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Effect of debranching and heat-moisture treatments on structural characteristics and digestibility of sweet potato starch

Ting-Ting Huang [a], Da-Nian Zhou [a], Zheng-Yu Jin [b], Xue-Ming Xu [b], Han-Qing Chen [a,*]

[a] School of Biotechnology and Food Engineering, Hefei University of Technology, 193 Tunxi Road, Hefei, Anhui 230009, PR China
[b] State Key Laboratory of Food Science and Technology, School of Food Science and Technology, Jiangnan University, 1800 Lihu Road, Wuxi, Jiangsu 214122, PR China

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ABSTRACT

The effects of debranching treatment (DT) and debranching-heat-moisture treatment (D-HMT) on the structural characteristics and *in vitro* digestibility of sweet potato starch were investigated. The results indicated that DT and D-HMT decreased the percentage of starch fraction with degree of polymerization (DP) $\leqslant 13$, increased the percentages of the other fractions, and decreased the molecular weight of starch sample. The D-HMT starch showed a considerable SDS content of 31.60%. Compared with the DT starch sample, the T_o, T_p, T_c, $T_c - T_o$ and ΔH of D-HMT starch samples for the second endothermal were increased significantly, crystalline pattern was altered from C_a to A type, the surface became more smooth. The pasting temperatures of DT and D-HMT starch samples were higher while the peak viscosities, breakdown and setback values were lower than that of native starch. These results suggested that structural changes of sweet potato starch by D-HMT significantly affected the digestibility.

1. Introduction

Sweet potato is one of the most common crops and staple food in China, and it is highly easy to manage and cultivate. Starch is one of the main components of sweet potato root. As a major source of carbohydrate in the human diet, starch plays a very important role in supplying metabolic energy and nutrition for humans. According to the rate and extent of starch digestion, starch is classified into rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) (Englyst, Kingman, & Cummings, 1992). RDS is the starch fraction that has been rapidly digested and absorbed in the gastrointestinal tract, which causes a sudden increase in blood glucose level after ingestion, whereas SDS is the starch fraction that is digested slowly but completely and sustains glucose release over time. RS has been defined as the starch portion that cannot be digested in the upper gastrointestine, but it can be fermented by microorganisms in the large intestine, which produces short-chain fatty acids that is beneficial to colonic health (Zhang & Hamaker, 2009). Food containing high content of SDS tends to sustain plasma glucose levels that may help to control and prevent diabetes. Such foods may also be beneficial to satiety, physical performance, improved glucose tolerance, and reduced blood lipid levels in both healthy individuals and those with hyperlipidaemia (Jenkins et al., 2002). Therefore, SDS has attracted much attention as a new functional food component in novel food development in recent years.

Recently, a number of methods have been applied to prepare SDS products from various sources of starch. These methods include enzymatic modification by debranching (Guraya, James, & Champagne, 2001a, 2001b; Miao, Jiang, & Zhang, 2009; Shin et al., 2004; Zeng et al., 2014), chemical modification by citric acid treatment (Shin et al., 2007), cross-linking (Woo & Seib, 2002), and esterification (Han & BeMiller, 2007), and physical modification by hydrothermal treatment (Ahn et al., 2013; Chung, Liu, & Hoover, 2009; Lee, Kim, Choi, & Moon, 2012; Lee, Shin, Kim, Choi, & Moon, 2011; Shin, Kim, Ha, Lee, & Moon, 2005; Song et al., 2014) and retrogradation treatment (Hu, Xie, Jin, Xu, & Chen, 2014; Hu et al., 2015; Park, Baik, & Lim, 2009; Tian et al., 2012, 2013; Xie, Hu, Jin, Xu, & Chen, 2014a, 2014b; Zhang, Hu, Xu, Jin, & Tian, 2011; Zhou, Baik, Wang, & Lim, 2010; Zhou & Lim, 2012). Among these methods, pullulanase debranching and hydrothermal treatment are safe and cost-effective techniques that have significant effect on the formation of SDS.

Enzymatic modification by debranching can cleave the branching point of α-1, 6-linkages and generate short linear α-1, 4-linked glucans, accompanying reforming of double helix structure at the temperature below the melting temperature (T_m). Some studies have indicated that high debranching enzyme concentration and short debranching time are suitable to prepare SDS from rice starch

* Corresponding author. Tel./fax: +86 551 62901516.
E-mail address: hanqchen@hfut.edu.cn (H.-Q. Chen).

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or waxy maize starch, whereas long debranching time is beneficial to RS formation (Guraya et al., 2001b; Miao et al., 2009). Guraya et al. (2001a) demonstrated that both waxy rice starch and non-waxy rice starch were suitable to prepare SDS, but the SDS content of waxy rice starch was higher than that of non-waxy rice starch after debranching and cooling treatments. Moreover, Zeng et al. (2014) reported that pullulanase debranching and subsequent temperature-cycled crystallization treatment produced a higher yield and more thermo-stable SDS product from rice starch compared with debranching combining isothermal crystallization treatment. However, heat-moisture treatment (HMT) can cause some gelatinization or other damage of the starch granules (Stute, 1992), which leads to the structural changes within amorphous and crystalline regions in the starch granules. Pullulanase debranching followed by HMT can cause the relatively short linear chains that located in amorphous and/or semi-crystalline regions to realign the new double-helical crystalline structures, while these short linear chains can also reassociate with the crystalline structure formed with long linear chains, which leads to more perfect the crystalline regions and the increment of SDS and RS contents (Trinh, Choi, & Moon, 2013). Trinh et al. (2013) also confirmed that debranching and hydrothermal treatments could significantly increase the boiling-stable SDS and RS contents of water yam starch.

Although some studies have reported the effect of hydrothermal treatment on formation and structural characteristics of SDS from sweet potato starch (Ahn et al., 2013; Shin et al., 2005; Song et al., 2014), however, few studies regarding the effect of pullulanase debranching combined HMT on formation and structural characteristics of SDS from sweet potato starch have been reported. Therefore, the objective of the present study was to investigate the effect of pullulanase debranching combined HMT on structural characteristics and *in vitro* digestibility of sweet potato starch.

2. Materials and methods

2.1. Materials

The fresh sweet potatoes were purchased from a local market of Hefei city, China. α-amylase type VI-B from porcine pancreas (EC 3.2.1.1, A3176) was purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). Amyloglucosidase (EC 3.2.1.3) and pullulanase (EC 3.2.1.41) OPTIMAX L-1000 from *Bacillus licheniformis* were purchased from Shanghai Yuanye Bio-Technology Co. Ltd. (Shanghai, China) and Genencor Bio-products Co. Ltd. (Wuxi, China), respectively. Isoamylase (Cat. No. I5284-1MU, ammonium sulfate suspension, ⩾3,000,000 units/mg protein) from *Pseudomonas* sp. was obtained from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). All other chemical reagents were of analytical grade (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China).

2.2. Isolation of starch from sweet potato

Sweet potatoes were washed, peeled and cut into cubes. The small pieces of sweet potato were soaked in 0.1% (w/v) sodium bisulfite solution for 10 min, and then smashed with the high speed blender containing sodium bisulfite solution. The resulting slurry was passed through 100-mesh sieve to remove the debris. Then, the suspension was filtered for three times using 180-mesh sieve, and allowed to settle at 8–10 °C for 24 h. The precipitated starch was suspended in distilled water and precipitated again. This procedure was repeated until the color of the precipitated starch was pure white. The starch layer was dried at 45 °C for 24 h in a drying oven. Then, it was milled and passed through a 100-mesh sieve.

2.3. Debranching treatment and heat-moisture treatment (HMT) of sweet potato starch

Starch (5.0 g) was dispersed with 45 ml phosphate buffer (pH 4.4) and cooked at 100 °C for 30 min in a water bath. The resultant gels were cooled to 58 °C and debranched by pullulanase at the concentration of 25 ASPU/g. After the reaction for 24 h, two volumes of 95% ethanol were added immediately to terminate the enzyme reaction. The mixture was centrifuged at 3500 rpm for 10 min and the precipitate was washed twice with distilled water. The collected precipitate pallet was dried in a drying oven at 45 °C for 24 h to reach final moisture content of around 10%, then milled and passed through a 100-mesh sieve.

The debranched starch sample was packed into the stainless steel can, and moisture content was adjusted to be 30% by adding an appropriate amount of distilled water, then the can was sealed and allowed to stand at room temperature overnight to reach an equilibrium state. The HMT was conducted by storing the can in an air-drying oven at 100 °C for 2 h. After the HMT, the starch sample in the can was dried in a drying oven at 45 °C for 24 h to reach final moisture content of around 10%, then milled and passed through a 100-mesh sieve.

2.4. High-performance anion-exchange chromatography analysis

The high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) was used to determine the chain length distribution of starch samples. The sample (10 mg) was added into sodium acetate buffer (2 ml, pH 3.5, 50 mM) and heated in a boiling water bath for 30 min. After cooled and debranched by isoamylase (0.5 U) for 24 h, the solution was heated in a boiling water bath for 20 min to deactivate the enzyme. The debranched starch sample solution was filtered through a 0.45-μm membrane filter and then injected into the HPAEC-PAD system (50 μl sample loop). The HPAEC-PAD system is a Dionex ICS-500 (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. The eluents were prepared in distilled and deionised water with helium sparging; eluent A was 100 mM NaOH, and eluent B consisted of 60 mM sodium acetate dissolved in 100 mM NaOH. The linear components were separated on a Dionex CarboPacPAC PA200 (250 × 4 mm I.D.) column with a gradient elution (20% of eluent B at 0 min, and 100% at 60 min) at 30 °C and a flow rate of 1 ml/min.

2.5. High-performance gel filtration chromatography analysis

The starch sample (10 mg) was added into 5 ml dimethyl sulfoxide (DMSO) containing 50 mM $NaNO_3$, stirred and boiled for 60 min and incubated at 50 °C for 24 h to completely dissolve the sample. The dissolved sample was filtered through a 0.45-μm cellulose acetate filter and then injected into a high-performance gel filtration chromatography system (HPGFC). The HPGFC instrument (Waters 600) consists of a connected column (Ultrahydrogel™ Linear 300 mm × 7.8 mm id × 2) and a 2410 differential refraction detector. The flow rate was 0.9 ml/min using 0.1 M $NaNO_3$ as the mobile phase. All data provided by HPGFC system were collected and analyzed using an Empower workstation.

2.6. Determination of in vitro digestibility of starch

The *in vitro* digestibility of the starch samples were determined according to the previously described method of Englyst et al. (1992) with a slight modification. Starch (200 mg) was dissolved in phosphate buffer (15 ml, 0.2 mol/l, pH 5.2) in centrifuge tube

by vortexing. Before seven glass balls (10 mm diameter) and 5 ml of enzyme solution (290 U/ml porcine pancreatic α-amylase and 15 U/ml amyloglucosidase) were added, the centrifuge tube was equilibrated in a water bath at 37 °C for 5 min. Subsequently the centrifuge tube was shaked (150 rpm) at 37 °C in a water bath, simultaneously keeping time. At time intervals of 20 and 120 min, aliquots of hydrolyzed solution (0.5 ml) were taken and mixed with absolute ethanol (4 ml) to deactivate the enzyme, then the mixture was centrifuged at 2000 rpm for 10 min. The glucose content in the supernatant was measured using 3, 5-dinitrosalicylic acid (DNS) method (Miller, 1959), and the percentage of hydrolyzed starch was calculated by multiplying the glucose content with a factor of 0.9. Each sample was determined in triplicate.

The percentages of RDS, SDS and RS fractions in each sample were obtained by the following equations:

$$\text{RDS}\ (\%) = [(G_{20} - FG)/TS] \times 0.9 \times 100$$

$$\text{SDS}\ (\%) = [(G_{120} - G_{20})/TS] \times 0.9 \times 100$$

$$\text{RS}\ (\%) = [(TS - RDS - SDS)/TS] \times 100$$

where G_{20} and G_{120} are the contents of glucose released within 20 and 120 min of hydrolysis, respectively; FG is the content of free glucose in starch; TS is total starch weight.

2.7. Differential scanning calorimetry (DSC)

The thermal properties of starch samples were investigated using differential scanning calorimetry (Q200, TA, New Castle, DE, USA). A starch sample (3 mg) was mixed with 6 μl deionized water and hermetically sealed in an aluminum pan, equilibrated at 4 °C for 24 h, and then equilibrated at 20 °C for 10 min. The pan was heated from 20 to 130 °C at a rate of 8 °C/min (Miao et al., 2009). An empty aluminum pan was used as the reference. The onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and gelatinization enthalpy (ΔH) were analyzed and calculated by DSC software (TA instruments, New Castle, DE, USA). Experiments were conducted in triplicate.

2.8. X-ray diffraction (XRD)

X-ray diffraction analysis was performed with an X-ray diffractometer (D/MAX 2500V, Rigaku Corporation, Japan) operating at 40 kV and 40 mA with Cu Kα radiation (k = 1.5406 Å). The starch sample was scanned at 2θ values from 3° to 30° at room temperature and the scanning rate was 2°/min. The degree of relative crystallinity was calculated using MDI-Jade 6.0 software (Material Date, Inc. Livermore, California, USA) according to the method of Nara and Komiya (1983).

2.9. Scanning electron microscopy (SEM)

The surface structure properties of starch samples were observed by the field-emission scanning electron microscopy (SU8020, Hitach Int., Japan). The dried and finely ground starch samples were coated with a thin film of gold (10 nm) in vacuum situations after mounted on a specimen holder with a silver plate, then examined and photographed using SEM at an accelerating voltage of 1.0 kV.

2.10. Pasting properties

The pasting property of each starch sample was determined by the Rapid Visco Analyser (RVA-4500, Perten Instruments, Sweden). The starch sample (2 g) was added to 25 ml distilled water to form the uniform starch suspension. After equilibration at 50 °C for 1 min, the starch suspension was heated from 50 °C to 95 °C at a rate of 12 °C/min, held at 95 °C for 2.5 min, then cooled to 50 °C at the rate described above, and held at 50 °C for 2 min. The paddle speed was 160 rpm for the experiment except for 960 rpm during the first 10 s.

2.11. Statistical analysis

Results are expressed as the mean ± standard deviation of triplicate experiments. Data were analyzed by one-way analysis of variance (ANOVA), followed by Duncan's multiple range test using SPSS 17.0 Statistical Software Program (SPSS Incorporated, Chicago). A value of $P < 0.05$ was considered statistically significant.

3. Results and discussion

3.1. Chain length analysis

The branched chain length distributions of native, DT and D-HMT sweet potato starch samples are presented in Table 1. On the basis of the cluster model of Hizukuri (1986), amylopectin molecules have A, B (B_1-B_4), and C chains, among them, A and B_1 chains are known as short chains which are composed of degree of polymerization (DP) < 13 and DP 13–30, and others (B_2-B_4) are collectively known as long chains which are composed of DP > 30. According to the report by Zhang, Ao, and Hamaker (2008), starch samples having either lower values of the weight ratio of amylopectin short-chain fraction (SF) (DP < 13) to long-chain fraction (LF) (DP ⩾ 13) or higher values of the weight ratio had a higher content of SDS, which meant amylopectin with a higher amount of either short chains or long chains had relatively high content of SDS. As shown in Table 1, DT and D-HMT sweet potato starch samples exhibited similar proportions of fractions of DP < 13, DP 13–30 and DP > 30, and had lower proportion of fraction of DP < 13 and higher proportion of fractions of DP 13–30 and DP > 30 compared with native starch. Theoretically, the minimum chain-length that is required to form double helices of starch is 10. The short chains (mostly DP < 10) that were too short to crystallize might be partly released during DT and the long chains (DP > 13) associated and crystallized preferentially, which may be the reason for the decrease in the proportion of fraction of DP < 13 and the increase in the proportion of fractions of DP 13–30 and DP > 30 of DT starch samples. After DT and D-HMT, the values of SF (DP < 13)/LF (DP ⩾ 13) became lower than that of native starch, which theoretically could be drawn the conclusion that DT and D-HMT can increase the content of SDS in sweet potato starch.

3.2. Molecular weight analysis

The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of native, DT and D-HMT sweet potato starch samples are also presented in Table 1. The M_w of the native starch was larger than those of DT and D-HMT starch samples. The M_n of the native starch was similar to that of DT starch sample. The decrease in the M_w of DT and D-HMT starch samples might be due to the degradation of some amylopectin. The smaller and similar M_n of the native and DT starch samples might be the result of that the native starch had smaller proportion of short branch-chains and DT changed the proportion of short branch-chains slightly.

The ratio of the weight-average molecular weight to the number-average molecular weight (M_w/M_n) is called the polydispersity index (PDI). The closer the PDI to 1.0 (the lower limit), the

Table 1
Chain length distribution and molecular weigh of native, DT and D-HMT sweet potato starch samples.

Starch samples	DP ⩽ 13 (%)	13 < DP ⩽ 30 (%)	DP > 30 (%)	$M_w \times 10^7$ (g/mol)	$M_n \times 10^5$ (g/mol)	M_w/M_n
NS	21.49	67.30	11.21	5.02	2.80	17.96
DT	13.94	71.03	15.03	3.07	2.81	10.92
D-HMT	14.32	71.10	14.58	3.09	3.00	10.31

DP represents the degree of polymerization.
M_w indicates weight-average molecular weight; M_n indicates number-average molecular weight.
NS indicates native starch; DT indicates debranching treatment; D-HMT indicates debranching-heat-moisture treatment.

narrower molecular weight distribution for the special polymers, which means the higher value of the PDI, the wider molecular weight distribution. Table 1 showed that the M_w/M_n values of DT and D-HMT starch samples were lower than that of the native starch, suggesting that the molecular chains of those had lower degree of polydispersity and more number of similar chains, which meant that the molecular chains of those were easy to form a double-helical structure. These results indicate that there are more interactions of amylose-amylose and amylose-amylopectin and the formation of the more stable and ordered double-helical structure.

3.3. Effect of debranching and heat-moisture treatment on in vitro digestibility of starch samples

The contents of RDS, SDS and RS fractions in native, DT and D-HMT sweet potato starch samples are presented in Fig. 1. As shown in Fig. 1, the RDS, SDS, and RS contents of native starch were 19.61%, 7.71%, and 72.68%, respectively. Compared with native starch, the DT starch sample exhibited higher RDS and SDS contents and much lower RS content. However, D-HMT significantly increased the contents of SDS and RS in starch sample and markedly decreased the RDS content compared with DT. During DT, the cleavage of α-1, 6-linkage accompanying the retrogradation were performed at 58 °C that was not ideal temperature for the recrystallization. Therefore, the DT starch sample might contain considerable amounts of amorphous crystallites, resulting in the higher contents of RDS and SDS and the lower content of RS. Ambigaipalan, Hoover, Donner, and Liu (2014) reported that HMT could change radial orientation of amylopectin crystallites due to increased amylopectin flexibility. In the present study, it could be concluded that the increment of SDS and RS contents of debranched starch sample by heat-moisture treatment has been attributed to the increase in the interactions of short linear chains which come from branch chain of amylopectin and crystallite perfection. Compared with DT starch sample, the lower enzyme susceptibility of D-HMT starch sample could also be attributed to its higher relative crystallinity (Fig. 2). During HMT, as the degree of association of starch chains in amorphous and crystalline regions increased, the disrupted crystallites may become more perfect. The content of SDS in starch sample reached the maximum (31.60%) after D-HMT, the higher content of SDS could be composed of large amount of amorphous components and partially disrupted crystalline components.

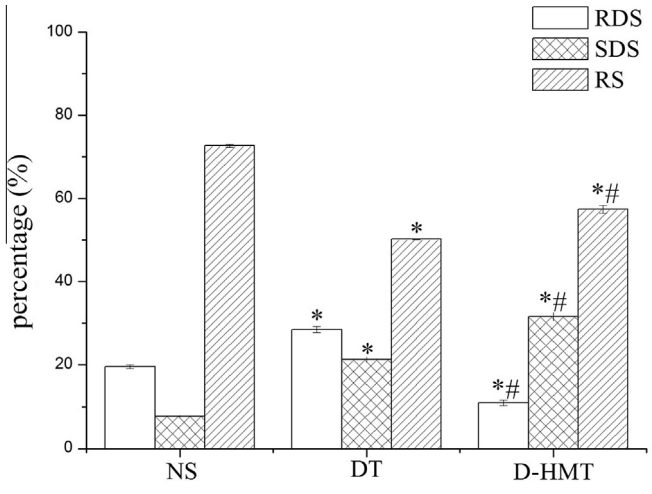

Fig. 1. The contents of RDS, SDS and RS fractions in native, DT and D-HMT starch samples. NS indicates native starch; DT indicates debranching treatment; D-HMT indicates debranching-heat-moisture treatment. $^*P < 0.05$ compared with native starch; $^{\#}P < 0.05$ compared with DT starch sample.

3.4. Thermal characteristics

The gelatinization transition temperatures (T_o, T_p and T_c), the gelatinization temperature range ($T_c - T_o$) and gelatinization enthalpy (ΔH) of native, DT and D-HMT starch samples were summarized in Table 2. The thermal properties of DT and D-HMT starch samples were significantly changed compared with the native starch. According to the report by Lopez-Rubio, Flanagan, Gilbert, and Gidley (2008), the transition temperatures represent crystalline stability, and the gelatinization enthalpy reflects the melting of crystals of amylopectin with potential contributions from both crystal packing and helix melting enthalpies. As shown in Table 2, compared with native starch, the starch samples by DT and D-HMT showed two endothermals, the transition temperatures and the gelatinization enthalpy of DT and D-HMT starch samples for the first endothermal were decreased significantly, suggesting that a number of double helices presented in the crystalline and non-crystalline regions were destroyed during the treatments. During the DT, the amylopectin was not completely debranched, which was mainly due to the characterization of pullulanase and retrogradation of amylose during debranching (Guraya et al., 2001b). Therefore, the second endothermal could be the melting of the

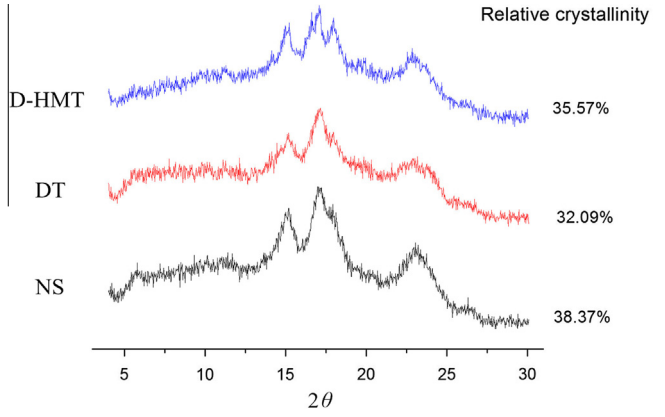

Fig. 2. X-ray diffraction patterns of native, DT and D-HMT starch samples. NS indicate native starch. DT and D-HMT indicate debranching treatment and debranching-heat-moisture treatment, respectively.

Table 2
Thermal properties of native, DT and D-HMT sweet potato starch samples.

Sample	Peak 1					Peak 2				
	T_o	T_p	T_c	$T_c - T_o$	ΔH	T_o	T_p	T_c	$T_c - T_o$	ΔH
NS	59.72 ± 0.57^c	71.85 ± 0.21^c	87.30 ± 0.64^c	27.58 ± 0.89^b	13.01 ± 0.61^b	–	–	–	–	–
DT	51.40 ± 0.51^a	60.25 ± 0.63^a	68.15 ± 0.51^a	16.74 ± 0.63^a	1.19 ± 0.20^a	80.63 ± 1.10^a	87.10 ± 0.11^a	99.36 ± 1.09^a	18.76 ± 0.61^a	1.19 ± 0.12^a
D-HMT	57.45 ± 0.26^b	65.63 ± 0.31^b	74.55 ± 0.38^b	17.10 ± 0.12^a	0.91 ± 0.91^a	82.88 ± 0.57^b	94.92 ± 0.07^b	107.87 ± 0.47^b	24.99 ± 0.42^b	3.24 ± 0.84^b

T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; $T_c - T_o$, gelatinization temperature range; ΔH, gelatinization enthalpy.
NS indicates native starch; DT indicates debranching treatment; D-HMT indicates debranching-heat-moisture treatment.
Values with different superscripts in the same column are significantly different ($p < 0.05$).

stronger crystallites which were formed as a result of amylose-amylose and amylose-amylopectin interactions during debranching accompanying retrogradation (Perera, Hoover, & Martin, 1997). Compared with DT starch sample, the T_o, T_p, T_c and ΔH of D-HMT starch samples for both endothermals were significantly increased except for the ΔH of the first endothermal, which was not significantly decreased, and the gelatinization temperature range ($T_c - T_o$) was obviously increased, which was in agreement with the results reported by Ambigaipalan et al. (2014). These results indicate that HMT may increase the stability of the crystallites and make more inter and intra helical hydrogen bonds formation, hence lead to the increase in the contents of SDS and RS in starch sample (Fig. 1), and may increase crystallite heterogeneity within the granules, thus form the crystallites with different stabilities (Wongsagonsup, Varavinit, & BeMiller, 2008). Furthermore, the starch samples with higher RS content had a higher ΔH value. In the present study, it was indicated that compared with DT, starch sample by D-HMT with the higher RS content (57.40%) had the higher ΔH value (3.24 J/g).

3.5. X-ray diffraction and relative crystallinity

Fig. 2 presents X-ray diffraction patterns and relative crystallinity of native, DT and D-HMT sweet potato starch samples. Tian, Richard, and Blanshard (1991) reported that sweet potato starch possessed different crystalline patterns (A and C or mixtures). According to a previous study by Hizukuri (1969), A and B crystalline patterns are independent forms, but C type structure is a mixture form of A and B types. In terms of the different ratio of A and B types, the X-ray diffraction patterns of C type can be categorized into 3 types (C_a, C_b and C_c types). As shown in Fig. 2, native sweet potato starch displayed a C_a-type pattern resulting from the reflection intensities at angle 2θ values of 5.7°, 15.2°, 17.1°, 17.9° and 23.0°, and the relative crystallinity was 38.37%. After DT, the X-ray diffraction pattern of starch sample maintained its C_a type, but the relative crystallinity was decreased. This change indicated that a number of double helices were destroyed, which was in agreement with the results from the *in vitro* digestibility and DSC analysis. When the debranched starch sample was treated with HMT, the crystalline pattern was altered from C_a to A type, and the relative crystallinity ranged from 32.09% to 35.57%. These results were similar to the report by Ambigaipalan et al. (2014), who reported that when pea, lentil and navy starches were treated with HMT, the crystalline patterns would be transformed from A + B type to A-type due to the interactions between amylose-amylose and amylose-amylopectin chains and the increase in relative crystallinity. These changes may result in the formation of imperfect crystallites and the increase in SDS content. Moreover, A-type crystallites have been shown to melt at a higher temperature than B-type crystallites, thus resulting in the increment of

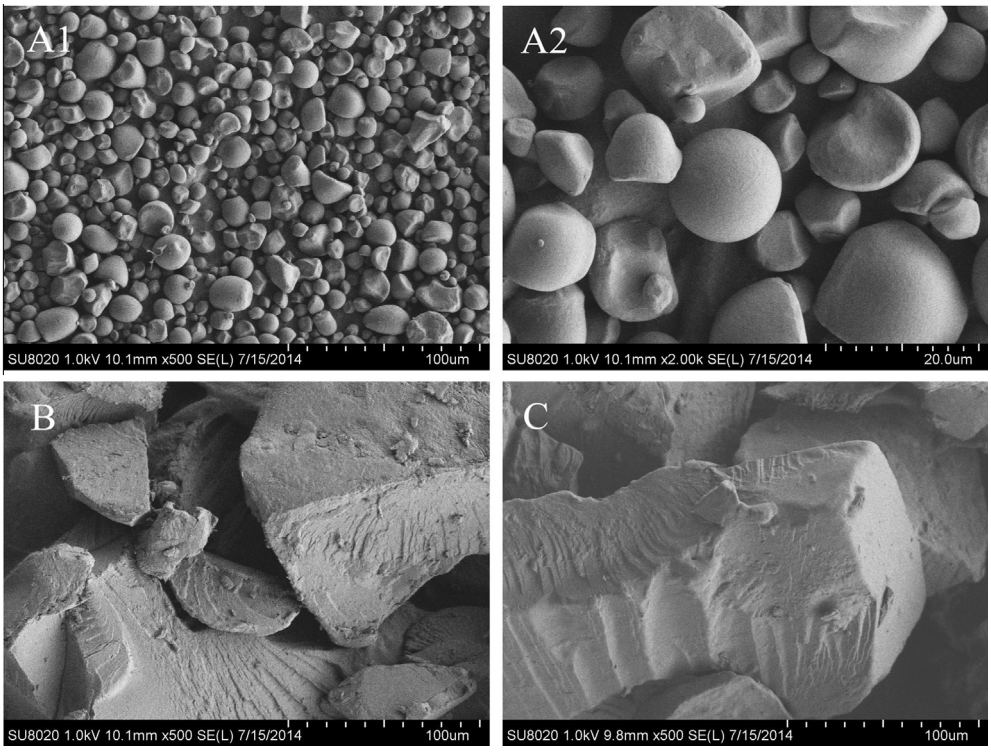

Fig. 3. Scanning electron microscopy (SEM) images of native, DT and D-HMT starch samples. (A1, A2) Native starch, (B) DT starch sample, (C) D-HMT starch sample. DT indicates debranching treatment; D-HMT indicates debranching-heat-moisture treatment. The magnification of images was 500× and 2000×, respectively.

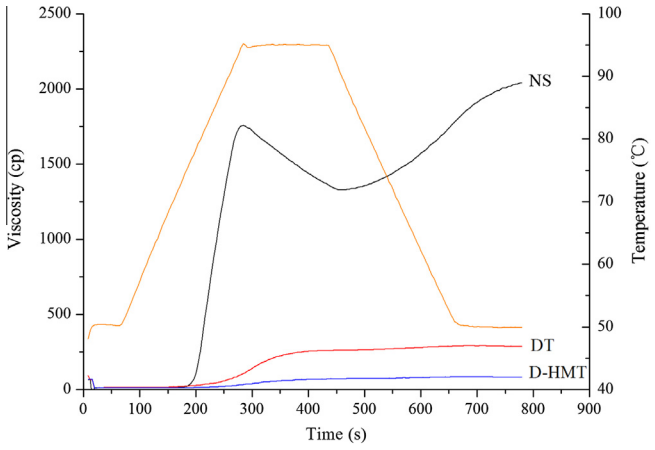

Fig. 4. Pasting properties of native, DT and D-HMT starch samples. NS indicate native starch. DT and D-HMT indicate debranching treatment and debranching-heat-moisture treatment, respectively.

T_o, T_p and T_c (Table 2). Compared with DT, the relative crystallinity of starch sample by D-HMT was increased, which was due to the formation of more ordered double helices within the crystalline domains during HMT. Furthermore, from Fig. 2, we found that starch sample by D-HMT with the higher RS content (57.40%) had the higher relative crystallinity (35.57%).

3.6. Scanning electron microscopy (SEM)

Fig. 3 exhibited the surface structural characteristics of native, DT and D-HMT sweet potato starch samples. The native starch showed round, oval, polygonal shapes with few fissures on the surface, and the tightness and smooth structure exhibited a high content of RS that was resistant to enzyme digestibility possibly. The process of cook in excess water induced the starch granules to swell and melt, which connected with each other. Heating led to further swelling and melting, ultimately the granules lost their identity, and the beams of neighboring deformed granules aggregated and formed a sponge-like structure (Ratnayake & Jackson, 2007). After DT, the granular structure disappeared, the surface of the starch sample became so rough and irregular, and the crystallites became much larger and more closely packed than the native starch. These changes indicated that the starch granule was completely destroyed. And the rough and irregular surface of DT starch sample was in accordance with the digestibility mentioned above. Compared with DT, the surface of starch sample by D-HMT became more smooth and the crystalline bodies became further larger, which may be the result of the decrease in RDS fraction in starch sample. The SEM images displayed the effects of DT and D-HMT on the morphological characteristics of starch samples, which may be combined with those results obtained from DSC, X-ray diffraction and digestibility mentioned above, suggesting that SDS consisted of amorphous region and a small portion of imperfect crystallites.

3.7. Pasting properties

The various pasting properties of native, DT and D-HMT sweet potato starch samples using the rapid visco analyzer (RVA) are presented in Fig. 4. DT and D-HMT have significant effects on pasting properties of sweet potato starch samples. After these treatments, the pasting temperatures were increased, the peak viscosities were declined, the values of breakdown were approached to zero, and the setback values were decreased significantly (D-HMT > DT). The higher pasting temperature indicated that the interactions between amylose-amylose and amylose-amylopectin chains increased, thus led to the intragranular bonds to be strengthened, so the starch samples required more heat for structural disintegration and paste formation (Stute, 1992). Peak viscosity and breakdown of starch samples, which reflected the swelling power and paste stability (Dengate & Meredith, 1984), respectively, were decreased significantly after the DT and D-HMT. The lower peak viscosities and breakdown indicated that the heat and shear stability of the starch paste were increased, and the granular swelling and amylose leaching were decreased, which were all desirable properties of sweet potato starch in the manufacturing of noodles (Jayakody & Hoover, 2008). The setback, which reflected the gelling ability or retrogradation tendency of amylose, was decreased after DT and D-HMT. The higher setback value suggests the presence of a more extensively hydrogen-bonded network structure formed by interactions among long amylopectin chains (DP 37–50) during the cooling cycle (Lan et al., 2008).

4. Conclusions

Debranching followed by heat-moisture treatment was used to modify the structure of sweet potato starch, and the structural characteristics and digestibility of native, DT and D-HMT starch samples were compared. The starch sample by D-HMT showed a considerable SDS content of 31.60%. After DT and D-HMT, the values of SF (DP < 13)/LF (DP ⩾ 13) of starch samples became lower than that of native starch, the molecular chains of DT and D-HMT starch samples had lower value of the PDI. Compared with native starch, the starch samples by DT and D-HMT showed two endothermals; the second endothermal could be due to melting of the stronger crystallites which were formed as a result of amylose-amylose and amylose-amylopectin interactions during debranching accompanying retrogradation. Native sweet potato starch displayed a C_a-type diffraction pattern, and the surface was tight and smooth. After DT, the X-ray diffraction pattern remained its C_a type, but the relative crystallinity was decreased, and the surface of the starch samples became so rough and irregular, the crystalline bodies became much larger and more closely packed than that of the native starch. When the debranched starch sample was further treated with HMT, the diffraction pattern was altered from C_a to A type, the relative crystallinity ranged from 32.09% to 35.57%, and the surface of starch sample became more smooth and the crystalline bodies became further larger. Compared with native starch, the starch samples by DT and D-HMT exhibited higher pasting temperatures, lower peak viscosities, no breakdown, and significant decrease in setback values (D-HMT > DT). These results suggested that structural changes in sweet potato starch by D-HMT significantly affected the digestibility and physicochemical properties.

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