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Effect of pullulan on the water distribution, microstructure and textural properties of rice starch gels during cold storage

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ABSTRACT

The effects of pullulan on the water distribution, microstructure and textural properties of rice starch gels during cold storage were investigated by low field-nuclear magnetic resonance (LF-NMR), scanning electron microscope (SEM), and texture profile analysis (TPA). The addition of pullulan reduced the transversal relaxation time of rice starch gels during cold storage. The microstructure of rice starch gel with 0.5% pullulan was denser and more uniform compared with that of rice starch without pullulan in each period of storage time. With regard to textural properties, 0.01% pullulan addition did not significantly change the texture of rice starch gels, while 0.5% pullulan addition appeared to reduce the hardness and retain the springiness of rice starch gels ($P \leqslant 0.05$). The restriction effects of pullulan on water mobility and starch retrogradation were hypothesized to be mainly responsible for the water retention, gel structure maintenance, and modification of the textural attributes of rice starch gels.

1. Introduction

Rice is one of the most important staple foods worldwide, and is mainly grown in Asian countries (Wani et al., 2012). In addition to direct cooking and eating, rice is processed into a variety of characteristic foods, such as rice noodle, rice cake, and rice flour, all of which are popular in China. The eating quality and nutritive value of foods made from rice are mainly dependent on the properties of the major component, i.e., starch. The gelatinization of rice starch (RS) endows the rice-based food with unique quality, nutritional (Tamura, Singh, Kaur, & Ogawa, 2016), and textural attributes (Ramesh, Zakiuddin Ali, & Bhattacharya, 1999). However, the reduction in the quality of these products inevitably occurs, and is mainly due to starch retrogradation. These irreversible changes take place during cold storage, and can be divided into two stages: amylose rearrangement, which occurs quickly upon cooling during the first few hours of cold storage (Doublier & Choplin, 1989), and amylopectin recrystallization, which proceeds slowly in the following weeks or even months (Gudmundsson, 1994). Starch retrogradation leads to increased hardness, opacity, and fragmentation, as well as decreased springiness, digestion, and water retention capacity in starch-containing gel products; these changes can severely affect the quality and storage stability of these products, thus resulting in the food wastage and economic losses (Karim, Norziah, & Seow, 2000; Wang, Li, Copeland, Niu, & Wang, 2015).

Various hydrocolloids have been incorporated in starch with the aim to modify the functionality of starch (BeMiller, 2011), especially to reduce starch retrogradation. For instances, four β-glucans, i.e., curdlan, oat, barley and yeast β-glucan have been reported to reduce the rate and extent of retrogradation of RS by increasing the viscosity of starch and interfering with the intermolecular associations among the starch molecules (Banchathanakij & Suphantharika, 2009). Charoenrein, Tatirat, Rengsutthi, and Thongngam (2011) added konjac glucomannan (KGM) to RS gel and observed a reduction in syneresis and gel

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hardness. Further, Schwartz et al. (2014) confirmed that KGM retarded the gelatinization and retrogradation of potato starch and broad bean starch by decreasing the amount of available water in the combination system. Xanthan remarkably inhibits the retrogradation of RS, and this inhibition is largely concentration dependent (Tang, Hong, Gu, Zhang, & Cai, 2013). The mechanisms for the inhibitory effect of hydrocolloids on starch retrogradation have been hypothesized to be explained in terms of the coating ability of hydrocolloids on starch granules (Chen et al., 2015; Funami et al., 2008), the electrostatic interactions between starch and hydrocolloids (Cai, Hong, Gu, & Zhang, 2011), the thickening effect of hydrocolloids on the starch paste (Achayuthakan & Suphantharika, 2008), and the possible molecular interactions (Funami et al., 2005; Shi & BeMiller, 2002) between hydrocolloids and starch, especially the amylose fractions. It is noteworthy that the extent to which starch retrogradation is retarded by hydrocolloids addition is remarkably influenced by the type and concentration of hydrocolloids (Wang et al., 2015).

There is no doubt that water also plays a crucial role in influencing the functional properties of starch, including gelatinization (Somboonchan, Lubbers, & Roudaut, 2016) and retrogradation (Schwartz et al., 2014), and also in determining the response of starch granules to processing treatments such as heating (Tester & Debon, 2000) and microwaving (Lewandowicz, Jankowski, & Fornal, 2000) etc.; this is because water is an excellent plasticizing agent of starch (Pouplin, Redl, & Gontard, 1999). In other words, the water content, location, mobility and even the interactions with other substances in the food matrix have a strong impact on stability and functional properties of starch-based foods during the conversion of dispersed starch paste to elastic starch gel, and then to retrograded starch composed of aggregated starch molecules (Wang, Li, Zhang, Copeland, & Wang, 2016). Low field nuclear magnetic resonance (LF-NMR) is a reliable, nondestructive, rapid and efficient technology to detect the distribution and mobility of water proton in the complex food system, and LF-NMR has been advantageously used for the characterization of water in polysaccharide solution or gel (Wu et al., 2016).

Despite many studies are focused on the effect of various hydrocolloids on the properties of starch and the macromolecular interactions between starch and hydrocolloids, there are few investigations on the effect of hydrocolloids addition on the water distribution/redistribution and mobility in starch paste/gel during gelatinization and retrogradation. We reported in previous studies that pullulan (PUL) exhibited some abilities to control the pasting and rheological properties of RS (Chen, Tong, Ren, & Zhu, 2014), thus retarding both the short-term retrogradation of amylose and the long-term retrogradation of amylopectin (Chen, Ren, Zhang, Tong, & Rashed, 2015). Therefore, the primary mission of the present work was to further investigate the effects of PUL on the water distribution, water mobility and textural attributes of RS gels during refrigerated storage at 4 °C using low-field nuclear magnetic resonance (LF-NMR) and texture profile analysis (TPA), respectively. Additionally, the microstructure transformation of gel samples during storage was evaluated using a scanning electron microscope (SEM) to give a comprehensive validation of the effect of PUL on the properties of RS.

Present work gave a detailed analysis of the water-starch interactions during cold storage with the aim of developing a starch gel with good cold storage stability. The understanding of these interactions could clarify the influence of PUL on starch gelatinization and retrogradation, and also allow the rational choice of the product formula for an application with optimal product quality and long shelf life in starch-rich foods. Additionally, the application amplification of PUL in food industry is also a logical aim of this study.

2. Materials and methods

2.1. Materials

Normal RS was supplied by Jiangsu Baby Co., Ltd. (Suqian, China). The purity of the starch was up to 98%. The moisture and amylose contents in this RS were 11.82% and 23.30%, respectively, which were determined using the AACC Method (2000). Purified PUL was purchased from Hayashibara Biochemical Inc. (Shanghai, China) with 4.50% moisture content and a molecular weight of 200,000 Da.

2.2. Sample preparation

RS (5%, w/v) and PUL (0, 0.01, and 0.5%, w/v) mixtures (RS-PUL) were prepared in accordance with the following procedure. In order to disperse the starch granules evenly in the PUL solution, two kinds of suspension were prepared in advance. Briefly, PUL was sprinkled into 50% of the total volume of water (50 mL) and stirred at 300 rpm for 30 min to thoroughly dissolve the PUL, while 5 g of RS was suspended in the remaining 50% of the total volume of water (50 mL) and stirred at 300 rpm for 30 min. Then, the RS suspension was added to the PUL solution, and the mixtures were dispersed by magnetic stirring for 60 min at room temperature.

The aforementioned RS suspensions with or without PUL were heated in a water bath at 95 °C for 20 min with continuous stirring at 200 rpm to allow the complete gelatinization of RS. During heating, the beaker mouth was sealed with three layers of plastic wrap to prevent water evaporation. After heating, the hot slurries were allowed to slowly cool down to 25 °C. RS without PUL was used as a control. Lastly, the prepared starch paste was stored at 4 °C for 0, 1, 3, 5, 7, 14, and 21 d to perform the retrogradation process. Gel samples were taken out from the refrigerator for further analysis after the specified number of days of storage.

2.3. LF-NMR

The LF-NMR measurements of the starch gels before and after cold storage for different lengths of time with or without pullulan addition were performed using a 23 MHz NMR analyzer (NMI20-015V-I, Niumag Co., Ltd., Suzhou, China). Approximately 2 g of different pasting samples prepared in Section 2.2 was transferred to a 10 mm diameter NMR glass tube and sealed with three layers of preservative film to prevent evaporation during the experiments or storage. These tubes were then stored at 4 °C for 0, 1, 3, 5, 7, 14, and 21 d. After cold storage, the tubes were taken out from the refrigerator and heated to 35 °C in a water bath. The temperature of the NMR instrument was set and maintained at 35 °C during the spin-spin relaxation time (T_2) measurements, which were performed using a sequence based on the Carr-Purcell-Meiboom-Gill (CPMG) sequence. Data from 1024 echoes were acquired as 8 scan repetitions, and the τ value was set at 50 μs between 90° and 180° pulses. Relaxation curves obtained from the CPMG sequence were analyzed using the exponential model (Eq. (1)). Exponential model was used to fit the experimental curves and it could provide a good fitting results (Tang et al., 2013). In a high moisture system, water can move freely and rapidly with typical time at a millisecond scale. Water mobility is often characterized by the transverse relaxation time under the low-resolution nuclear magnetic resonance, and this transverse relaxation time is also called spin-spin relaxation time (T_2) (Wu et al., 2016).

$$S(t) = \sum A_i \exp\left(-\frac{t}{T_{2i}}\right) \quad (1)$$