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Effects of charge-carrying amino acids on the gelatinization and retrogradation properties of potato starch

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ABSTRACT

The objective of this study was to evaluate the effects of charge-carrying amino acids (lysine (Lys), arginine (Arg), aspartic acid (Asp) and glutamic acid (Glu)) on the gelatinization and retrogradation properties of potato starch. Acidic amino acids (Asp and Glu) showed a decreasing trend in swelling power and granule size of potato starch, but increased amylose leaching and gelatinization temperature. Alkaline amino acid (Arg) showed an increasing trend in swelling power and granule size of potato starch, but decreasing amylose leaching and gelatinization temperature. Lys had no effect on the swelling power of potato starch, except at a high content (0.2 mol/kg). Like other two acidic amino acids, Lys also increased gelatinization temperature. Moreover, the addition of alkaline amino acids (Arg) decreased syneresis value of potato starch but acidic amino acids (Asp and Glu) increased it. Compared to Arg, the syneresis of potato starch with Lys was similar to that of its native starch.

1. Introduction

As an abundant polysaccharide source, starch is widely used to improve the qualities of food products (Lu, Luo, & Xiao, 2012). Potato starch has low gelatinization temperature and high water-binding capacity (Cai, Hong, Gu, & Zhang, 2011; Sandhu, Kaur, & Mukesh, 2010; Zaidul et al., 2008). Because of its unique properties, potato starch has been widely used in the food industry (Yusuph, Tester, Ansell, & Snape, 2003). There is a weak internal organisation in potato starch due to the presence of negatively charge-carrying phosphate ester groups (Li & Vasanthan, 2003). Native starch is often modified with various chemical reagents or through acid, alkali, enzymatic or hydrothermal treatments for applications in foods and non-foods. Alkali treatment, such as sodium hydroxide, is widely used in the production of many traditional food products, including tortillas, waxy rice dumplings and yellow alkaline noodles, to improve the colour, flavour and texture of those products (Cai et al., 2014). Acid treatment can also influence the gelatinization behaviour of the starch. For example, the starch used in gum candies is generally modified with hydrochloric acid, citric acid and lactic acid (Whistler & Daniel, 2000). Thin-boiling starch, normally prepared by acid treatment, is used extensively in the food, textile and paper industries (Sandhu, Singh, & Lim, 2007).

Amino acids are increasingly applied as nutrient supplements and additives in the food industry and play a crucial role in human nutrition and health maintenance (Chávez-Béjar, Báez-Viveros, Martínez, Bolívar, & Gosset, 2012; Mitsuhashi, 2014). Aspartic acid (Asp) and glutamic acid (Glu) with negative charges are acidic in the solution, while lysine (Lys) and arginine (Arg) with positive charges are alkaline. Amino acids showed significant influences on the pasting and gelatinization characteristics of potato starch (Ito, Hattori, Yoshida, & Takahashi, 2004, 2006; Ito, Hattori, Yoshida, Watanabe, et al., 2006), sweet potato starch (Lockwood, King, & Labonte, 2008), and rice starch (An & King, 2009). The addition of positively and negatively charge-carrying amino acids had stronger effect on the pasting properties of rice starch than the neutral one (Liang & King, 2003).

Despite the numerous observations on pasting properties of starch-amino acid mixture, there is no systematic study about effects of charge-carrying amino acids on pasting and ageing

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properties of potato starch. The pH values of those amino acids in the solution can be either acid or alkaline, so they could potentially influence the characteristics of potato starch. Therefore, the objective of this study was to investigate the effects of charge-carrying amino acids on the gelatinization and retrogradation properties of potato starch.

2. Materials and methods

2.1. Materials

Potato starch (Xue Guan Starch Company, Ning Xia, China) was used after drying in the oven at 80 °C for 24 h. Amino acids included two alkaline amino acids (Lys and Arg) and two acidic amino acids (Asp and Glu) (Biosharp, Seoul, Korea).

2.2. Swelling power and amylose leaching

The swelling power of starches with amino acids (0, 0.05, 0.1 and 0.2 mol/kg on a starch weight basis) was determined between the temperature range from 60 to 90 °C according to the method of Leach, McCowen and Schoch (1959). Amino acids in the required concentration were prepared and starch was added on 2% (w/v) starch suspension. The pH values of samples were measured, respectively. The suspension of starch was heated at 60, 70, 80, 90 °C for 20 min, respectively, followed by rapid cooling in an ice water to room temperature. The suspension was then centrifuged at 3500*g* for 20 min. Supernatant was decanted carefully and residue weighed for swelling power determination. The ratio between the residue and initial starch dry matter was calculated (g/g of starch on dry weight basis) as the swelling power (Leach et al., 1959). Amylose leaching was estimated as described by Hoover and Ratnayake (2002).

2.3. Differential scanning calorimetry

Differential Scanning Calorimeter (DSC) measurement was performed using a DSC-204F1 (Netzsch, Bavarian, Germany). Potato starch (5 mg each) with charge-carrying amino acids (0.2 mol/kg on a starch weight basis) was weighed and placed into aluminum DSC pan. Distilled water (10 μL) was then added to each pan. Empty pan was served as a reference. The cells were equilibrated at 30 °C and then heated to 100 °C at 10 °C/min. The onset, peak, and conclusion temperatures (T_0, T_p, and T_c) with gelatinization enthalpy (ΔH) were obtained.

2.4. Particle sizes

Potato starch (6 g) with different charge-carrying amino acids (0.2 mol/kg on a starch weight basis) was dissolved in 100 mL distilled water and then heated in water bath (50 and 65 °C) for 2 h. The samples were suspended in water and stirred at 2000 rpm. The particle sizes of potato starch were determined with the Malvern Mastersizer 2000 (Malvern Instruments Limited, UK).

2.5. Syneresis

Potato starch pastes (6% w/v) with different levels of amino acids (0, 0.05, 0.1 and 0.2 mol/kg on a starch weight basis) were prepared by heating at 95 °C for 20 min in a water bath with stirring. Then the paste (30 g) was added into 50 ml centrifuge tubes and stored in a freezer (−24 °C) for 22 h and then thawed at water bath (30 °C) for 2 h. The pastes were centrifuged at 3500*g* for 10 min. The percentage of water separated was measured and expressed as the syneresis (%). The freeze–thaw cycles were up to 4 cycles as described by Schmitz et al. (2006).

2.6. Statistical analysis

All experiments were replicated three times. The statistical analyses were performed using a SPSS package (SPSS 17.0 for Windows, SPSS Inc, Chicago, IL, USA). Differences among the mean values of various treatments were compared using Duncan's multiple range test ($p < 0.05$).

3. Results and discussion

3.1. Swelling power and amylose leaching

Fig. 1 shows swelling power of potato starch with and without charge-carrying amino acids at different temperatures. All samples exhibited a sharp increase of swelling power with heating temperatures from 60 to 80 °C and followed by a slight increase from 80 to 90 °C. Moreover, the swelling power values of potato starch with Asp and Glu were significantly lower than those of the control. As their concentrations in potato starch were increased, more reduction was observed in the swelling power of potato starch. However, the swelling power of potato starch with Lys was similar to that of the control ($p > 0.05$), while that of potato starch with Arg was much higher than the control ($p < 0.05$). Fig. 2 illustrates the leaching of amylose in the starch fortified with charge-carrying amino acids. The higher the concentration of acidic amino acids (Asp and Glu) resulted more amylose leaching from potato starch. The leaching increased with the concentration of acidic amino acids, but was not basically affected by Lys, until the concentration was more than 0.2 mol/kg. The leaching power decreased with Arg ($p < 0.05$).

The swelling behaviour of starch is primarily due to its amylopectin, while amylose acts as both a diluent and an inhibitor of starch granule swelling (Cai et al., 2014). Amylose restricts the swelling of starch and maintains the integrity of swollen granules (Xie et al., 2007). However, the acidic environment (pH < 3.95) could accelerate amylose leaching from the starch granules and decrease the amylose content in the starch granules because the acid preferentially attacks the amorphous regions (Komiya & Nara, 1986). Moreover, the branch points of B-type amylopectin, like in potato starch, are mainly located in the amorphous region and easily susceptible to acid hydrolysis (Jane, Wong, & McPherson, 1997). The hydrochloric acid (0.14 M, HCl) caused a decrease in swelling power of corn and waxy corn starches (Sandhu et al., 2007). The increase of HCl concentration from 0.1 to 1 M gradually decreased swelling power of potato starch (Gunaratne & Corke, 2007). As acidic amino acids were added into the starch, Asp (e.g., 0.2 mol/kg, pH = 2.83) and Glu (e.g., 0.2 mol/kg, pH = 3.34) might facilitate amylose leaching from the starch granules, respectively. However, acidic amino acids caused the reduction of swelling power of potato starch (Fig. 1). There was no obvious relationship between swelling power and leaching of starch ($R2 = 0.197$ for linear correlation) (Bordenave, Janaswamy, & Yao, 2014). Acidic amino acids were added into potato starch solution, bringing more hydrogen ions into starch granules. It could probably reduce the negative charges from phosphate ester groups inside the potato starch granules, resulting in the reduction of the repulsion or the increase of the attraction among molecules inside the granule. Therefore, potato starch with acidic amino acids became more stable than the control, decreasing its swelling power.

Arg (e.g., 0.2 mol/kg, pH = 11.01), alkaline amino acid, could probably decrease the content of apparent amylose and restrain amylose leaching from potato starch granules, causing more