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Disruption and molecule degradation of waxy maize starch granules during high pressure homogenization process

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ABSTRACT

The mechanism underlying the fragmentation of waxy maize starch (WMS) granules during high-pressure homogenization (HPH) was studied and the results were interpreted in terms of granular and molecular aspects. The diameter of disrupted starch granules decreased exponentially with increasing HPH pressure, but decreased linearly with increasing of HPH cycles. Scanning electron microscopy revealed a cone-like inside-out disruption pattern through the channels that resulted in separation of blocklets fragments or starch fragments. The M_w of amylopectin was reduced by ~half following treatment at 150 MPa with two cycles, or at 100 MPa for eight cycles, and the decrease was in accordance with the disruption of starch granules. This indicated that amylopectin was "protected" by blocklets, and the disruption of WMS granules mainly occurred close to the linkage among blocklets. Increasing the HPH pressure appeared to be more effective for breaking starch granules than increasing the number of HPH cycles.

1. Introduction

High pressure homogenization (HPH) is extensively used to emulsify, disperse and mix substances in the chemical, pharmaceutical, specialty food and biotechnology industries (Floury, Desrumaux, Axelos, & Legrand, 2002). During HPH treatment, liquids simultaneously experience high shear, turbulence, cavitation, and velocity gradients caused by a rapid change in pressure (Brookman & James, 1974). At a specific energy output, HPH treatment can introduce novel changes to products, and high pressure technologies not only affect the emulsion stability, but also other processed constituents such as particles, colloids or macromolecules (Paquin, 1999). Based on the economic and efficient benefits of HPH approaches, researchers are now exploring novel applications involving microorganism and enzyme inactivation, modification, extraction/isolation and the preparation of new products. (1) HPH is used widely to disrupt microorganism cell walls, resulting in membrane debris and/or collapsed cells (Donsì, Ferrari, Lenza, & Maresca, 2009; Gogate & Pandit, 2008; Maresca, Donsì, & Ferrari, 2011; Tribst, Franchi, Cristianini, & De Massaguer, 2009). (2) Furthermore, HPH treatments can improve the properties of processed constituents and introduce novel changes. For example, Ulbrich and Flöter found that HPH treatment had a profound effect on the water binding capacity of a cellulose-based fibrous material (Ulbrich & Flöter, 2014), and homogenates display surface activity at the water-oil and water-air interfaces that contribute to a change in the digestibility of products (Le Thanh-Blicharz, Lewandowicz, Błaszczak, & Prochaska, 2012). (3) In terms of extraction and isolation, HPH can be used to de-agglomerate rice starch-protein aggregates, isolate nanocellulose from sugarcane bagasse, and extract peanut proteins and phenolic acids (Dong et al., 2011; Guraya & James, 2002; Li et al., 2012; Zhu et al., 2016). (4) Additionally, HPH can be used in the preparation of new products through force-induced cavitation, shear, turbulence and temperature rises. Consequently, new products with novel changes would be prepared (An, Lee, Choi, Kim, & Shin, 2014).

As one of the most abundant naturally occurring polysaccharides, starch is widely used in the paper, textile, adhesive, and food industries. Currently, starches are frequently processed by HPH either individually or with other components to: (1) impart novel functional properties, (2) prepare new products or (3) isolate starch from other constituents. Wang et al. (2008) investigated the effects of HPH on the thermal characteristics of normal maize starch, and described a decrease in gelatinization temperature or gelatinization enthalpy with increasing homogenizing pressure

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(Wang et al., 2008). Meanwhile, Augustin, Sanguansri, and Htoon (2008) investigated the effect of high-pressure microfluidization on a suspension of resistant starch (RS), and identified a novel functional RS ingredient with increased viscosity and water-holding capacity (Augustin et al., 2008). HPH can also alter the digestibility of maize starch paste and starch water sorption isotherms (Le Thanh-Blicharz et al., 2012; Santos et al., 2014). Liu, Wu, Chen, and Chang (2009) prepared starch nanoparticles with a particle size in the range of 10–20 nm using HPH at a pressure of 207 MPa, without affecting the crystal structure or thermal stability (Liu et al., 2009). HPH was also used to facilitate the preparation of starch-fatty acid complexes (Meng, Ma, Cui, & Sun, 2014; Meng, Ma, Sun, Wang, & Liu, 2014). Guraya and James (2002) demonstrated that rice starch-protein agglomerates could be physically disrupted in the presence of water using high-pressure microfluidization (Guraya & James, 2002). Similarly, Kasemwong, Ruktanonchai, Srinuanchai, Itthisoponkul, and Sriroth (2011) studied the effects of high-pressure microfluidization on the structure of cassava starch in granular state and found that the crystalline order was disrupted, larger starch granules were partially gelatinized, and a gel-like structure was formed on the granular surface (Kasemwong et al., 2011). During HPH, starch granules experience a very high energy input per mass of product. Consequently, it is expected that HPH can not only influence the structure and physical properties of starch, but also the quality and quantity of molecules (amylose/amylopectin) in the final product. However, limited information is available on the molecular degradation of starch granules despite some studies on the changes occurring in granules (Blaszczak, Fornal, Valverde, & Garrido, 2005; Kasemwong et al., 2011; Modig, Nilsson, Bergenståhl, & Wahlund, 2006; Oyeyinka, Singh, Ma, & Amonsou, 2016; Tu et al., 2010; Wang, Li, Wang, Liu, & Adhikari, 2012). A detailed understanding of the molecular mechanism underlying the disruption of starch granules by HPH therefore remains of fundamental importance.

In our previous study, we explored the degradation mechanism of gelatinized amylopectin during HPH treatments (Wei, Cai, Jin, & Tian, 2016). Whereas, the amylopectin in waxy maize starch (WMS) granules show the properties of crystallinity, which was quite different from that in the gelatinized state. Consequently, it could be proposed that the degradation of amylopectin lies in the aspects of granule and molecules. In the present study, WMS granules, a common raw material in the food, medicine and cosmetic industries, were investigated to study its disruption mechanism during HPH treatments. A WMS suspension was homogenized under different pressure-cycle regimes at 4 °C and the resulting samples were characterized by particle size distribution, scanning electron microscopy (SEM), X-ray diffraction (XRD) and high-performance size-exclusion chromatography (HPSEC) equipped with multi-angle laser light scattering (MALLS) and refractive index (RI) detectors. The results could provide important information for developing modified starch using HPH approaches, and might help to broaden the use of HPH in industries utilizing starch products.

2. Materials and methods

2.1. Materials

WMS was donated by Tianjin Tingfung Starch Development Co., Ltd. (Tianjin, China). Dimethyl sulfoxide (DMSO, HPLC grade) was purchased from Sigma Chemical Co., (Shanghai, China). Dextran T40 and T2000 standards were purchased from GE Healthcare/Pharmacia (Code Nos. 17-0270-01 and 17-0330-01, respectively). All other reagents (analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Suzhou, China).

2.2. HPH treatments of WMS granules

In order to explore the interacting effects of pressure and the number of cycles, HPH was performed at 50, 100, and 150 MPa for two cycles. Additionally, 2, 4, 6, and 8 cycles were performed at 100 MPa. WMS granules were homogenized at 4 °C in order to avoid gelatinization using a high-pressure homogenizer equipped with an online cooling system (LABOR-PILOT 2000/4-SH5, IKA, Germany). A WMS suspension (1%, w/v) was prepared by adding starch to deionized water at 4 °C. A 200 mL suspension was processed in each pressure-cycle interval at a flow rate of 20 mL/min.

2.3. Particle size distribution (PSD)

Native or homogenized WMS suspensions (1%, w/v, 4 °C) were pretreated by Ultra-Turrax T20 (IKA, Germany) for 3 min at 3000 rpm to prevent aggregation, and samples were tested immediately. The dispersion was analysed from triplicate samples using a Microtrac S3500 particle size analyser (Microtrac Inc., North Largo, FL, USA). The amount and direction of light scattered by the particles were quantified using optical detector arrays, and further processed and analyzed using Microtrac Software. The Bluewave S5118 analysis mode was used, and the refractive index for fluid and particle were set to 1.33 and 1.53, respectively. A spherical particle shape was assumed.

2.4. Field emission scanning electron microscopy (FE-SEM)

FE-SEM was performed using an S-4800 instrument (Hitachi, Japan) at an acceleration voltage of 1 kV. A drop of starch and homogenized WMS suspensions were spread onto a copper grid coated with carbon support film and allowed to dry at room temperature. Samples were then coated with gold by ion sputtering (40 s) using a Hitachi E-1010 apparatus for observation.

2.5. XRD and relative crystallinity (RC)

Native and homogenized starches were lyophilized, milled into powder (200 mesh) and hydrated in a sealed vessel at relative humidity of 75% (using saturated sodium chloride). Samples (0.8 g) were pressed into a pellet (10 × 25 mm) using a hydraulic press. XRD patterns were obtained using a Bruker D8-Advance XRD instrument (Bruker AXS Inc., Karlsruhe, Germany). Diffractograms were obtained at 40 kV and 30 mA using nickel-filtered Cu-K_α radiation (wavelength = 1.5405 Å). The samples were scanned from 3° to 35° (2θ) at a rate of 4°/min and in triplicate. The ratio of the crystalline portion as a fraction of the sum of crystalline and amorphous portions (RC) and the diffraction angle (2θ) from XRD patterns were analyzed by Jade 5.0 software (Materials Data Inc., CA, USA), and quantitatively estimated as described previously (Nara & Komiya, 1983).

2.6. Sample preparation for HPSEC-MALLS-RI

Solutions of native and homogenized starch granules were obtained by solubilizing 60 mg (dry basis) of lyophilized samples with the mobile phase in a boiling water bath with constant stirring (1 h). Then it was continually stirred for another 24 h at 25 °C. Each sample was filtered by PTFE membrane filter (5.0 μm) and a 200 μL was injected into the HPSEC system for analysis.

The HPSEC system include an LC-20AB pump and a manual injection valve (200 μL) (Hewlett-Packard, Valley Forge, PA, USA). The detection parts include a MALLS detector (Dawn EOS, Wyatt Technology, Santa Barbara, CA, USA) with a He–Ne laser source (k = 658.0 nm), RI detector (model 2414, Waters, USA) and a K-5 flow cell. Two organic *SEC* columns (Styragel HMW 6E DMF 250