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Physically modified common buckwheat starch and their physicochemical and structural properties

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ABSTRACT

Structural and physicochemical properties of physically modified buckwheat starches prepared using alcoholic-alkaline, drum-drying and ball-milling treatment were investigated and compared. The results showed that all of the treatments caused a significant increase in solubility and swelling power. SEM observations revealed that the starch granules obtained by different modified method exhibited a various morphological characteristics. X-ray diffraction showed that the crystallinity pattern of granular cold water soluble starch (GCWS) and micronized starch (MBS) changed from A-type to V-type, whereas pre-gelatinized starch (PGBS) granule exhibited a minor B-type pattern. DSC analysis showed that different treatments caused a significant lowering of the gelatinization enthalpy. RVA measurements revealed that the starch suspension viscosity of GCWS and MBS granules decreased compared to native starch, while PGBS granules exhibited an opposite trend. The present study will provide fundamental information of the GCWS, MBS and PGBS starch for their potential industrial application.

1. Introduction

Buckwheat is a member of the Polygonaceae family, which includes common buckwheat (*Fagopyrum esculentum*) and tartary buckwheat (*Fagopyrum tataricum*). Buckwheat has been widely cultivated in Asia, Eastern, Central Europe and North America as an important constituent of foods such as pancakes, noodles, pasta, salad, tea and buckwheat bread blended with flour from other cereals, and has many beneficial health aspects (Neethirajan, Tsukamoto, Kanahara, & Sugiyama, 2012; Takahama & Hirota, 2010). Common buckwheat has proved to be a good source of carbohydrate, protein, lipid, vitamin, dietary fiber and minerals (Zieliński, Michalska, Amigo-Benavent, del Castillo, & Piskula, 2009). Among these nutrients, starch hold the highest content, buckwheat flour contains 70–91% (w/w) of starch depending on the flour types, and buckwheat starch consists of about 25% amylose and 75% amylopectin (Qin, Wang, Shan, Hou, & Ren, 2010). In specially, buckwheat starch also has a unique structural property by containing a substantial amount of long-chain amylopectin fractions (12–13%) (Yoshimoto et al., 2004).

Like any other variety of starch, native buckwheat starch could be widely applied in food and nonfood industry as a thickener, binder, film and foam. However, the applications of native starch in modern industry have suffered from a limited degree because of their disadvantages such as insolubility in cold water, low shear and thermal resistance, thermal decomposition, and high tendency toward retrogradation (Majzoobi et al., 2011). These shortcomings could be overcome through modification of native starch. Starch modification is mainly applied to alternate the original physicochemical properties of native starch and make them suitable for specific food and industrial application. The properties and functionalities of starch modification can be modified through chemical, physical, enzymatic and genetic methods or a combination of them (Hong & Gu, 2010; Singh, Kaur, & McCarthy, 2006). Amongst the different methods available for production of modification starch, physical methods have received more attention since they are chemical free and fairly easier compared to the other methods (Majzoobi et al., 2011). The purpose of physical modification of starch is to change the granular structure and convert native starch into cold water-soluble starch or small-crystallite starch (Lewandowicz & Soral-Śmietana, 2004).

The physical modification of starch can be achieved through alcoholic-alkaline, drum-drying and micronization method (Hong & Gu, 2010; Majzoobi et al., 2011; Ren, Li, Wang, Özkan, & Mao, 2010). Pre-gelatinized starch (PGS) is one of the most common

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types of physically modified starch with wide applications, especially in food industry. PGS starches, also referred to as instant starches, is generally produced through produced by drum drier, spray drier and extruder (Karapantsios, 2006; Majzoobi et al., 2011). Granular cold water soluble starches (GCWS) can be prepared by various patterns such as heating of starches in aqueous alcohol, high temperature, high pressure and alcoholic-alkaline treatment (Singh & Singh, 2003). GCWS starches exhibit greater viscosity, smoother texture and have more processing tolerance as compared to traditional pre-gelatinized starches (Hong & Gu, 2010). Micronized starch generally made by a vacuum ball-grinding machine. In the process of micronization, starch granules flake off layer by layer from their surface edge to the interior, ultimately break into anomalous, small granules by means of forces between grinding balls and starch granules (Ren et al., 2010).

During the process of different kinds of modifications, starch granules underwent degradation, hydration, swelling, loss of crystallinity, and changes in viscosity (Hong & Gu, 2010; Lewandowicz & Soral-Śmietana, 2004; Ren et al., 2010). These changes made the structural and physicochemical properties of modified starches different from native starches. As the physicochemical properties of starch will affect the functional properties of starch-based foods, the understanding of structural and physicochemical properties of starch is vital for the development of new starch applications. In present study, the structural and physicochemical properties of modified buckwheat starch prepared by alcoholic-alkaline, drum-dried and micronizated treatment were evaluated, individually. The results could serve as a theoretical basis to introducing new applications for buckwheat starch in food and non-food applications.

2. Materials and methods

2.1. Materials

Buckwheat flour used in this study was obtained from Huan County in Gansu Province, China. All chemicals reagents used in experiments were of analytical grade (Chemical Company, Beijing, China).

2.2. Isolation of starch

Buckwheat flour was presoaked in 0.02 M anhydrous sodium sulfite solution water for 2 h at 50 °C. The flour was then blended and centrifuged at 4000 rpm for 10 min. The supernatant was discarded and the top yellow protein layer was removed. The white starch layer was resuspended in distilled water and centrifuged, and this process was repeated until the yellow layer was no longer visible. The sedimented starch was re-suspended in 0.05 M sodium hydroxide aqueous solution for three times to remove the protein and lipids. The extracted buckwheat starch was then suspended in the wash buffer (1 M Tris–HCl, pH 6.8; 0.1 M EDTA Na_2; 4% SDS) for two times. The starch was washed with distilled water 3 times and air-dried at 45 °C to obtain the dry isolated buckwheat starch. The extracted buckwheat starch had starch, protein, fat and ash contents of 90.9%, 0.43%, 0.6 and 0.39%, respectively.

2.3. Preparation of starch samples

2.3.1. Preparation of cold water soluble buckwheat starch

The granular cold water soluble starches (GCWS) were prepared according to Singh and Singh (2003) using alcoholic-alkali method with some modifications. A mixture of dry buckwheat starch (50 g) and 1000 ml of 80% ethanol (w/w) was heated to 70 °C and with a continuously stirring until the starch granules are fully dispersed. Then 200 ml of 15.75 M NaOH solution was weighed and added in the starch–ethanol slurry slowly under stirring. The mixture was held at the reaction temperature of 70 °C for 80 min with gentle stirring. The slurry obtained was then left at room temperature (25 °C) until the starch granules settle down. The clear supernatant was decanted, while the sediment starch was re-suspended in another 500 ml of 80% ethanol solution and neutralized with 3 M HCl. The starch was then washed with 85% ethanol solutions for two times and dehydrated with absolute ethanol. The dehydrated starch obtained was dried at 45 °C in an air oven. The dried starch was grounded and passed through no: 100 (BSS) sieve to obtain the granular cold water soluble buckwheat starch.

2.3.2. Preparation of pre-gelatinized buckwheat starch

Pre-gelatinized buckwheat starches (PGS) were prepared through a twin drum drier. Buckwheat starch was first dispersed in cold water (37%, w/v), then, it was dried using a twin drum drier at drum speed of 3 rpm, steam pressure of 5 bar, clearance between the drums of 0.4 mm and the surface temperature was 150 °C. The dried starch sheet was milled and then passed through no: 100 (British standard screen scale, BSS) sieve to obtain the pre-gelatinized buckwheat starch.

2.3.3. Preparation of micronized buckwheat starch

A high-energy nano impact mill (Laboratory-type, CJM-SY-B, Taiji Nano Products Co. Ltd., Qinhuangdao, China) was used for the preparation of micronized buckwheat starch samples. Buckwheat starch was dried at 60 °C in an air oven to ensure that the moisture content was less than 6%. The volume ratio of grinding media and starch was 2:1, and milled for 8 h.

2.4. Microscopy analysis

2.4.1. Scanning electron microscopy (SEM)

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

2.4.2. Light microscopy

Starch sample was suspended in a glycerol/H_2O solution (1:1, V/V) and was observed using a polarizing light microscope (DMBA400, Motic China Group Co., Ltd, Guangzhou, China) with a ×40 objective.

2.5. X-ray diffraction analysis

X-ray powder diffraction (XRD) measurements were performed 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. To avoid the influence of relative humidity on relative crystallinity, the starch samples were equilibrated in a 100% relative humidity chamber for 48 h at room temperature.

2.6. Determination of light transmittance

Light transmittance of starch solution (1%, w/w in water) was measured according to the method of Craig, Maningat, Seib, and Hoseney (1989).