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Physicochemical Characteristics of Acid Thinned and High Pressure Treated Waxy Rice Starch for *Yugwa* (Korean Rice Snack) Production

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Abstract The acid modification of waxy rice starch was conducted to improve the *yugwa* production process. The intrinsic viscosity, paste viscosity, and differential scanning calorimetry characteristics of acid modified starch were measured, and *bandaegi* and *yugwa* prepared from acid modified starch were evaluated. The intrinsic viscosities of acid thinned starches were 1.48, 1.27, 1.15, and 0.91 mL/g after reaction times of 1, 2, 3, and 4 hr, respectively. The gelatinization enthalpy was reduced from 16.3 J/g in native starch to 15.8, 15.3, 14.7, and 14.5 J/g in acid thinned starches as the time of acid thinning increased. The peak viscosity and final viscosity decreased with increasing the time of acid thinning, but the pasting temperature was slightly increased in acid thinned starches. The hardness of *bandaegi* from acid thinned starches under high pressure greatly decreased relative to the control, typical *yugwa*. *Yugwa* from acid thinned starch under high pressure maintained a homogeneous structure containing tiny and uniform cells similar to that of native waxy rice starch used for typical *yugwa*. Acid thinning under high pressure appears to be a good alternative to the existing steeping process for better *yugwa* quality.

Key words: starch, acid thinning, physicochemical property, *yugwa*

Introduction

Yugwa is a traditional Korean oil-puffed snack made of waxy rice (*Oryza sativa*). It is eaten as a popular snack due to its soft texture and unique taste, and there has been more than a 10-fold increase in its production during the last 15 years in Korea. Traditionally, *yugwa* is prepared as follows. The milled waxy rice is steeped for 2 to 14 days (1) and then washed, drained, and crushed by mill into a fine powder. After steaming, the waxy rice dough is kneaded and pounded for aeration and then cooled, cut into small pieces, and dried. These dried small pieces (*bandaegi*) are fried through 2 consecutive deep-frying processes and coated with honey and puffed or coated cereal grits. The resulting *yugwa* product is quite different from western and other Asian rice-based snacks in the aspects of texture and taste.

The qualities of *yugwa* depend entirely on the processing conditions, such as the steeping period of waxy rice in water, milling method, conditions of pounding, drying, frying, and so on (2). In particular, the steeping period of waxy rice in water involves several distinct physicochemical changes. First is the hydration of waxy rice grains enabling it to be gelatinized during processing. Steeping also affects the texture and volume expansion, which are the most important characteristics of *yugwa* (3). Finally, steeping acidifies the character of glutinous rice, affecting the starch's α-amylase activity and bringing about component's changes (4). In a study of the steeping periods of waxy rice during the preparation of *yugwa* (5), it was reported that steeping influences the physical and sensory properties of *yugwa*.

However, many problems occur during steeping including off-flavor, undesirable microorganisms, water pollution, and the extended consumption of water. Thus, many manufacturers of *yugwa* seek to improve the process by the substitution of raw materials (waxy rice or starch) or the fast and continuous manner. One such method, we may suggest, is the use of waxy rice starch which can be used as a raw material for the production of *yugwa* instead of waxy rice grains. In this case, waxy rice starch can be modified through a chemical modification to eliminate or reduce undesirable characteristics. In recent times, many types of chemically modified starches have been prepared by acid hydrolysis, oxidation, acetylation, esterification, etherification, and cross-linking (6-8). It is well known that acid modification changes the physicochemical properties of starch without destroying its granule structure, and the properties of acid-thinned starches can be variable (9). In fact, the waxy rice starch resulting from the steeping of waxy rice exhibits differences in physicochemical properties such as viscosity and the degree of damage or gelatinization. High pressure treatment also can be used as a powerful tool for the fast and continuous modification of starch including gelatinization, homogenization, incorporation, and separation (10, 11).

The objective of this study was to investigate the effects of acid thinning and high pressure on the physicochemical properties of waxy rice starch and the quality characteristics of *yugwa*, and to develop a new process to improve the production of *yugwa*.

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Materials and Methods

Waxy rice starch Waxy rice starch (*Indica*) was purchased from Bangkok Starch Industrial Co. (Nakornprathom, Thailand). All other chemicals used were of analytical grade.

Acid thinning and acid thinning treatment under high pressure Four-hundred g of waxy rice starch was slurried in 6 L of 0.4 M HCl by stirring with an impeller mixer for 4 hr, while maintaining a temperature at 45°C. The slurry was passed 1-3 times through a microfluidizer (model 110-T; MFIC Corporation, Newton, MA, USA) at 18,000 psi. The waxy rice starch modified by acid thinning treatment under high pressure was neutralized and then filtered. The residue obtained was washed 3 times with distilled water and air dried at 30°C for 48 hr.

Intrinsic viscosity Waxy rice starches were dissolved (0.2-0.3%) in 90% dimethyl sulfoxide (DMSO), held at 100°C for 4 min, and then filtered through 0.45 μm Millipore filter. The viscosity of solutions was measured by a Cannon-Fenske capillary viscometer (size 100; Cannon Instrument Co., State College, PA, USA) at 25°C. Prior to measurement, the solution was placed for 30 min in a 25°C water bath to equilibrate the temperature. Specific viscosity (η_{sp}) and intrinsic viscosity ([η]) were determined as follows:

$$\eta_{sp} = (\eta - \eta_s)/\eta_s \text{ and } [\eta] = \lim_{c\to 0} \eta_{sp}/C$$

where η is the solution viscosity, η_s is the solvent viscosity, and C is the solution concentration.

Differential scanning calorimetry (DSC) DSC characteristics were carried out using a Perkin-Elmer DSC-7 (Perkin-Elmer, Waltham, MA, USA). Starch sample (16 mg) was weighed in a large volume stainless steel pan and then distilled water (48 mg) was added. The pan was hermetically sealed and heated at a scan rate of 10°C/min and a heating range of 25 to 120°C. An empty pan was used as reference.

Paste viscosity The paste viscosity of waxy rice starch was measured by a rapid visco analyzer (RVA, Newport Scientific Instruments and Engineer, Sydney, Australia). Waxy rice starch suspension in water (1% dry solid) was heated from 25 to 95°C at a rate of 3.5°C/min, held at 95°C for 10 min, cooled to 50°C at 3.5°C/min, and then held at 50°C for 10 min.

Texture analysis Texture analysis was performed on the samples using a rheometer (Compac-100; Sun Scientific Co., Tokyo, Japan). The conditions for measurements were a maximum weight of 2 kg and a speed of 240 mm/min using a no. 9 cutting-type probe. Ten samples for each testing group were measured.

Preparation of *yugwa* Acid thinned and high pressure treated waxy rice starches were adjusted for moisture content and steamed at 100°C for 30 min. After that, the dough was kneaded at 250 rpm for 5 min using a screw kneader (Kyung Chang Machine Works, Seoul, Korea). The kneaded dough was pressed into a sheet 5 mm thick using the screw kneader and dried by hot air at 60-65°C for 2 hr. The dried sheet was cut into small pieces with an average dimension of 30×8.5×3.0 mm by using a cutting machine (Kyung Chang Machine Works), and dried again by hot air at 60-65°C for 2 hr. These small dried pieces (called *bandaegi*) were fried in 2 consecutive deep-frying pans. The frying time and temperature were 1.5 min at 100±5°C in the first pan and 1.5 min at 165±5°C in the second pan. The fried *yugwa* was used for texture measurement and appearance tests.

Results and Discussion

Intrinsic viscosity of acid thinned waxy rice starches The intrinsic viscosities of acid thinned starch (ATS) with different reaction times of acid thinning, and acid thinning under the high pressure treatment are listed in Table 1. The intrinsic viscosities of acid thinned starches were 1.48, 1.27, 1.15, and 0.91 mL/g after treatment times of 1, 2, 3, and 4 hr, respectively, when compared to raw waxy rice starch (1.56 mL/g). It is well known that the hydroxonium ion (H_3O^+) attacks the glycosidic oxygen atoms and hydrolyses the glycidic linkages during the process of acid thinning. Acid gradually degrades the surface of the starch granule first before entering the inner region. According to Shon *et al.* (12), the rice starch dispersions in DMSO solution displayed rheological behaviors similar to those of weak gels. The viscosity of starch pastes changed depending on the pH due to the addition of various sour substances (citric acid, acetic acid, lactic acid, malic acid, tartaric acid, and ascorbic acid) to corn starch pastes. The hydrolysis of amylose and amylopectin chains occurred by adding sour substances and also led to a decrease in viscosity at lower pH. However, the addition of a small amount of sour substances promoted the leaching out of amylose and amylopectin chains and led to an increase in viscosity (13). On the other hand, the intrinsic viscosity of acid thinned starch under high pressure (ATP) following a combination of acid thinning and high pressure treatment in 1 to 3 passes decreased as much as the viscosity of acid thinned starch for 1 hr (AT1) or acid starch for 2 hr (AT2). This result shows that the combination of acid thinning and high pressure might be effective for preparing ATS within only a few minutes as opposed to the 1-2 hr of reaction time required for acid thinning. According to Stute *et al.* (14), most starches show very little swelling and maintain their own granular character such as that after heat gelatinization under high pressure treatment. Under high pressure, the pressure acts immediately and independent of the size and the shape of the product, and it does not break covalent bonds (15).

Generally, the intrinsic viscosity of waxy rice starch, which is isolated from waxy rice grains after steeping in the commercial production of *yugwa*, was within a range of 1.65-1.82 mL/g. The intrinsic viscosities of all ATS were lower than that of waxy rice starch produced from waxy rice grains by the steeping process. The acid thinning of waxy rice starch might provide a great advantage in the commercial production of *yugwa*. Although the intrinsic viscosity of ATS is somewhat lower, it is noteworthy from the commercial viewpoint that waxy rice starch may be a good alternative to waxy rice grains. The use of waxy rice starch could be expected to solve the sanitary and economical problems associated with traditional *yugwa* production.

DSC characteristics The onset temperature and gelatinization enthalpy (ΔH) of native starch and ATS are listed in Table 1. The onset temperature shifted to lower values in ATS compared to that in native starch but increased slightly with increasing reaction times of acid thinning. Gelatinization enthalpy, which represents the amount of thermal energy involved in the gelatinization process, was reduced from 16.3 J/g in native starch to 15.8, 15.3, 14.7, and 14.5 J/g in ATS as the reaction time of acid thinning increased. The onset temperature and gelatinization enthalpy of acid thinned starch under high pressure (ATP starches) was generally lower than that of ATS (Table 1). Acid thinning treatment under high pressure was more effective at reducing both the onset temperature and the gelatinization enthalpy of starch. In view of this direct relationship between double helix content and crystallinity, it is thought that leaching of the amorphous region by acid hydrolysis increases starch crystallization and consequently increases both the gelatinization temperature and enthalpy. Enthalpy might be involved in the cleavage of hydrogen bonds and other associative bonding forces among starch molecules, and such bonds must be limited by oxidation and acetylation. This accounts for the reduction of enthalpy following chemical modification (16). The decrease in gelatinization temperature and enthalpy are in agreement with the of intrinsic viscosity values.

Table 1. Intrinsic viscosity and DSC characteristics of native starch and ATS

Starch sample[1)]	Intrinsic viscosity	DSC characteristics	
	(mL/g)	Onset (°C)	Enthalpy (J/g)
Native	1.56	65.28	16.31
AT1	1.48	64.01	15.75
AT2	1.27	64.53	15.34
AT3	1.15	64.83	14.65
AT4	0.91	65.84	14.54
ATP1	1.37	62.04	15.25
ATP2	1.31	61.43	14.70
ATP3	1.20	61.29	14.50

[1)]Native, native waxy rice starch; AT1, acid thinned starch for 1 hr; AT2, acid thinned starch for 2 hr; AT3, acid thinned starch for 3 hr; AT4, acid thinned starch for 4 hr; ATP1, acid thinned starch under high pressure with 1 pass; ATP2, acid thinned starch under high pressure with 2 passes; ATP3, acid thinned starch under high pressure with 3 passes.

Paste viscosity The paste viscosities of native starch and ATS are listed in Table 2. When the pasting characteristics of ATS were compared with those of native starch, it was apparent that the acid thinning treatment changed the overall pasting characteristics of starch. The peak viscosity and final viscosity decreased with increasing reaction times of acid thinning treatment. The decrease in paste viscosity might be due to the shorter chains produced by acid thinning. Similar results were reported for the oxidation, acetylation, and acid thinning of starch (17, 18). Breakdown, which is defined as the difference between the peak viscosity and the final viscosity after holding for 10 min at 95°C and measuring the fragility of the starch (19), decreased proportionally as the reaction time of acid thinning increased. This accounts for the degradation that occurred in modified waxy rice starches during acid thinning. This setback, an index of retrogradation tendency in the paste.of starch (20), was also greatly reduced by acid thinning. There might be a higher degree of depolymerization in the AT starch paste than in the native starch paste. The peak, minimum (holding strength) breakdown, final, and setback viscosities of ATP starches were higher than those of AT starches, however, the pasting temperature showed a lower value regardless of the number of passes. There was no difference in peak times among native starch, AT and ATP starches. These results suggest that it is possible to use acid thinning treatment under high pressure to produce modified starch with the least amount of starch damage.

Quality characteristics of *yugwa* The hardness and color values of *bandaegi* prepared from AT starch are listed in Table 3. The hardness of *bandaegi* made from AT starch was much higher than that of the control, typical *yugwa*. However it exhibited a much lower value relative to native starch and decreased with increased times of acid

Table 2. RVA characteristics of native starch and acid thinned waxy rice starches

Starch sample[1)]	Peak1 (RVU)	Holding strength (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)	Peak time (min)	Pasting temp. (°C)
Native	262.9±0.9	114.6±1.1	148.3±1.8	148.5±1.7	33.9±0.9	3.5±0.0	71.9±0.0
AT1	188.3±0.5	80.4±0.6	107.9±0.5	100.9±0.9	20.5±0.9	3.5±0.0	74.3±0.1
AT2	156.5±0.5	64.3±0.8	92.3±0.4	81.6±0.7	17.4±0.3	3.5±0.0	73.8±0.5
AT3	125.1±0.4	49.9±0.5	75.2±0.5	63.5±0.4	13.6±0.3	3.5±0.0	-
ATP1	275.3±2.5	121.0±2.0	154.4±2.7	146.7±1.0	25.7±2.1	3.4±0.0	66.2±0.1
ATP2	263.4±2.1	115.3±1.0	148.2±2.2	140.3±0.7	25.0±0.3	3.5±0.0	66.3±0.1
ATP3	246.4±3.2	111.8±1.4	134.6±1.8	134.8±1.1	23.0±1.2	3.5±0.0	66.2±0.1

[1)]Native, native waxy rice starch; AT1, acid thinned starch for 1 hr; AT2, acid thinned starch for 2 hr; AT3, acid thinned starch for 3 hr; ATP1, acid thinned starch under high pressure with 1 pass; ATP2, acid thinned starch under high pressure with 2 passes; ATP3, acid thinned starch under high pressure with 3 passes.

Table 3. Textural properties and color values for *bandaegi* prepared from native and acid-thinned waxy rice starches

Bandaegi[1)]	Hardness (g/cm²)	Color value		
		L	*a*	*b*
CON	53,819.45	72.47	-0.90	3.38
Native	387,807.53	71.28	-0.44	0.91
AT1	293,229.19	73.18	-0.59	1.77
AT2	104,759.84	69.92	-0.65	2.16
AT3	63,043.90	67.86	-0.89	3.21
ATP1	86,098.37	77.61	-0.83	4.07
ATP2	74,081.30	78.75	-0.59	3.81
ATP3	41,522.33	63.05	-0.53	4.48

[1)]CON, *bandaegi* for typical *yugwa*; native, *bandaegi* from native waxy rice starch; AT1, *bandaegi* from acid thinned starch for 1 hr; AT2, *bandaegi* from acid thinned starch for 2 hr; AT3, *bandaegi* from acid thinned starch for 3 hr; ATP1, *bandaegi* from acid thinned starch under high pressure with 1 pass; ATP2, *bandaegi* from acid thinned starch under high pressure with 2 passes; ATP3, *bandaegi* from acid thinned starch under high pressure with 3 passes.

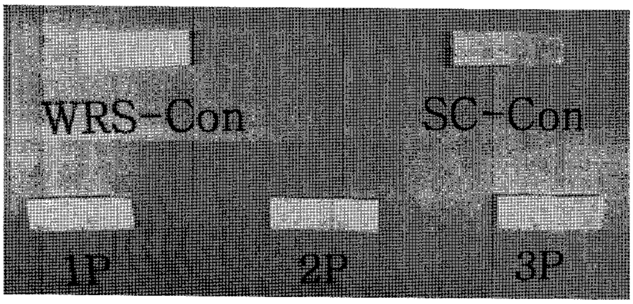

Fig. 1. Appearance of *bandegi.* WRS-Con, *yugwa* from raw waxy rice starch; SC-Con, control of typical *yugwa*; 1P, *yugwa* from acid thinned starch under high pressure with 1 pass; 2P, *yugwa* from acid thinned starch under high pressure with 2 passes; 3P, *yugwa* from acid thinned starch under high pressure with 3 passes.

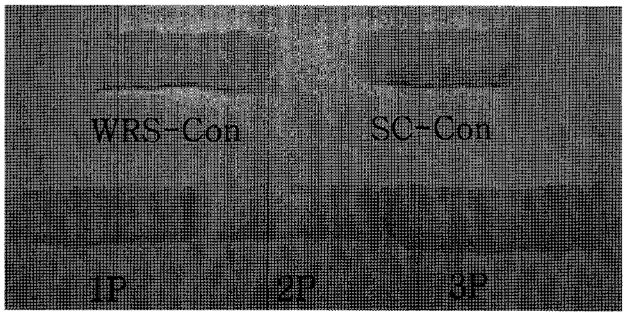

Fig. 2. Appearance of *yugwa*. WRS-Con, *yugwa* from raw waxy rice starch; SC-Con, control of typical *yugwa*; 1P, *yugwa* from acid thinned starch under high pressure with 1 pass; 2P, *yugwa* from acid thinned starch under high pressure with 2 passes; 3P, *yugwa* from acid thinned starch under high pressure with 3 passes.

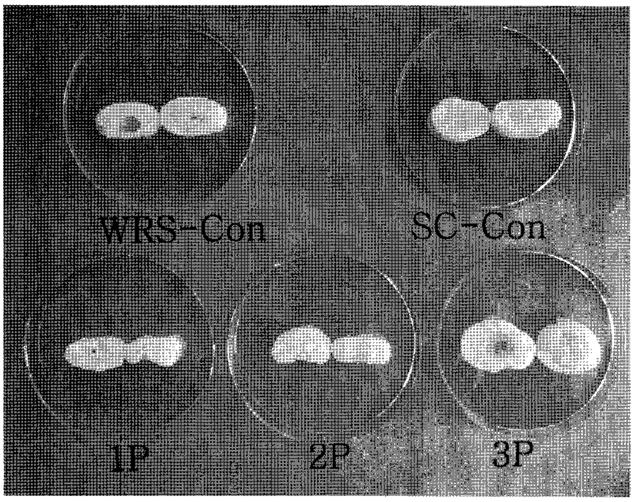

Fig. 3. Cross-section of *yugwa*. WRS-Con, *yugwa* from raw waxy rice starch; SC-Con, control of typical *yugwa*; 1P, *yugwa* from acid thinned starch under high pressure with 1 pass; 2P, *yugwa* from acid thinned starch under high pressure with 2 passes; 3P, *yugwa* from acid thinned starch under high pressure with 3 passes.

thinning. In particular, the hardness of *bandaegi* from AT3 was much closer to that of the control *yugwa*. The *L* value of *bandaegi* from AT starches decreased with increasing times of acid thinning compared to the control *yugwa*. The *a* and *b* values also showed a contrary tendency as the time of acid thinning increased from 1 to 3 hr. Hardness decreased greatly in *bandaegi* from ATP starches compared to the control *yugwa* (Table 4). The hardness of *bandaegi* from ATP3, having the lowest value of 41,522 g/cm², was significantly lower than that of the control (p= 0.05). The *L* values of *bandaegi* made from ATP1 and ATP2 were similar to the control *yugwa*, while the *L* value of *bandaegi* made from ATP3 was lowest.

Pieces of *bandaegi* prepared from native and ATP starches are shown in Fig. 1. Both types of *bandaegi* prepared from native and ATP starches had a good appearance. Figure 2 shows *yugwa* expanded by oil-frying the *bandaegi*. The appearance of typical *yugwa* was better than that of *yugwa* prepared from native starch. The expansion degree for ATP3, similar to that of typical *yugwa*, was better than those of ATP1 and ATP2 when the acid thinning treatment was conducted under high pressure. The photographs of cross-sections of *yugwa* (Fig. 3) show that acid thinning treatment under high pressure is rather effective for preparing *yugwa*. As the time of acid thinning treatment under high pressure increased, the expansion of *yugwa* increased and maintained a homogeneous structure containing tiny and uniform cells compared to native waxy rice starch or typical *yugwa*. The production time for *yugwa* can be improved by acid thinning treatment under high pressure instead of the traditional steeping process. Therefore, acid thinning under high pressure appears to be a good alternative to the existing steeping process for improving the quality of traditional *yugwa* production.

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