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Determination of optimum experimental conditions for preparation and functional properties of hydroxypropylated, phosphorylated and hydroxypropyl-phosphorylated glutinous rice starch

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ABSTRACT

Optimization of the preparation of hydroxypropylated, phosphorylated and hydroxypropyl-phosphorylated glutinous rice starch was performed using a response surface methodology comprising three variables at three levels. Multi-linear regression was used to fit the degree of substitution and molar substitution against. Optimal reaction conditions were 9 h, 42 °C, 10% (hydroxypropylated), 148 min, 150 °C, 7% (phosphorylated) and 95 min, 140 °C, 7.8% (hydroxypropyl-phosphorylated). For hydroxypropylated, predicted optimal and experimental molar substitution values were found to be identical: 0.20. Both the phosphorylated and hydroxypropyl-phosphorylated, the predicted optimal and experimental degree of substitution values was 0.02. Static rheological analysis revealed a pseudoplastic nature for native and modified starches and an increase in apparent viscosity following modification. Dynamic rheological analysis indicated an entanglement network system for native glutinous rice starch suspension, but weak elastic gel-like structure for modified starches as the storage modulus (G') exceeded the loss modulus (G"). Additionally, chemical modification improved the freeze-thaw stability, swelling power, solubility and paste clarity.

1. Introduction

Glutinous rice, one kind of rice, is usually used as raw material in various traditional foods such as sweet dumpling, rice cakes, and desserts [1]. Because of the indigestibility, it usually can't be used as principal food, resulting in its low value-added. But the economic value can get improved through deep processing. Starch, an environmentally friendly biodegradable material, is the main component of glutinous rice, and has its unique characteristics compared to other starch, such as small granule morphology, no off-odor, having smooth taste and hypoallergenic, which make it become irreplaceable [2]. However, there are still some disadvantages for the application of native starch, such as the lack of pasting consistency and stability, which restrict the further use of glutinous rice starch and pave the way for development of modified starch having desirable functional properties such as solubility, texture, adhesion and dispersion [3].

Chemical modification involves the introduction of functional groups into the starch molecule, including esterification, etherification, cross-linking, oxidization and decomposition (acid or enzymatic hydrolysis), resulting in markedly altered physicochemical properties [4], depending on the degree of substitution (DS) or molar substitution (MS). Hydrophilic moieties such as hydroxypropyl and phosphate groups increase the viscosity, paste clarity, and freeze-thaw stability [5]. Kim & Yoo reported that hydroxypropylated starch is a popular modified form that is widely used in the food industry [6], due to the resultant low gelatinization temperature and enthalpy, increased paste clarity, freeze-thaw stability and solubility in cold water [6,7]. Phosphorylation is another common chemical modification that introduces an ionic group [8,9], and this can have a major impact on rheological and other properties by increasing viscosity and generating a clearer gel that is beneficial for many industrial applications, such as in frozen foods, in bread and cakes, in meat products, and so on [10]. Dual modification introducing two different functional groups can be used to improve native starch properties above those afforded from separate modifications [11].

The MS or DS of chemically modified starch depends on several process parameters such as reaction time, reaction temperature,

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and addition of reagents. Since these parameters often interact, their optimization during preparation and processing is important. To this end, a response surface empirical modelling approach can be used to evaluate the relationship between experimental parameters and observed results. This powerful mathematic approach facilitates a rapid and efficient analysis of the effects of multiple variables or factors, alone or in combination [12]. Based on our previous study [2], the objective of this study was to further optimize reaction conditions for the preparation of hydroxypropylated, phosphorylated and hydroxypropyl-phosphorylated glutinous rice starch evaluating MS and DS, and to generate reference values for the preparation of modified glutinous rice starches. The functional properties of native and three types of modified glutinous rice starch were investigated to provide information on their application in the food industry and exploited a new field for the application of glutinous rice.

2. Material and methods

2.1. Materials

Glutinous rice (Wankennuo NO. 1, Wandao 2010025, widely cultured in Anhui Province) as the material to prepare glutinous rice starch was kindly provided by Bengbu Brothers Grain and Oil Co,. Ltd (Anhui, China).

Glutinous rice starch was isolated in the laboratory by the alkali steeping method. The main components of glutinous rice starch were as follows: moisture 7.76%, ash 0.29%, protein 0.62%, fat 0.75%, amylose 8.02%, amylopectin 91.98%.

Chemical compounds: Sodium dihydrogen phosphate dihydrate (PubChem CID: 23673460); Disodium hydrogen phosphate anhydrous (PubChem CID: 24203); Propylene oxide (PubChem CID: 6378); Sodium Sulfate (PubChem CID: 24436).

2.2. Preparation of modified waxy rice starches

2.2.1. Preparation of hydroxypropylated glutinous rice starch

Hydroxypropylated glutinous rice starch was prepared according to the method described by Pham & Naofumi [13] with slight modifications. The water-bath time changed to 0, 8, 12, 16, 20 h, the temperature changed to 30, 35, 40, 45, 50 °C, and the concentration of propylene oxide changed to 6, 10, 14, 18, 22%.

2.2.2. Preparation of phosphorylated glutinous rice starch

Glutinous rice starch was phosphorylated using the method of Mahmoud et al. [9] and Hu [14] with some modifications. The oil-bath time changed to 0, 90, 120, 150, 180 min, the temperature changed to 120, 130, 140, 150, 160 °C, and the concentration of phosphate changed to 1, 4, 7, 10, 13%.

2.2.3. Preparation of hydroxypropyl-phosphorylated glutinous rice starch

We firstly prepared hydroxypropylated glutinous rice starch under the optimal reaction condition (9 h, 42 °C, 10%), and then the hydroxypropylated glutinous rice starch was phosphorylated using the method in section 2.2.2 to prepare the hydroxypropyl-phosphorylated glutinous rice starch.

2.3. Determination of the molar substitution (MS) of hydroxypropylated waxy rice starch

The molar substitution (MS) of hydroxypropylated starch was determined as reported by Zhao et al. [15], and the hydroxypropyl content was calculated using the following formula [16]:

$$\text{Hydroxypropylgroups}\,(\%) = \frac{c \times 0.7763 \times 10 \times F}{w} \quad (1)$$

In which 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 the following formula [17]:

$$\text{MS} = \frac{162 \times W}{100M - (M - 1) \times W} \quad (2)$$

where W is the equivalent number of hydroxypropyl groups in 100 g of starch and M is the molecular weight of C_3H_6O.

2.4. Determination of the degree of substitution (DS) of phosphorylated waxy rice starch and hydroxypropyl-phosphorylated waxy rice starch

The phosphorus content of phosphorylated and hydroxypropyl-phosphorylated glutinous rice starch was determined by the method described by Jiang et al. [18]. Degree of substitution (DS) was calculated using the following formula [19]:

$$DS = \frac{162 \times P}{3100 - 102 \times P} \quad (3)$$

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

2.5. Characterisation of functional properties

2.5.1. Static rheological properties

Static shear rheological properties were investigated using an R/S + CC rheometer

(Brookfield Corporation, USA). Static shear (shear stress and shear rate) data were obtained over a shear rate range of 0-1000/s s-1 at 25 °C. Shear stress versus shear rate was used to characterize flow behaviour by fitting to the power law model as follows:

$$\tau = \mathrm{k} \cdot \gamma^n \quad (4)$$

where τ is the shear stress (Pa), γ is the shear rate (s^{-1}), k is the consistency index (Pa s^n), and n is the flow behaviour index.

2.5.2. Dynamic rheological properties

Dynamic rheology properties were analyzed with a HAAKE RheoStress 6000 (Thermo Scientific, USA) by the method described by Capitani et al. [20] with some modifications. The oscillation measurement procedure was selected with the strain set at 10%, a frequency sweep range of 0.1–10 Hz and a temperature of 25 °C. The rheometer data analysis software was used to obtain experimental data and calculate the storage modulus (G') and loss modulus (G"). The tangent of phase difference, or loss tangent (tan δ = G"/G') was calculated to provide additional information on the relationship between elastic and inelastic components.

2.5.3. Freeze-thaw stability

Freeze-thaw stability was determined by the method reported by Yang et al. [2]. The freeze-thaw cycles of native and modified starches were repeated 21 times.

2.5.4. Swelling power and solubility

The method described by Rungtiwa et al. [21] was adopted for the determination of both swelling power and solubility of native and modified glutinous rice starches.

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