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Shear degradation of corn starches with different amylose contents

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ABSTRACT

This work investigated the effect of shear on the starch degradation, with a particular focus on the changes in molecular and lamellar structures. Corn starches with different amylose/amylopectin ratios (waxy corn starch, or WCS: 1:99; normal corn starch, or NCS: 25:75; and Gelose 80 starch, or G80: 80:20) were used as model materials to be processed using a Haake twin-rotor mixer for different times. Molecular and lamellar structural analysis was performed using size-exclusion chromatography (SEC) and small-angle X-ray scattering (SAXS). The degree of damage of starch at the granule level was evaluated by an assay kit. The results showed that amylose molecules in starch granules did not change significantly, while amylopectin molecules degraded to a stable size caused by the shear treatment. The average thickness of semi-crystalline lamellae disappeared rapidly during processing. A typical positive deviation from Porod's law at a high q region was observed, attributed to the presence of thermal density fluctuations or mixing within phases. Nonetheless, the degree of mixing within phases for the processed samples was lower than the native starch. The study of the mass fractal structure indicated that the scattering objects of the processed starches were more compact than those of the native counterparts. Furthermore, waxy corn starch (containing mostly amylopectin) experienced the greatest granule damage than the other starches. All the results showed that the rigid crystal structure in amylopectin is more sensitive to the shear treatment than the flexible amorphous structure in amylose. This mechanistic understanding at the microstructure level is helpful in designing the processing of starch-based foods or plastics with desired functional properties.

1. Introduction

Starch is the main component of cereal-based foods, which is a primary source of energy for humans. Besides, due to its total biodegradability, low cost, and wider availability, starch has attracted much attention as an important raw material for producing biodegradable plastics to replace some petroleum-based polymers (Yu, Dean, & Li, 2006). Extrusion is commonly used in industry for the processing of starch-based foods and materials. Gelatinization and degradation are two most important phenomena in extrusion processing, affecting the material performance (Liu et al., 2013). Starch degradation during processing has shown to be strongly correlated to the mechanical properties of starch-based materials (Li, Hasjim, Xie, Halley, & Gilbert, 2014; Liu, Halley, & Gilbert, 2010).

It is well known that the multi-scale structure of the starch granule is mainly composed of amylose and amylopectin. These two macromolecules are the basis of the aggregation and granule structure of starch and provide an excellent conceptual approach to the understanding of the structure-processing-property relationships of natural polymers (Pérez & Bertoft, 2010; Wu, Witt, & Gilbert, 2013; Liao et al., 2014). Amylose is a linear molecular with a few long branches, whereas amylopectin is highly branched, containing ~5% branching points and a large number of short branches (Damager, Engelsen, Blennow, Lindberg Møller, & Motawia, 2010). The outer parts of amylopectin branches (A and B_1 chains) form clusters of double helices, which build up the

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crystalline lamellae; and the internal parts (B_2, B_3 and C chains) locate in the amorphous lamellae (Jane, Xu, Radosavljevic, & Seib, 1992). The alternating crystalline and amorphous lamellae with a ~9 nm repeat distance collectively form the semi-crystalline growth rings in a starch granule (Calvert, 1997; Damager et al., 2010). Amylose is in either amorphous or single helical conformation and is interspersed among amylopectin molecules (Jane et al., 1992; Lopez-Rubio, Flanagan, Gilbert, & Gidley, 2008).

The mechanical shear in extrusion processing induces gelatinization, with the breakage of the crystalline structure of starch (Xie, Halley, & Avérous). This process is entirely different from the usual gelatinization process under heat-moisture treatment (Zhang, Chen, Liu, & Wang, 2010) or annealing (Liu, Yu, Simon, Dean, & Chen, 2009). In our previous paper, the lamellar structure of starch during gelatinization process was studied by synchrotron-SAXS/WAXS (Kuang et al., 2017; Zhang et al., 2015). It was observed that, before the gelatinization temperature, the lamellar peak intensity decreased, and the thickness of crystalline lamellae increased, whereas the size of both amorphous and crystallinity lamellae disappeared rapidly around the gelatinization temperature. However, there have been no comprehensive studies on the change of starch lamellar structure under shear treatment.

On the other hand, shear may also induce the change in the molecular size of starch. Liu et al. (2010) and Li et al. (2014) have used size-exclusion chromatography (SEC) to investigate the degradation mechanism of corn starch during extrusion. They found that the mechanical energy played a dominant role in reducing the starch molecular size, and amylopectin in starch granules was more susceptible to shear degradation than amylose. However, as extrusion is a process involving a complex flow and multiple temperature sections, it is difficult to obtain a precise understanding of the relationship between processing conditions and the resultant structure of starch.

Recently, an internal twin-rotor mixer has been used to understand the gelatinization (Wang et al., 2010; Xue, Yu, Xie, Chen, & Li, 2008) and chemical modification (Qiao et al., 2014; Qiao et al., 2012) of starch during processing. A HAAKE Rheomix twin-rotor mixer can not only be used a processing device, but also serves as a rheometer to accurately monitoring the processing conditions (Yang, Bigio, & Smith, 1995). This device can represent a short section of an extruder so it could be useful to understand the processing-structure relationship in a simpler manner. Yet, the change of the multi-level starch structure during kneading using a twin-rotor mixer has not been reported.

In this study, corn starches with different amylose/amylopectin ratios were used as model materials to reveal the shear-induced starch degradation during kneading. The molecular and lamellar structures were studied by SEC and small-angle X-ray scattering (SAXS), respectively. The information obtained from this study would help to understand the shear degradation mechanism and to design new starch materials with accurately-controlled structures.

2. Material and method

2.1. Sample and sample prepared

Commercially-available corn starches with different amylose contents were used in this experimental work. Waxy corn starch (WCS) (1% amylose content) was supplied by Lihua Starch Industry Co., Ltd. Normal corn starch (NCS) (25% amylose content) was provided by Huanglong Food Industry Co., Ltd. Gelose 80 starch (G80) (80% amylose content) was supplied by National Starch Pty Ltd. (Lane Cove, NSW 2066, Australia).

Starch and water were pre-mixed in a high-speed mixer (capacity 10 L, SRLW 10/25, Fanchang machinery Co. LCD, China) at 1000 rpm for 5 min. An infrared heating balance (Model DHS-20, Longway & Yueping, Shanghai, China) was used to measure the moisture content during heating the sample to 110 °C for 20 min. The total moisture content (about 35%) of a specimen was taken as the sum of the original starch moisture content and the added water.

2.2. Haake rheometer

A Haake Rheocord Polylab RC500p system incorporating a HAAKE Rhemix 600p twin-rotor mixer (ThermoHaake, Germany) was used in the experimental work. This equipment was described in detail previously (Wang et al., 2010; Xue et al., 2008). The material was introduced into the mixer through a top-mounted loading hopper, and torque and temperature were recorded immediately after loading. The roller speed of 75 rpm and initial temperatures 70 °C were used. The samples were collected at different times (0, 2, 5, 7, 10 and 15 min) and ground into power using a cryo-grinder (ZM200, Retsch) under liquid nitrogen for further analysis.

2.3. Size-exclusion chromatography

The molecular size and size distribution of fully-branched and debranched starch molecules were measured using size-exclusion chromatography (SEC) (Tran et al., 2011). The extracted native starch granules (about 6 mg) were dissolved in DMSO/LiBr solution and then debranched using isoamylase in acetate buffer (pH ~3.5), following the method of Li, Hasjim, Dhital, Godwin, and Gilbert (2011). Then, the weight size distributions of fully-branched and debranched starch molecules were analyzed in duplicate using SEC (Agilent 1260 series, Agilent Technologies, Santa Clara, California, USA) equipped with a refractive index detector (Optilab T-rEX, WYATT Corp., USA). The injection volume was 100 μL, the flow rate was 0.3 mL/min, and the column oven temperature was at 80 °C. A series of columns (GRAM precolumn, GRAM 30, and GRAM 3000 analytical columns, Polymer Standard Services, Mainz, Germany) were used to analyze the size distribution of fully-branched starch molecules. Another series of columns (GRAM precolumn, GRAM 100, and GRAM 1000 analytical columns, Polymer Standard Services, Mainz, Germany) were used to analyze the size distribution of debranched starch molecules. A series of pullulan standards (Polymer Standard Services, Mainz, Germany) with varying molecular weights ranging from 342 to 2.35×10^6 Da were used for calibration to obtain the relationship between the SEC elution volume and the hydrodynamic volume V_h (which is the separation parameter for SEC). Data are presented as the SEC weight distribution, $w(\log V_h)$, as a function of the corresponding hydrodynamic radius R_h, with $V_h = (4/3)\pi R_h^3$. Because the largest standard had a hydrodynamic radius of ~50 nm, this is the maximum size at which calibration is reliable. The dependence of R_h on elution volume for larger sizes was obtained by extrapolation of the calibration curve and thus are only semi-quantitative, and also sensitive to day-to-day variations (Wang, Hasjim, Wu, Henry, & Gilbert, 2014).

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

Synchrotron small-angle X-ray scattering (SAXS) measurements were carried out at the BL16B1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF), China. Distilled water was added to the starch in a glass vial to obtain a starch suspension with the starch:water ratio being 1:3 (w/v). The suspension was equilibrated for 24 h before SAXS tests. Then, the starch suspension (0.70 mL) was loaded into a 2-mm-thick sample cell, of which both the front and back windows were covered with the Kapton tape. Two-

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