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Effects of amylose and phosphate monoester on aggregation structures of heat-moisture treated potato starches

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ABSTRACT

For three cultivars of potato starch, heat-moisture treatment (HMT) displayed an influence on the aggregation structures at different scale levels. With HMT, the granular morphology of potato starch granules remained similarly, and an increase in the average repeat distance of semi-crystalline lamellae was observed. The crystalline structure and birefringence were also affected. Moreover, the polymorphic transformation (B → A + B) could be related to dehydration, whereas the decrease in the degree of crystallinity might be resulted from the rupture of hydrogen bonds. Interestingly, amylose could act as the backbone of the aggregation structures of potato starch to provide resistance to HMT, but phosphate monoester could promote the destruction during HMT. In addition, compared with amylose, phosphate monoester played a more significant role in changing the average repeat distance of semi-crystalline lamellae (long period) during HMT.

1. Introduction

Starch is a natural polymer and is widely used in many industrial fields, either as a main raw material or as an additive. In general, starch consists of two major polymer components, namely amylose and amylopectin. Amylose is a relatively long linear D-glucan containing 99% α-1,4 linkages and 1% α-1,6 linkages, whereas amylopectin is a highly branching D-glucan containing 95% α-1,4 linkages and 5.0% α-1,6 linkages (Damager, Engelsen, Blennow, Møller, & Motawia, 2010; Pérez & Bertoft, 2010). These two polymers form the amorphous and crystalline regions in the starch granule (Zhang, Zhao, et al., 2014). Due to the diversities in starch source, composition, structure, and properties, starches are suitable for various applications contributing to different functionalities (Hoover, 2010). However, the application of native starch is limited because of the undesirable defects caused by the structural characteristics, such as poor solubility, low heat and shear resistance, uncontrolled paste consistency, high tendency toward retrogradation and gelling, and low freeze–thaw stability of pastes (BeMiller, 1997; Lawal, 2009). To overcome these shortcomings, various techniques of starch modification, including chemical, physical and enzymatic methods, are widely used to improve the inherent characteristics of starch (BeMiller, 1997; Pu et al., 2011; Zhang, Chen, Zhao, & Li, 2013).

Heat-moisture treatment (HMT) is defined as a physical modification method that involves the treatment of starch granules at a low moisture level (<35%) and at a temperature (84–120 °C) above the glass transition temperature (T_g) but below the gelatinization temperature for a certain period of time (15 min–16 h) (Gunaratne & Hoover, 2002). HMT has gained great attention as one of the physical modification techniques to modify the physicochemical properties of starch without destroying its granular structure. According to a previous report (Hoover, 2010), HMT had an influence on the crystalline structure, starch chain interactions, granular swelling, amylose leaching, viscosity, gelatinization parameters, retrogradation, and susceptibility toward acid and α-amylase hydrolysis of cereal, tuber, and legume starches. Furthermore, there are many factors that can affect the extents of changes in the structure and properties of starch during HMT, such as the starch composition, organization of amylose and amylopectin within the native granule, and conditions (e.g. temperature, moisture, and time). It is worth noting that the semi-crystalline lamellae of starch can be disrupted by HMT (Vermeylen, Goderis, & Delcour, 2006). Additionally, HMT can lead to a reduction in the gelatinization endotherm and total crystallinity of potato starch (Hoover &

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Vasanthan, 1994; Miyoshi, 2002; Stute, 1992), and a shift from B- to A-type crystalline structure (Vermeylen et al., 2006). Therefore, the aggregation structural characteristics of starch can be affected by HMT. The aggregation structures (mainly lamellar structure and crystalline structure) of starch play a key role in determining the properties (Kim & Huber, 2010; Zhang, Li, Liu, Xie, & Chen, 2013b). Particularly, the crystalline structure can affect the enzymatic resistivity of starch (resistant starch content) (Zhang, Chen, et al., 2013) which displays a nutritional relevance and potential health benefits.

Potato starch is one of the worldwide starch resources and has been widely used in foods and non-food industries. For further improving the properties of native potato starch by using HMT and thus extending the industrial applications of potato starch, it is indispensable to investigate the influences of starch granular components (amylose, and phosphate monoester, etc.) on the aggregation structures of HMT treated potato starch. However, there have been few studies on the detailed comparison of the changes in aggregation structures of HMT treated potato starch as affected by the amylose and phosphate monoester contents. Normally, potato starch contains more phosphate monoester than cereal starches (Blennow & Engelsen, 2010; Wickramasinghe, Blennow, & Noda, 2009) and the crystallites of potato starch are more susceptible to disruption by HMT (Hoover, 2010). This indicates that phosphate monoester may be a determinant on the extent of influence by HMT on the structures of potato starch. Nonetheless, the role of amylose during HMT, especially the concurrent effect of amylose and phosphate monoester on the aggregation structures of potato starch, has not been clarified so far. This is undesirable for further investigations of the relationship between the aggregation structures and the properties of potato starch to extend the application of potato starch in foods and other starch-based products. Therefore this work involves the selection of three cultivars of potato starch which had different amylose and phosphorus contents for HMT, in order to investigate the HMT-induced changes in the granular morphology, lamellar structure, and crystalline structure of these starches as affected by the amylose and phosphorus contents.

2. Materials and methods

2.1. Materials

Three cultivars of potato starch (Qing 168, Qing 5, and Feiwuruita) from Qinghai Province, China were used in this experiment, and were referred to as Potato-1, Potato-2, and Potato-3 respectively. They were supplied by Sanjiang Group Co., Ltd. (Xining, China). A moisture analyzer (MA35, Sartorius Stedim Biotech GmbH, Germany) was used to determine the moisture content (MC) of each sample.

2.2. Amylose content

The apparent amylose contents of native and HMT treated potato starches were determined using the AACC method 61-03 (10) through the spectrophotometric detection, which is based on blue color formation upon the reaction of amylose with iodine. A UV-3802 spectrophotometer (UNICO, New Jersey, USA) was used to measure the color at 620 nm. All the measurements were done in triplicates.

2.3. Phosphorus content

The phosphorus contents of potato starches were obtained with an energy dispersive X-ray spectrometer (EDX) of EVO18 scanning electron microscope (ZEISS, Oberkochen, Germany) operated at a voltage of 10.0 kV.

2.4. Heat-moisture treatment

Each potato starch was premixed with distilled water to reach certain moisture content (MC, ~30%) and treated in a reactor (Model No. 4545, Parr Instrument Company, Moline, Illinois, USA) at 110 °C with stirring for 30 min. After that, all the samples were air dried at 45 °C for 48 h and ground for further analysis. The HMT treated potato starches were referred to as Potato-1-HMT, Potato-2-HMT, and Potato-3-HMT, respectively.

2.5. Aggregation structures of native and heat-moisture treated potato starches

2.5.1. Scanning electron microscopy (SEM)

Granular morphology was observed using an EVO18 scanning electron microscope (ZEISS, Oberkochen, Germany) operated at a voltage of 10.0 kV. All the samples were coated with a thin gold layer before the microscopic examination.

2.5.2. Small-angle X-ray scattering (SAXS)

SAXS experiments were performance according to the method in our previous reports (Zhu, Li, Chen, & Li, 2012; Zhang, Xiong, et al., 2014) with proper modification. An SAXSess system (Anton-Paar GmbH, Austria) equipped with a PW3830 X-ray generator (PANalytical B.V., The Netherlands), operated at 50 mA and 40 kV, using Cu Kα radiation with a wavelength of 0.1542 nm as the X-ray source was used. The starch slurries with a MC of about 60% were prepared and equilibrated at 20 °C for 24 h before the analysis. Each sample was placed into a paste sample cell and measured for 10 min. The data, recorded using an image plate, were collected by the IP Reader software program with a PerkinElmer® Storage Phosphor System. All data were normalized, and the background intensity and smeared intensity were removed using the SAXSquant 3.0 software program for further analysis.

2.5.3. Polarized light microscopy (PLM)

A polarized light microscope (Axioskop 40 Pol/40A Pol, ZEISS, Oberkochen, Germany) equipped with a 35 mm SLA camera (Power Shot G5, Canon, Tokyo, Japan) was used to obtain the polarized light microscopic images. Each sample was dispersed as 10 mg of starch in 1 mL of distilled water in a glass vial and observed at 500× magnification (50 × 10). A drop of starch suspension was transferred onto a slide, covered by a cover slip.

2.5.4. X-ray diffraction (XRD)

XRD analysis was performed with a Xpert PRO diffractometer (PANalytical B.V., The Netherlands), operated at 40 mA and 40 kV, using Cu Kα radiation with a wavelength of 0.1542 nm as the X-ray source. The scanning of diffraction angle (2θ) was from 5° to 40° with a scanning speed of 10°/min and a scanning step of 0.033°. The samples were equilibrated in an oven (DHG-9145A, Shanhai Bluepard Instruments Co., Ltd., China) at 40 °C for 24 h and the MC of all the samples was about 15% before the analysis. The relative crystallinity (RC) of each sample was calculated using the method by Hermans and Weidinger (1948).

3. Results and discussion

3.1. Amylose and phosphorus contents

Table 1 shows the amylose and phosphorus contents of the different native potato starches. The amylose content is one of the main factors that affect the physicochemical properties of