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Recrystallization characteristics of high hydrostatic pressure gelatinized normal and waxy corn starch

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ABSTRACT

High hydrostatic pressure (HHP) can lead to starch gelatinization at room temperature, while the retrogradation mechanism of HHP gelatinized starch is not well known. HHP gelatinized normal and waxy corn starches were stored at room temperature for 192 h in order to investigate the retrogradation characteristics. The scanning electron microscopy (SEM), polarised light microscopy and differential scanning calorimetric (DSC) analysis showed that the pressurization of normal and waxy corn starch suspensions with concentration of 30% (w/v) at 600 MPa for 15 min resulted in a complete gelatinization. In addition, the pressure-gelatinized normal and waxy corn starch gels were stored and subjected to X-ray diffraction (XRD) analysis, resistant starch content determination, swelling power and pasting behavior. The retrograded normal maize and waxy maize starch showed a substantial loss of A-type crystallinity. Both pressure-gelatinized normal and waxy corn starches showed an increase in resistant starch content and relative crystallinity degree with the increase of storage time. In addition, restricted starch swelling power and lower pasting viscosities were observed for these two retrograded starches. The amylose molecule within starch granules has been regarded as the main factor to affect the structural and physicochemical properties during the retrogradation process of HHP-gelatinized starch granules.

1. Introduction

Starch retrogradation is an inevitable property of gelatinized starch and is more likely to occur during the storage of starch-based products. Through the process of retrogradation, the starch molecules change from a disordered state to a more ordered or apparent crystalline form. Retrograded starch has some unique properties such as lower solubility, poor susceptibility to acid and enzyme hydrolysis, and not easy to form complex with iodine ions [1,2]. The uses of native starches have been largely restricted due to their high retrogradation tendency during storage, transportation and distribution that decrease their shelf lives and consumer acceptance. However, starch retrogradation technology has been used to prepare resistant starch (RS) or slowly digestible starch (SDS) [3], which is beneficial to the prevention of diabetes diseases, and controlling or preventing hyperglycaemia-related diseases [4,5].

Retrogradation involves amylose and amylopectin chains forming an ordered helical aggregation and an increasing crystalline state between amylose and amylopectin molecules [6]. Starch retrogradation can be divided into short-term and long-term retrogradation. Amylose is attributed to the short-term retrogradation, while the long-term retrogradation is mainly related to amylopectin. Long-term retrogradation is a much slower process, could decrease the digestibility of the starch by amylase [7,8]. Traditionally, it is believed that heat processing is the most common technique for starch gelatinization, thus the scientific researchers have always concentrated more on the retrogradation mechanism of thermal gelatinized starch.

However, as an alternative to conventional thermal processing, high pressure technology has been extensively used to gelatinize or physically modify different kinds of starch suspensions [9–12]. Moreover, if pressure is high enough, starch gelatinization can be performed at room temperature. It is generally believed that high pressure technology provides a new possibility for processing of starch-based food and applying starch to food products [13]. For example, the HHP-treated starch granules maintain an intact granular form and possess partially and/or completely gelatinized granule interiors, which may have great potential to be used as a carrier to protect and/or transport nutrients [16]. Recently, this technology has activated a new dimension in the field of food

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sciences and technology in relation to the modification of macromolecule such as starch gelatinization and protein denaturation, preserving foods or modifying their eating and functional properties [14,15].

Over the past two decades, application of HHP as a means of gelatinization or physical modification of starch has been focused on effects of various treatment parameters including pressure level, starch source, starch concentration, temperature, and treatment time, on the physicochemical and structural properties of HHP-treated starch granules to elucidate the mechanism of pressure-induced gelatinization of starch granules [11,12,16]. The results from the previous studies suggest that HHP gelatinized starch showed different physicochemical and structural properties and a different molecular mechanism of gelatinization compared to the heat-gelatinized one. However, published articles with respect to retrogradation mechanism of HHP gelatinized starch are very limited. Therefore, the aim of the present study was to investigate the physicochemical and structural properties of HHP gelatinized starch during their retrogradation process at room temperature. Accordingly, the changes in starch swelling power, gelatinization, pasting behavior and crystalline structure of HHP gelatinized normal and waxy corn starch were investigated during storage for 196 h at room temperature for retrogradation. The changes in resistant starch content at different retrogradation time were also analyzed.

2. Materials and methods

2.1. Materials

Normal corn starch was purchased from Xi'an Guowei Starch Co., Ltd., Xi'an, China, while the waxy corn starch was purchased from Shandong Huanong Special Corn Development Co., Ltd., Dezhou China. The amylose/amylopectin ratios for normal and waxy corn starch are 22/78, and 0/100, respectively. Other chemical reagents used in this study were of analytical grade.

2.2. High pressure treatment

Starch dispersions with concentration of 30% (w/w) were sealed (about 200 mL) in 500 ml polyethylene bags under vacuum and pressure treated at 300, 450, and 600 MPa for 15 min using a high pressure vessel (L2-600/0.6, Tianjin Huatai Senmiao Biotechnology Co., Ltd., Tianjin, China). The rate of pressure rise was about 350 MPa/min. The pressure-transmitting liquid medium was deionized water. Immediately after 15 min of HHP treatment, pressure was released automatically to atmospheric pressure. Then the 300 and 450 MPa treated samples were vacuum-filtered and freeze-dried to obtain dry starch samples, while the 600 MPa pressurized starch gels were stored at room temperature for 0, 3, 6, 12, 24, 48, 96 and 192 h to conduct the retrogradation studies. After each storage time, each of resulting starch gels was freeze-dried and ground with a laboratory-scale grinder (FW100, Tianjin Test Instrument Co., Ltd., Tianjin, China). The retrograded starch samples were passed through a 100-mesh sieve and stored in an airtight container at room temperature for further analysis.

2.3. Microscopy observation

2.3.1. Scanning electron microscopy (SEM)

A starch sample was mounted on an SEM stub using double sided adhesive tape and coated with a thin layer of gold to make the sample conductive. SEM micrographs were taken using a scanning electron microscope (JSM-6360LV, JEOL, Japan).

2.3.2. Light microscopy

Starch sample was suspended in a 1:1 glycerol solution (glycerol/H_2O, v/v) and was observed under a microscope (DMBA400, Motic China Group Co., Ltd, Guangzhou, China) using polarised light at 40-times magnification.

2.4. Determination of thermal properties

Thermal properties were performed using a differential scanning calorimeter (DSC Q2000; TA Instruments, New Castle, USA) under ultra high-purity nitrogen atmosphere. 3 mg (dry base, db) of each starch sample was directly measured into the aluminum pan and 12 μL of distilled water was added with a microsyringe, and an empty pan was used as reference for all measurements. The scanning temperature and the heating rates were 30–120 °C and 10 °C/min, respectively.

2.5. X-ray diffraction analysis

X-ray powder diffraction (XRD) measurements were analyzed using an X-ray diffractometer (Rigaku d/max2200pc, Rigaku Corporation, Tokyo, Japan) under the following conditions: radiation source, CuKa (40 kV, 50 mA); angle of diffraction scanned from 5° to 60°; step size, 0.02; step time, 2 s. Prior to the XRD test, the starch samples were equilibrated in a 100% relative humidity chamber for 48 h at room temperature to avoid the influence of relative humidity on relative crystallinity. The relative crystallinity degrees of the starch granules were calculated as the percentage of the area of peaks to the total area of the diffractogram.

2.6. Determination of resistant starch content

Resistant starch (RS) content was determined with the Megazyme Resistant Starch Assay Kit (Megazyme Int. Ireland Ltd. Co., Wicklow, Ireland) using AACC-approved method 32–40 [17]. Starch sample (100 mg) was hydrolyzed by the mixture of α-amylase and amyloglucosidase (AMG) at 37 °C for 16 h in a shaking water bath. The reaction was stopped by the addition of ethanol, and resistant starch was recovered as a pellet by centrifugation. The pellet was dissolved in 2 M KOH by vigorously stirring in an ice water bath. This solution was neutralised with acetate buffer, and the starch was quantitatively hydrolyzed to glucose with AMG. Glucose released, which is a measure of resistant starch content, was determined spectrophotometrically at 510 nm using a glucose oxidase assay (GOPOD reagent).

2.7. Granule swelling power

Starch swelling power (SP) was determined at 50 °C, 60 °C, 70 °C, 80 °C, and 90 °C, respectively, according to the procedure described by Leach et al. [18]. Aqueous suspensions of 2% starch (w/v) were heated in a water bath at 50, 60, 70, 80, and 90 °C for 30 min. Each suspension was cooled and centrifuged at 3000 × g for 15 min; the decanted supernatant was weighed and was placed in a vacuum stove at 105 °C for 16 h. The SP was determined as follows: SP = weight of sediment × 100/(weight of dry sample solids × (100 − solubility)).

2.8. Determination of pasting properties

Pasting characteristics of starches were determined using a Rapid Visco Analyser (RVA, Super-4, Newport Scientific, Pty Ltd, Australia), and Thermocline for Windows software. Each 3.0 g (dry basis, db) of starch sample was directly weighed into RVA canisters, followed by the addition 25 ml of distilled water. The slurry was then manually homogenized using the plastic paddle to avoid