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Thermal and rheological properties of brown flour from *Indica* rice

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ABSTRACT

The thermal, paste and rheological properties of brown flours from four *Indica* rice subspecies with different amylose content were examined using Differential scanning calorimetry (DSC), Brabender Viscometer and rheometer. Peak, final and setback viscosities ($p < 0.05$) increased with increasing amylose content from Brabender micro Visco-Amylo-Graph (MVA), but the phase transition temperatures of brown rice flour from DSC ($p < 0.05$) decreased with increasing amylose content. Rheological properties were determined by steady shear, small amplitude oscillatory shear (SAOS) and thixotropic experiments. SAOS results showed a gel-like viscoelastic behavior with G' higher than G''. Steady-shear results showed that the brown rice flour exhibited a non-Newtonian shear-thinning behavior and the flow curves can be well described by the Herschel-Bulkley model. The upward-downward rheograms showed that brown rice flour gel, except IR-1, had a hysteresis loop, indicating a strong thixotropic behavior.

1. Introduction

Rice is an excellent source of energy for about half world's human and it is particularly important in Asia's food consumption. Brown rice, produced by dehulling the grain, is considered as a whole grain food and its color may be light brown, green, reddish or black (Gunaratne et al., 2013). White rice, also known as milled rice or polished rice, is currently the most common form consumed. Compared with white rice, brown rice flour has an amount of fiber (non-starch polysaccharides, NPS) and bioactive molecules such as polyphenol, which can reduce the risk of chronic diseases including hypercholesterolemia, cardiovascular disease, and type II diabetes (Frolich et al., 2013). Recently, brown rice has drawn increasing attention due to its additional health benefits.

The thermal and rheological properties are important to understand brown rice processing and digestion in human. For example, flow behavior, thixotropy and dynamical viscoelastic properties are most important properties in rheology, which are related to production processing and application. In detail, small oscillatory frequency sweep is extremely sensitive to the structure information of samples, which makes it useful to evaluate gelation behavior and kinetics (Liu et al., 2015), and it can provide some additional information such as structure and energy consumption. The rheological properties are also important to the analysis of flow conditions in product processes and prediction of product stability (Li et al., 2014). Rheological properties also correlate to the textural attributes, which in turn determine the sensory characteristics and consumer acceptability of the products (Li et al., 2014).

The thermal, pasting and rheological properties of brown rice flour have been reported (Ibáñez et al., 2007; Varavinit et al., 2003; Wu et al., 2013; Zhu et al., 2010). Wu et al. (2013) showed that the gelatinization temperature exhibited no significant differences between the brown rice flour and isolated starch. However, the pasting viscosity of starch is several times higher than that of brown flour (Zhu et al., 2010). Ibáñez et al. (2007) have studied the viscoelastic properties of waxy and non-waxy rice flours. After removal of protein and lipids with aqueous alkaline or detergent solutions, pasting temperatures decreased, but the viscosities of both starches increased. The rheological properties of rice flour are also shown to be affected by damaged starch content and particles size (Asmeda et al., 2016) as well as apparent amylose content (Kong et al., 2015a).

Rheological properties of rice flour are of high importance to design new products with desired sensory and textural attributes. However, the comprehensive and systematic study on the

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rheological properties of brown rice flour is still limited. In this work, *Indica*, a main rice subspecies cultivated in South China, was used to investigate the rheological properties of gels produced from brown rice flour using steady and oscillatory shear experiments. This work provides an important reference to the brown rice application.

2. Material and methods

2.1. Raw materials

Four *Indica* rice (IR) cultivars from China main rice production area (such as Guangdong, Hunan province) were used in this study (Table 1). All the brown rice was harvested in the year of 2014 and stored at 4 °C. Beihan1# was kindly provided by Shandong Academy of Agricultural Science, while Jinnongsimiao and Yuxiangyouzhan were kindly provided by Guangdong Academy of Agricultural Science, China. Xing2# was supplied by Hunan Jinjian Seed Industry Science & Technology Co., Ltd.

2.2. Sample preparation

Before all tests, the raw rice grains were dehulled to produce brown rice (with bran layers and germ still intact). In this study, rice grains were de-husked (BLH-3250, Zhejiang Bethlehem, China) and grounded to pass through a 100-mesh sieve on a Cyclone Sample Mill (CT410, Foss Scino, China) for further use.

2.3. Chemical analyses

Protein content (N content x5.95) was determined by combustion (AACC method 46-11A) using Automatic Kjeldahl Nitrogen Analyser (Kjeltes2300, FOSS, Inc, USA). Total starch content was measured by Megazyme assay kit (K-TSTA 09/14) from Megazyme International Ireland Ltd. (Co. Wicklow, Ireland) following the manufacturer's instructions. Amylose content of starches was analyzed in triplicate with an amylose/amylopectin assay kit (Megazyme International Ireland Ltd., Bray, Co. Wicklow, Ireland). Total fat was measured using a Soxhelt extractor, with petroleum ether as the extraction solvent (AACC method 08-01).

2.4. Pasting properties of brown rice flour

The pasting properties were monitored using a Brabender Micro Visco-Amylo-Graph (MVA) (Brabender OHG, Duisburg, Germany) according to the classic method (Mariotti et al., 2005, 2009). 12 g of the sample was dispersed in 100 mL of distilled water, scaling both flour and water weight on 14% flour moisture basis. The suspensions were subjected (stirring at 250 RPM/min and using a 300 cm·gf cartridge) to the following standard temperature profile: heating from 30 °C up to 95 °C at a rate of 7.5 °C/min, holding at 95 °C for 5 min, cooling from 95 °C to 50 °C at a rate of 7.5 °C/min and holding at 50 °C. The pasting temperature range was obtained as the range between the temperature at the start of increase of viscosity and that at which it remains constant. The peak, breakdown, and setback viscosity were also recorded.

2.5. Differential scanning calorimetry

Thermal transition measurements of brown rice flour were determined using a Modulated Differential Scanning Calorimeter MDSC 2920 instrument (TA Instruments Inc., Delaware, USA) equipped with a thermal analysis data station and data recording software. The sample was prepared according to the procedure of Wang et al. (Wang et al., 2014) with a slight modification. Briefly, about 3 mg of samples was weighed into 40 μL aluminum pans. Distilled water was added with a pipette to obtain a water/sample ratio of 3:1 in the DSC pans. The starch-water mixtures were blended gently and left overnight at room temperature before DSC analysis. The pans were heated from 30 to 120 °C at a scanning rate of 10 °C/min and an empty pan was used as a reference. The Universal Analysis 2000 software was used to analyze the main endotherm of the DSC traces for start (T_o), peak (T_p) and conclusion (T_c) temperatures and enthalpy change ($\triangle H$).

2.6. Rheological properties

Starch dispersions (5% w/w) were moderately stirred for 15 min, then heated at 95 °C for 30 min by a magnetic stirrer. The hot paste obtained was immediately transferred to the rheometer plate and cooled down to 25 °C for rheological tests. All the tests were performed in an MCR 301 rheometer (Anton-paar Austria, DE) using a parallel plate geometry (d = 50 mm).

2.6.1. Small amplitude oscillatory shear (SAOS)

Frequency sweep was carried out at 25 °C in a frequency range of 1–100 rad/s with a strain of 0.1, which was within the identified linear viscoelastic regime. The storage modulus (G'), loss modulus (G''), loss tangent ($\tan\theta = G''/G'$) and complex viscosity (η^*) were recorded as a function of frequency (ω).

2.6.2. Steady-shear

Steady shear flow measurements were carried out at 25 °C, and the shear rate increased from 0.01 to 100^{-1}. Shear stress (τ) and steady shear viscosity (η) were recorded as a function of shear rate. Tests were carried out in automatic mode to ensure that steady state at each shear rate was reached.

2.6.3. Thixotropic properties

The thixotropic properties of brown rice flour gel were characterized by using hysteresis experiments which consisted of a three-step operation (upward curve, plateau curve and downward curve). An increasing shear rate ramp at a constant shear rate of 1 s^{-1} to 100 s^{-1}, followed by a plateau at the maximum shear rate for 50 s^{-1}, and thereafter, the ramp was reversed to measure downward flow curve from 100 to 1 s^{-1}, the upward and downward flow curves should be the same for a time-independent liquid and should not superpose in the case of a time-dependent liquid. The area enclosed between up curves and down curves obtained by increasing and decreasing shear rate measurements was calculated by the software in Rheometer of MCR 301.

Table 1
Sources and chemical composition of brown rice power samples.

Code	Cultivar	Protein (%)	Total fat (%)	Total starch (%)	Apparent amylose (%)
IR-1	Beihan1	11.94 ± 0.05^a	3.86 ± 0.16^a	75.52 ± 1.16^a	10.40 ± 0.19^d
IR-2	Xing2	9.28 ± 0.01^b	2.18 ± 0.20^c	75.75 ± 0.89^a	15.90 ± 0.01^c
IR-3	Zhongguangxiang	8.38 ± 0.11^c	2.77 ± 0.21^b	78.21 ± 2.22^a	20.56 ± 1.33^b
IR-4	Yuxiangyouzhan	7.77 ± 0.15^d	2.65 ± 0.02^b	76.95 ± 1.22^a	26.50 ± 0.26^a