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Development of maize starch with a slow digestion property using maltogenic α-amylase

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ABSTRACT

In this study, maltogenic α-amylolysis was used to modulate the fine structure of starch responsible for the slow digestion property. The normal maize starch was treated using maltogenic α-amylase for 6 h and showed an increase of slowly digestible starch from 11.1% to 19.6%. Compared to the control starch, the iodine binding analysis showed that the wavelength of maximum absorption and the absorbance was substantially reduced with initial maltogenic α-amylase treatment. The maltogenic α-amylolysis decreased in molecular weight from 32.5×10^7 to 9.0×10^4 g/mol and increased in the number of shorter chains (DP < 13) from 25.5% to 44.8%, which was also accompanied by a reduction of longer chains (DP > 13). The increase in the amount of shorter chains was attributed to the slow digestion property of starch. These results suggest that the normal maize starches modified with partial maltogenic α-amylolysis produced new, fine structures with slow digestible characteristics.

1. Introduction

Starch is a major glycaemic carbohydrate of foods and its nutritional property is related to its rate and extent of digestion as well as glucose absorption in the small intestine. Based on the Englyst assay, starch is generally classified into three major categories to specify its nutritional quality: 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 levels, whereas SDS provides a slow and extended release of glucose into the blood stream (Björck, Liljeberg, & Ostman, 2000; Englyst et al., 1992; Ludwig, 2002; Miao, Jiang, Cui, Zhang, & Jin, 2013; Miao, Xiong, Jiang, Jiang, Cui, & Zhang, 2013). Food containing a substantial amount of SDS has been associated with regulating glucose delivery to the body and its associated metabolic effects, triggering gut hormones that affect gastrointestinal tract motility and satiety (Ells, Seal, Kettlitz, Bal, & Mathers, 2005; Harbis et al., 2004; Ludwig, 2002; Miao, Jiang, 2013; Miao, Xiong, 2013; Seal et al., 2003; Venkatachalam, Kuschnick, Zhang, & Hamaker, 2009). Therefore, a great deal of attention is being given to SDS as a novel, functional material for processed food to effectively control postprandial glucose levels and provide potential health benefits. Currently, there are no commercial SDS-based products available in the food market, and there are limited reports on techniques used for SDS preparation (Ao et al., 2007; Chai, Wang, & Zhang, 2013; Chung, Liu, & Hoover, 2009; Emami, Meda, Pickard, & Tyler, 2010; He, Liu, & Zhang, 2008; Lee, Shin, Kim, Choi, & Moon, 2011; Miao, Jiang, & Zhang, 2009; Miao, Jiang, Zhang, Jin, & Mu, 2011; Miao, Jiang, 2013; Miao, Xiong, 2013).

Maltogenic α-amylase (glucan 1,4-α-maltohydrolase, EC 3.2.1.133) is known to catalyze the hydrolysis of (1 → 4)-α-D-glucosidic linkages in polysaccharides to remove successive-maltose residues from the non-reducing ends of the chains (Christophersen, Otzen, Norman, Christensen, & Schafer, 1998; Goesaert, Leman, Bijttebier, & Delcour, 2009; Min et al., 1998). This enzyme is typically hydrolysed randomly in an external portion (exo-action), however it can hydrolyse internally (endo-action). In addition, maltogenic α-amylase is used in the baking industry as an anti-staling agent because of its ability to reduce the retrogradation of amylopectin (Dauter et al., 1999; Goesaert et al., 2009; Hug-Iten, Escher, & Conde-Petit, 2003; Leman, Goesaert, Vandeputte, Lagrain, & Delcour, 2005). However, little has been reported on maltogenic α-amylase as a tool to sculpt the structure of starch with slow digestion properties. The objectives of the current study were to investigate the impact of maltogenic α-amylase modification of maize starch on its slow digestible property, to study the structure and functional

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properties of enzymatic treated starch and to determine whether it is possible to produce specific SDS, which would provide a method for increasing the SDS content in processed food products and provide potential health benefits.

2. Materials and methods

2.1. Materials

The normal maize starch was a generous gift from Changchun Dacheng Industrial Group Co. Ltd. (Jilin, China). The maltogenic α-amylase from *Bacillus stearothermophilus* (Novamyl® 10,000 BG) was donated by Novozymes (Beijing, China). The α-amylase from porcine pancreas (type VI-B) was purchased from Sigma–Aldrich Chemical Co. (St. Louis, USA). The amyloglucosidase, isoamylase and the glucose oxidase-peroxidase assay kits were purchased 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. Modification of starch samples

The normal maize starch slurry (10%, w/v in diluted pH 5.0, 0.02 M sodium acetate buffer solution) was heated in a water bath at 95 °C for 60 min. The temperature of the starch sample was adjusted to 55 °C and the maltogenic α-amylase (5 U/g dry weight of starch) was added to the solution. The enzymatic reaction was incubated for 1, 2, 3, 6, 12 or 24 h. Immediately after the reaction, the solutions were autoclaved at 121 °C for 30 min to stop the reaction; the solution was then cooled to room temperature and 1 volume of 90% ethanol (v/v) was added to facilitate the precipitation of reactant. The precipitated starch was centrifuged at 5000 *g* for 10 min, washed with deionised water and re-centrifuged twice before collecting and freeze-drying. The collected material was ground to form a powder (120 mesh) and stored in a desiccator for further analysis. These enzymatically hydrolysed samples were named MS1, MS2, MS3, MS4, MS5 and MS6, respectively for enzymatic reaction times of 1, 2, 3, 6, 12 and 24 h. The supernatant of the hydrolysed starch product was collected by stopping the enzymatic reaction at different times and the degree of hydrolysis was determined using the phenol–sulphuric acid method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956).

2.3. In vitro digestibility analysis

The digestibility of starch was analyzed according to the procedure of Englyst et al. (1992) with a slight modification. The amyloglucosidase solution (0.14 ml) was diluted to 6.0 ml with deionised water to prepare Enzyme Solution I. 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 and then centrifuging the mixture for 10 min at 3000 *g*. Finally, a portion (54.0 ml) of the supernatant was transferred to a beaker. Enzyme Solution 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).

The starch sample (200 mg) was dissolved in 15 ml of phosphate buffer (0.2 M, pH 5.2) by vortex mixing. After the starch solution was equilibrated at 37 °C for 5 min, seven glass balls (10 mm diameter) and Enzyme Solution III (5.0 ml) were added. The samples were then shaken in a 37 °C water bath at 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 hydrolysate was determined using the glucose oxidase/peroxidase assay kits. The percentage of hydrolysed starch was calculated by multiplying the glucose content by a factor of 0.9. Each sample was analyzed in triplicate.

The values of the different carbohydrate nutritional fractions (rapidly digestible starch, RDS, slowly digestible starch, SDS and resistant starch, 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) using the following formulas:

$$\%RDS = (G120 - FG) \times 0.9 \times 100$$

$$\%SDS = (G120 - G20) \times 0.9 \times 100$$

$$\%RDS = (TG - FG) \times 0.9 \times 100 - \%RDS - \%SDS$$

2.4. Iodine binding analysis

The iodine binding analysis was measured using a UV/visible Spectrophotometer (UV-2102PC, Unico Instrument Co., Ltd., Shanghai, China). An iodine reagent was prepared by adding 2 mg of I_2 and 20 mg of KI to 1 ml deionised water; the solution was stored in a non-actinic bottle at room temperature. The dried starch sample (50 mg) was dissolved in deionised water in 10 ml screw-cap vials. The diluted starch solution (0.5 ml) was mixed with the iodine solution (1.5 ml) and was then adjusted to a final volume of 2 ml with water. The absorbance spectra and wavelength of maximum absorption (λ_{max}) were analyzed via a wavelength scan from 500 to 800 nm.

2.5. High-performance size-exclusion chromatography (HPSEC) analysis

The starch samples (10 mg) were added to 5 ml deionised water, stirred and boiled for 15 min to completely dissolve the samples. The dissolved samples were filtered through 5 μm cellulose acetate filters (Whatman, Maidstone, UK) and were injected into a high-performance size exclusion chromatography system with a multi-angle laser light scattering detector and a refractive index detector (HPSEC-MALLS-RI) (Wyatt Technology, Santa Barbara, CA, USA). Two series tandem columns (300 mm × 8 mm, Shodex OH-pak SB-806 and 804, Showa Denko K.K., Tokyo, Japan) with an OH-pak SB-G guard column, a DAWN HELEOS II laser photometer fitted with a He–Ne laser (λ = 632.8 nm) with a K-5 flow cell, and an OPTILAB® T-rEX Interferometric Refractometer were used. The flow rate was set at 0.5 ml/min with a mobile phase of distilled-deionised water (pH 6.8, 18.2 MΩ cm) containing 0.02% NaN_3. A d*n*/d*c* value of 0.138 was used in molecular weight calculations, and data processing was performed using ASTRA software (Version 5.3.4.14, Wyatt Technology, Santa Barbara, CA, USA).

2.6. High-performance anion-exchange chromatography (HPAEC) analysis

The chain length distribution of starch was determined by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The samples (10 mg) were dissolved with 2 ml sodium acetate solution (pH 4.0, 0.1 M) and heated in a boiling water bath for 10 min. Isoamylase (0.5 U) was added to each dispersion, and the mixtures were incubated at 40 °C with shaking for 24 h. Then, the solution was heated in a boiling water bath for 10 min to deactivate the enzyme. The debranched sample solutions were filtered through a 0.45-μm membrane filter and then injected into the HPAEC-PAD system (50 μl sample loop). The HPAEC-PAD system consisted of a Dionex DX 600 equipped with an ED 50 electrochemical detector with a gold working electrode, GP 50 gradient pump, LC 30 chromatography oven, and an AS 40 automated sampler (Dionex Corporation, Sunnyvale, CA, USA). The standard triple potential waveform was utilized, with the following period and pulse potentials: T1 = 0.40 s, with 0.20 s sampling time, E1 = 0.05 V; T2 = 0.20 s, E2 = 0.75 V; T3 = 0.40 s, E3 = –0.15 V.

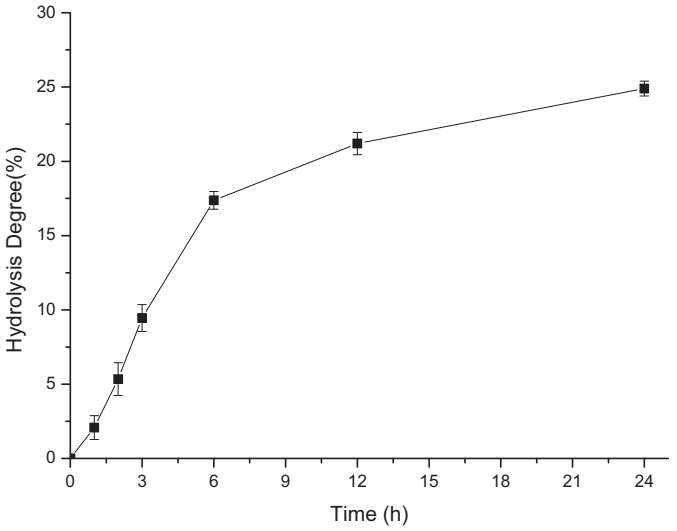

Fig. 1. Hydrolysis of normal maize starch after cooking by maltogenic α-amylase over time.

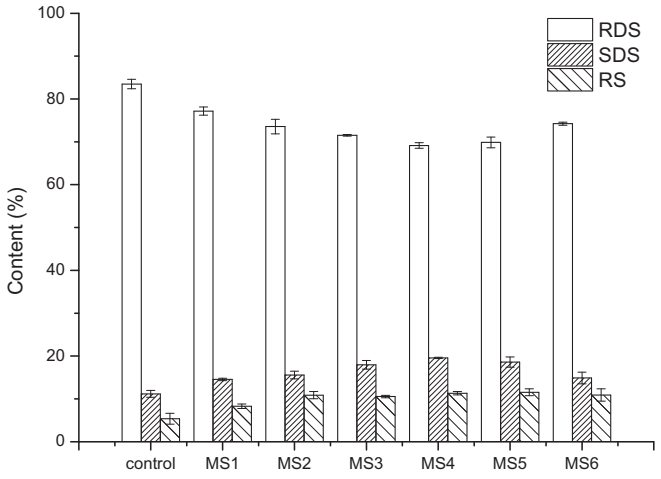

Fig. 2. Nutritional starch fractions of maltogenic α-amylase treated starches.

The data were collected using Chromeleon software (version 6.50, Dionex Corporation, Sunnyvale, CA, USA). The eluents were prepared in distilled deionised water with helium sparging; eluent A consisted of 150 mM NaOH, and eluent B consisted of 50 mM sodium acetate in 150 mM NaOH. The linear components were separated on a Dionex CarboPac™ PA1 column with a gradient elution (40% of eluent B at 0 min, 50% at 2 min, 60% at 10 min, and 80% at 40 min) at 30 °C and a flow rate of 1 ml/min.

2.7. Statistical analysis

The data were analyzed by the Duncan test using the statistical analysis system (SAS Institute, Cary, NC). A level of 0.05 was set to determine statistical significance.

3. Results and discussion

3.1. Enzymatic hydrolysis

The hydrolysis profile of normal maize starch during maltogenic α-amylase treatment over 24 h is presented in Fig. 1. The degree of hydrolysis of normal maize starch increased substantially up to 17.4% in the first 6 h and then incrementally increased to the values of 24.9% at 24 h. As previously shown by Christophersen et al. (1998), maltogenic α-amylase shows sequence homology to cyclo-glycosyl transferases and is clearly different from exoglucanases, such as β-amylase and glucoamylase. Maltogenic α-amylase is a retaining enzyme, and able to degrade both amylopectin and amylose to maltose and oligosaccharides; in addition, the enzymatic modification does not require an unblocked, non-reducing end by an endo-type mechanism, which shows that maltogenic α-amylase can degrade β-limit dextrin. Additionally, the enzyme activity is inhibited by high product concentration, indicative of a secondary maltodextrin binding site or unproductive binding in the active site. Yun and Matheson (1993) reported that the upper limit of maltose produced from β-amylolysis of normal maize starch was approximately 56%, which was higher than maltogenic α-amylase treatment. Based on these observations, the difference in the degree of hydrolysis might be attributed to the substrate inhibition of maltogenic α-amylase as suggested by Christophersen et al. (1998). According to Min et al. (1998), maltogenic α-amylase from *Bacillus subtilis* SUH 4–2, which selectively produces maltose and maltotriose from the starch solution, and another amylase from *Streptomyces albus* KSM-35, which primarily produces maltotetraose and maltotriose, have been used as antistaling agents for bread. They also found that as the incubation time increases, the content of maltose and maltodextrins show an initial rapid increase up to 10 h and then gradually increases, which confirmed our results.

3.2. In vitro starch digestibility

The enzymatic digestibility of maltogenic α-amylase treated starch samples are shown in Fig. 2. The Englyst assay is a classic method used to categorize starch fractions based on the rate of glucose released and its absorption in the gastrointestinal tract. RDS, SDS and RS are the three consecutive nutritional starch fractions divided by reaction time. As illustrated in Fig. 2, the maltogenic α-amylase treated starch samples had an increase in slow digestion property, which was higher than the normal maize starch (control sample). The heated maize starch (control sample) contained 83.5% RDS, 11.1% SDS and 5.4% RS. Compared to the control sample, the content of the RDS was reduced 6.3%, 9.9%, 12.0%, 14.3%, 13.6% and 9.3% for MS1, MS2, MS3, MS4, MS5 and MS6, respectively, whereas, the content of the SDS was 14.6%, 15.6%, 18.0%, 19.6%, 18.6%, 14.9% for these six samples, respectively. Ao et al. (2007) also reported that normal maize starch subjected maltogenic α-amylase (7.0 U/g dry weight of starch) for 5 h produced 18.8% SDS with a reduction of 19.8% RDS, which was similar to the data obtained in this study. The maltogenic α-amylase modified starch also had a greater RS than the control sample but different content, which might be attributed to the branched oligosaccharide production by maltogenic α-amylase via transglycosylation (Min et al., 1998; Kwon et al., 1999). The branched oligosaccharides are oligomers of α-D-glucopyranose linked primarily by 1,4-bonds and containing at least one 1,6-glycosidic linkage, which are primarily composed of isomaltose, isomaltotriose, panose and several others composed of four or five glucose residues. According to Miao et al. (2014), amylolytic hydrolysis of α-1,6 linkages takes place at a slower rate than that of α-1,4 linkages, which indicates that the branched oligosaccharides can be used as prebiotics to promote health and treat diseases (Swennen, Courtin, & Delcour, 2006).

3.3. Iodine binding

The wavelength scanning profiles of maltogenic α-amylase treated starches binding iodine are shown in Fig. 3. Shen, Bertoft, Zhang, and Hamaker (2013) have shown that amylose and amylopectin can bind iodine to form a blue complex, which can be

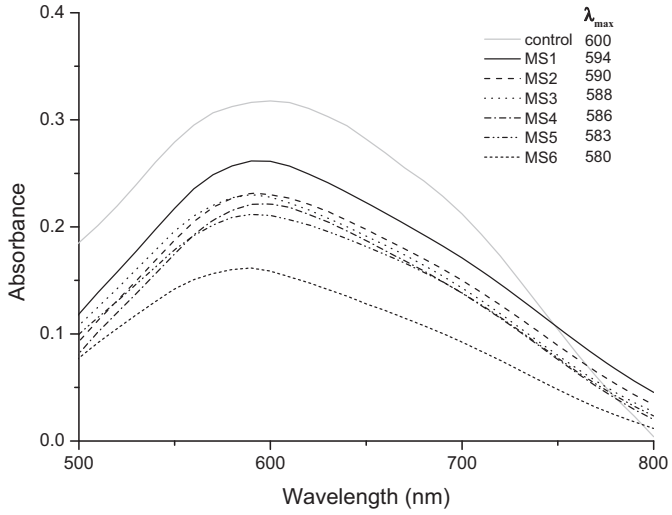

Fig. 3. Wavelength scanning profile of maltogenic α-amylase treated starches binding iodine.

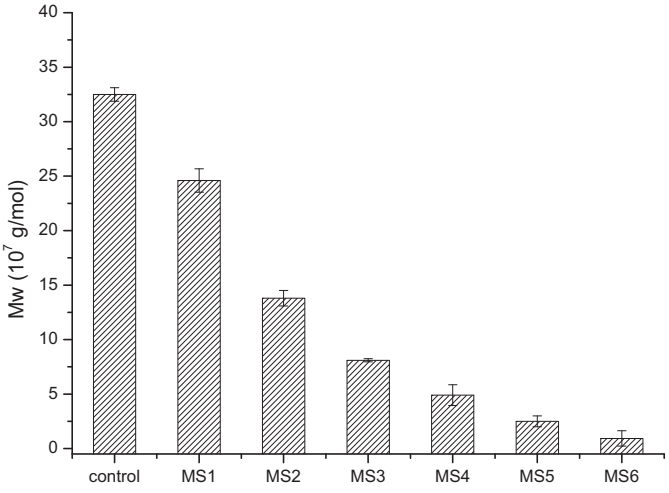

Fig. 4. Changes of molecular weight of maltogenic α-amylase treated starches.

measured spectrophotometrically to estimate the affinity of the polysaccharide structure. There are variations in terms of absorptivity and λ_{max} depending on the degree of polymerization (DP) and the structural properties of starch molecules, which determine the composition of the poly-iodine chains complexed with the linear chain helices. As illustrated in Fig. 3, the iodine binding with native maize starch (control) showed a λ_{max} of approximately 600 nm and an absorbance of 0.32, while both λ_{max} and absorbance reduced substantially with initial maltogenic α-amylase treatment. When the length of the starch chain decreased with the extent of enzymatic modification (Table 1), the number of helical turns reduced, and the number of iodine molecules that could be accommodated also decreased with a resulting lower iodine binding capacity (absorbance reduced from 0.32 to 0.16). This decreased binding resulted in a shift in the λ_{max} (from 600 to 580 nm). According to Bailey and Whelan (1961), $1/\lambda_{max}$ has been shown to be directly proportional to 1/DP up to a DP of approximately 100 in linear chains, and the absorbance value of the complex decreases with decreased molecular weight of α-1,4 linked starch, which was in line with the results obtained in this study.

3.4. Molecular weight analysis

Fig. 4 shows the changes in molecular weight (Mw) of maize starch during maltogenic α-amylolysis. The Mw rapidly decreased after the 6 h enzymatic treatment (from 32.5×10^7 to 4.9×10^7 g/mol), and then very slowly decreased, tapering off at approximately 9.0×10^4 g/mol. According to BeMiller and Whistler (2009), the native starch presented two molecular weight fractions: amylopectin, which indicates larger molecule (10^7–10^8), and amylose, which represents smaller molecule (10^4–10^6). The data demonstrated that maltogenic α-amylase hydrolysis induced a shift in the amylopectin Mw to the low Mw region, which indicated that the enzyme treated starch had lower proportions of larger molecules and greater proportions of smaller molecules than the native starch. Leman, Goesaert, and Delcour (2009) found that the SEC chromatogram of maltogenic α-amylolysis treated starch could be divided into two regions, with a marked shift in iodine binding at Kav of approximately 0.2, which indicated a sharp transition from amylopectin to amylose. The addition of maltogenic α-amylase reduced the levels and Mw of amylose and amylopectin. According to Christophersen et al. (1998), maltogenic α-amylase quickly reduced the peak DP of amylose with only a minor formation of glucose, maltose and other low Mw oligosaccharides. They reported that only 3% of low Mw oligosaccharides were produced, but the DP was drastically reduced from DP 350 to DP 123. Bijttebier, Goesaert, and Delcour (2010) reported that the maltogenic α-amylase from *Bacillus stearothermophilus* preferentially hydrolysed the exterior chains of amylopectin during the early stages of hydrolysis, and also hydrolysed inner chains using high multiple attack action during the later phases. The data suggested that endo-mechanism of maltogenic α-amylase was in line with the reduced Mw of the starch molecule.

Table 1
Chain length distribution of maltogenic α-amylase treated starches.

Sample	Fr I (DP > 30, %)	Fr II (13 < DP < 30, %)	Fr III (DP < 13, %)
Control	29.6 ± 2.4[a]	44.8 ± 0.4[a]	25.6 ± 0.3[a]
MS 1	28.6 ± 0.2[a]	42.8 ± 0.3[b]	28.6 ± 0.7[b]
MS 2	28.0 ± 0.3[b]	40.9 ± 1.1[c]	31.1 ± 0.1[b]
MS 3	27.2 ± 0.0[c]	37.8 ± 0.6[a]	35.0 ± 0.2[c]
MS 4	26.7 ± 0.5[b]	34.5 ± 0.2[b]	38.8 ± 0.3[a]
MS 5	25.4 ± 0.3[a]	33.0 ± 0.4[c]	41.6 ± 0.0[c]
MS 6	22.3 ± 1.0[b]	32.9 ± 0.5[a]	44.8 ± 0.8[b]

Significant difference in each column is expressed as different superscript letters ($p < 0.05$).

3.5. Chain length analysis

The proportion of fraction I (long, DP > 30), II (intermediate and short, 13 < DP < 30), and III (very short, DP < 13) linear chains of maltogenic α-amylase treated starch samples is present Table 1. According to the Hizukuri cluster model, amylopectin molecules have A, B (B1–B4), and C chains, in which the fractions of DP < 13 and DP 13–30 together compose the short chains and correspond to A + B1 chains; the other longer chain fractions (DP > 30) correspond to B2–B4 chains (Hizukuri, 1986). The maltogenic α-amylase treatment increased the percentage of fraction III from 25.6% to 44.8% and accompanied a reduction of fraction II and fraction I with increasing time of hydrolysis treatment, which indicated that both amylose linear chains and amylopectin branch chains (A and B1–B4 chains) were shortened by the action of the hydrolysis enzyme. However, the maltogenic α-amylolysis of maize starch markedly decreased fraction II content compared to the control, and somewhat decreased fraction I. When the starch sample was prepared with maltogenic α-amylase, the A + B1 chains of amylopectin were more a proportion of degradation than B2–B4 chains, in line with the result of Bijttebier et al. (2010). They found the appearance of several subpopulations of DP 2, DP 5–6, and DP 8 in the case

of maltogenic α-amylase was most likely typical for a multiple attack action on exterior chains of amylopectin. Leman et al. (2009) reported that maltogenic α-amylase had a marked influence on the side chain distribution of the starch sample, which especially led to a decrease of short B chains. The enzyme increased the relative levels of the short chains (DP < 9) from 23.7% to 44.2%, and the reduction was most pronounced for the side chains with DP 10–11 and 12–16; the relative levels of these chains in the control wheat sample (56.9%) was reduced by 16% after maltogenic α-amylolysis. The results showed that maltogenic α-amylase reduced the level of the outer chains (primarily A and B1) by 50% compared to the control sample with little effect on the internal chain length. Based on these observations, it might be concluded that the addition of maltogenic α-amylase reduced the molecular weight and level of the amylopectin fraction to a lesser extent, but had a significant influence on the side chain distribution of the residual amylopectin with increased relative levels of short chains.

In some earlier studies, differences in the digestibility of starch has been attributed to the interplay of many factors, such as starch source, granule size, crystallinity, molecular fine structure, surface pores and interior channels (Miao et al., 2013a, 2013b; Tester, Karkalas, & Qi, 2004). Our data showed that the enzyme modified starch sample MS4 with higher SDS content (19.6%) had a higher proportion of short chains after maltogenic α-amylolysis modification (Table 1). Zhang, Ao, and Hamaker (2008) found a parabolic relationship between the chemical structure of starch and the slow digestion property of maize starch mutants, indicating that starch with either a high amount of short chains (DP < 13) or a high amount of long chains (DP ≥ 13) had a higher content of SDS. The above results suggest that fine structure differences of starch could drive the amount of SDS and starch with a high content of short chains could have a higher content of SDS.

4. Conclusions

Partial maltogenic α-amylolysis of the normal maize starch reduced starch digestibility, which was related to the molecular weight and chain length. A maximum SDS content (19.6%) was obtained using maltogenic α-amylase hydrolysis over 6 h. An increase of the shorter chain fractions (DP < 13) led to more SDS and RS. Further work is underway to obtain an accurate and quantitative structure-property relationship model for modulating starch digestibility by enzymatic modification. The experimental data that can be obtained with such a model could help determine a process to design a novel glycaemic starch, which may have potential health benefits.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.12.041.

References

Ao, Z., Simsek, S., Zhang, G., Venkatachalam, M., Reuhs, B. L., & Hamaker, B. R. (2007). Starch with a slow digestion property produced by altering its chain length, branch density, and crystalline structure. *Journal of Agricultural and Food Chemistry*, *55*, 4540–4547.

Bailey, J. M., & Whelan, W. J. (1961). Physical properties of starch. *Journal of Biological Chemistry*, *236*, 969–973.

BeMiller, J. N., & Whistler, R. L. (2009). *Starch: Chemistry and technology* (3rd ed.). New York: Academic Press.

Bijttebier, A., Goesaert, H., & Delcour, J. A. (2010). Hydrolysis of amylopectin by amylolytic enzymes: Structural analysis of the residual amylopectin population. *Carbohydrate Research*, *345*, 235–242.

Björck, I., Liljeberg, H., & Ostman, E. (2000). Low glycaemic-index foods. *British Journal of Nutrition*, *83*, 149–155.

Chai, Y., Wang, M., & Zhang, G. (2013). Interaction between amylose and tea polyphenols modulates the postprandial glycemic response to high-amylose maize starch. *Journal of Agricultural and Food Chemistry*, *61*, 8608–8615.

Christophersen, C., Otzen, D. E., Norman, B. E., Christensen, S., & Schafer, T. (1998). Enzymatic characterisation of Novamyl® a thermostable α-amylase. *Starch*, *50*, 39–45.

Chung, H.-J., Liu, Q., & Hoover, R. (2009). Impact of annealing and heat-moisture treatment on rapidly digestible, slowly digestible and resistant starch levels in native and gelatinized corn, pea and lentil starches. *Carbohydrate Polymers*, *75*, 436–447.

Dauter, Z., Dauter, M., Brzozowski, A. M., Christensen, S., Borchert, T. V., Beier, L., et al. (1999). X-ray structure of Novamyl, the five-domain "maltogenic" α-amylase from *Bacillus stearothermophilus*: maltose and acarbose complexes at 1.7 Å resolution. *Biochemistry*, *38*, 8385–8392.

Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., & Smith, F. (1956). Colorimetric method for determination of sugars and related substances. *Analytical Chemistry*, *28*, 350–356.

Ells, L. J., Seal, C. J., Kettlitz, B., Bal, W., & Mathers, J. C. (2005). Postprandial glycaemic, lipaemic and haemostatic responses to ingestion of rapidly and slowly digested starches in healthy young women. *British Journal of Nutrition*, *94*, 948–955.

Emami, S., Meda, V., Pickard, M. D., & Tyler, R. T. (2010). Impact of micronization on rapidly digestible, slowly digestible, and resistant starch concentrations in normal, high-amylose, and waxy barley. *Journal of Agricultural and Food Chemistry*, *58*, 9793–9799.

Englyst, H. N., Kingman, S. M., & Cummings, J. H. (1992). Classification and measurement of nutritionally important starch fractions. *European Journal of Clinical Nutrition*, *46*, 30–50.

Goesaert, H., Leman, P., Bijttebier, A., & Delcour, J. A. (2009). Antifirming effects of starch degrading enzymes in bread crumb. *Journal of Agricultural and Food Chemistry*, *57*, 2346–2355.

Harbis, A., Perdreau, S., Vincent-Baudry, S., Charbonnier, M., Bernard, M. C., Raccah, D., et al. (2004). Glycemic and insulinemic meal responses modulate postprandial hepatic and intestinal lipoprotein accumulation in obese, insulin resistant subjects. *American Journal of Clinical Nutrition*, *80*, 896–902.

He, J., Liu, J., & Zhang, G. (2008). Slowly digestible waxy maize starch prepared by octenyl succinic anhydride esterification and heat-moisture treatment: Glycemic response and mechanism. *Biomacromolecules*, *9*, 175–184.

Hizukuri, S. (1986). Polymodal distribution of the chain lengths of amylopectin and its significance. *Carbohydrate Research*, *147*, 342–347.

Hug-Iten, S., Escher, F., & Conde-Petit, B. (2003). Staling of bread: Role of amylose and amylopectin and influence of starch-degrading enzymes. *Cereal Chemistry*, *80*, 654–661.

Kwon, K. S., Auh, J. H., Choi, S. K., Kang, G. J., Kim, J. W., & Park, K. H. (1999). Characterization of branched oligosaccharides produced by *Bacillus licheniformis* maltogenic amylase. *Journal of Food Science*, *64*, 258–261.

Lee, C. J., Shin, S. I., Kim, Y., Choi, H. J., & Moon, T. W. (2011). Structural characteristics and glucose response in mice of potato starch modified by hydrothermal treatments. *Carbohydrate Polymers*, *83*, 1879–1886.

Leman, P., Goesaert, H., & Delcour, J. A. (2009). Residual amylopectin structures of amylase-treated wheat starch slurries reflect amylase mode of action. *Food Hydrocolloids*, *23*, 153–164.

Leman, P., Goesaert, H., Vandeputte, G. E., Lagrain, B., & Delcour, J. A. (2005). Maltogenic amylase has a non-typical impact on the molecular and rheological properties of starch. *Carbohydrate Polymers*, *62*, 205–213.

Ludwig, D. S. (2002). The glycemic index physiological mechanism relating to obesity, diabetes, and cardiovascular disease. *JAMA*, *287*, 2414–2423.

Miao, M., Jiang, B., Cui, S. W., Zhang, T., & Jin, Z. (2013). Slowly digestible starch—A review. *Critical Reviews in Food Science and Nutrition*, http://dx.doi.org/10.1080/10408398.2012.704434 (in press)

Miao, M., Jiang, B., & Zhang, T. (2009). Effect of pullulanase debranching and recrystallization on structure and digestibility of waxy maize starch. *Carbohydrate Polymers*, *76*, 214–221.

Miao, M., Jiang, B., Zhang, T., Jin, Z., & Mu, W. (2011). Impact of mild acid hydrolysis on structure and digestion properties of waxy maize starch. *Food Chemistry*, *126*, 506–513.

Miao, M., Li, R., Jiang, B., Cui, S. W., Lu, K., & Zhang, T. (2014). Structure and digestibility of endosperm water-soluble α-glucans from different sugary maize mutants. *Food Chemistry*, *143*, 156–162.

Miao, M., Xiong, S., Jiang, B., Jiang, H., Cui, S. W., & Zhang, T. (2013). Improved the slow digestion property of maize starch using partially β-amylolysis. *Food Chemistry*, http://dx.doi.org/10.1016/j.foodchem.2013.11.148 (in press)

Min, B.-C., Yoon, S.-H., Kim, J.-W., Lee, Y.-W., Kim, Y.-B., & Park, K. H. (1998). Cloning of novel maltooligosaccharide-producing amylases as antistaling agents for bread. *Journal of Agricultural and Food Chemistry*, *46*, 779–782.

Seal, C. J., Daly, M. E., Thomas, L. C., Bal, W., Birkett, A. M., Jeffcoat, R., et al. (2003). Postprandial carbohydrate metabolism in healthy subjects and those with type 2 diabetes fed starches with slow and rapid hydrolysis rates determined *in vitro*. *British Journal of Nutrition*, *90*, 853–864.

Shen, X., Bertoft, E., Zhang, G., & Hamaker, B. R. (2013). Iodine binding to explore the conformational state of internal chains of amylopectin. *Carbohydrate Polymers*, *98*, 778–783.

Swennen, K., Courtin, C. M., & Delcour, J. A. (2006). Non-digestible oligosaccharides with prebiotic properties. *Critical Reviews in Food Science and Nutrition*, *46*, 459–471.

Tester, R. F., Karkalas, J., & Qi, X. (2004). Starch—Composition, fine structure and architecture. *Journal of Cereal Science*, *39*, 151–165.

Venkatachalam, M., Kuschnick, M. R., Zhang, G., & Hamaker, B. R. (2009). Starch-entrapped biopolymer microspheres as a novel approach to vary blood glucose profiles. *Journal of the American College of Nutrition*, *28*, 583–590.

Yun, S., & Matheson, N. (1993). Structures of the amylopectins of waxy, normal, amylose-extender, and wx-ae genotypes and of the phytoglycogen of maize. *Carbohydrate Research*, *243*, 307–321.

Zhang, G., Ao, Z., & Hamaker, B. R. (2008). Nutritional property of endosperm starches from maize mutants: A parabolic relationship between slowly digestible starch and amylopectin fine structure. *Journal of Agricultural and Food Chemistry*, *56*, 4686–4694.