

RESEARCH ARTICLE

Structure and digestibility of debranched and hydrothermally treated water yam starch

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Debranched water yam starch was subjected to repeated hydrothermal treatment (HTT), and its physicochemical and structural properties and digestion pattern were investigated. The B-type crystalline pattern of raw starch was recrystallized to B- and C_A-type patterns by debranching and repeated HTT. The degree of relative crystallinity of debranched starch gradually increased and reached its maximum (43.3%) after five repetitions of HTT. The thermal transition temperatures and melting enthalpy of recrystallized starches increased progressively, reflecting the perfection of their crystalline structure, leading to the accumulation of boiling-stable crystalline structure under repeated HTT conditions. As a result, RS of HTT starches reached a very high level (>92.2%). The boiling-stable RS content depended on the repetition of this treatment and was maximized (81.0%) after five repetitions.

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1 Introduction

Starch is a major source of carbohydrate in the human diet. Based on the extent and rate of starch digestion, starch is generally classified into three fractions [1]: rapidly digestible starch (RDS), slowly digestible starch (SDS), and RS. SDS is digested completely but slowly in the small intestine. SDS has potential physiological benefits such as stable glucose metabolism, diabetes management, satiety, and mental performance [2]. RS is a starch fraction that is not digested completely by human digestion enzymes in the small intestine [1, 3]. RS positively correlates with low glycemic index food, colonic health, and metabolic responses such as glucose and blood metabolisms. Also, RS is a food ingredient that enhances

crispness in foods [3, 4]. In general, RS is categorized into four types [1, 5]. RS1 represents physically enclosed and inaccessible starches and is found in partially milled grains, seeds, and legumes. RS2 is native granular starch normally found in unripe bananas and raw potatoes, and can be easily digested after gelatinization. RS3 is the starch fraction formed through retrogradation after gelatinization, and RS4 is the chemically modified starch. Heat treatment such as ANN, HMT, and pyroconversion, enzymatic treatment for chain-extension and debranching, and chemical treatment for cross-linking have been used to produce RS [3]. It is also well-known that repeated hydrothermal treatment (HTT) is associated with increased formation of RS [3]. Further, their combinations have been applied to the preparation of a novel starch containing high SDS and/or RS [6–9].

Thermal stability is an important factor in the food applications of RS. RS1, RS3, and RS4 are considered to be thermally stable [3, 5]. It has also been reported that HTT enhances the thermal stability of RS2 [10]. However, information is sparse about the effect of repeated HTT on

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Abbreviations: DRC, degree of relative crystallinity; HTT, hydrothermal treatment; IS, isoamylase-treated starch; RDS, rapidly digestible starch; SDS, slowly digestible starch

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structural properties and digestibility of the debranched and retrograded starch [8, 9].

Therefore, the objectives of the present study were: to investigate the effects of repeated HTT on the starch modified through debranching, in regard to the structural and physicochemical properties, especially, the thermal stability; and to determine the relationship between the structural changes during dual modification and the digestion pattern of the modified starch. Water yam starch was chosen for this study because, in our preliminary study, it showed peculiar branched chain length distribution, longer average DP, and higher relative crystallinity compared with corn, rice, potato, Hylon V, and Hylon VII starches after gelatinization followed by HTT. Also, its RS content was greater than the reported values for other tuber and root starches including cassava and yam starches [11, 12].

2 Materials and methods

2.1 Preparation of isoamylase-treated starch (IS)

Raw water yam starch suspension (5% on dry basis) in 0.1 M sodium acetate buffer (pH 4.0) was boiled for 30 min with continuous mixing for the complete gelatinization. The starch slurry was cooled down to 40°C. Isoamylase from *Pseudomonas* sp. (E-ISAMY, 280 U/mg, Megazyme International Ireland, Bray, Ireland) was added to starch slurry to be 20 U/g starch. Debranching reaction was conducted at 40°C for 48 h. To stop the isoamylase reaction, two volumes of 95% ethanol were added, and the mixture was centrifuged at $12\,000 \times g$ for 10 min. The supernatant was decanted. The precipitate was suspended with the distilled water and centrifuged at $12\,000 \times g$ for 10 min. This washing step was repeated twice. The collected precipitate was dried in an air-drying oven at 40°C for 24 h to reach final moisture content of around 11%. All samples were ground and passed through a 150- μm sieve for the further experiment.

2.2 Hydrothermal treatment of IS

IS (5%) was suspended in distilled water, boiled for 30 min, and dried in an air-forced oven at 40°C for 24 h to reach final moisture content of around 11%. After drying, the starch sample was ground, passed through a 150- μm sieve, transferred to a glass container, and its moisture content was adjusted to 30% by adding an appropriate amount of distilled water. The glass container was sealed and allowed to stand at room temperature for 24 h to reach equilibrium. HTT was conducted by storing the glass container in an air-drying oven at 100°C for 24 h. The glass container was opened and the HTT starch was dried in an air-drying oven at 40°C for 24 h to reach final moisture content of around 11%. After drying, the

starch sample was ground and passed through a 150- μm sieve. The boiling and HTT steps were repeated (one, three, and five times) to produce IS-HTT1, IS-HTT3, and IS-HTT5 starch samples.

2.3 Determination of AML

To measure AML [13], 10 mL of distilled water was added into a screw cap tube containing 20 mg of starch sample. The tube was then heated at 95°C for 30 min. After cooling to ambient temperature, the sample was centrifuged at $2000 \times g$ for 10 min. AAM content in 0.1 mL of supernatant was estimated according to the method of Chrastil [14].

2.4 X-ray diffractometry and degree of relative crystallinity (DRC)

XRD analysis was performed with a powder X-ray diffractometer (Model D5005, Bruker, Karlsruhe, Germany) operating at 40 kV and 40 mA with Cu-K α radiation of 0.15406 nm (Nickel filter; time constant, 4 s). The sample was scanned through 2θ range from 3 to 30°. The DRC was calculated using the equation $\text{DRC} = A_c / (A_c + A_a)$, where A_c is the area of crystalline portion and A_a is the area of amorphous portion, according to the method of Nara and Komiya [15] with peak-fitting software (Origin-version 7.5, OriginLab, Northampton, MA, USA).

2.5 Differential scanning calorimetry (DSC)

The thermal properties of starch samples were determined using a differential scanning calorimeter (Diamond DSC, Perkin-Elmer, Waltham, MA, USA). A 10 mg sample was placed in a high-pressure stainless steel DSC pan and 40 μL of distilled water were directly added into a DSC pan containing starch sample. The sample pan was sealed hermetically and kept at room temperature for 24 h to equilibrate. The sample pan was heated from 30 to 195°C at 5°C/min with an empty pan as reference. The endothermic transition parameters including onset (T_o), peak (T_p), and conclusion (T_c) temperatures of melting, melting temperature range ($T_r = T_c - T_o$), and melting enthalpy (ΔH) were determined.

2.6 Determination of amylopectin branch-chain length distribution

Raw starch (30 mg) was dissolved in 3 mL of DMSO and boiled for 20 min with vortexing. Ethanol (15 mL) was added and centrifuged at $10\,000 \times g$ for 10 min. After decanting the supernatant, the pellet was redissolved in 1.5 mL distilled water and boiled for 20 min. Then, 1.5 mL of 60 mM sodium acetate buffer (pH 4.3) and 30 μL (30 U) of isoamylase (Megazyme International Ireland) were added. The mixture

was incubated at 45°C for 2 h, and the reaction was stopped by adding 6 mL of pure DMSO and by boiling for 10 min. In cases of IS and IS-HTT starches, starch sample (30 mg) was dissolved in 6 mL of DMSO and boiled for 20 min. Then, 1.5 mL of distilled water and 1.5 mL of 50 mM sodium acetate buffer (pH 4.3) were added. The sample was passed through a 0.45- μ m membrane filter, and the analysis was performed as described by Oh et al. [16].

2.7 Starch digestibility

Starch digestibility was determined following the method described by Englyst et al. [1], as modified by Shin et al. [17]. Pancreatin (2 g, Sigma–Aldrich, St. Louis, MO, USA) was dissolved in distilled water (24 mL) and stirred for 10 min. It was centrifuged at 1500 \times g for 10 min, and then 20 mL of supernatant was mixed with 3.6 mL of distilled water and 0.4 mL (120 U) of amyloglucosidase (AMG 300L, Novozymes A/S, Bagsvaerd, Denmark). This enzyme solution was stored in a 37°C water bath for at least 10 min. Each starch sample (30 mg) was placed in a 2-mL microtube with a glass bead. After adding 0.75 mL of sodium acetate buffer (pH 5.2), the tube was boiled for 0, 10, 20, 40, and 60 min and cooled to 37°C in a shaking incubator. Then, 0.75 mL of the prepared enzyme solution was added to the tube, and the tube was shaken continuously. The reaction was stopped after 10 and 240 min by boiling for 10 min. The glucose present in the supernatant obtained by centrifugation (5000 \times g, 5 min) was measured using a GOD-POD kit (BCS, Anyang, Korea). Starch fractions were classified based on the rate of hydrolysis. RDS and SDS were measured by the glucose concentration after enzyme reaction for 10 and 240 min, respectively. RS was the fraction undigested after 240 min.

2.8 Statistical analysis

Experiments were conducted in triplicate, and the mean value and the SD are reported. Data were analyzed using analysis of variance (ANOVA), and the mean separations were determined by Duncan's multiple-range test ($p < 0.05$). All

statistical analyses were carried out using SPSS software (Ver. 17.0, SPSS, Chicago, IL, USA).

3 Results and discussion

The proximate analysis of water yam starch, carried out by Approved Methods (08–17, 30–25, and 46–10) of the AACC [18], showed dry weight percentages of 0.09, 0.12, 0.05, and 99.74% for crude ash, crude fat, crude protein, and nitrogen-free extract, respectively.

3.1 Branch-chain length distributions

The branch-chain length distributions of IS and IS-HTT starches are listed in Table 1. According to Hanashiro et al. [19], the branch-chains of amylopectin can be categorized into four fractions: f_a , DP 6–12; f_{b1} , DP 13–24; f_{b2} , DP 25–36; and f_{b3} , DP > 37. The proportions of f_a and f_{b1} of IS were lower than those of the raw starch, whereas the proportions of f_{b2} and f_{b3} and average DP were higher than those of the raw starch. Theoretically, the minimum chain-length required for crystallization was 10, although oligomers as short as maltohexaose could co-crystallize in the presence of longer chains [20]. Thus, the preferential association and crystallization of long chains could be a reason for the increase in the average DP of IS. In addition, some amount of short chains classified as f_a and f_{b1} released during isoamylase treatment might not take part in reassociation and may be removed during the washing step. As a result, the proportions of f_{b2} and f_{b3} , and average DP increased. Compared to IS, IS-HTT1 starch showed a very similar branch-chain length distribution. As the number of HTT repetitions increased, the proportions of chains with DP ≤ 5 and f_a increased and the proportions of f_{b1} and f_{b2} decreased. The extent of thermal degradation depended on the starch structure; amylose was more susceptible to thermal degradation than short linear amylopectin chains [21]. Therefore, the increase in the content of short chains and the decrease in the content of long chains could result from the thermal degradation of long linear chains in our starch samples during the repeated HTT.

Table 1. Branch-chain length distribution of raw, IS, and IS-HTT starches^{a)}

Starch sample	Degree of polymerization (DP)					Average DP
	DP ≤ 5	DP 6–12 (f_a)	DP 13–24 (f_{b1})	DP 25–36 (f_{b2})	DP ≥ 37 (f_{b3})	
Raw	1.5 \pm 0.8 ^c	14.1 \pm 0.8 ^{ab}	61.3 \pm 1.2 ^a	17.6 \pm 0.2 ^c	5.5 \pm 0.9 ^b	20.5 \pm 1.0 ^d
IS	2.2 \pm 0.2 ^{bc}	7.9 \pm 0.1 ^d	57.4 \pm 0.6 ^{bc}	23.0 \pm 0.1 ^a	9.5 \pm 0.2 ^a	22.3 \pm 0.0 ^{ab}
IS-HTT1	1.4 \pm 0.7 ^c	7.5 \pm 0.3 ^d	57.3 \pm 0.8 ^{bc}	23.2 \pm 0.1 ^a	10.7 \pm 0.5 ^a	22.8 \pm 0.2 ^a
IS-HTT3	2.9 \pm 0.9 ^b	11.8 \pm 1.1 ^{bc}	55.3 \pm 0.4 ^c	21.0 \pm 0.4 ^b	9.1 \pm 0.6 ^a	21.4 \pm 0.6 ^{bc}
IS-HTT5	5.9 \pm 0.2 ^a	11.4 \pm 0.7 ^{bc}	51.5 \pm 1.2 ^d	22.0 \pm 0.2 ^{ab}	9.2 \pm 0.6 ^a	21.2 \pm 0.5 ^{bc}

a) Values followed by different superscript letters in the same column are significantly different ($p < 0.05$).

3.2 XRD pattern and DRC

The XRD patterns of starch samples are depicted in Fig. 1. Raw starch and IS showed typical characteristics of a B-type XRD pattern. However, a B-type crystalline structure with different intensity was detected for IS. The temperature (40°C) used for the isoamylase reaction in our study was not ideal for recrystallization, although recrystallization could occur to some extent during the isoamylase reaction. Therefore, both the cleavage of α -1,6-linkage and the retrogradation during debranching reaction performed at 40°C could induce the B-type XRD pattern of IS. The polymorphic form found in debranched starch depends on chain length, concentration, and temperature [20, 22, 23]. Our finding of the B-type XRD pattern for IS is in good agreement with a previous study that identified B-type crystallites in debranched starch having an average DP of 22 [24]. The HTT of IS made the peaks at 14.9° and 17.1° more pronounced and combined the peaks at 22.2° and 24.1° into a single peak at 23°. A polymorphic transition due to HTT was observed in IS. All IS-HTT starches showed general characteristics of an A-type XRD pattern, together with a small peak at 5.8°, indicating that IS-HTT starches had a C_A-type (A- and weak B-type). The melting temperature for amylose crystals is around 150°C [25]. However, the HTT conditions applied in this study, especially the temperature, were not ideal for recrystallization. Also, the temperature was not high enough to melt the crystallites formed from linear long chains, although recrystallization could occur to some extent during HTT. The short linear chains forming the crystalline structure in IS could be partially disintegrated during the first cycle of

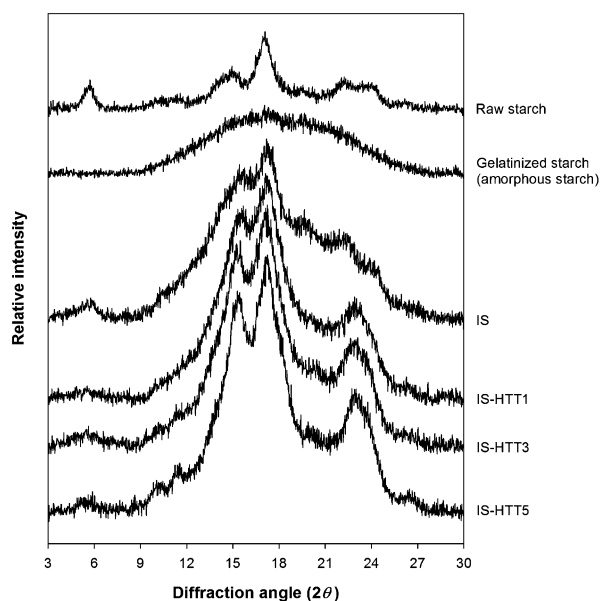


Figure 1. X-ray diffractograms of raw, gelatinized, IS, and IS-HTT starches.

HTT. During storage at 100°C, the crystallites formed from the long linear chains could maintain their structure with slight transition by the reassociation of the short linear chains. Therefore, during HTT, nucleation was limited and propagation was favored. The phase-transition of crystalline structure from B- to A-type was reported when the crystallites formed from short amylose chains (average DP 15) were stored at temperatures around 90–130°C [20, 26].

Among the starch samples investigated, raw starch showed the highest DRC (Table 2). IS showed 26.0% of DRC, almost twofold higher than that of gelatinized water yam starch (10.1%, data not shown). The relatively high DRC of IS is indicative of reassociation between the amylose and the linear chains released from amylopectin to a considerable extent [4]. After the first cycle of HTT of IS, DRC increased from 26.0 to 34.4% and the XRD pattern changed from B- to C_A-type. Also, after three repetitions of HTT, DRC increased further but the XRD pattern remained as C_A-type. A previous study [9] reported the change of XRD pattern from C- to A-type and the increase of DRC by HTT of debranched retrograded cassava starch. After more than three repetitions of HTT, all IS-HTT starches showed a similar DRC and the same crystalline structure. Furthermore, by HTT, the rapid attachment of linear chains (released from amylopectin) to nuclei (formed from long linear amylose) resulted in a perfect and well-arranged crystalline structure. This well-developed crystalline structure during the first HTT was very rigid and stable against dissociation by boiling.

3.3 Thermal properties and crystalline structure of modified starch

The thermal properties of the samples are presented in Table 3. Raw water yam starch showed a typical gelatinization endothermic peak, significantly sharper than that of all IS and IS-HTT starches (data not shown). The endothermic peak for IS ranged from 93 to 122°C, indicating the formation of a crystalline structure during starch debranching. Also, the IS melted at a higher temperature, although the ΔH was twofold lower than that of the raw starch. The crystallinity of amylose molecules may be visible as an endothermic peak at around 150°C [25]. However, in the present study, an endothermic

Table 2. AML, DRC, and XRD pattern of raw, IS, and IS-HTT starches^{a)}

Starch sample	AML (%)	DRC (%)	XRD pattern
Raw	38.9 ± 1.2 ^a	49.4 ± 0.5 ^a	B
IS	27.2 ± 1.0 ^b	26.0 ± 0.5 ^d	B
IS-HTT1	5.7 ± 0.1 ^c	34.4 ± 0.2 ^c	C _A
IS-HTT3	0.02 ± 0.1 ^d	41.8 ± 0.7 ^b	C _A
IS-HTT5	0.01 ± 0.1 ^d	43.3 ± 0.5 ^b	C _A

a) Values followed by different superscript letters in the same column are significantly different ($p < 0.05$).

Table 3. Thermal properties of raw, IS, and IS-HTT starches^{a)}

Starch sample	T_o (°C)	T_p (°C)	T_c (°C)	T_r (°C)	ΔH (J/g)
Raw	76.3 ± 0.2 ^a	79.5 ± 0.3 ^a	83.0 ± 1.0 ^e	6.7 ± 1.2 ^a	18.7 ± 1.5 ^a
IS	93.3 ± 0.0 ^d	107.2 ± 0.0 ^d	121.9 ± 0.2 ^c	28.6 ± 0.2 ^b	6.5 ± 0.2 ^c
IS-HTT1	98.1 ± 0.1 ^c	108.0 ± 0.0 ^c	116.5 ± 0.1 ^d	18.4 ± 0.2 ^c	14.2 ± 0.3 ^b
IS-HTT3	108.6 ± 0.2 ^b	115.4 ± 0.0 ^b	126.9 ± 0.0 ^b	18.3 ± 0.2 ^c	14.3 ± 0.5 ^b
IS-HTT5	110.6 ± 0.1 ^a	118.1 ± 0.0 ^a	146.2 ± 0.1 ^a	35.7 ± 0.1 ^a	15.1 ± 0.1 ^b

a) Values followed by different superscript letters in the same column are significantly different ($p < 0.05$).

peak for IS was observed at a lower temperature (93–122°C). The reason for this may be amylose reassociation as well as the reassociation of shorter linear chains released from debranched amylopectin. Considering the results of AML, DRC, and endothermic transition parameters, the IS might contain an amorphous region to a considerable extent, although the crystallites in IS were more stable than those in the raw starch. On the contrary, the endothermic peak of IS shifted to a higher temperature by HTT. Further HTT repetitions raised T_o , T_p , and T_c significantly. This observation was in good agreement with the results of AML and DRC. The decrease in AML and the increases in DRC with HTT repetition suggest the presence of more perfect crystalline structures in IS-HTT starches.

The slightly lower ΔH of IS-HTT starches compared to that of the raw starch could be due mainly to a lesser extent of ordered structures compared to the raw starch [27]. The broad T_r of IS and IS-HTT starches indicated that crystallites with high heterogeneity, having various degrees of perfection and stability, developed during these treatments [28]. Thus, under repeated HTT conditions, the crystalline structure in the treated starches gradually became more stable, dense, and rigid. Christopher et al. [9] also reported the broadening of the transition endotherms by HMT of cassava starch recrystallized via debranching and incubation or temperature cycling, stating that the exact melting region and enthalpy were dependent upon recrystallization method.

3.4 Amylose leaching

The absolute amylose content of water yam starch was 18.6%, as determined using an amylose/amylopectin assay kit (K-AMYL, Megazyme International Ireland), whereas the AAM content was 38.9% as determined by the colorimetric method of Chrastil [14]. This difference could be due to different measurement conditions [29]. In the case of the raw starch, the amount of AML (39.0%) was twice the amylose content (18.6%), but was similar to the AAM content (38.9%). This means that most small amylose and amylopectin molecules could leach out under the conditions for AML measurement (Table 2). The AML value for IS was 27.2%, lower than the AML and AAM content of the raw starch. Generally, AML is attributed to changes in the interaction

between amylose–amylose and/or amylose–amylopectin chains and the amount of amylose–lipid complex [30]. However, no evidence of amylose–lipid complex formation during HTT was observed in the results of DSC and XRD (Fig. 1 and Table 3). All HTT starches showed lower AML values than the raw starch and IS. The decrease in AML after HTT was caused mainly by the changes in the interaction between amylose molecules and/or between amylose and short linear chains released from amylopectin during debranching reaction. During recrystallization by repeated HTT, the originally existing amylose molecules and the short linear chains derived from amylopectin could be reassociated much faster than amylopectin molecules. Co-crystallization is promoted by a high amount of amylose and that the presence of amylopectin can restrict the reassociation of amylose [31]. Besides, the crystallites formed by recrystallization at high temperatures are more perfect than those formed at low temperatures [20]. Therefore, the temperature (<150°C) used for AML measurement in the present study could not fully destroy the crystallites in HTT starches [25], and consequently, amylose molecules could not be leached from the undestroyed crystallites.

3.5 In vitro digestion patterns

The in vitro digestion profiles of raw, IS, and IS-HTT starches are illustrated in Fig. 2. Raw starch had very low contents

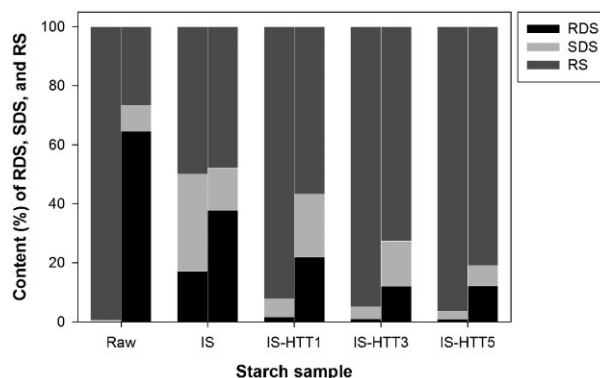


Figure 2. In vitro digestion pattern of raw, gelatinized, IS, and IS-HTT starches with (right bar) or without (left bar) boiling for 20 min.

of RDS (0.2%) and SDS (0.3%), and a very high content of RS (99.5%). It has been suggested that B-type starches without pores and channels allow enzymes to digest starch granules through a layer-by-layer mechanism, and that those starches are more resistant to enzyme digestion [32]. The IS showed higher RDS and SDS contents and a much lower RS content than the raw starch. However, compared to the boiled raw starch, the contents of RS and SDS in the IS were higher because of the formation of new boiling-stable crystallites during isoamylase treatment, as represented by the elevation of DRC (26.0%), thermal transition temperatures, and melting enthalpy (Table 3). On the other hand, all IS-HTT starches showed very low RDS and SDS contents (Fig. 2) and a very high RS content (92.2, 95.0, and 96.5% for IS-HTT1, IS-HTT3, and IS-HTT5 starches, respectively), independent of the repetition of HTT. The positive effect of HTT on the increase of RS content was also reported for debranched retrograded cassava starch [9].

Compared to IS, both RDS and SDS contents of IS-HTT starches decreased, but their RS content increased significantly. During the boiling step in the HTT, the crystalline structure, having a melting temperature higher than the boiling temperature, was maintained. During storage at 100°C, the relatively short linear chains, located in amorphous and/or semi-crystalline regions, were promoted to form the new double-helical crystalline structures. The crystalline structure formed with the long linear chains could maintain its structure with a slight transition by the reassociation of the short linear chains. Furthermore, the crystalline regions of IS-HTT starches gradually became more perfect as the number of repetitions increased, as reflected by their higher thermal transition temperatures (Table 3). The repetition of HTT resulted in the accumulation of the highly enzyme-resistant portion consisting of a perfect double-helical crystalline structure, as indicated by their gradual increase of DRC (Table 2). Among all starch samples, the highest SDS content (32.9%) was observed in IS.

In contrast, after boiling with excess water, the digestion patterns of all starch samples were quite different from those before boiling. The boiling time was controlled from 10 to 60 min. However, beyond 10 min of boiling, there was no significant difference in the digestion patterns among starch samples. The digestion patterns for all starches after 20 min of boiling are presented in Fig. 2. When raw starch was boiled, it lost its digestion-resistant properties, and there was a dramatic increase in RDS content. Such an increase in RDS content and reduced RS content are generally observed in gelatinized starch because the boiling destroys the semi-crystalline structure of raw starch granules [4]. The RS levels in IS were similar before and after boiling. However, an increase in RDS content and a decrease in SDS content were observed in the boiled IS. The change in the digestibility pattern of IS

indicated that its boiling-stable crystallites mostly remained under boiling, as reflected by the higher gelatinization temperature (107.2°C). The IS-HTT starches also showed a reduction in RS content after boiling, which was similar to that of the raw starch. However, in the case of IS-HTT starches, the RS content remained >56.8% after boiling. The content of remaining (boiling-stable) RS increased with the repetition of HTT. Obviously, the repeated HTT promoted the accumulation of boiling-stable crystalline regions, as evidenced by the gradual increases of DRC and thermal transition temperatures and a reduction of AML (Tables 2 and 3). The changes in SDS contents of IS-HTT starches before and after cooking were interesting. The SDS content in IS-HTT starches increased after cooking, unlike the raw starch and IS. These changes in SDS content could be caused by the reassociation of linear chains after boiling resulting in the formation of the mixture of semi-crystallites and amorphous material [2]. The repetition of HTT reduced the SDS content in cooked IS-HTT starch. Both raw and IS-HTT starches had very high RS contents, but they belonged to different types of RS [1]. Raw water yam granular starch is classified as type 2 RS. However, the IS-HTT starch could be classified as type 3 RS (gelatinized and crystallized), implying no granular structure. The dense crystalline structure is a major factor for the enzyme resistance of type 3 RS like IS-HTT starch. Compared to the raw starch, IS-HTT starches showed higher thermal stability (Table 3). As described above, the RS content in raw starch decreased to less than 30% after cooking. The gelatinization temperature (79.5°C) of raw water yam starch was lower than the cooking temperature (95°C) and the enzyme-resistant granular structure could be destroyed during boiling. In contrast, the IS-HTT starches showed much higher melting temperatures (108.0–118.1°C), indicating their better thermal stability.

4 Conclusions

Raw, IS, and IS-HTT starches showed different physicochemical and structural properties and digestibility. IS displayed high contents of SDS and RS fractions, which remained high under boiling conditions. Through repeated HTT, boiling-stable crystalline materials accumulated and resulted in nearly pure RS product. Both IS and IS-HTT starches had low RDS contents and high boiling-stable RS contents; thus, these modified starches could be used as an RS ingredient in heat-processed foods.

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The authors have declared no conflict of interest.

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