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RESEARCH ARTICLE

Digestibility and Physicochemical Properties of Granular Sweet Potato Starch as Affected by Annealing

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Abstract The effects of annealing on the digestibility, morphology, and physicochemical characteristics of four types of granular sweet potato starches [Yulmi (YM), Yeonwhangmi (YHM), sweet potato starch from Samyang Genex (SSPS), and commercial sweet potato starch (CSPS)] were investigated. Annealing was performed at 55°C and 90% moisture content for 72 h. Morphology, the branched chain distribution of amylopectin, and the X-ray diffraction pattern remained unchanged during the annealing process. The slowly digestible starch content in annealed YM, YHM, and SSPS starches increased, but did not change in annealed CSPS. The gelatinization temperatures increased, but the gelatinization temperature range decreased with annealing. The swelling factor and amylose leaching decreased, while the close packing concentration increased. Rapid Visco Analyser analysis revealed that annealed starches possessed thermal stability and higher pasting temperatures. It is suggested that the enhanced packing arrangement formed during annealing impacts the digestibility and physicochemical properties of sweet potato starches.

Keywords: annealing, digestibility, slowly digestible starch, structural analysis, sweet potato starch

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Introduction

Sweet potato [*Ipomoea batatas* (L.) Lam.] is the seventh most important food crop in annual production in the world. However, its role has changed dramatically, from a staple food to a health food. Sweet potato is used as powder, snack, sweet jelly, drink, source of starch (bread, cakes, noodles, and confectioneries), source of ethanol, and food coloring, as well as for other applications (1). At present, orange-fleshed sweet potato is very popular in Korea due to its sweet taste, appearance, and flavor compared to the yellow-fleshed sweet potato. Among various varieties, Yeonwhangmi (used in this study) is known to be of high quality. Lee *et al*. (2), who developed this variety, reported that steamed Yeonwhangmi has a higher polyphenol content, which improves bioactivity in humans and a higher degree of enzymatic browning. Its total sugar content is higher than that of Yulmi (2), which is another Korean sweet potato variety used in the current study. Although the nutritional aspects of orange-fleshed sweet potato have been reported, including the β-carotene content (3), its physicochemical properties have rarely been reported. Modification of orange-fleshed sweet potato starch has not been attempted.

Raw starches are not widely utilized in the food industry due to various disadvantages including low solubility; high viscosity of starch gel at room temperature; poor thermal, shear, and acid stability; and a high rate and extent of retrogradation (4). In addition, there has recently been much interest in the digestibility of starches. Therefore, starches have been modified chemically, physically, and

enzymatically to improve their functional properties and induce low digestibility. Among various physical modifications, annealing and heat-moisture treatments are considered to be natural, easy to apply, economical, and non-toxic. Moreover, starch granules remain intact after annealing when with excessive (>60%, w/w) or intermediate (40%-55%, w/w) amounts of water for a long period below the gelatinization temperature and above the glass transition temperature (5,6). Changes in various physicochemical properties such as granular stability, crystalline perfection, starch chain interactions within the amorphous and crystalline domains of the granule, gelatinization temperatures, granular swelling, and amylose leaching normally occur after annealing (5-12).

For nutritional purposes, starch is generally classified into rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch depending on the rate of digestion (13). SDS is digested completely but at a very slow rate compared to RDS. The physiological effects of SDS are helpful in prolongation of satiety and diabetes control. Moreover, SDS can function as a longer, more consistent source of systemic glucose (14). RS is defined as the sum of starch and the products of starch degradation not absorbed in the small intestine of healthy individuals. Sajilata *et al*. (15) reported that RS can prevent colonic cancer, has hypoglycemic and hypocholesterolemic effects, inhibits fat accumulation, and increases the absorption of minerals. Different annealing conditions have been used to produce RS by physical modification (16). However, only a few studies have assessed the generation of SDS by annealing (17,18). Shin *et al*. (17) obtained sweet potato starch by hydrothermal treatment in which the content of SDS was doubled. Chung *et al*. (18) showed that the annealing of several starches (corn, pea, and lentil) decreased the SDS content in granular starches but increased the SDS content after gelatinization. Therefore, the objectives of the present study were to determine the changes in structure and digestibility of granular sweet potato starches following an annealing treatment, to compare the effects of annealing on orange-fleshed sweet potato starch to those on commercial sweet potato starches, and to determine the relationship between the structure developed by annealing and digestibility.

Materials and Methods

Materials Korean native sweet potato cultivars, Yulmi (YM) and Yeonwhangmi (YHM), were obtained from Bioenergy Crop Research Center, National Institute of Crop Science, Rural Development Administration. A sweet potato starch (SSPS) was provided by Samyang Genex (Daejeon, Korea), and a commercial sweet potato starch (CSPS) was bought from a local market. The apparent amylose contents were 27.3, 26.6, 26.5, and 26.6% for YM, YHM, SSPS, and CSPS, respectively.

Starch isolation Washed sweet potato was peeled and cut into cubes. Small pieces of sweet potato were ground in a blender with 0.2% sodium hydroxide at full speed, and was filtered through 35-, 50-, and 100-mesh sieves. The suspended solution was centrifuged at 6,000×*g* for 10 min, and the supernatant was decanted. This procedure was repeated until no protein in supernatant was detected using ninhydrin reaction (19). The starch layer was resuspended in distilled water, shaken and centrifuged as described above. For neutralizing the starch slurry, washing with distilled water was repeated. Then, it was dried at 30°C in a drying oven and passed through a 100-mesh sieve.

Preparation of annealed starch The initial moisture contents of YM, YHM, SSPS, and CSPS were 10.8, 8.5, 11.5, and 12.3 %, respectively. Raw starches (5 g) were weighed into glass containers. Then, moisture contents of sweet potato starches was adjusted to 90% by adding appropriate amounts of distilled water with 0.02% sodium azide as a bacteriostatic agent. The glass containers were sealed, stored at room temperature for 24 h for equilibration. After equilibration, all samples were stored at 55°C in a water bath for 72 h. All samples were recovered by centrifugation at 1,500×*g* for 5 min and the supernatant was poured off. The annealed starches were washed with distilled water and air-dried at room temperature, ground and passed through a 100-mesh sieve.

Microscopic observation Microscopic observations of raw and annealed sweet potato starches was performed using a scanning electron microscope (JSM 5410LV; JEOL Ltd., Tokyo, Japan) as described by Shin *et al*. (17). Light microscopy was conducted using a CSB-HP3 light microscope (Sam Won Scientific, Seoul, Korea) equipped with a polarizer. Images were captured using a digital camera (E8400; Nikon, Tokyo, Japan).

Gelatinization properties using differential scanning calorimetry (DSC) The gelatinization properties of starch samples were determined using a differential scanning calorimeter (Diamond DSC; Perkin-Elmer, Waltham, MA, USA). Starch (10 mg) was weighed in a hermetic aluminum pan, and 40 mL of distilled water was added. The sample pan was sealed and kept at room temperature overnight. DSC scan was made as the sample was heated from 30°C to 130°C at a rate of 5°C/min. As a reference, an empty pan was used.

X-ray diffraction and relative crystallinity X-ray

diffraction analysis was performed using an X-ray diffractometer (Model D5005; Bruker, Karlsruhe, Germany) operating at 40 kV and 40 mA with Cu-Kα radiation of 0.15406 nm (nickel filter; time constant, 4 s). The sample was scanned through 2θ range from 3° to 30°.

Relative crystallinty was calculated using Origin 5.0 (MicroCal, Northampton, MA, USA) according to the following equation:

$$\text{Relative crystallinity (\%)}=\frac{A_c}{A_a+A_c}\times 100$$

where, A_a is the area of amorphous region, and A_c is the area of crystalline region.

Swelling factor Starch (100 mg) was suspended in 5 mL of distilled water and incubated in a water bath at 30, 50, 60, 70, and 80°C for 30 min. After cooling the sample on ice, 0.5 mL of blue dextran solution (5 mg/mL) was added. The solution was gently vortexed, centrifuged at 3,000×*g* for 10 min, and the absorbance of the supernatant was measured at 620 nm. Swelling factor (SF) was calculated as follows:

$$SF=1+\frac{7{,}700}{w}\times\frac{A_S-A_R}{A_S}$$

where, w is the sample weight, A_S is the absorbance of the supernatant, and A_R is the absorbance of reference (without starch).

Close packing and amylose leaching Close packing (*C**) and amylose leaching (AML) were determined by the method of Eerlingen *et al.* (21) with slight modification. Starch suspension (0.5% dry matter) was heated for 15 min in a water bath at 80°C. After cooling on ice, the starch sample was centrifuged at 2,400×*g* for 15 min. The supernatant was transferred to other tube with a pipette for the measurement of amylose content (21). The sediment was weighed and *C** was calculated as follows:

$$C^*\ (\%)=\frac{\text{starch weight (dry matter)}\times 100}{\text{sediment weight}}$$

For the determination of amylose content, supernatant (1.0 mL) was taken into a 50.0 mL tube. After adding 0.1 M NaOH (0.5 mL), the sample was boiled for 3 min and immediately cooled on ice. Following neutralization with 0.1 M HCl (0.5 mL), 20.0 mL of potassium hydrogen tartrate solution (5.0 g/L) and distilled water (27.5 mL) were added. Then, 0.5 mL of an iodine solution (0.2 g I_2 and 2.0 g KI/100 mL) was added. After thorough mixing, the solution was kept at room temperature for 20 min. The absorbance of the solutions was measured at 680 nm. Pure potato amylose was used for the calibration curve.

Starch digestibility Starch digestibility was determined following the method of Brumovsky and Thompson (16) with slight modification. To prepare enzyme solution, 2 g of pancreatin (P-7545, activity 8×USP/g; Sigma-Aldrich, St. Louis, MO, USA) was added to 24 mL of distilled water and stirred for 10 min. After centrifugation at 1,500×*g* for 10 min, 20 mL of the supernatant was transferred into a beaker containing 3.6 mL of distilled water and 0.4 mL of amyloglucosidase (AMG 300L, activity 300 AGU/mL; Novozymes, Bagsvaerd, Denmark). The enzyme solution was stored in a shaking incubator at 37°C for at least 10 min prior to use. The enzyme solution was freshly prepared for each batch of digestion.

Each starch sample (30 mg) was weighed into a 2-mL microtube containing 0.75 mL of sodium acetate buffer (pH 5.2) and a glass ball. Each tube containing starch and buffer was stored in a shaking incubator at 37°C for 10 min. After storage, prepared enzyme solution (0.75 mL) was added to each tube and all samples were incubated in a shaking incubator with a shaking speed of 240 rpm at 37°C. The microtube was taken at certain time (10 and 240 min) and boiled for 10 min to stop enzyme reaction. The hydrolyzed glucose content in the supernatant obtained after centrifugation (5,000×*g*, 5 min) was measured using a GOP-POD kit (BCS Co., Anyang, Korea).

Starch fractions were classified based on the rate of hydrolysis. RDS and SDS fractions were measured after incubation for 10 min and 240 min, respectively. The undigested fraction after 240 min was determined as RS fraction.

Pasting properties Pasting properties of starch suspensions were measured with a Rapid Visco Analyser (RVA-3D; Newport Scientific, Warriewood, Australia). The starch suspension (8%, w/w) was equilibrated at 50°C for 1 min, heated from 50°C to 95°C at a rate of 12°C/min, held at 95°C for 2.5 min, cooled to 50°C at the same rate, and held at 50°C for 2 min. The paddle speed was 960 rpm for the first 10 s, then 160 rpm for the remainder of the experiment.

Statistical analysis Experiments were conducted in triplicate, and the mean value with the standard deviation are reported. SigmaPlot for windows (version 10.0; Chicago, IL, USA) was used for graphs.

Results and Discussion

Microscopic observation Scanning electron microscopy revealed that these raw sweet potato starches had irregular, oval, round, polygonal, spherical, and bell-shaped granules

and there were no pores on their surfaces. The granule shape rarely changed after annealing (data not shown). Under polarized light, the retention of granule crystallinity was observed by birefringence. All annealed starches maintained their birefringence and showed similar intensities of birefringence under polarized light (data not shown). This suggests that there are only minor changes to the organized structure and its orientation during annealing. Studies of several starches have also shown no significant changes in the birefringence of starch during annealing treatments (5,18).

Gelatinization properties Among the raw sweet potato starches, onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) were highest in CSPS followed by YM/YHM and SSPS (Table 1). Gelatinization properties are normally affected by amylose content and the distribution of amylopectin chains of different length (22). There were no significant differences in chain length distribution and amylose content among the samples (data not shown). These results suggest that there are other factors that affect gelatinization properties. A possible reason for the different gelatinization parameters is the varying amounts of imperfect crystallites with different thermal stability. The gelatinization temperature range (T_r=T_c−T_o) of raw SSPS was broader than for the other starches, which could be due to the presence of crystallites that are disordered at different temperatures. The ΔH was the highest in SSPS followed by CSPS and YM/YHM. Gelatinization enthalpy may be due to the melting of imperfect amylopectin-based crystals, with potential contributions from the crystal packing and helix melting enthalpies (23). All sweet potato starches used in this study had similar amylose contents (26.8%) and showed similar amylopectin chain length distributions (data not shown). Thus, they presumably had a different internal structure with respect to the starch granules.

The T_o and T_p of all annealed starches were higher than in the raw starches and the T_c of annealed starches was slightly higher or similar to that of raw starches. T_r decreased during annealing. The T_r value represents the degree of heterogeneity of crystallites. Thus, the crystallites in annealed starches displayed higher homogeneity than raw starches. This can be been attributed to the perfection of pre-existing crystallites (5). There was a more pronounced increase in T_o than in T_p and T_c. This suggests that the weakest crystallites were affected by annealing and were made more stable during the annealing process. The slightly higher or similar T_c values for annealed starches compared to raw starches suggests that the strong crystallites were unlikely to be affected by annealing. These results are consistent with previous reports (5-9,11). The extent of the increases in T_o and T_p was the highest in SSPS followed by YM/YHM and then CSPS. ΔH decreased during annealing in all starches except for CSPS. The decrease in the ΔH of YM, YHM, and SSPS suggests that the double helical structures in amylopectin-based crystals, which contain loosely associated crystallite defects, were disrupted during annealing. However, the increase in the ΔH of CSPS may have been due to the increased extent of the helical structure after annealing. This could be caused by the differences in the packing structures among sweet potato starches during biosynthesis. Annealing appears to allow the partial melting of some crystallites and a general realignment of starch chains in the amorphous phase. Therefore, weak crystallites or crystallite defects in the original packing structures of YM, YHM, and SSPS were likely to have melted and to have not readily realigned

Table 1. Gelatinization parameters of raw and annealed sweet potato starches

Sample[1)]		T_o (°C)	T_p (°C)	T_c (°C)	T_r (°C)	ΔH (J/g)
YM	Raw	64.9±0.4	73.2±0.0	79.7±0.3	14.8±0.1	9.3±0.2
	Annealed	72.1±0.1	76.4±0.1	81.0±0.2	8.9±0.1	7.8±0.2
	ΔT[2)]	7.2±0.4	3.2±0.1	1.3±0.4	-5.9±0.1	-1.5±0.3
YHM	Raw	62.4±0.6	73.8±0.4	80.1±0.2	17.8±0.5	9.3±0.3
	Annealed	70.0±0.4	77.2±0.6	81.9±0.4	9.9±0.6	8.2±0.5
	ΔT	7.6±0.7	3.4±0.7	1.8±0.4	-7.9±0.8	-1.1±0.6
SSPS	Raw	57.2±0.2	68.1±0.3	78.2±0.8	21.0±0.8	14.8±0.6
	Annealed	70.7±0.1	74.4±0.1	78.9±0.3	8.1±0.3	12.0±0.7
	ΔT	13.5±0.2	6.3±0.3	0.7±0.9	-12.9±0.9	-2.8±0.9
CSPS	Raw	67.1±0.3	74.2±0.5	83.2±0.5	16.1±0.7	12.0±0.7
	Annealed	72.2±0.2	78.3±0.4	83.9±0.2	11.8±0.1	16.1±0.4
	ΔT	5.1±0.4	4.1±0.6	0.7±05	-4.3±0.7	4.1±0.8

[1)]YM, Yulmi; YHM, Yeonwhangmi; SSPS, sweet potato starch produced by Samyang Genex; CSPS, commercial sweet potato starch
[2)]ΔT denotes the degree of difference in onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) gelatinization temperature (T_r), and enthalpy (ΔH) before and after annealing treatment, calculated by subtracting the values for annealed starch from those for raw starch.

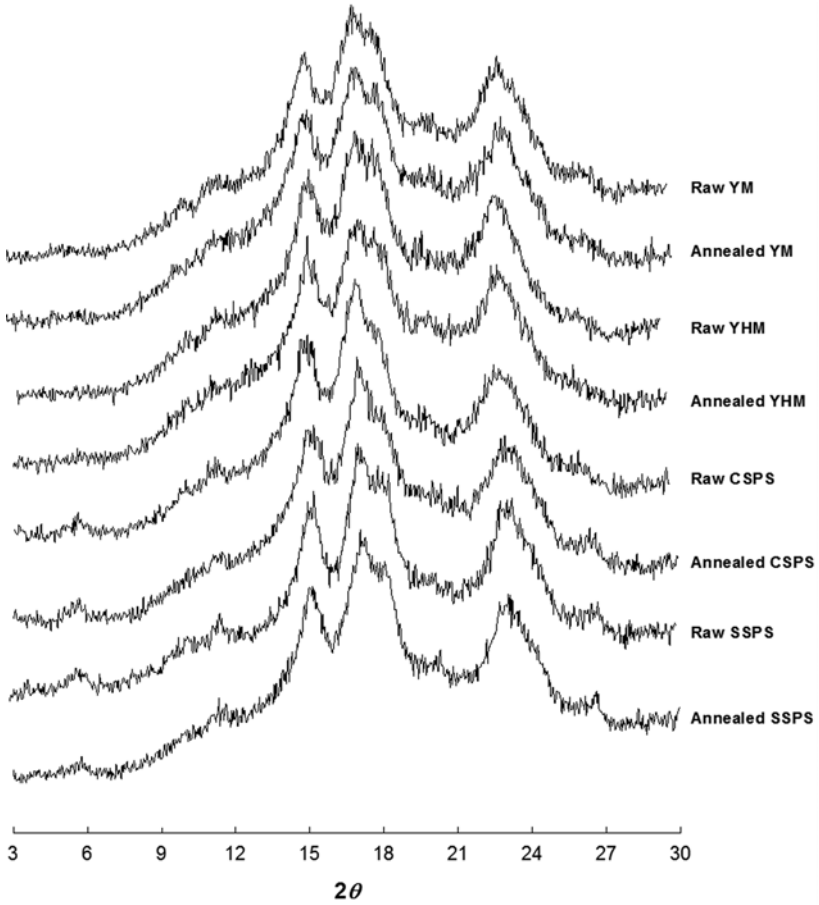

Fig. 1. X-ray diffractograms of raw and annealed sweet potato starches. YM, Yulmi; YHM, Yeonwhangmi; SSPS, sweet potato starch produced by Samyang Genex; CSPS, commercial sweet potato starch

whereas those in CSPS likely realigned more easily, and these realigned crystallites had a more ordered structure than those in raw CSPS. Many researchers have reported conflicting results regarding changes in ΔH after annealing treatment (5,7,8,18,24,25). These studies have suggested that the extent of change in ΔH after annealing depends on the annealing conditions and the origin of the starch.

X-ray diffraction pattern and crystallinity The X-ray diffraction patterns and the relative crystallinities of raw and annealed sweet potato starches are shown in Fig. 1 and Table 2, respectively. Starch can be classified into A, B, and C types based on the X-ray diffraction pattern. According to Hizukuri *et al*. (26), X-ray diffraction peaks at 5.5, 15, 17, and 22° or 23° are characteristic of C type starch that is common to most sweet potato starches. They also sub-classified C type starch into C_a, C_b, and C_c types on the basis of their resemblance to either type A, B, or an intermediate type between A and B, respectively. According to this classification, raw YM and YHM are C_a type starches. The X-ray diffraction patterns of raw SSPS and CSPS allowed them to be classified as C_b and C_c types, respectively. After annealing, the X-ray diffraction pattern remained unchanged.

Table 2. Relative crystallinity of sweet potato starches before and after annealing

Sample[1)]		Relative crystallinity (%)
YM	Raw	25.5±0.1
	Annealed	23.5±0.3
YHM	Raw	29.7±0.4
	Annealed	28.5±0.3
SSPS	Raw	25.5±0.1
	Annealed	23.2±0.2
CSPS	Raw	24.9±0.2
	Annealed	26.7±0.3

[1)]YM, Yulmi; YHM, Yeonwhangmi; SSPS, sweet potato starch produced by Samyang Genex; CSPS, commercial sweet potato starch

The relative crystallinities of raw starches were similar. Relative crystallinity can be influenced by the content ratio of amylose to amylopectin, average amylopectin chain length, and crystallite size (4). After annealing, the relative

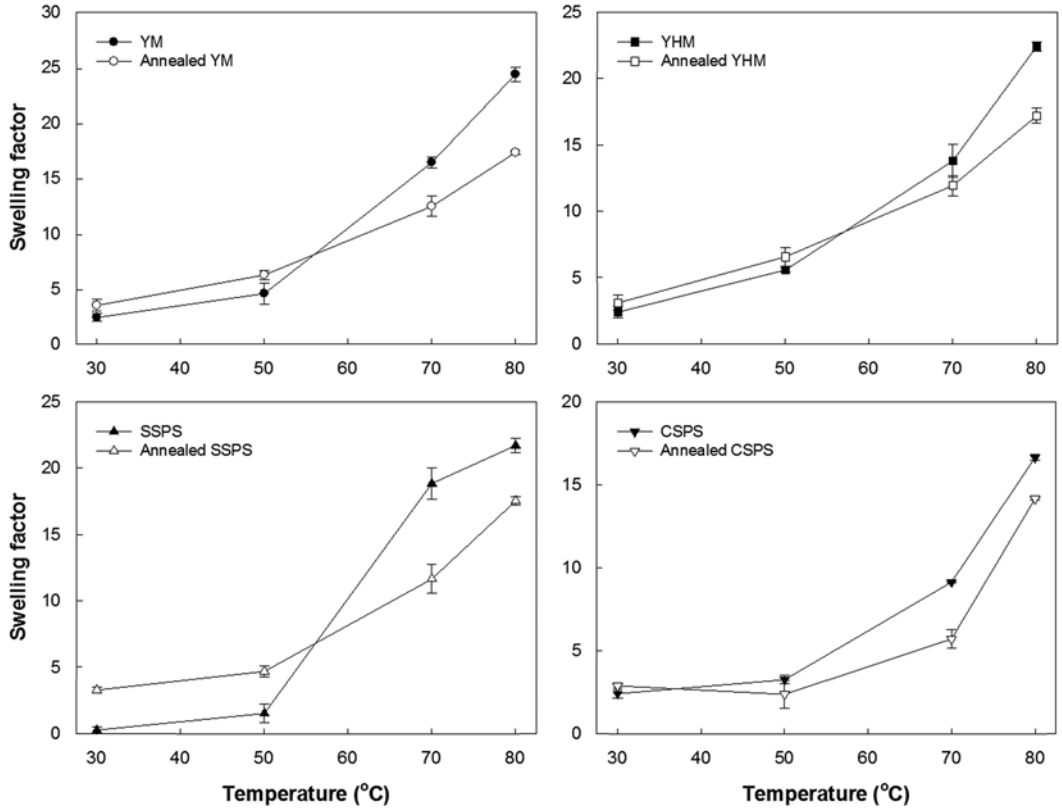

Fig. 2. Swelling factors of raw and annealed sweet potato starches. YM, Yulmi; YHM, Yeonwhangmi; SSPS, sweet potato starch produced by Samyang Genex; CSPS, commercial sweet potato starch

crystallinities of annealed YM, YHM, and SSPS slightly decreased, but the relative crystallinity of annealed CSPS slightly increased. This is consistent with the ΔH results. Vermeylen *et al*. (27) reported that a slight decrease in crystallinity might be a reflection of crystallite disruption or reorientation. The increase in ΔH and relative crystallinity of CSPS after annealing may have been due to an increase in crystal perfection or the formation of new crystallites. The increase in crystallinity during annealing might also be influenced by the enhanced ordering of the amylose-lipid complex (11,25). However, the peak intensity at 19.5°, which is characteristic of the amylose-lipid complex, was rarely changed by annealing in the present study.

AML, SF, and *C** Studies regarding AML and SF have provided information regarding the extent of interaction between starch chains in the amorphous and crystalline domains of raw granules (18,25). AML at 80°C decreased with annealing. The extent of this reduction was greatest in SSPS followed by YM, YHM, and CSPS (Table 2). Low values indicated that only a fraction of amylose had leached out. Many researchers have reported that a reduction in AML after annealing may be due to additional interactions between amylose-amylose and/or amylose-amylopectin and an enhanced ordering of amylose-lipid complexes (5,11,18,25). As mentioned above, the peak intensity of amylose-lipid complexes in the X-ray pattern rarely changed after annealing. This suggests that the change in the amount of amylose-lipid complex was not the main reason for the decrease in AML after annealing and that the additional interactions between the amylose and amylopectin chains could be the main reason for the increase in AML. During annealing, imperfect and weak crystallites are easily melted and then reassociated (4). During reassociation, they may interact with amylose and/or amylopectin. Therefore, new crystallites formed by reassociation could decrease AML after annealing. However, newly formed crystallites in annealed starches may have a less ordered structure and packing energy. This does not apply to CSPS, because only the ΔH and crystallinity of CSPS increased upon annealing.

The swelling of starch granules may begin in the bulk, relatively mobile amorphous fraction and in the more restrained amorphous regions immediately adjacent to crystalline regions (28). In the present study, SF increased as temperature increased up to 80°C, but decreased upon annealing (Fig. 2). At 80°C, the decrease in SF of annealed YM, YHM, SSPS, and CSPS was 7.1, 5.1, 4.2, and 2.5%, respectively. This decline upon annealing was likely due to

Table 3. Amounts of amylose leaching (AML) and close packing concentrations (*C) of sweet potato starches before and after annealing**

Sample[1)]		AML	*C** (%)
YM	Raw	60.7±1.5	3.3±0.5
	Annealed	40.2±1.7	6.7±0.1
YHM	Raw	62.4±1.0	3.2±0.0
	Annealed	46.3±2.3	5.7±0.1
SSPS	Raw	49.9±1.5	4.2±0.1
	Annealed	23.2±1.3	7.2±0.3
CSPS	Raw	39.8±0.9	4.8±0.1
	Annealed	25.4±0.9	7.3±0.4

[1)]YM, Yulmi; YHM, Yeonwhangmi; SSPS, sweet potato starch produced by Samyang Genex; CSPS, commercial sweet potato starch

Table 4. Relative amounts of RDS, SDS, and RS in raw and annealed sweet potato starches

Sample[1)]		RDS (%)	SDS (%)	RS (%)
YM	Raw	20.0±2.2	34.2±2.2	45.8±0.0
	Annealed	28.3±0.5	44.8±0.6	26.9±0.1
YHM	Raw	22.0±0.6	35.4±0.4	42.6±0.1
	Annealed	29.3±0.3	45.3±0.8	25.4±0.6
SSPS	Raw	14.2±0.7	38.5±0.2	47.4±0.9
	Annealed	20.6±0.2	46.5±0.6	32.9±0.6
CSPS	Raw	5.0±0.1	30.9±1.0	64.1±1.0
	Annealed	5.6±0.2	32.2±1.4	62.2±1.2

[1)]YM, Yulmi; YHM, Yeonwhangmi; SSPS, sweet potato starch produced by Samyang Genex Co.; CSPS, commercial sweet potato starch

interplay among several factors, such as an increase in crystal perfection, the formation of new crystallites through interactions between starch chains (amylose-amylose, amylose-amylopectin, and amylopectin-amylopectin), and an increase in crystallite size and crystallite reorientation (5,11).

After annealing, *C** increased because of the strong decrease in swelling power caused by annealing (20). The higher *C** of annealed starch indicates that it needs a larger number of granules to fill the total space compared to raw starch. Therefore, the swollen granules of annealed sweet potato starches used in this study may be smaller than those of raw starch. These results are consistent with the results of the SF.

Digestibility The *in vitro* digestibility of raw and annealed starches is presented in Table 4. After annealing, the changes in the digestibility of YM, YHM, and SSPS were similar. Annealing increased RDS and SDS levels but decreased RS content. However, the digestibility of CSPS was not significantly different before and after annealing. Starch-degrading enzymes mainly attack the amorphous regions of starch granules in the initial period. Subsequently, if some crystalline regions are exposed, the enzymes attack the exposed crystalline region (29). In YM, YHM, and SSPS, the amorphous region increased after annealing. At the same time, crystalline defects, which are more resistant to starch-degrading enzymes than are amorphous regions, appeared to melt during annealing (based on the results of DSC and X-ray diffractometry). A possible reason for the increased RDS content is the easy and rapid attack on the amorphous region and melted crystalline defects during the initial period of digestion. The increase in SDS content and the decrease in RS content could be due to the loss of some α-helical structures and the crystalline region. These changes could also be attributed to the partial gelatinization of starch during annealing. However, as stated above, after annealing, all annealed sweet potato starches retained their birefringence under polarized light microscopic observation. The partial or full swelling and gelatinization of starch granules are indicated by the loss of birefringence, that is, the disappearance of Maltese cross. Therefore, the swelling or gelatinization during annealing could be negligible in our study.

Unlike the other samples, the annealed CSPS had higher ΔH and crystalline perfection. Chung *et al*. (18) reported that annealing decreases the SDS content and increases the RS content of corn, pea, and lentil starches. This discrepancy could be due to the differences in starch source, digestive enzyme source, and method of digestibility measurement (25).

Pasting properties Figure 3 shows Rapid Visco Analyser (RVA) viscosity curves for raw and annealed sweet potato starches. The starch pasting properties are influenced by the interplay among various factors including granule swelling, amylose leaching, starch crystallinity, and the branch chain length distribution of amylopectin (28). Jacobs *et al*. (9) reported that both the formation of a tightly packed array of swollen and deformable granules and the leaching of amylose can contribute to the development of viscosity in starch paste during heating. Peak viscosity and breakdown, which reflect the swelling power and fragility of swollen granules, respectively, were highest in YM followed by YHM, SSPS, and CSPS. As an indicator of the tendency for retrogradation, CSPS had the highest setback value (747 cp) and YM had the lowest (552 cp). The higher setback value suggests the presence of a more extensively hydrogen-bonded network structure formed by the interactions among long amylopectin chains (DP 37-50) during the cooling cycle (25). YM and YHM had sharp peaks and high breakdown values, implying granule fragility at higher temperatures and shear rates.

Annealing decreased peak viscosity and setback but increased pasting temperature. The peaks were not well

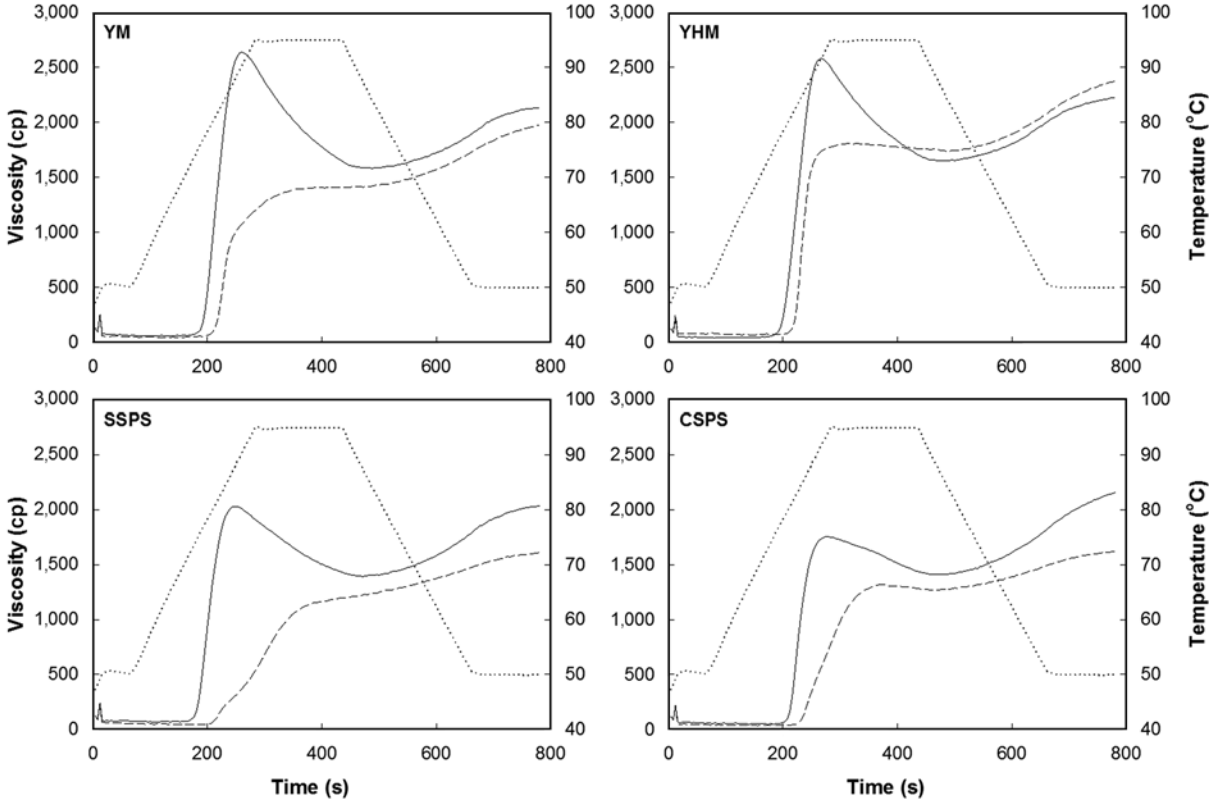

Fig. 3. Viscograms of raw and annealed sweet potato starches. YM, Yulmi; YHM, Yeonwhangmi; SSPS, sweet potato starch produced by Samyang Genex; CSPS, commercial sweet potato starch; Solid line, raw starch; dashed line, annealed starch; dotted line, temperature

defined. The final viscosities of annealed YM, SSPS, and CSPS were lower than those of the raw starches, whereas annealed YHM had a higher viscosity than raw starch. The pasting temperature of all annealed starches increased by 4.75, 3.95, 8.05, and 5.45°C in YM, YHM, SSPS, and CSPS, respectively. Hydrothermal treatment may make the granules resistant to deformation by strengthening the intragranular binding forces (8). Higher pasting temperature and lower peak viscosity and breakdown may be due to enhanced crystallinity and limited starch swelling and structural disintegration, which significantly contributes to starch viscosity (30). In annealed YHM, the increased final viscosity was probably a consequence of swollen gelatinized granules being more rigid, which significantly contributes to high cold viscosities (31). Therefore, annealing increased the paste stability and gelatinization temperature. This result is consistent with previous studies (5,8,9).

Regarding a potential industrial application of the annealed sweet potato starch, because the annealing process can decrease granular swelling and amylose leaching and increase heat and shear stability, which are all desirable properties for preparing good quality noodles, it can be of use in the manufacturing of noodles containing sweet potato starch (4).

In conclusion, the annealing process enhanced the packing arrangement in sweet potato starch granules and thus affected their physicochemical properties and digestibility by increasing the SDS content, although the extent of its influence varied depending on the cultivar. Our results will help lead to the development of new foods containing a healthy functional starch ingredient from orange-fleshed sweet potato.

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References

1. Palomar LS, Perez JA, Pascual JA. Wheat flour substitution using sweet potato or cassava in some bread and snack items. Ann. Trop. Res. 3: 8-17 (1981)
2. Lee JS, Ahn YS, Kim HS, Chung MN, Kim JJ, Kim JM, Jeong BC, Bang JK. A new sweetpotato cultivar for table use, "Yeonhwangmi". Korean J. Breeding 38: 149-150 (2006)
3. Teow CC, Truong V-D, McFeeters RF, Thompson RL, Pecota KV, Yencho GC. Antioxidant activities, phenolic and β-carotene contents of sweet potato genotypes with varying fresh colours. Food Chem. 103: 829-838 (2007)
4. Jayakody L, Hoover R. Effect of annealing on the molecular structure and physicochemical properties of starches from different

botanical origins - A review. Carbohyd. Polym. 74: 691-703 (2008)
5. Hoover R, Vasanthan T. The effect of annealing on the physicochemical properties of wheat, oat, potato and lentil starches. J. Food Biochem. 17: 303-325 (1994)
6. Jacobs H, Delcour JA. Hydrothermal modifications of granular starch, with retention of the granular structure: A review. J. Agr. Food Chem. 46: 2895-2905 (1998)
7. Krueger BR, Knutson CA, Inglett GE, Walker CE. A differential scanning calorimetry study on the effect of annealing on gelatinization behavior of corn starch. J. Food Sci. 52: 715-718 (1987)
8. Stute R. Hydrothermal modification of starches: The difference between annealing and heat/moisture-treatment. Starch-Starke 44: 205-214 (1992)
9. Jacobs H, Eerlingen RC, Clauwaert W, Delcour JA. Influence of annealing on the pasting properties of starches from varying botanical sources. Cereal Chem. 72: 480-487 (1995)
10. Tester RF, Morrison WR. Swelling and gelatinization of cereal starches. II. Waxy rice starches. Cereal Chem. 67: 558-563 (1990)
11. Waduge RN, Hoover R, Vasanthan T, Gao T, Li J. Effect of annealing on the structure and physicochemical properties of barley starches of varying amylose content. Food Res. Int. 39: 59-77 (2006)
12. Nazakawa F, Noguchi S, Takahashi J, Takada M. Thermal equilibrium state of starch-water mixture studied by differential scanning calorimetry. Agr. Biol. Chem. Tokyo 48: 2647-2653 (1984)
13. Englyst HN, Kingman SM, Cummings JH. Classification and measurement of nutritionally important starch fractions. Eur. J. Clin. Nutr. 46: E33-E50 (1992)
14. Lehmann U, Robin F. Slowly digestible starch-its structure and health implications: A review. Trends Food Sci. Tech. 18: 346-355 (2007)
15. Sajilata MG, Singhal RS, Kulkarni PR. Resistant starch-a review. Compr. Rev. Food Sci. F 5: 1-17 (2006)
16. Brumovsky JO, Thompson DB. Production of boiling-stable granular resistant starch by partial acid hydrolysis and hydrothermal treatments of high-amylose maize starch. Cereal Chem. 78: 680-689 (2001)
17. Shin SI, Kim HJ, Ha HJ, Lee SH, Moon TW. Effect of hydrothermal treatment on formation and structural characteristics of slowly digestible non-pasted granular sweet potato starch. Starch-Starke 57: 421-430 (2005)
18. Chung HJ, Liu Q, Hoover R. Impact of annealing and heat-moisture treatment on rapidly digestible, slowly digestible and resistant starch levels in native and gelatinized corn, pea and lentil staches. Carbohyd. Polym. 75: 436-447 (2009)
19. Moore S, Stein HW. Photometric ninhydrin method for use in the chromatography of amino acids. J. Biol. Chem. 176: 367-388 (1948)
20. Eerlingen RC, Jacobs H, Block K, Delcour JA. Effects of hydrothermal treatments on the rheological properties of potato starch. Carbohyd. Res. 297: 347-356 (1997)
21. Gilbert GA, Spragg SP. Iodimetric Determination of Amylose. Methods in Carbohydrate Chemistry. Academic Press, New York, NY, USA. pp. 168-169 (1964)
22. Vandeputte GE, Vermeylen R, Geeroms J, Delcour JA. Rice starches I. Structural aspcets provide insight into crystallinity characteristics and gelatinisation behaviour of granular starch. J. Cereal Sci. 38: 43-52 (2003)
23. Lopez-Rubio A, Flanagan BM, Gilbert EP, Gidley MJ. A novel approach for calculating starch crystallinity and its correlation with double helix content: A combined XRD and NMR study. Biopolymers 89: 761-768 (2008)
24. Knutson CA. Annealing of maize starches at elevated temperatures. Cereal Chem. 67: 376-384 (1990)
25. Lan H, Hoover R, Jayakody L, Liu Q, Donner E, Baga M, Asare EK, Hucl P, Chibbar RN. Impact of annealing on the molecular structure and physicochemical properties of normal, waxy and high amylose bread wheat starches. Food Chem. 111: 663-675 (2008)
26. Hizukuri S, Abe JI, Hanashiro I. Starch: Analytical Aspects. Carbohydrates in Food. CRC Press, Boca Raton, FL, USA. pp. 305-390 (2006)
27. Vermeylen R, Goderis B, Delcour JA. An X-ray study of hydrothermally treated potato starch. Carbohyd. Polym. 64: 364-375 (2006)
28. Hoover R, Manuel H. The effect of heat-moisture treatment on the structure and physicochemical properties of normal maize, waxy maize, dull waxy maize and amylomaize V starches. J. Cereal Sci. 23: 153-162 (1996)
29. O'Brien S, Wang YJ. Susceptibility of annealed starches to hydrolysis by α-amylase and glucoamylase. Carbohyd. Polym. 72: 597-607 (2008)
30. Vieira FC, Sarmento SBS. Heat-moisture treatment and enzymatic digestibility of Peruvian carrot, sweet potato and ginger starches. Starch-Starke 60: 223-232 (2008)
31. Collado LS, Corke H. Heat-moisture treatment effects on sweet potatostarches differing in amylose content. Food Chem. 65: 339-346 (1999)