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Supramolecular structure of A- and B-type granules of wheat starch

Binjia Zhang [a], Xiaoxi Li [a], Jia Liu [a], Fengwei Xie [b], Ling Chen [a,*]

[a] Ministry of Education Engineering Research Center of Starch & 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

The supramolecular structure of the A- and B-type granules of wheat starch was compared. Polarized light microscopy, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) were used to study the granular, crystalline, and short-range structures. The A- and B-type granules displayed a typical A-type crystalline structure with the degrees of crystallinity of 31.95% and 29.38% respectively. In addition, the B-type granules had some V-type crystallites. The nanostructure and fractals were characterized by small angle X-ray scattering (SAXS), which showed that the average thickness of the lamellae of the A-type granules was larger, while the B-type granules possessed a higher degree of ordering in the lamellar regions. A second order reflection was found in both A- and B-type granules, which was proposed due to the crystalline lamellae of the semicrystalline lamellae. The A- and B-type granules had mass and surface fractal structures respectively.

1. Introduction

Starch is the main material in the food industry, and is one of the most important energy sources for humans (Juansang, Puttanlek, Rungsardthong, Puncha-arnon, & Uttapap, 2012). It is a mixture of two major D-glucan polymers, i.e. amylose, a mostly linear 1,4-α-D-glucan, and amylopectin, mainly 1,4-α-D-glucan but having 1,6-α linkages at the branch points (Jiang, Gao, Li, & Zhang, 2011; Karim, Norziah, & Seow, 2000; Zobel, 1988). These two kinds of polymers form amorphous and crystalline regions in starch granules (Oates, 1997).

The supramolecular structure of starch mainly contains the granular morphology, the crystalline structure, the short-range order, and the nanostructure. It has been shown that the structure of native starch was organized in four length scales: the molecular scale (~0.1 nm), the lamellar structure (8–9 nm), the growth rings (~0.1 μm), and the whole granular morphology (μm) (Pikus, 2005). Two main types of crystalline structures have been shown by X-ray diffraction (XRD) (Kim & Huber, 2010; Nara & Komiya, 1983), i.e. the A-type crystalline structure of cereal starches such as wheat and rice starches, and the B-type crystalline structure of tuber, fruit and stem starches such as potato and banana starches. An additional C-type crystalline structure is actually a combination of both A- and B-type structures (Gernat, Tadosta, & Damaschun, 1990; Sarko & Wu, 1978). A V-type crystalline structure was also detected by XRD, which describes the amylose single helices co-crystallized with compounds such as iodine, dimethyl sulfoxide (DMSO), alcohols, or fatty acids (Buleon, Colonna, Planchot, & Ball, 1998).

Wheat starch contains two kinds of starch granules, i.e. the large, disk-shaped A-type granules and the small, spherical and irregular B-type granules (Ao & Jane, 2007; Hayashi, Kiribuchi-Otobeb, & Seguchi, 2005; Wei et al., 2010). Both the A- and B-type granules of wheat starch display predominantly an A-type crystalline structure. However, the A- and B-type granules have different morphology, granular specific surface area, composition, relative crystallinity, amylopectin branch chain length distribution, and physical properties (swelling, gelatinization, and pasting behaviors) (Kim & Huber, 2010). Compared to the B-type granules, the A-type granules possess a different gelatinization temperature and higher crystallinity. A structural difference between amylopectin molecules of the two types of granules was also reported, and the crystalline lamellae of the B-type granules are denser than the A-type granules (Vermeylena, Goderis, Reynaers, & Delcour, 2005).

The properties of wheat starch are related to the structures of the A- and B-type granules. A previous study (Kim & Huber, 2010) showed that the swelling, gelatinization, and pasting properties of wheat starch are obviously affected by the ratio of A/B-type granules, which can be explained by the different amylopectin chain length distributions of the A- and B-type granules. Furthermore, the correlations between the structural and functional parameters were less significant for the unseparated wheat starch than for the isolated A- and B-type granules (Salman et al., 2009). Besides above, the supramolecular structures of the A- and B-type granules

* Corresponding author. Tel./fax: +86 20 8711 3252.
E-mail addresses: felchen@scut.edu.cn, zbw9383@163.com (L. Chen).

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of wheat starch play a key role in determining the properties and applications of wheat starch in the food industry. Nonetheless, no study has been reported on the detailed comparison of the supramolecular structures of the A- and B-type granules of wheat starch.

In this study, the A- and B-type granules were purified from wheat starch, and their granular morphology, crystalline structure, short-range order, nanostructure, and fractals are compared. The results of this study would form the basis for the further investigations on the supramolecular structures of the A- and B-type granules to widen the industrial application of wheat starch.

2. Material and methods

2.1. Material

Wheat starch (food grade) was obtained from Foshan Suiyang Food Material Co., Ltd. (Foshan, China).

2.2. Separation of the two types of granules of wheat starch

Wheat starch was fractionated into the A- and B-type granules by sedimentation using 1 L graduated cylinders as described by Takeda et al. (Takeda, Takeda, Mizukami, & Hanashiro, 1999). Wheat starch (100 g) was suspended in 800 mL deionized water for 1 h. Then, the upper 500 mL suspension was collected as the B-type granules before 500 mL deionized water was added to the cylinder. The above processes were repeated 8–9 times until the upper suspension was clear. The rest precipitate in the cylinder was collected as the A-type granules. The A- and B-type granules fractions obtained were centrifuged at 3500 *g* for 30 min and then air dried at 30 °C for 48 h. A light microscope was used to verify the separation.

2.3. Microscopy

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 in the study. The magnification was 500 (50 × 10). The A- and B-type granules were dispersed as 10 mg starch in 1 mL of distilled water in glass vials. Then, a drop of starch suspension was transferred onto a slide and covered by a cover slip. Polarized light was used to for observation.

2.4. X-ray diffraction (XRD)

XRD analysis was performed by an X'Pert PROX diffractometer (Panalytical, Almelo, Netherlands) operated at 40 mA and 40 kV, using Cu Kα radiation with a wavelength of 0.1542 nm as the X-ray source. Data were obtained at 2θ (θ being the angle of diffraction) of 4–40° using sequential scanning with a scanning speed of 10°/min and scanning step of 0.033°. The samples were equilibrated at 40 °C for 24 h and the moisture of all the samples was about 10% before the analysis. The method by Hermans and Weidinger (1948) was used to calculate the relative crystallinity of each sample.

2.5. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the A-type and B-type granules of wheat starch were measured using a Tensor 37 spectrometer (Bruker, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector. The KBr pellet method was used for the sample preparation. The spectra, recorded against an empty cell as the background, were acquired at wavelength between 400 and 4000 cm^{-1} with 4 cm^{-1} resolution with OPUS software. All spectra were the averages of 64 scans and were baseline corrected and normalized. The absorbance intensities of the bands at about 1047, 1035 and 1022 cm^{-1} were used to investigate the crystalline structures of the A- and B-type granules of wheat starch. All samples had the same moisture content (MC).

2.6. Differential scanning calorimetry (DSC)

A PerkinElmer DSC Diamond-I with an internal coolant (Intercooler 1P) and nitrogen purge gas were used in the experimental study to determine the gelatinization characteristics. A constant MC was maintained during DSC measurements by using a high-pressure stainless steel pan (PerkinElmer No.: B0182901) with a gold-plated copper seal (PerkinElmer NO. 042-191758). The samples were prepared by premixing the A-type or B-type starch granules with added water in glass vials. Starch was weighed accurately into each empty glass vial. Then, the desired mass of water was injected to the vial by a micro-syringe, and was mixed well with the starch granules using a small spatula. The vials were sealed and kept at 20 °C for 24 h before DSC measurements to achieve homogeneous samples. The added water together with the original MC of the starch was taken as the MC of the mixture. About 25 mg sample, scanned from 30 to 100 °C, was used in the study. The slow heating rate of 5 °C/min was used to minimize any temperature lag due to the large mass of the stainless steel pan. The onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and enthalpy (ΔH) of starch gelatinization were recorded. All the results are reported as the averages of 3 replicates. The enthalpy was calculated based on the weight of dry starch.

2.7. Small angle X-ray scattering (SAXS)

SAXS measurements were performed according to our previously method (Zhu, Li, Chen, & Li, 2012) with proper modification using a SAXSess small angle X-ray scattering system (Anton Paar, Austria), operated at 50 mA and 40 kV, using Cu Kα radiation with a wavelength of 0.1542 nm as X-ray source. Each sample was placed in a paste sample cell and was exposed at the incident X-ray monochromatic beam for 10 min. The data, recorded using an image plate, were collected by the IP Reader software with a PerkinElmer storage phosphor system. The samples used for the SAXS measurements were prepared by premixing the starch with added water in glass vials as described above in the DSC study and were equilibrated at 20 °C for 24 h before the analysis. The total MC of each sample was 60%.

The background scattering and smeared intensity were removed by applying the SAXSquant 3.0 software to analyze the SAXS data. The average repeat distance of the amorphous and crystalline lamellae of each sample was calculated by:

$$d = 2\pi/q \quad (1)$$

where d (nm) is the lamellar repeat distance and q (1/nm) is the scattering vector (Suzuki, Chiha, & Yano, 1997). The relationship between q and θ can be calculated by:

$$q = (4\pi \sin\theta)/\lambda \quad (2)$$

where λ (nm) is the wavelength of the X-ray source (Suzuki et al., 1997). The Lorentz method (Stribeck, 2007) was applied to correct SAXS date for further analysis.

3. Results and discussion

3.1. Microscopic morphology

An anisotropic phenomenon normally exists in starch granules because of the orderly arranged starch molecules of crystalline