



## Pasting and rheological properties of rice starch as affected by pullulan



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### ABSTRACT

Effect of pullulan (PUL) on the pasting, rheological properties of rice starch (RS) was investigated. The swelling power, amylose leaching, and confocal laser scanning microscopy (CLSM) observation of the samples were also conducted to explore the possible interaction between starch and pullulan. Rapid visco-analysis (RVA) showed that PUL significantly changed viscosity parameters of rice starch–pullulan (RS–PUL) mixtures. Dynamic rheological measurements revealed that the modulus ( $G'$ ,  $G''$ ) of the mixtures increased with the increase of pullulan concentration from 0.01% to 0.07%, but then decreased with the increase of pullulan concentration from 0.07% to 0.50%. The pasting and rheological properties of samples indicated that pullulan could blend well with rice starch and promote the gelatinization of starch granules at low concentration of pullulan, but suppress the gelatinization of starch granules at high concentration of pullulan. The results of swelling power, leached amylose and CLSM observation of samples further suggest that the interaction between starch and pullulan occurred in the RS–PUL system and the interaction was hypothesized to be responsible for these results.

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### 1. Introduction

Starch is one of the most important and abundant materials in nature, and possesses extensive applications, such as thickening, gelling, stabilizing, and binding agent in food industry [1]. However, native starch sometimes does not satisfy the requirements of production due to its retrogradation tendency [2–4] and instability under shear and acidic conditions [5]. These changes would bring undesirable effects on the quality of starch-based products.

Physical blending starch with non-starch polysaccharides, as a safe and effective method to modify the quality of native starch, was extensively reported by many researchers. The specific modification of the properties of starch is significant. Wang et al. [6] investigated the effect of flaxseed gum on the rheological properties of maize starch and found that the addition of flaxseed gum was in favor of forming stronger gels and could be used together with starch to get a high apparent viscosity in industrial production. Kim and Yoo [7] indicated that xanthan gum could promote the recrystallization at the beginning of aging, and so increased the modulus of the rice starch–xanthan gum mixtures. Also, Sasaki and Kohyama [8] reported the effects of different non-starch polysaccharides on the characteristics of mixture systems and Tischer et al.

[9] reported on the influence of iota-carrageenan on the rheological properties of different starches. It was widely accepted that the addition of non-starch polysaccharides in starch system evidently changed the characteristics of starch and the interaction between starch and non-starch polysaccharides was considered to play an important role in determining the properties of these combination systems [10,11].

Pullulan is a typical linear exocellular polysaccharide produced by *Aureobasidium pullulans*. It has a starch-like structure of linkage  $\alpha$ -D-glucan primarily consisting of maltotriose repeating units interconnected by  $\alpha$ -(1→6) linkages, resulting in a stair-step structure [12]. The regular structure conferred pullulan some distinctive properties compared to other polysaccharides, such as enhanced solubility and preferable film forming ability [13,14]. Pullulan, as an important non-starch polysaccharide, has been widely used in food industry, especially the production of edible film [15]. Physicochemical properties of pullulan have been extensively studied in model aqueous system [16,17].

However, researches focused on the effect of pullulan on the physicochemical properties of starch were limited, and the knowledge about the interaction between pullulan and starch was still insufficient. Rice and rice starch products are staple foods in oriental countries, therefore, in the present study, the rice starch was chosen as a model to assess the interaction between starch and pullulan. The main objectives of this work were: (1) to investigate the effect of pullulan on the pasting, and rheological properties of

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rice starch; (2) to explore the interaction between rice starch and pullulan; (3) to offer the possibility of modifying the quality of rice starch by means of blending starch with pullulan. Such studies are meaningful in exploring the potential utilization of microbiological polysaccharides to improve the processing characteristics, storage stability of rice starch-based foods.

## 2. Materials and methods

### 2.1. Materials

Rice starch was obtained from Jiangsu Baby Corporation (Suqian, China). It contained 0.23% proteins, 0.68% free lipids, 23.30% amylose, and 11.82% moisture. Pullulan was purchased from Hayashibara Biochemical Inc. (Shanghai, China). The moisture content and molecular weight of pullulan were 4.50%, and 200,000 MW, respectively.

### 2.2. Sample preparation

The rice starch (5%, w/v)–pullulan (0.01, 0.04, 0.07, 0.1, 0.3, and 0.5%, w/v) mixtures (RS–PUL) were prepared as follows. Briefly, various quantities of pullulan were dissolved thoroughly in 100 mL of distilled water in closed tubes, and then 5 g of rice starch (dry weight) was added. The mixtures were dispersed at room temperature by magnetic stirring for 30 min. Then, the RS–PUL mixtures were heated at 95 °C in a water bath for 20 min with continuous stirring to obtain a complete gelatinization of the rice starch. Lastly, the hot mixtures were allowed to cool down slowly to 25 °C. Rice starch without pullulan was used as a control.

### 2.3. Pasting properties

Pasting properties of RS and RS–PUL mixtures were determined by using a rapid visco-analyzer (RVA-RECHMASTER, Newport Scientific Pty. Ltd., Sidney, Australia). The pasting parameters were measured following the general pasting method (STD 2). Sample was equilibrated at 50 °C for 1 min, heated to 95 °C within 7.5 min, and then held at 95 °C for 5 min. The hot sample was subsequently cooled to 50 °C within 7.5 min, and maintained at 50 °C for 4 min. Paddle speed was 960 rpm for the beginning 10 s to disperse the sample, and then the speed of paddle was set at 160 rpm during the measurement. Pasting parameters included peak viscosity, trough viscosity, final viscosity, breakdown value, and setback value and the viscosity parameters were expressed in cP units in present study.

### 2.4. Rheological measurements

Rheological measurements were carried out using an AR G2 rheometer (TA instrument Inc., USA). Parallel plate geometry (60 mm) at gap 500  $\mu\text{m}$  was used for both steady shear and small amplitude oscillatory measurements. Samples were transferred to the rheometer plate at 25 °C. The excess material was wiped off with a spatula. Silicon oil was applied to the exposed surfaces of samples to prevent evaporation during experiments. The sample was allowed to rest for 5 min in order to equilibrate stresses before starting the test.

Steady shear experiments were performed over the shear rate range of 0.1–10  $\text{s}^{-1}$ . According to Barnes et al. [18], the shear rate range of present study included three parts and could simulate the shear effect which the food materials subjected in producing procedures.

The frequency sweep tests were performed at 25 °C over the frequency range of 0.1–10 Hz, and the strain value for

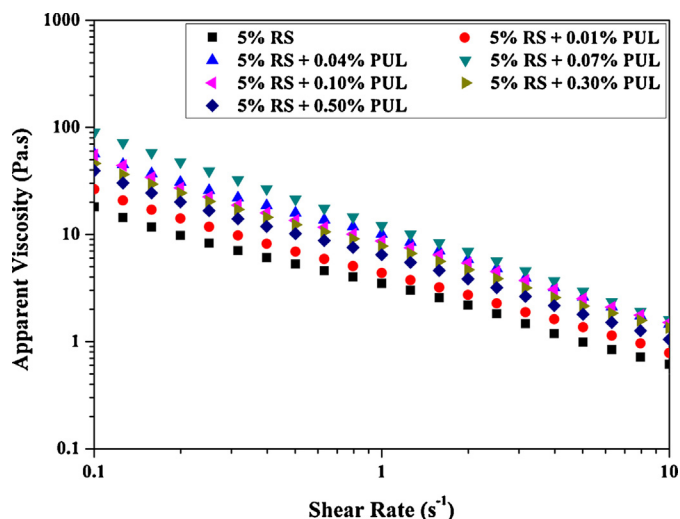


Fig. 1. Effect of pullulan on the apparent viscosity of rice starch (RS) and rice starch–pullulan (RS–PUL) mixtures at 25 °C.

measurements was selected as 3%. The 3% strain was in the linear viscoelastic region according to the strain sweep results (data not shown).

For the rheological properties of samples, one representative datum was drawn in Figs. 1 and 2, because there were no differences in data from triplicate measurements. For the power law parameters in Table 2, however, data were presented as means of triplicate.

### 2.5. Determination of swelling power and amylose leaching

Swelling power of samples during heating was determined following the method reported by Chaisawang and Suphantharika [19] with a slight modification. Firstly, suspensions of 5% rice starch alone and rice starch (5%)–pullulan (0.01, 0.04, 0.07, 0.10, 0.30, and 0.50%) blends were prepared in centrifuge tubes with closed screw caps. Then the samples were heated in a shaking water bath at designated temperatures in the range of 50–90 °C for 30 min. After heating, samples were cooled to room temperature and then centrifuged at 10,000  $\times g$  for 30 min. The supernatant was separated to determine the leached amylose by the iodine colorimetric reaction according to the method described by Chrastil [20], and the results should be regarded as “apparent amylose”, which included not only amylose but also segmental amylopectin leached from starch granules during gelatinization [21]. The leached amylose was calculated by dividing the amylose content in the supernatant by the original weight of the rice starch. The precipitate was weighed and then dried to constant weight in a hot air oven at 105 °C. The swelling power was expressed as the ratio of the wet weight of the residue to its dry weight.

### 2.6. Confocal laser scanning microscopy (CLSM)

The ultrastructure observation of samples was carried out using confocal laser scanning microscopy (Carl Zeiss Inc., Braunschweig, Germany) to visualize the distribution pattern of pullulan around the surface of starch granules according to the method proposed by Funami et al. [21] with a slight modification. The rice starch (5%), rice starch (5%)–pullulan (0.01%, 0.5%) and pullulan (0.5%) were dispersed and heated in boiling water bath for 20 min to gelatinize the rice starch. Two types of fluorescent dyes, fluorescein isothiocyanate (FITC) (20  $\mu\text{L}$  at 2 mg/mL) and rhodamine B (20  $\mu\text{L}$  at 2 mg/mL) were used to identify pullulan and starch. It had been proved that

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