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Preparation and physicochemical properties of three types of modified glutinous rice starches

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ABSTRACT

Hydroxypropylated, phosphorylated, and hydroxypropyl-phosphorylated starches were prepared from glutinous rice starch, and their physicochemical and structural properties were investigated. With increasing reaction time, the molar or degree of substitution of modified starches increased. SEM micrographs revealed that phosphorylated starch granules retained their relative integrity, while some cracks appeared on the surface of hydroxypropylated and hydroxypropyl-phosphorylated starch granules. RVA analyses revealed that pasting properties improved after chemical modification. Additionally, chemical modification improved freeze-thaw stability, especially in hydroxypropyl-phosphorylated starch. DSC analyses showed that onset temperature and gelatinization enthalpy decreased with increasing reaction time, especially in the dual-modified starch. X-ray diffraction patterns revealed that native and modified starches had A-type crystalline patterns. FT-IR spectra showed some minor spectral differences after modification. ^{13}C CP/MAS NMR spectra showed that a novel peak appeared at 20 ppm after hydroxypropylation and that the relative intensity signals in the C4 region increased after phosphorylation.

1. Introduction

Glutinous rice, a.k.a., waxy or sweet rice, is characterized by the lack of amylose (Lian, Wang, Zhang, & Li, 2014). In China, glutinous rice is commonly used as raw material in traditional food products including sweet dumplings, sweets, desserts, rice cakes, and baked rice crackers (Gao, Li, Bi, Mao, & Adhikari, 2014a; Gao, Zhang, & Zhou, 2014b). Due to its indigestibility, glutinous rice is not used in main dishes, leading to lower economic value. However, the value-added of glutinous rice can be improved through deep processing. Starch, which is the main component of glutinous rice, has several unique characteristics: small granule morphology, no off-odors, and pleasant taste. In addition, glutinous rice starch is hypoallergenic (Ma & Sun, 2009). However, glutinous rice starch has some disadvantages, which limit its applications. Glutinous rice starch granules are normally insoluble in cold water, requiring thermal heat to achieve dissolution. Moreover, gelatinized glutinous rice starch molecules are easily losing their viscosity and thick power, forming stiff and non-transparent gels during cooling and storage (Mahmoud, Salah, Said, Mohamend, & Zagazig, 2000a). Starch modification is often used to overcome these limitations (Balasubramanian, Sharma, Kaur, & Bhardwaj, 2014).

Chemical modification, including acid-modified, oxidation, esterification, etherification, crosslinking, and enzymatic modification, was commonly used in starch modification (Zhang, Liao, & Gui, 2007). It usually improves the properties of native starches via the introduction of functional groups (Karim, Sufha, & Zaidul, 2008). The introduction of functional groups contributes to the stabilization of starch pastes and gels and reduces retrogradation (Singh, Kaur, & McCarthy, 2007). Hydroxypropylation is a commonly used starch chemical modification method. The etherification of starch with propylene oxide in alkaline environments results in hydroxypropylated starch, which has lower gelatinization temperature and enthalpy, higher paste transparency, higher cold water solubility, and improved freeze-thaw stability compared with native starch (Gunaratne & Corke, 2007; Kim & Yoo,

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2010; Monireh, Abdorreza, Marzieh, & Abd, 2013). Phosphorylation represents another starch modification method, which improves starch emulsification, gelling, and digestibility (Mahmoud, Said, Salah, Mohamed, & Zagazig, 2000b). Nel and Wang (2005) reported that the freeze-thaw stability, swelling ability, and water binding capacity of the phosphorylated glutinous corn starches were improved and the retrogradation decreased.

Dual chemical modification introduced two kinds of functional groups, the functional properties benefits from each individual modification (Thewika, Piyarat, & Thawien, 2014). To the best of our knowledge, few studies have investigated glutinous rice starch chemical modification. To improve the physicochemical properties of glutinous rice starch, the aim of the present work was to modify glutinous rice starch by hydroxypropylation, phosphorylation, and hydroxypropyl-phosphorylation, and further studied the effect of reaction time on their thermal properties, freeze-thaw stability, and pasting properties.

2. Materials and methods

2.1. Raw materials

The glutinous rice starch was isolated in our laboratory by the alkaline method following the procedures of Lin, Xiao, Zhao, Li and Yu (2009). The main components of glutinous rice starch are as follows: moisture 9.97%, ash 0.28%, protein 0.64%, fat 0.85%, amylose 8.58%, and amylopectin 91.42%.

2.2. Preparation of modified glutinous rice starch

2.2.1. Hydroxypropylation

The preparation of hydroxypropylated glutinous rice starch was performed according to the method reported by Pham and Naofumi (2005) with some modifications. Starch (100 g, dry basis) was suspended in 150 ml distilled water containing 1 g NaOH and 10 g Na_2SO_4 in a 500-ml round-bottom flask. After adjusting the pH to 11.5 with 0.1 M NaOH and replacing the air with nitrogen gas, 10 g propylene oxide was added to the mixture, and the flask was immediately sealed. The flask was kept in a 40 °C water bath with continuous shaking for 0, 30, 60, 90, 120, and 150 min, and 12, 18, and 24 h, respectively, in order to produce different products. The slurry was adjusted to pH 6.0–6.5 with 1 M HCl. The hydroxypropylated starch was isolated by centrifugation (3000*g*, 10 min), washed three times with water, oven-dried at 40–45 °C, ground, and sieved.

2.2.2. Phosphorylation

The preparation of phosphorylated glutinous rice starch was performed by the method reported by Mahmoud et al. (2000a) and Hu (2014) with some modifications. Phosphorylation was allowed to take place for 0, 30, 60, 90, 120, and 150 min. Anhydrous disodium hydrogen phosphate (Na_2HPO_4, 4.5 g) and sodium dihydrogen phosphate dehydrate ($NaH_2PO_4{\cdot}2H_2O$, 2.5 g) were dissolved in 200 ml distilled water. After adjusting the pH to 5.5–6.0, glutinous rice starch (100 g, dry basis) was suspended in the solution. The mixture was stirred for 20–30 min, and the slurry was vacuum-filtered using a Büchner funnel. The retentate was dried at 55–60 °C for 10–12 h. Subsequently, the mixture was ground, dried at 60–65 °C for 90 min, transferred into an airtight container under vacuum, and heated at 150 °C for 0, 30, 60, 90, 120, and 150 min in an oil bath, respectively. Following the heat treatment, the product was allowed to cool and mixed with 50% (v/v) aqueous methanol for 30 min. Subsequently, the product was vacuum-filtered using a Büchner funnel, and the resulting retentate was mixed with anhydrous ethanol and deionized water. Following vacuum filtration, the phosphorylated starch was dried in an oven at 40–45 °C, ground, and sieved.

2.2.3. Hydroxypropylation-phosphorylation

We firstly prepared hydroxypropylated glutinous rice starch by using the method described in Section 2.2.1 with the reaction time of 24 h, and then we conducted the phosphorylation of the hydroxypropylated glutinous rice starch based on the method described in Section 2.2.2 to prepare hydroxypropyl-phosphorylated glutinous rice starch.

2.3. Determination of molar substitution in hydroxypropylated glutinous rice starch

The molar substitution (MS) of hydroxypropylated starch was determined by the method reported by Zhao, Liu and Liu (2011). Hydroxypropyl content was calculated using the following formula (Bongkot, Chureerat, & Vilai, 2007):

$$\text{Hydroxypropyl groups } (\%) = \frac{c \times 0.7763 \times 10 \times F}{w}$$

where, c is the amount of propylene glycol in the sample, F is the dilution factor, and W is the weight of the sample. MS was calculated using following formula (Monireh et al., 2013):

$$\text{MS} = \frac{162 \times W}{100 - (M-1) \times W}$$

where, W is the equivalent hydroxypropyl group amount in 100 g of starch and M is the molecular weight of C_3H_6O.

2.4. Determination of degree of substitution in phosphorylated and hydroxypropyl-phosphorylated glutinous rice starch

The phosphorus content in phosphorylated and hydroxypropyl-phosphorylated glutinous rice starch was determined by the method reported by Jiang, Ni and Wu (1999). Degree of substitution (DS) was calculated using the following formula (Khanitta & Syed, 2010):

$$\text{DS} = \frac{162 \times P}{3100 - 102 \times P}$$

where, P is the % phosphorus content (w/w, dry basis) in the starch samples.

2.5. Starch granule morphology

SEM micrographs were obtained with a Hitachi S-4800 cold field emission SEM (Tokyo, Japan) operated at an accelerating voltage of 3.0 kV. The samples were added to double-sided adhesive tape mounted on an aluminum stub and coated under vacuum with a thin film of platinum.

2.6. Pasting properties

Pasting properties were determined with a Rapid Viscosity Analyzer (RVA, Super3 Newport Co. Ltd., Australian) using the method reported by Pawinee et al. (2008) with some modifications. Aqueous starch dispersions (3.5 g dried starch in 25 ml distilled water) were held at 50 °C for 1 min, heated from 50 °C to 95 °C within 4 min, held at 95 °C for 2.5 min, allowed to cool to 50 °C within 4 min, and held at 50 °C for 1.5 min. The RVA plot, i.e., viscosity (cP) versus time (min), was used to determine the pasting properties of the starches (Balasubramanian et al., 2014).