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In vitro digestion and physicochemical characteristics of corn starch mixed with amino acid modified by heat-moisture treatment

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ABSTRACT

Corn starch was modified with amino acid by heat-moisture treatment (HMT) to investigate the formation of slowly digestible starch (SDS). SDS content in native corn starch and heat-moisture treated corn starch were 17.91% and 4.35% respectively, while the maximum SDS content in amino acid-heat treated starches (HMT-amino acid) reached 41.07%. HMT-Lys displayed reduced birefringence brightness at the periphery, while for HMT-Asp, a weaker birefringence region was observed but without apparent Maltese crosses. HMT-amino acid showed higher gelatinization temperature and lower gelatinization enthalpy. After HMT, relative crystallinity of amino acid-heat treated starches decreased. The lower ΔH and the lowest relative crystallinity had the highest SDS content (41.07%). The results indicated that structural changes of corn starch mixed with amino acid by HMT significantly affected the digestibility.

1. Introduction

Starch is the main energy reserve in the human diet. Nutritionally, starch is divided into rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) (Englyst, Kingman, & Cummings, 1992). SDS is generally the most desirable form of dietary starch, which received much attention in novel food development. Currently, Preparation of SDS can be achieved by structural alteration through different physical modification. Among these methods, many researchers have applied heat-moisture treatment (HMT) for preparing SDS from various sources of starch (Chen, He, Fu, & Huang, 2015; Huang, Zhou, Jin, Xu, & Chen, 2015; Lee, Kim, Choi, & Moon, 2012). HMT represents a means for enhancing thermo-stable SDS contents, which likely result from altered starch chain associations in crystalline and/or amorphous regions of granules.

All of the amino acids are vital for the construction of proteins, regulating the acid–base balance in the human body. Studies have shown that the binding interaction between starch molecules and amino acids can be used to produce novel starch derivatives (Chen, Zhou, Yang, & Cui, 2015; Ito, Hattori, Yoshida, & Takahashi, 2004; Ito et al., 2006; Liang & King, 2003; Lockwood & King, 2008). Studies have also shown that starch modified with amino acids could be used as health-enhancing functional food ingredients which are resistant to hydrolysis (Pizzoferrato, Paci, & Rotilio, 1998). Yang, Hattori, Kawaguchi, and Takahashi (1998) introduced a Maillard Reaction to conjugate native potato starch, carboxymethyl potato starch and corn starch phosphate monoester granules with lysine or poly(lysine). They reported that the digestibility of each conjugate with α-amylase was lower than that of the original starch.

We expected that the amino groups of amino acids could be conjugated with the reducing-end groups of starch by the heat moisture treatment. In order to promote the reaction, we selected two kinds of amino acids with high solubility. Lysine, one of the essential amino acids, is the most reactive amino acid, and aspartic acid, charged amino acids, could have caused a greater effect on pasting characteristics of starch. In this study, starch mixed with amino acid was first modified by HMT: (1) to determine the effect of lysine and aspartic acid on the *in vitro* digestibility characteristics of

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corn starch, and (2) to study the structure characteristics of corn starch mixed with amino acids modified by HMT.

2. Materials and methods

2.1. Materials

Corn starch (amylose content: 29%; moisture content:10%) was a gift of National Starch and Chemical Co. (ShangHai, China). The amino acid used included lysine (Lys) and aspartic acid (Asp), which were purchased from Sigma Chemical Co. (Shanghai, China). All other chemicals were analytical grade.

2.2. Starch modification

The amino acid (0.3 g, dry basis) was slowly added to distilled water (40 mL) with vigorous stirring. Corn starch (9.7 g, dry basis) was dispersed into the amino acid solution and stirred for 30 min at room temperature. The whole dispersion was transferred to a glass dish and dried at 40 °C in a convection oven for 48 h and ground. The moisture levels of the dried starch-amino acid mixture were adjusted to 30% by adding appropriate volumes of distilled water and the mixtures were sealed in containers and equilibrated at 4 °C for 24 h. After the incubation, the containers were heated at 100 °C for 10 h, then cooled to room temperature and the samples were air dried at 40 °C for 48 h and ground for further analysis. Each formulation was prepared in duplicate.

2.3. In vitro digestion properties of starch

2.3.1. Uncooked samples

RDS, SDS, and RS were determined using the method of Englyst et al. (1992) with some modification. Briefly, starch sample (200 mg, dry base) was hydrolyzed by a mixed enzyme solution of porcine pancreatic a-amylase (290 U/mL) and amyloglucosidase (15 U/mL). Phosphate buffer (15 mL, 0.2 mol/L, pH 5.2) and five glass balls (10 mm in diameter) were added to each of the conical tubes containing starch samples (200 mg, dry base). After equilibration at 37 °C for 5 min, the enzyme solution (10 mL) was added to the sample tube, followed by incubation in a water bath at 37 °C with shaking (170 rpm). Aliquots (0.5 mL) were taken at intervals of 20 and 120 min and mixed with 4 mL of 80% ethanol to deactivate the enzymes. The mixed solution was centrifuged at 2000 rpm for 10 min, and the glucose content in the supernatant was measured using the 3,5- dinitrosalicylic acid (DNS) method. The percentage of hydrolyzed starch was calculated by multiplying a factor of 0.9 with the glucose content. Each sample was analyzed in triplicate.

The values of different starch fractions of RDS, SDS and RS were obtained by combining the values of G_{20} (glucose released after 20 min), G_{120} (glucose released after 120 min), FG (free glucose) and TG (total glucose) and using the following formulas:

$$RDS = \left[\frac{(G_{20} - FG) \times 0.9}{\text{Weight of sample}}\right] \times 100$$

$$SDS = \left[\frac{(G_{120} - G_{20}) \times 0.9}{\text{Weight of sample}}\right] \times 100$$

$$RS(\%) = \left[\frac{(TG - FG) \times 0.9}{\text{Weight of sample}}\right] \times 100 (RDS + SDS)$$

2.3.2. Cooked samples

Starch sample (200 mg) and water (15 mL) were added to the screw-capped polypropylene centrifuge tubes (50 mL) and mixed by vortexing for 5 min. The tubes were heated in boiling-water bath for 20 min while gently stirring magnetically at low speed. After that the tubes were placed in 37 °C water bath and equilibrated for 10 min. Then starch sample was hydrolyzed by a mixed enzyme solution by the experimental method for determining RDS, SDS, and RS.

2.4. Polarised light microscopy

Native and HMT starch suspensions (water-glycerol, 50:50,v/v) were viewed using a binocular microscope (Nikon Microscope, Eclipse 80i, NY, USA) fitted with a real time viewing (Q-capture Pro™, BC, Canada). Observations were conducted under cross polarised light (magnification 100×). All tests were carried out in triplicate.

2.5. Thermal properties

The thermal properties of each starch sample were examined using a differential scanning calorimetry (Pyris-1, Perkin Elmer Inc., USA). The sample (3 mg, dry weight basis) were accurately weighed into aluminum DSC pans, and deionized water was added by micropipette in order to achieve a water-sample ratio of 2:1. The sample pans were sealed and equilibrated at room temperature for 24 h before analysis. The samples were heated at a rate of 10 °C/min in a temperature range of 10–95 °C using an empty pan as reference. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy of gelatinization were calculated automatically. All tests were carried out in triplicate.

2.6. X-ray diffraction

The X-ray diffraction patterns were performed with an XRD-6000 X-ray diffractometer (Shimadzu Co., Japan). X-ray diffraction patterns were acquired at room temperature over the 2q range of 4–40° (2θ) with a step size of 0.02. All tests were carried out in triplicate.

2.7. Statistical analysis

Results are expressed as the mean ± standard deviation of triplicate experiments. All the test data were analyzed by the analysis of variance and multiple comparison tests with the least significant difference (ANOVA; SAS Statistic Package; SAS, Cary, NC, USA). Differences were defined at a significance level of 95% ($P < 0.05$).

3. Results and discussion

3.1. In vitro digestion

This study showed that values for RDS, SDS and RS fractions in native corn starch are 21.03%, 17.91% and 61.06%, respectively (Table 1). By simply blending the starches with amino acid (Lys and Asp), both RDS and SDS contents were increased, whereas the RS content decreased. However, the ratio in RDS, SDS and RS fraction of corn starch added with amino acids did not show any significant different. More recently it has been shown that addition of amino acids strongly affect the physic-chemical properties of starch, such as gelatinization, retrogradation and pasting behavior (Cui, Fang, Zhou, & Yang, 2014; Lockwood & King, 2008).

Cooked starch has the greatest RDS, which is expected since

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