 120 min) and resistant starch (RS, undigested starch after 120 min).

2.10. Statistical analysis

All analyses were replicated at least twice and mean values and standard deviation values are reported. Analysis of variance (one-way ANOVA) by Duncan's test ($p < 0.05$) were conducted using the SPSS 10.0 Statistical Software Program (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

3.1. Apparent amylose content

The apparent amylose content of maize starches before and after annealing treatment is presented in Table 1. Annealing treatment did not significantly alter the apparent amylose content of the three maize starches. For example, normal maize starch had an amylose content of 23.0%, which was 22.5% and 23.2% after 24 and 72 h of annealing treatment, respectively. The little change in amylose content indicated that annealing treatment did not trigger any significant swelling or a gelatinization process. Annealing treatment is generally taken to be a pure physical process, during which no amylose leaching occurs. Similar results have also been observed with corn, wheat, potato, cassava and Peruvian Carrot starches (Chung, Hoover, & Liu, 2009; Kohyama & Sadaki, 2006; Rocha, Cunha, Jane, & Franco, 2011; Rocha, Gelizardo, Jane, & Franco, 2012; Tester, Debon, & Karkalas, 1998). However, annealing treatment has been shown to decrease the amylose content of peas (Wang et al., 2013), wheat (Lan et al., 2008), normal corn, high-amylose corn and potato starches (O'Brien & Wang, 2008). The decreased amylose content of annealed starch could be attributed to amylose leaching (O'Brien & Wang, 2008; Wang et al., 2013) or the weakened iodine binding to the amylose helix as a