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Annealing improves paste viscosity and stability of starch

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ABSTRACT

The effect of annealing treatments at different temperatures on structural and functional properties of wheat, potato, and yam starches was investigated. Annealing had little effect on the long- and short-range ordered structures of three starches, except for the annealing of wheat starch at 50 °C. Annealing increased the gelatinization temperatures of three starches, but had little effect on the enthalpy changes. Annealing at 30 and 40 °C increased the overall paste viscosity of wheat starch, while the treatment at 50 °C reduced the paste viscosity substantially. There was a continuous increase in paste viscosity of potato starch after annealing at 50 °C during the whole RVA (rapid viscosity analyser) testing. The increases in gelatinization temperatures and paste viscosities were attributed to the increased ordering of starch chains in amorphous regions. Our results showed that annealing is an effective method to increase the paste viscosity of starch, which is very important for the application of annealed starch.

1. Introduction

Annealing, a physical modification means of starch, has attracted much attention for its chemical safety, low-cost and environment-friendliness. Annealing can modify greatly the functional properties of starch without disrupting its granular structure (Dias, da Rosa Zavareze, Spier, de Castro, & Gutkoski, 2010; Rocha, Felizardo, Jane, & Franco, 2012; Singh, Chang, Lin, Singh, & Singh, 2011). The changes in granular structure are often observed with surface roughening, increased granule size, and a small increase or decrease in crystallinity, amount of double helices and short-range molecular order (Chung, Hoover, & Liu, 2009; Dias et al., 2010; Gomand et al., 2012; Liu, Yu, Simon, Dean, & Chen, 2009; Liu, Yu, Simon, Zhang, Dean, & Chen, 2009; Waduge, Hoover, Vasanthan, Gao, & Li, 2006). The obvious changes in functional properties of starch after annealing treatment include increased gelatinization temperatures, especially onset temperature, and narrowed gelatinization temperature range (Jayakody & Hoover, 2008; Wang, Wang, Yu, & Wang, 2014; Zhang et al., 2015). Other changes in gelatinization enthalpy, swelling power, starch solubility, amylose leaching, pasting properties, and *in vitro* enzyme hydrolysis have been shown not to follow a consistent trend, especially for pasting properties (Jayakody & Hoover, 2008; Zavareze & Dias, 2011).

Although the effect of annealing on starch properties has been studied extensively, the exact mechanism behind starch annealing is still not fully understood. Several hypothesis have been proposed to interpret the annealing effect on starch properties, which include crystalline perfection (Chung, Hoover, et al., 2009), crystal thickening (Gomand et al., 2012), increased interaction between starch chains (Chung, Liu, & Hoover, 2009; Rocha, Cunha, Jane, & Franco, 2011), elongation of double helix or crystalline lamellae (Tester, Debon, & Karkalas, 1998), and stabilization or weakening of starch structure through amylose reorganization or removal (Wang et al., 2014; Wang, Jin, & Yu, 2013). Due to the complexity of annealing mechanism, further studies are required to understand comprehensively the annealing-induced changes in starch properties.

Starch is a naturally occurred semi-crystalline polymer, which presents three types of X-ray diffraction patterns, corresponding to A-, B-, and C-type polymorphs. A- and B-type polymorphs are different in double helix packaging and water content in the unit cell (Tester, Karkalas, & Qi, 2004; Zeeman, Kossmann, & Smith, 2010). C-type polymorph is considered a mixture of A- and B-type polymorphs, mostly occurring in legume and tuber (like yam) starches. Starches with different crystalline polymorphs have been shown to respond differently to thermal or non-thermal treatments (Bogracheva, Morris, Ring, & Hedley, 1998; Stute, Klingler,

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Boguslawski, Eshtiaghi, & Knorr, 1996; Wang, Sun, Wang, Wang, & Copeland, 2016). To the best of our knowledge, there is a dearth of information on how starches with different crystalline polymorphs respond to annealing treatment. In this study, three starches with A-, B- and C-crystalline polymorphs are used to investigate their susceptibility to annealing treatment. This study provides new insights into the annealing-induced changes in functional properties of starch.

2. Materials and methods

2.1. Materials

Wheat grains were provided by China Agricultural Science Institute, Beijing, China. Potato and yam (*Dioscorea opposite)* tubers were purchased from the local supermarket. α-Amylase (Sigma, EC 3.2.1.1, type VI-B from porcine pancreas, 15 U/mg) was purchased from Sigma Chemical Co. (St. Louis, MO, USA). *Aspergillus niger* amyloglucosidase (3260 U/mL) and D-Glucose Assay Kit (GOPOD format) were purchased from Megazyme International Ireland Ltd. (Co. Wicklow, Ireland). Other chemical reagents are all of analytical grades.

2.2. Starch isolation

Wheat starch was isolated from wheat grains according to a method by Wang et al. (2015). Potato and yam starches were isolated according to the method of Ek, Wang, Copeland, and Brand-Miller (2014). Apparent amylose content of the starch was determined according to the method of Chrastil (1987). The moisture, lipid and protein contents were measured by the methods of AOAC (2002)-International. The amylose, moisture, protein and lipid contents of three starches are summarized in Table 1.

2.3. Annealing treatment

12 g starch was weighed accurately into a polyethylene bag and 60 ml distilled water was added to obtain a ratio of starch:water = 1:5 (w/v). The polyethylene bag was vacuum-sealed before annealing treatment in a water bath at 30, 40, and 50 °C for 24 h. After treatment, starches were freeze-dried, ground into powder and passed through a 75 μm sieve. The annealed starches were stored in a sealed container at 4 °C before further analysis. Freeze drying was shown to have a significant effect on structural properties of B-type potato starch (Zhang et al., 2014). Hence, another set of annealed potato starch, which was dried by ethanol dehydration following annealing treatment, was prepared to investigate the effect of freeze-drying on starch properties.

2.4. Scanning electron microscopy (SEM)

The morphology of starch granules was imaged using a LEO 1530 scanning electron microscope (LEO, Germany). Starch samples were mounted on the aluminum stub using the double-sided carbon adhesive tapes and sputter-coated with gold. An accelerating voltage of 5 kV was used during imaging.

2.5. X-ray diffraction (XRD)

X-ray diffraction analysis was performed using a D/max-2500vk/pc X-ray diffractometer (D8FOCUS, Bruker, Germany) operating at 40 kV and 30 mA. Starches were equilibrated over a saturated NaCl solution at room temperature for one week before analysis. The X-ray diffraction patterns were measured from 4 to 35° as a function of 2θ and at a scanning speed of 1°/min and a step size of 0.02°. The relative crystallinity was quantitatively estimated as a ratio of the crystalline area to the total area between 4° and 35° (2θ) using the Origin software (Version 8.0, Microcal Inc., Northampton, MA, USA).

2.6. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of native and annealed starches were obtained using a Tensor 27 FTIR spectrometer (Bruker, Germany) equipped with a DLATGS detector. The sample preparation and operation conditions were described elsewhere (Wang, Luo, Zhang, Zhang, He, & Wang, 2014). The spectra were analyzed by OMNIC7.0. The baseline of spectra was corrected firstly and then the spectra from 1200 to 800 cm^{-1} was deconvoluted with a peak width of 38 and an enhance factor of 2.1. The ratio of absorbances at 1047/1022 cm^{-1} was calculated to characterize the short-range molecular order of starch granules.

2.7. Laser confocal micro-Raman (LCM-Raman) spectroscopy

A Renishaw Invia Raman microscope system (Renishaw, Gloucestershire, United Kingdom) equipped with a Leica microscope (Leica Biosystems, Wetzlar, Germany) and a 785 nm green diode laser source was used in this study. Spectra were taken from the same spot size of each sample in the range of 3200–100 cm^{-1} with a resolution of approximately 7 cm^{-1}. The full width at half maximum (FWHM) of the band at 480 cm^{-1} was calculated by using the software of WiRE 2.0.

2.8. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) measurements were performed using a differential scanning calorimeter (200 F3, Netzsch, Germany) equipped with a thermal analysis data station. Approximately 3 mg of starch were accurately weighed into an aluminum sample pan. Distilled water was added with a pipette to obtain a starch:water ratio of 1:3 (w/w) in the DSC pans. The pans were sealed and allowed to stand overnight at room temperature before analysis. The samples were heated from 20 to 130 °C at a heating rate of 10 °C/min. An empty aluminum pan was used as the reference. The onset (T_o), peak (T_p), conclusion (T_c) temperatures and enthalpy change of gelatinization ($\triangle H$) were obtained through data recording software. All measurements were performed in triplicate.

2.9. Pasting properties

The pasting profiles were monitored using a Rapid Visco

Table 1
The basic composition of three starches.

Starch	Moisture content (%)	Protein content (%)	Lipid content (%)	Amylose content (%)
Potato	12.0 ± 0.0c	0.29 ± 0.09a	0.06 ± 0.01a	30.8 ± 0.1b
Yam	10.3 ± 0.1b	0.16 ± 0.04a	0.06 ± 0.02a	37.1 ± 0.3c
Wheat	8.7 ± 0.1a	0.22 ± 0.09a	0.18 ± 0.04b	27.7 ± 0.7a

Values are means ± SD. Values with the same letters in the same column are not significantly different ($p < 0.05$).