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Effect of microwave irradiation on internal molecular structure and physical properties of waxy maize starch

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ABSTRACT

Native waxy maize starch was treated at a moisture content of 30% by microwave irradiation for 5 min, 10 min and 20 min, respectively. The molecular structure and physical properties of waxy maize starch were characterized. Compared with native maize starch, lower population of short chains of amylopectin (A chain), higher proportion of short B_1 and long B_2 and B_3 were observed in irradiated starches. ^{1}H NMR data showed that α-(1,6) glycosidic linkages were destroyed more easily than α-(1,4) glycosidic linkages during microwave treatment. A increase in gelatinization temperatures and a decrease in the molecular weight, the relative crystallinity, ΔH, viscosities and syneresis were observed after microwave treatment. Gelatinization temperatures were positively correlated with long chains B_3 with DP > 36, while ΔH and syneresis were negatively correlated with them. The extent of the changes induced by microwave treatment for different times revealed that the major degradation occurred in internal chain (amorphous region) at the first stage (microwave treatment for 5 min), the external chain (crystalline region) mostly destroyed at the second stage (microwave treatment for above 10 min). The foregoing data indicated that the molecular structure of amylopectin is a critical factor determining physical properties.

1. Introduction

Starch is one of the most important storage reserve of carbohydrates in plants. Starch contains mainly two types of biomacromolecules: amylopectin and amylose, of which amylopectin is commonly considered as the major component in starch (Gayin, Abdel-Aal, Manful, & Bertoft, 2016). Amylose is essentially a linear α-1,4-linked D-glucopyranosyl chain of approximately 1000 residues, whereas amylopectin has numerous branch points that form by a-1,6 linkages joining linear chains (Yang et al., 2015; Yao, Zhang, & Ding, 2002). The amylopectin is an extremely large branched molecule, but there is extensive order of the fine structure of amylopectin molecules in native starch granule and it is believed to adopt an efficiently packed, cluster structure (Sanderson, Daniels, Donald, Blennow, & Engelsen, 2006). These starch chains can be classified as either the unbranched outermost chains (A chain) or the branched inner chains (B chain) (Syahariza, Li, & Hasjim, 2010; Yao et al., 2002). Meanwhile, there is a single chain (C chain) per molecule which contains a sole reducing residue (Van Hung, Phi, Thi, Vy, & Thi, 2012). The B chains were further divided into short B_1 chain (DP 12–24), B_2 chain (DP 24–36) and B_3 chain (DP > 36) (Kong et al., 2015; Van Hung et al., 2012; Yoo & Jane, 2002).

There are three broad classifications of starch modifications: chemical, physical, and enzymatic modifications. Microwave irradiation creates heat deep inside the materials being processed as a result of rapid alterations of the electromagnetic field at high

Abbreviations used: HPAEC-PAD, High performance size exclusion chromatograph; GPC-MALS, Gel permeation chromatography coupled with multiangle light scattering; XRD, X-Ray diffraction; DSC, Differential scanning calorimetry; CLD, Chain length distribution; DB, Degree of branching; wms-ns, Native maize starch; wms-m5, Waxy maize starch treated by microwave irradiation for 5 min; wms-m10, Waxy maize starch treated by microwave irradiation for 10 min; wms-m20, Waxy maize starch treated by microwave irradiation for 20 min; PT, Pasting temperature; PV, Peak viscosity; BD, Breakdown; SB, Set back; FV, Final viscosity; BU, Brabender unit.

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frequency (Chandrasekaran, Ramanathan, & Basak, 2013; Zhu, Li, Zhang, Li, & Zhang, 2016). Hence, it results in a shorter process time, higher yield and better quality of products than that obtained by conventional processing techniques (Colman, Demiate, & Schnitzler, 2014). So far, many researchers study the effect of microwave irradiation on the properties of waxy maize starch including granular properties, gelatinization and pasting properties, molecular weight distributions, ratio of amylose to amylopectin, thermal dynamics and dielectric properties, etc (Chandrasekaran et al., 2013; Colman et al., 2014; Man et al., 2012; Sanderson et al., 2006; Szepes et al., 2005; Zeng et al., 2016). It is evident that microwave irradiation can induce the rearrangement of crystalline regions within the starch granules and lead to physicochemical properties change, including water absorption ability, swelling power, and paste viscosity, to an extent (Braşoveanu & Nemţanu, 2014). Microwave irradiation causes a shift in the gelatinization range to higher temperatures, and a drop in viscosity and crystallinity which may be due to the molecular rearrangements restricted to sections of the starch molecules (Luo, He, Fu, Luo, & Gao, 2006). The pasting properties of both waxy and non-waxy starches show significant changes after microwave irradiation (Xie, Yan, Yuan, Sun, & Huo, 2013; Zhang, Chen, Zhao, & Li, 2013; Zhu et al., 2016). However, few works have been given for chain length distribution in waxy maize starch, the change of α-1,6 glycosidic bond and α-1,4 glycosidic bond, the relationship between molecular structure and physical properties under microwave irradiation.

The aims of this work were to investigate the influence of microwave irradiation on chain length distribution, molecular weight, the change of α-1,6 glycosidic bond and α-1,4 glycosidic bond, particle size distribution, crystalline structure, thermal properties, pasting properties and freeze-thaw stability. The relationship between internal molecular structure and physical properties were also discussed.

2. Materials and methods

2.1. Materials

Waxy maize starch was purchased from Qinhuangdao Lihua Co. Ltd., (Hebei, China) with a moisture content of 12.85%. Isoamylase (Megazyme, 1000 U/mL) and pullulanase (Megazyme, 700 U/mL) in this study were purchased from Megazyme (Wicklow, Ireland). All other reagents were of analytical grade.

2.2. Microwave irradiation treatment of waxy maize starch

Waxy maize starches were adjusted to 30% (w/w) moisture content by the addition of an appropriate amount of water to native maize starch of known moisture content. The moistened starch samples were placed in glass Petri dishes with the diameter 15.4 cm which were put in the center of the microwave chamber to form a circle, and sealed with a perforated polyethylene film designed for microwave ovens. 10 g of samples put in one Petri dish were irradiated with microwave at 1600 W (160 W/g) for 5 min using a Galanz microwave oven (DG26T-016C2, Shunde, China) at 2450 MHz frequency and repeated 7 times. And then, 7 samples were mixed for the further analysis. The samples irradiated for 10 min and 20 min were prepared according to the foregoing procedure. The experiments were repeated three times.

2.3. Amylopectin fractionation and chain length distribution (CLD) determination

Amylopectin fractionation and purified amylopectin from native and irradiated waxy maize starches followed previous methods based on butanol-alcohol precipitation with a slight modification (Kong, Bertoft, Bao, & Corke, 2008; Kong et al., 2015). Purified amylopectin (9 mg) was dissolved in 450 μL of 100% DMSO with constant stirring overnight. The solution was then diluted with 2250 μL of Milli-Q water, and 300 μL of 0.1M sodium acetate buffer (pH 4.5), 1 μL of isoamylase and 1 μL of pullulanase were added. The debranching reaction was conducted at room temperature with constant stirring overnight and was terminated by heating. The sample was centrifuged and filtered (pore size 0.45 μm) before injected into the HPLC system.

The chain length distributions of debranched samples were analyzed with a method modified from a previous report using a high performance anion-exchange chromatography (HPAEC) system (Dionex ICS-5000+, Sunnyvale, CA) coupled with a BioLC gradient pump and a pulsed amperometric detector (PAD) (Kong et al., 2008). The PAD signal was recorded by Chromeleon software (Version 6.8) and corrected to carbohydrate content. Prior to loading of the sample, the column (250 mm × 4 mm, Carbo-Pac PA-100 with a guard column) was eluted at a rate of 1 mL/min with 150 mM NaOH for 20 min and then with a mixture of 150 mM NaOH (eluent A, 93%) and 150 mM NaOH containing 1 M NaOAc (eluent B, 7%) for 20 min. The elution gradient with a rate of 1 mL/min was as follows: from 0 to 1.3 min, 93% eluent A; from 1.3 to 10 min, eluent A changed from 93 to 82% linearly; from 10 to 19 min, from 82 to 78%; from 19 to 111 min, from 78 to 50%; from 111 to 113 min, from 50 to 93% (after which it returned to the starting mixture). The sample was injected during the initial 1.2–1.3 min.

2.4. Gel permeation chromatography coupled with multiangle light scattering (GPC-MALS)

Starch samples were prepared as described with some modifications (Man et al., 2012; Zhang et al., 2013). A GPC coupled with MALS (Waters, America) and refractive index detector was used to determine the molecular weight and mean square radius of gyration. The mobile phase was pure DMSO which had been filtered through a 0.45 mm membrane filter (Millipore Co., USA) and degassed by ultrasound before use. A certain amount of sample (5 mg) was heated in 10 mL of DMSO with LiBr (50 mmol/L) at 60 °C for 12 h and then the sample solutions were filtered using a 5 mm membrane filter (Millipore Co., USA) and transferred to sample bottles. A chromatographic column (Styragel HMW 6E, Waters, America), and a wavelength of 623.8 nm laser were used in the experiment. The flow speed was 0.5 mL/min. The data of light scattering were collected and analyzed using Astra V software.

2.5. ^{1}H nuclear magnetic resonance (NMR) spectroscopy

Starch samples were prepared according to the method described by Park, Kim, Cho, Lee, and Kim (2016). Starch samples were dissolved in DMSO-d_6, which is accepted to be one of the most popular solvents in solution. The analysis was carried out at the Laboratory for NMR structural studies on a Bruker Avance II 600 MHz spectrometer. Before proceeding with the NMR measurement, 10 mg of starch samples were completely dissolved in 1 mL DMSO-d_6 for 10–60 min. In this context, the starch samples were kept in oven (60 °C) for 1 h to completely dissolve the sample before NMR test. The NMR data was collected for 16 scans at 25 °C. The chemical shift scale was calibrated using the residual DMSO-d_6 signal at 2.549 ppm (Hoffman, Arzuan, Pemberton, Aserin, & Garti, 2008).

$$\text{Degree of branching (DB) (\%)} = \text{(I-1,6)/(I-1,6 + I-1,4)} \times 100 \quad (1)$$