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Effect of planetary ball-milling on multi-scale structures and pasting properties of waxy and high-amylose cornstarches

Xiaoyan Tan [a], Binjia Zhang [a], Ling Chen [a,*], Xiaoxi Li [a,*], Lin Li [a], Fengwei Xie [b]

[a] Ministry of Education Engineering Research Center of Starch and Protein Processing, Guangdong Province Key Laboratory for Green Processing of Natural Products and Product Safety, College of Light Industry and Food Sciences, South China University of Technology, Guangzhou 510640, China
[b] Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, QLD 4072, Australia

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ABSTRACT

Waxy and high-amylose cornstarches were mechanically modified, and the effects of planetary ball-milling treatment on the multi-scale structures and pasting properties of these cornstarches were investigated. The ball-milling could hardly change the structures and properties of high-amylose cornstarch but result in distinct changes to that of waxy cornstarch. With the thicker semi-crystalline lamellae, larger crystalline amylopectin lamellae, thinner amorphous amylopectin lamellae and more structural rigidity amylose amorphous background region, high-amylose cornstarch showed high resistance to the mechanical disruption during the planetary ball-milling treatment. Consistent with the structural changes, the paste properties of high-amylose starch has negligible changes, but the treated waxy cornstarch showed a reduced pasting temperature and paste viscosity, increased pasting stability and a reduced tendency to retrogradation. The results suggest that planetary ball-milling could be a potential physical method to obtain starch products with relatively low viscosity at high concentration and enhanced pasting stability.

Industrial relevance: Ball-milling is an eco-friendly and cost-effective physical technique which regulates the structure and therefore the physicochemical properties of polymers. Starch is a natural polysaccharide and has been widely used in foods and non-food products. As starch structure plays a key role in determining its properties, it is highly important to ensure a desirable structure and thus properties to be achieved for specific applications. The present study reveals that planetary ball-milling is an attractive technique to alter the multi-scale structures of starch (in particular waxy starch) and therefore its paste properties. In particular, the treatment displayed a reduced pasting temperature and paste viscosity, an enhanced paste stability at different temperatures and a smaller tendency to retrogradation, which makes starch suitable for a wide range of products such as confections, instant desserts and canned and bottled foods. This enables planetary ball-milling to be a potential physical technique to produce starch products with desired paste behaviors and to expand the industrial applications of starch.

1. Introduction

Starch as a natural polysaccharide has been widely applied in foods and non-food products. Since the starch structure plays a key role in determining its properties (Sandhu & Singh, 2007), it is highly important to ensure a desirable structure and thus properties to be achieved for specific applications. However, this has always be challenging regarding the inherent complex structure of native starch, which greatly limits the expansion of starch applications. Regarding this, various techniques involving chemical, physical and enzymatic methods are useful in improving the functional and other physicochemical properties of starch such as pasting properties and gelatinization behaviors. Besides, in recent years, physical techniques for starch modification (e.g., heat-moisture, ultrasound, microwave, high-pressure and ball-milling) have attracted great attention due to their advantages such as increased safety and reduced waste-generation (Blaszczak et al., 2007; Huang, Xie, Chen, Lu, & Tong, 2008; Szepes et al., 2005; Zhang, Zhao, Li, Li et al., 2014; Zhu, Li, Chen, & Li, 2012).

Ball-milling has been reported as an eco-friendly and cost-effective physical technique, which could regulate the starch structure and therefore modify the physicochemical properties of starch and cereal flour (Liu, Ma, Yu, Shi, & Xue, 2011; Loubes & Tolaba, 2014). Ball-milling normally can provide a mechanochemical effect on the characteristics of materials, through combined friction, collision and shear resulting from the grinding balls and the container wall. As reported earlier, the granule morphology, granule size distribution, crystallinity, molecular weight and amylose/amylopectin ratio of starch could be significantly modified by ball-milling, together with the resultant changes in the starch properties, including solubility, digestibility, pasting properties

* Corresponding authors. Tel./fax: +86 20 8711 3252.
E-mail addresses: felchen@scut.edu.cn (L. Chen), xxlee@scut.edu.cn (X. Li).

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and rheological properties (Huang et al., 2008; Kim, Suzuki, Hagiwara, Yamaji, & Takai, 2001; Liu et al., 2011; Tamaki, Hisamatsu, Teranishi, Adachi, & Yamada, 1998). Therefore, ball-milling shows potentials as a physical approach to modulate the starch structure and functionalities (e.g., reduced crystallinity and increased solubility), for expanding the applications of starch (Liu et al., 2011).

As a heterogeneous material, starch is normally a mixture of two biopolymers, i.e., 10–30% amylose, a mostly linear 1,4-α-D-glucan with a small number of long branches, and 90–70% amylopectin, mainly1,4-α-D-glucan but having a large number of 1,6-α linkages at the branch points (Karim, Norziah, & Seow, 2000; Zhang, Zhao, Li, Zhang et al., 2014). In addition, high-amylose starch can possess amylose content up to 85%, while waxy starch may contain 100% amylopectin after genetic modification (Liu, Halley, & Gilbert, 2010). These two biopolymers form the hierarchical structure of starch which is organized on multi-length scales, from different supramolecular structures (whole granule, growth rings, semi-crystalline lamellae and crystalline structure) to the molecular structure (chain characteristics) (Oates, 1997). Due to the different amylose/amylopectin ratio, waxy, regular and high-amylose starches often display prominent differences in their hierarchical structure. In particular, while waxy and regular starches have a large amount of A-type crystallites, high-amylose starch predominantly displays a B-type crystalline structure. It is noteworthy that starch with a higher amylose content is less susceptible to various physicochemical treatments such as hydrothermal treatment, despite its lower crystallinity (Liu, Yu, Xie, & Chen, 2006; Zhang, Zhao, Li, Li et al., 2014). Therefore, to improve the functional properties (e.g., pasting properties) of starch by ball-milling, it is extremely important to understand the effects of ball-milling on the hierarchical structure and properties of starches with different amylose/amylopectin ratios.

Compared with other conventional milling methods, planetary ball-milling can result in more apparent alteration to starch characteristics and thus can be considered as a more suitable method for starch modification. It has been reported that planetary ball-milling is capable to reduce starch crystallinity and double-helices (Liu et al., 2011). However, the changes induced by this method in the starch multi-scale structures (especially including, on the nano-scale, semi-crystalline lamellae), and in its functionalities such as pasting properties, have not been well understood. This is especially true when starches with different amylose/amylopectin ratios are involved.

In present work, waxy and high-amylose (Gelose 80, or G80) cornstarches were selected and treated by a planetary ball mill for different times. By comparing starch samples without and with the planetary ball-milling treatment, the related changes in the granule morphology, granule size distribution, semi-crystalline lamellae, crystalline structure and molecular structure as well as the pasting properties of waxy and high-amylose cornstarches were explored.

2. Materials and methods

2.1. Materials

Waxy cornstarch (the amylose/amylopectin ratio, 0/100) was obtained from Lihua Starch Industry Co., Ltd. (Qinhuangdao, China), and a high-amylose cornstarch, Gelose 80 (G80) (the amylose/amylopectin ratio, 80/20), was supplied by Penford (Australia). The moisture content (MC) (about 10%) of each sample was determined using a moisture analyzer (MA35, Sartorius Stedim Biotech GmbH, Germany). Anhydrous ethanol, in reagent grade, was supplied by Nanjing Chemical Reagents Co., Ltd. (Nanjing, China).

2.2. Planetary ball-milling treatment

A QM-BP planetary ball mill (Nanda, Nanjing, China) with four ceramic milling cylinders (100 mL) was used. About 15 g of starch and zirconia balls (a mixture of balls with diameters of 2, 5 and 10 mm) of which the weight was three times that of starch were placed into each ceramic container, filling about 1/3 capacity of the container, followed by addition of 12 mL of anhydrous ethanol. The cylindrical container was tumbled at a rotation speed of 1032 rpm (the ratio of rotation/revolution speed, 2/1) for 4, 8, 15 or 20 h. After treatment, the sample was collected after removing the balls and ethanol (by evaporation) and then was sealed for further analyses. In the following discussion, the code typically as "Waxy-0h" is used, in which "Waxy" represents the type of cornstarch and "0h" indicates the ball-milling treatment time.

2.3. Scanning electron microscopy (SEM)

Granule morphology was observed using an EVO18 scanning electron microscope (ZEISS, Germany), operated at 10.0 kV. All the samples were coated with a thin gold film before the microscopic observation.

2.4. Laser diffraction analysis

Granule size distribution was analyzed by a Malvern Mastersizer 2000 laser diffraction analyzer (Version 5.22, Malvern, UK) using a 1000 mL flow-through reservoir. Each ball-milled starch sample was added to the reservoir and fully dispersed in anhydrous ethanol until an obscuration value between 12% and 17% was achieved. The pump speed was set at 2050 r/min. The refractive index of the starch samples and the dispersing reagent ethanol was 1.54 and 1.36, respectively. Volume size distribution between 0.10 and 104.71 μm was recorded for all samples. All the results are reported as the averages of three replicates.

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

SAXS experiments were performed on a SAXSess small-angle X-ray scattering system (Anton-Paar, Austria) equipped with a PW3830 X-ray generator (PANalytical), operated at 50 mA and 40 kV, using Cu-Kα radiation with a wavelength of 0.1542 nm as the X-ray source. The samples (ca. 60% MC) used for the SAXS measurement were prepared by premixing the starches with added water in glass vials and were equilibrated at 20 °C for 24 h before the analysis. Each sample was placed in a paste sample cell and was exposed at the incident X-ray monochromatic beam for 5 min. The data, recorded using an image plate, were collected by the IP Reader software 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 for further analysis.

2.6. Light microscopy

Both ordinary and polarized light micrographs were recorded using a light microscope (Axioskop 40 Pol/40APol, ZEISS, Oberkochen, Germany) equipped with a camera (PowerShot G5, Canon, Tokyo, Japan). The magnification was set at 500 (50 × 10). Each sample was dispersed as 10 mg of the starch in 1 mL of distilled water in a glass vial. Then a drop of the starch suspension was transferred onto a slide, covered by a cover slip.

2.7. X-ray diffraction (XRD)

X-ray diffraction patterns of the starch samples were measured using an Xpert PRO diffractometer (PANalytical, 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 diffraction angle (2θ) scanning was from 5° to 40° with a scanning speed of 10°/min and a scanning step of 0.033°. The MC of each sample was about 10%.