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Effect of controlled gelatinization in excess water on digestibility of waxy maize starch

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ABSTRACT

An aqueous dispersion of waxy maize starch (5%, w/w) was controlled gelatinized by heating at various temperatures for 5 min. The treated samples were analysed using *in vitro* Englyst assay, light microscopy, differential scanning calorimetry, X-ray diffraction, and Fourier-transform infrared spectroscopy. When heated, SDS and RS levels were decreased inversely with RDS. A high SDS content (>40%) was kept prior to the visible morphological and structural changes (before 60 °C). Swelling factor began to increase slightly at 50–60 °C and continued to maximum value at 80 °C. A large decrease in ΔH, crystallinity, and ratio of 1047/1022 cm^{-1} attributed to partially dissociation of crystalline clusters and double helices occurred at 65–80 °C. These changes showed that controlled gelatinized starch with slow digestion property occurred in the molecular rearrangement process before granule breakdown and SDS mainly consists of amorphous regions and a small portion of less perfect crystallites.

1. Introduction

Starch is the main source of digestible carbohydrates in the human diet and contributes a substantial amount of calories for human metabolism. The slow rate of glucose release from food products inducing low glycemic responses is considers to be beneficial for dietary management of metabolic disorders, including diabetes, prediabetes, glycogen storage disease, cardiovascular disease, and obesity (Björck & Asp, 1994; FAO/WHO, 1998; Miao, Jiang, & Zhang, 2008). The concept of glycemic index (GI) describing the level of the postprandial glucose rise in blood as compared to a reference food (white bread or glucose), was introduced to classify carbohydrate-based foods (FAO/WHO, 1998). Low-GI meals (GI $\leqslant$ 55) yield a more stable diurnal profile, reducing postprandial hyperglycaemia and hyperinsulinemia, as well as attenuating late postprandial rebound in circulating non-esterified fatty acids, all of which are factors that exacerbate these metabolic syndromes (Björck, Liljeberg, & Östman, 2000; FAO/WHO, 1998; Ludwig, 2002). A food product with a low-GI is preferable, not only in individuals with hypoglycaemia or hyperglycaemia, but also in healthy individuals.

It is well known that starch is composed of a mixture of two distinct macromolecules with α-D-glucopyranosyl unit, a linear fraction linked by the α-1,4 bonds, amylose, and a highly branched fraction linked by α-1,4 and α-1,6 linkages, amylopectin. From a nutritional physiological point of view, starch is generally classified into three major fractions depending on the rate and extent of digestion *in vitro*: rapidly digestible starch (RDS), the portion of starch digested within the first 20 min of incubation, slowly digestible starch (SDS), the portion of starch digested from 20 to 120 min, and resistant starch (RS), the remaining portion that cannot be further digested (Englyst, Kingman, & Cummings, 1992). RDS induces a fast increase of postprandial blood glucose and insulin level and is correlated to high GI, whereas SDS provides a slow and extended release of glucose into the blood stream and a low glycemic response (Björck et al., 2000; Englyst et al., 1992; Miao et al., 2008). Foods containing a substantial amount of SDS result in a diet with a low-GI, which may be advantageous to satiety, physical performance, improved glucose tolerance, as well as reduced blood lipid levels and insulin resistance through lessening the stress on regulatory systems related to glucose homoeostasis (Björck et al., 2000; Ludwig, 2002). Therefore, much attention is being given to SDS as a new functional material in novel food product development.

There have been reports on making SDS by chemical, physical, enzymatic, genetic, or multiple modifications (He, Liu, & Zhang, 2008; Miao et al., 2008). However, most of the reported SDS materials are also sensitive to thermal processing which is most often used in food preparation and SDS-based product is not commercially available in the current food market. Thus a challenge for the food industry is to develop new technologies to make heat-stable SDS. Zhang, Ao, and Hamaker (2006) reported that native cereal starches are ideal SDS (about 50%) and the semicrystalline A-type structure determines the slow digestion property. When crystalline structure is destroyed with processing, such as cooking, baking, and autoclaving, starch is more easily digested than raw

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starch (Holm, Lundquist, Björck, Eliasson, & Asp, 1988; Noda et al., 2008; Slaughter, Ellis, & Butterworth, 2001; Zhang et al., 2006). The objective of the present study is to determine the effect of controlled gelatinization in excess water on digestibility of waxy maize starch and to investigate the slow digestion property and structural characteristics for SDS. It is demonstrated that different digestibility of starch can be achieved by controlling the moist heat processing and containing rich-SDS diets for practical applications may be provided.

2. Materials and methods

2.1. Materials

Waxy maize starch was obtained from Changchun Dacheng Industrial Group Co., Ltd. (Changchun, Jilin, China). α-Amylase type VI-B from porcine pancreas and amyloglucosidase Dextrozyme® GA from *Aspergillus niger* were purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO) and Novozymes (Tianjin, China), respectively. Glucose assay reagents were from Megazyme International Ireland Ltd. (Wicklow, Ireland). All chemicals were of reagent grade and were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.2. Preparation of starch samples

Starch samples, having different degree of gelatinization, were prepared by controlling moist heat treatment. A dispersion of starch (5 g) in distilled water (100 ml) was treated in a water bath at specific temperatures (ranging from 50 to 80 °C at 5 °C increments) for 5 min with shaking (200 rpm). The samples were filtered through Whatman Grade No.1 filter papers, and the residue was subjected to dry in an air oven at 50 °C for 24 h.

2.3. In vitro digestibility of starch samples

The digestibility of starch was analysed according to the procedure of Englyst et al. (1992) with a slight modification. To prepare enzyme solution I, amyloglucosidase solution (0.14 ml) was diluted to 6.0 ml with deionized water. Enzyme solution II was prepared by suspending porcine pancreatic α-amylase (12.0 g) in water (80.0 ml) with magnetic stirring for 10 min, centrifuging the mixture for 10 min at 1500*g*, then transferring a portion (54.0 ml) of the supernatant into a beaker. Enzyme III was prepared immediately before use by mixing water (4.0 ml), enzyme solution I (6.0 ml), and enzyme solution II (54.0 ml).

A starch sample (200 mg) was dissolved in phosphate buffer (15 ml, 0.2 mol/l, pH 5.2) by vortexing. After equilibrated at 37 °C for 5 min, seven glass balls (10 mm diameter) and enzyme solution III (5.0 ml) were then added, followed by incubation in a water bath at 37 °C with shaking (150 rpm). Aliquots of hydrolysed solution (0.5 ml) were taken at different time intervals and mixed with 4 ml of absolute ethanol to deactivate the enzymes. The glucose content of the hydrolyzates was determined using glucose oxidase/peroxidase assay kits. Percentage of hydrolysed starch was calculated by multiplying a factor of 0.9 with the glucose content. Each sample was analysed in triplicate.

The values of different starch fractions of RDS, SDS and RS were obtained by combining the values of G20 (glucose released after 20 min), G120 (glucose released after 120 min), FG (free glucose) and TG (total glucose) and using the following formulas:

$$\%\mathrm{RDS} = (\mathrm{G120} - \mathrm{FG}) \times 0.9 \times 100$$
$$\%\mathrm{SDS} = (\mathrm{G120} - \mathrm{G20}) \times 0.9 \times 100$$
$$\%\mathrm{RS} = (\mathrm{TG} - \mathrm{FG}) \times 0.9 \times 100 - (\mathrm{RDS} + \mathrm{SDS})$$

2.4. Light microscopy

Diluted starch samples (1 g in 25 ml of water) in a glass Petri dish on a hot plate for 5 min. After reaching the experimentally specified temperature (between 50 and 80 °C at 5 °C intervals, i.e., 55, 60, and 65 °C, etc.) the Petri dish was promptly viewed using an XP-201 light microscope (Shanghai Caikon Optical Instruments Factory, Shanghai, China) and observed at a 10×40 magnification.

2.5. Swelling factor (SF)

The swelling factor (SF) of the starches was measured according to the blue dextran dye exclusion method of Tester and Morrison (1990). The SF is reported as a ratio of the volume of swollen granules to the volume of dry starch. Starch (100 mg) in water (5.0 ml) was heated in a water bath at the required temperature for 30 min with constant shaking. The tube was then cooled rapidly to 20 °C, 0.5 ml of blue dextran (Pharmacia, M_r 2×10^6, 5 mg/ml) was added, and then contents mixed by gently inverting the closed tubes several times. After centrifuging at 2000*g* for 10 min, the absorbance of the supernatant (A_S) was measured at 620 nm. The absorbance of reference tubes (A_R) that contained no starch was also measured.

Calculation of SF was based on starch weight corrected to 12% moisture, assuming a density of 1.4 g/ml. Free or interstitial-plus-supernatant water (FW) is given by:

$$\mathrm{FW}\ (\mathrm{ml}) = 5.5(A_R - A_S) - 0.5$$

The initial volume of the starch (V_0) of weight W (in mg) is

$$V_0(\mathrm{ml}) = W/1400$$

The volume of absorbed intragranular water (V_1) is

$$V_1 = 5.0 - \mathrm{FW}$$

The volume of the swollen starch granules (V_2) is

$$V_2 = V_0 + V_1$$

The SF can be calculated as:

$$SF = V_2/V_0$$

This can also be expressed by the single equation:

$$SF = 1 + (7700/W)[(A_\mathrm{S} - A_\mathrm{R})/A_\mathrm{S}]$$

2.6. Differential scanning calorimetry (DSC)

The thermal properties of each starch sample were examined using differential scanning calorimetry (Pyris-1, Perkin Elmer Inc., Norwalk, CT, USA). Approximately 3 mg anhydrous starch sample was mixed with 6 mg deionized water and hermetically sealed in an aluminIum pan. The samples were allowed to equilibrate for 12 h at room temperature, then scanned at a heating rate of 5 °C/min from 40 to 120 °C. The differential scanning calorimetry analyser was calibrated using indium as a standard and an empty aluminIum pan was used as the reference. The onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and enthalpy of gelatinization (ΔH) were calculated automatically.

2.7. X-ray diffraction (XRD)

X-ray diffraction analysis was performed with an X' Pert PRO X-ray powder diffractometer (PANalytical, Almelo, The Netherlands) operating at 40 kV and 40 mA with Cu Kα radiation (λ = 1.5406 Å). The starch powder was packed tightly in a rectangular