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Effect of pullulan on the short-term and long-term retrogradation of rice starch☆

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ABSTRACT

The effect of pullulan (PUL) on the retrogradation of rice starch (RS) was investigated by means of rapid visco-analyzer (RVA), rotational rheometer, differential scanning calorimetry (DSC), and X-ray diffraction (XRD). RVA results showed that addition of pullulan significantly decreased the breakdown and setback values, which meant that the short-term retrogradation of RS was inhibited. The dynamic time sweep of samples also proved the retarding effect of pullulan on the retrogradation of RS. DSC curves showed clearly that pullulan significantly reduced the retrogradation enthalpy of amylopectin, and the kinetics of retrogradation was analyzed using the Avrami model. XRD results showed that recrystallinity of RS was reduced from 11.565% to 8.841% with the addition of pullulan and this was in line with the DSC results. It could be concluded that the addition of pullulan apparently influenced not only the short-term retrogradation of amylose, but also the long-term retrogradation of amylopectin.

1. Introduction

Rice is one of the most common crops in the world, the staple food and the major energy source of people in East Asian countries (James & Roy, 2009; Wani et al., 2013). Rice consists mostly of starch, and therefore it is very prone to retrogradation after cooking. The term retrogradation is used to describe the changes that occur in gelatinized starch during storage, especially at low temperature. The components of rice starch, amylose and amylopectin, have unique roles in the retrogradation of starch. Generally, amylose is responsible for the short-term retrogradation, while the long-term retrogradation is ascribed to the reordering of amylopectin which is a much slower process involving mainly the recrystallization of the outer branched-chains of amylopectin (Miles, Morris, Orford, & Ring, 1985; Ring et al., 1987). The retrogradation during production or storage profoundly affects quality, acceptability and shelf-life of starch or starch-containing foods (Karim, Norziah, & Seow, 2000). The firmness of starch gel increases markedly due to the fact that starch molecules in pastes associate together on aging (Seow & Teo, 1996). The phase separation between polymers and water appeared and resulted in the phenomenon of syneresis (Karim et al., 2000). What's more, retrogradation could change the nutritional value of starch with increasing the level of enzyme-resistant starch (Haralampu, 2000).

This tendency of retrogradation limited the large-scale production of rice products in commercial and industrial field, and therefore, effective measures were urgently required to overcome this problem. Blending starch with hydrocolloids, as a safe and effective method, was widely applied in food industry to modify and control the rheological properties (Chaisawang & Suphantharika, 2006; Chen, Tong, Ren, & Zhu, 2014; Pongsawatmanit, Chantaro, & Nishinari, 2013; Wang et al., 2008), retrogradation behavior (Banchathanakij & Suphantharika, 2009; Funami et al., 2005; Tang, Hong, Gu, Zhang, & Cai, 2013), texture (Charoenrein, Tatirat, Rengsutthi, & Thongngam, 2011), syneresis and freeze-thaw stability (Chen et al., 2014; Lee, Baek, Cha, Park, & Lim, 2002; Sae-kang & Suphantharika, 2006). Possible interactions among hydrocolloids, starch molecules, and starch granules, i.e. hydrocolloid molecules interacted with leached starch molecules,

☆ Please note: As pullulan is not a specific chemical, it is a polymer of repeating maltotriose units; it will not have a specific record in PubChem.

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were hypothesized to play an important role in modifying the properties of starch–hydrocolloid combinations (BeMiller, 2011), including retarding the granule swelling and the aggregation of amylose that led to retrogradation (Chen et al., 2014; Fredriksson, Silverio, Andersson, Eliasson, & Åman, 1998).

In the aspects of natural neutral polysaccharide, pullulan is attracting the attention of more and more people, not only because of its preferable film forming ability (Wu & Chen, 2013; Xiao, Tong, & Lim, 2012), but also its unique and multiple benefits on human beings (Singh, Saini, & Kennedy, 2008). Pullulan is a typical linear exocellular polysaccharide produced by *Aureobasidium pullulans* with a starch-like structure of linkage α-D-glucan primarily consisting of maltotriose repeating units interconnected by α-(1 → 6) linkages (Singh et al., 2008). The regular structure confers pullulan the aforementioned distinctive properties compared to other polysaccharides.

Although many efforts have been made to investigate the properties and applications of pullulan in many fields such as food and pharmaceutical industry (Singh et al., 2008), there are very few reports focused on the effect of pullulan addition on the properties of starch. Xiong, Song, Yao, and Lu (2013) reported that pullulan reduced the retrogradation enthalpy, the peak viscosity, and final viscosity of high amylose RS by reducing the water mobility and the interactions between starch and water. Our previous study (Chen et al., 2014) investigated the effect of pullulan on the gelatinization and rheological properties of RS, and found that pullulan adsorbed onto the surface of starch granules and coated around these granules during heating when the concentration of pullulan was greater than 0.07%, resulting in the reduction of granule swelling, leached amylose, the subsequent gelatinization and setback values of RS. However, the information about the effects of pullulan on the retrogradation behavior of starch is still insufficient, and relevant investigations and farther quest of deep-seated mechanisms behind these phenomena are still needed.

The objective of this study was to investigate the role and potential usefulness of pullulan in controlling retrogradation of starch-based foods. Since retrogradation was a complex process affected by many factors, it was unlikely that any single method could be able to give a complete picture of the retrogradation properties of starch gels. Therefore, multiple methods including RVA, rheological properties, DSC, and XRD were applied, and the independent evidence derived from those methods might allow us to obtain a comprehensive understanding of the effect of pullulan on both the short-term and long-term retrogradation of rice starch. Furthermore, the Avrami model fitting the DSC data was employed to study the isothermal crystallization kinetics of long-term retrogradation in RS, and the relative crystallinity dada of retrograded samples obtained from the XRD diffraction patterns were also given.

2. Materials and methods

2.1. Materials

Normal rice starch was obtained from Jiangsu Baby Co., Ltd. (Suqian, China). The contents of moisture, ash, protein, lipid and amylose in this rice starch were 11.82%, 0.14%, 0.23%, 0.68%, and 23.30%, respectively. Pullulan was purchased from Hayashibara Biochemical Inc. (Shanghai, China) with 4.50% moisture content and 200,000 MW.

2.2. Pasting properties

RS–PUL mixtures were prepared as follows. RS–PUL ratios were 5/0, 5/0.07, 5/0.10, 5/0.30, and 5/0.50 (w/w), respectively. The calculated amounts of pullulan powder were primarily dissolved thoroughly in distilled water with continuous stirring for 1 h, and then RS was slurried in pullulan solutions at room temperature by magnetic stirring for 30 min to avoid the formation of starch lump. The prepared slurry was transferred into an aluminum canister and stirred using a plastic paddle. The pasting parameters of samples were measured by a rapid visco-analyzer (RVA-RECHMASTER, Newport Scientific Pty. Ltd, Sidney, Australia) in the following manner. The slurry 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. Breakdown value representing the differences between peak viscosity and trough viscosity, and setback value representing the differences between trough viscosity and final viscosity were calculated from the RVA curves. The viscosity was expressed in cP units.

2.3. Dynamic viscoelastic measurements

The dynamic time sweep was performed following the method reported by Funami et al. (2005) with a slight modification by using an AR G2 rheometer (TA instrument Inc., USA) isothermally at 4 °C. Parallel plate geometry (60 mm) at gap 500 μm was used for rheological measurements. The slurries, which went through the RVA measurements, were immediately transferred to the rheometer plate. The excess material was wiped off with a spatula. Silicon oil was applied to the exposed surfaces of samples to prevent evaporation during experiments. Prior to measurement, samples were held for 5 min to equilibrate stresses and temperature. G' values were monitored during aging at a constant frequency of 6.28 rad/s and at a constant strain of 3%. The 3% strain was in the linear viscoelastic region according to the strain sweep results (data not shown).

2.4. Differential scanning calorimetry (DSC)

The thermal analysis of RS with different pullulan ratios during storage at 4 °C was performed by using a differential scanning calorimetry (SII NanoTechnology Inc., Japan) under an ultrahigh-purity nitrogen atmosphere. The instrument was calibrated using indium as a standard and an empty aluminium pan was used as the control. The gelatinization and retrogradation properties of samples were determined form the DSC curves. Rice starch containing 0%, 1.4%, 2%, 6%, and 10% pullulan (based on rice starch weight) were prepared, respectively. Three milligrams of prepared samples were mixed with 6 μL of deionized water and hermetically sealed in an aluminium pan. All sealed samples were equilibrated at room temperature for 12 h to hydrate and then heated over a temperature range of 30–100 °C at a constant rate of 10 °C/min to perform the gelatinization process. Subsequently, the gelatinized samples were stored at 4 °C for 1, 3, 5, 7, 14, 21, and 28 days to perform the retrogradation process and then rescanned from 30 to 100 °C to melt the retrograded amylopectin crystallites. Melting enthalpy (ΔH) was calculated from the area of the main endothermic peak and expressed in terms of J/g of dry starch using the equipment software. Measurements were performed in triplicate.

The Avrami equation, which deals with crystallization at temperatures above the glassy region, has been extensively used by many researchers to provide a convenient empirical means of representing the process of starch retrogradation (Xu et al., 2012).

Therefore, the Avrami's equation, Eq. (1), was used to illustrate the kinetics of retrogradation of starch (especially amylopectin).

$$X(t) = \frac{\Delta H_t - \Delta H_0}{\Delta H_\infty - \Delta H_0} = 1 - \exp\left(-kt^n\right) \quad (1)$$