Lamellar structure change of waxy corn starch during gelatinization by time-resolved synchrotron SAXS

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ABSTRACT

In situ experiment of synchrotron small- and wide-angle X-ray scattering (SAXS/WAXS) was used to study the lamellar structure change of starch during gelatinization. Waxy corn starch was used as a model material to exclude the effect of amylose. The thicknesses of crystalline (d_c), amorphous (d_a) regions of the lamella and the long period distance (d_{ac}) were obtained based on a 1D linear correlation function. The SAXS and WAXS results reveal the multi-stage of gelatinization. Firstly, a preferable increase in the thickness of crystalline lamellae occurs because of the water penetration into the crystalline region. Then, the thickness of amorphous lamellae has a significant increase while that of crystalline lamellae decreases. Next, the thickness of amorphous lamellae starts to decrease probably due to the out-phasing of starch molecules from the lamellae. Finally, the thickness of amorphous lamellae decreases rapidly, with the formation of fractal gel on a larger scale (than that of the lamellae), which gradually decreases as the temperature further increases and is related to the concentration of starch molecular chains. This work system reveals the gelatinization mechanism of waxy corn starch and would be useful in starch amorphous materials processing.

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1. Introduction

Starch is the main component of food and provides an essential energy for humans. Recently, starch has attracted much attention as a renewable polymer resource for eco-friendly uses due to its advantages of biodegradability and low costs (Yu, Dean, & Li, 2006). Starch granules are always heated in water before used, and this results in an order-disorder phase transition, termed “gelatinization”. Gelatinization is one of the most significant processing methods in industry and food application of starch, which determines the proper conversion of starch in the processing of food and emerging biodegradable starch-based materials (Liu et al., 2011).

The structure of native starch granules is a unit entirety and organized in different length scales, i.e., whole granule (μm), growth rings (~0.1 μm), lamellar structure (8–11 nm) and molecular scale (~0.1 nm) (Pérez & Bertoft, 2010; Tran et al., 2011). It is widely recognised that the native starch granule is composed of alternating amorphous and semi-crystalline growth rings. The semi-crystalline growth ring consists of the repeats of alternating amorphous and crystalline lamellae. The amorphous lamellae are related to branch points of the amylopectin side chains, and the crystalline lamellae are formed by the short-chain fractions of amylopectin arranged as double helices and packed in small crystallites, respectively (Witt, Doutch, Gilbert, & Gilbert, 2012). Also, linear amylose molecules and probably less ordered amylopectin are present in an amorphous state within each native granule (Fan et al., 2013; Pérez & Bertoft, 2010).

In our previous papers (Chen, Yu, Kealy, Chen, & Li, 2007; Chen et al., 2011), the changes of granule and growth rings of starch during gelatinization have been studied by light microscopy and confocal light scanning microscopy (CLSM). However, there had been no non-destructive and efficient methods to observe the lamellar structure of starch until the use of SAXS. SAXS measures...
the variations in electron density distributions of amorphous and crystalline lamellae in granule starch (Blazek & Gilbert, 2011). Although the lab SAXS is widely used in starch lamellar structure characterization (Zhang, Chen, Zhao, & Li, 2013), the lab SAXS is still rarely used for in-situ experiments due to its lower light brightness.

Compared with lab-bench SAXS instruments, synchrotron SAXS may offer much higher spectral brilliance, small source size and high beam flux (Koch, 2006). Therefore, synchrotron SAXS is very effective to study the in-situ (real time) lamellar structure change during gelatinization. Vermeylen et al. (2006a & 2006b) have studied the gelatinization behavior of rice starch and potato starch with bound or limited water by in-situ SAXS experiments. It was found that the water content plays a major role in gelatinization and the change of lamellar and crystalline structures during gelatinization. Waigh, Gidley, Komanshek, and Donald (2000) also studied the starch structure change during gelatinization by in-situ SAXS and found two different processes for the A-type and B-type starches. However, the SAXS analysis in their study did not investigate the changes in the amorphous and crystalline layers. Yang et al. (2016) have used synchrotron SAXS coupled with diamond anvil cell (DAC) to study the effect of high hydrostatic pressure on starch gelatinization and used the correlation function to reveal the change in thickness of the crystalline and amorphous layers during this process.

In this study, synchrotron SAXS and WAXS were used to in-situ study the lamellar structure of waxy corn starches during gelatinization. Waxy starches were selected as a model material since there is nearly no amylose starch in its lamellar structure and waxy starch shows a clear peak corresponding to the lamellar phase. The correlation function was used to analyze the in-situ synchrotron SAXS results of waxy starch in excess water. Those studies would help to probe the changes in waxy starch amorphous and crystalline layers during gelatinization.

2. Material and method

2.1. Sample and sample prepared

Waxy corn starch with the amylose/amylopectin ratio of 0/100 was obtained from Lihua Starch Industry Co. Ltd. (Qinhuaingdao, China). The amylose content was determined by the method of concanavalin A while the moisture content (MC) (about 10%) of each sample was determined using a moisture analyzer (MA35, Sartorius Stedim Biotec GmbH, Germany). Distilled water was added to the starch to obtain a starch: water ratio of 1:3 (w/v) in a glass vial and equilibrated 24 h for SAXS/WAXS tests.

2.2. Differential scanning calorimetry

The gelatinization behavior of starch was determined by a differential scanning calorimeter (200 F3, Netzsch, Germany) equipped with a thermal analysis data station. Exactly 3 mg of starch were weighed into an aluminum sample pan. Distilled water was added to the starch in the DSC pans with a pipette to obtain a starch: water ratio of 1:3 (w/v) in the DSC pans. When water was added, care was taken to ensure that the starch granules were completely immersed in the water by gentle shaking. The pans were sealed, and the sealed pans were allowed to stand overnight at room temperature before DSC analysis. An empty pan was used as a reference. The pans were heated from 20 to 120 °C at a scanning rate of 10 °C/min. The analysis was undertaken in triplicate. The software of Netzsch Proteus Thermal Analysis Version 6.1.0 was used to analyze the DSC traces.

2.3. Small and wide angle X-ray scattering (SAXS/WAXS)

Synchrotron time-resolved small and wide-angle X-ray scattering (SAXS/WAXS) measurements were carried out at BL16B1 beamline at Shanghai Synchrotron Radiation Facility (SSRF), China. We loaded the suspension (0.70 mL) into 2-mm-thick sample cells, of which the front and back windows were both covered with Kapton tape. Two-dimensional (2D) Mar165 were used to collect the 2D SAXS and WAXS patterns. The wavelength of the incident X-ray was 1.24 Å for both SAXS and WAXS, and the sample to detector distance (SDD) was 1940 mm for SAXS and 115 mm for WAXS measurements. A beef tendon specimen and Cerium oxide (CeO2) were used as standard materials for the calibration of the scattering vector of SAXS and WAXS, respectively. The air and water scattering were subtracted from the original SAXS and WAXS data. A Linkman (STC200) hot stage was used to control sample temperatures, which was calibrated by a temperature calibrator (Fluker 724) with a K type thermocouple (Omega) before use. The temperature rose from 35 to 85 °C, at a speed of 2 °C/min, with a holding time of 1 min. Data were collected at each degree rise and were measured for 60 s 2D SAXS and WAXS patterns were recorded by a Mar165 charge-coupled device (CCD) detector. By measuring sample adsorption using ionization chambers in front and back of the sample cell, we performed data correction, calibrated the SAXS data from the background scattering, and normalized the data on the primary beam intensity. Background subtraction follows the equation: \( I_{bs}(\theta) = I_{rs}(\theta) - \frac{I_{sc}(\theta) + I_{so}(\theta)}{2} \) and \( I_{bs}(\theta) \) and \( I_{rs}(\theta) \) represent the distribution of scattering intensity of samples held in cells, sample cells and pure samples respectively. \( I_{sc}(\theta) \) and \( I_{so}(\theta) \) represent the values of samples held in cells and sample cells, read from the ionization chambers in front of sample cell. \( T_{r} \) and \( T_{f} \) represent the transmissivity of samples held in cells and sample cells.

2.4. SAXS analysis

The normalized 1D correlation function \( \gamma_1(r) \) is defined as

\[
\gamma_1(r) = \frac{\int I(q)q^2 \cos(qr)dq}{Q}
\]

where \( I(q) \) is scattering intensity, \( q \) is scattering vector defined as \( q = 4\pi\sin(\theta)/\lambda(2\theta \text{ is the scattering angle} and r \text{ is the direction along the lamellar stack.}

The scattering invariant, \( Q \), is defined as

\[
Q = \int_{0}^{\infty} I(q)q^2dq
\]

Because of the finite \( q \) range of experimental SAXS data, extrapolation of the 1D SAXS data to both the low and high \( q \) ranges are necessary for the integration of the intensity, \( I(q) \). Extrapolation to low \( q \) was performed using an intensity profile based on Guinier’s law, and the extension of the intensity to large \( q \) values can be accomplished using the Porod-Ru land model (Yang, Liang, & Han, 2015; Yang, Liang, Luo, Zhao, & Han, 2012). The parasitic scattering and thermal fluctuation were corrected using a normalized 1D correlation function.

3. Result and discussion

3.1. Thermal behavior by DSC

DSC is a quick and efficient method to test gelatinization
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