Rheological properties of rice flour treated with mild solutions of citric acid

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Abstract Effects of milling methods and organic acids treatments on rheological properties of rice flour were investigated. The average particle-size of wet-milled rice flour was lower and showed lower pasting temperature, peak viscosity, and storage modulus values than those of dry-milled rice flour. Wet-milled rice flour treated with citric acid showed significantly low viscosity and viscoelastic properties, as the concentration of citric acid increased, whereas wet-milled rice flour treated with acetic acid was not significantly affected by the acetic acid concentration. Rheological property of *baekseolgi* (Korean rice cake) made with wet-milled citric-acid-treated rice flour showed a similar trend in viscoelasticity, wherein citric acid treatment lowered the hardness of the rice. However, cohesiveness increased with increasing citric acid concentration. Overall, milling method affected the particle size, which influenced the viscosity and heat stability, whereas citric acid treatment affected the rheological properties of rice flour. These results are expected to contribute to the development of an appropriate method for rice flour application.

Keywords: wet-milled rice flour, citric acid, particle size, viscosity, viscoelasticity

Introduction

Rice has long been a staple food source in Korea and is consumed by 40% of the world's population (1). However, as the food consumption pattern has gradually changed, the domestic rice consumption has gradually decreased (2). Thus, the pressure to develop processed rice products to increase rice consumption is growing (3). In addition, the importance of processed rice products is growing because of wheat allergies in individuals (4) and the recognition of the nutritional value of rice, including its ease of digestion and high essential amino acid content (5).

A powdered rice form rather than the whole grain is usually used in processed foods. As the rice powder can be directly supplemented into processed foods, there has been research aimed to improve processing of the rice powder and make distribution easier. Studies have reported on processed rice products on the basis of their soaking time and particle size (6), effect of the grinding method (7), properties of the extruded rice powder (8), properties after enzymatic treatment (9), properties of rice powder treated with acetic acid (10), and retrograde inhibition of Korean rice cake (*garaedduk*) with modified starch (11), all of which are involved with various milling methods of rice with high processability and modifications for rice powder production (12).

In this study, physicochemical properties of rice powder produced by different milling methods and rheological properties of wet-milled rice flour treated with citric acid were investigated.

Materials and Methods

Materials The *Boramchan* cultivar purchased from Agricultural Union (MIDM, Pyeongtaek, Korea) in 2014 was used in this study.

Preparation of dry- and wet-milled rice powder, and particle-size determination Wet-milled rice flour was prepared by soaking rice in distilled water for 8 h followed by drying at room temperature for 1 h and milling with a roll mill (KM-18; Kyungchang, Seoul, Korea) (13). Dried wet-milled rice flour was sealed in a plastic bag and stored at 20°C. The stored rice flour was thawed at 4°C for 24 h until use. Dry-milled rice flour was obtained from a pin mill (SC-1B; Kyungchang) and stored at 4°C.

The particle size of rice flour was analyzed using a particle-size analyzer, (CILAS 1190; CILAS, Orléans, France) with distilled water as the dispersant (14).

Acid treatment of the wet-milled rice The acid treatment method

and acid concentrations for wet-milled rice flour were modified from Hirashima *et al.* (15). Citric and acetic acid solution with concentrations of 0.5, 1.0, 1.5, and 2.0% (w/v) were prepared. The rice flour was treated with the organic acid solutions at a ratio of 1:4 in a 35°C heated water bath for 3 h. The supernatant was removed by centrifugation at 1,500×*g* for 1 min. The pellet was dried at 40°C for 2 day to produce a powder, and the powder was sifted using a 20 mesh sieve before storing in a polythene bag.

Rapid Visco Analysis (RVA) of the rice powder during heating Rice powder (3 g with 12% water content) was dispersed in 22 mL of distilled water and changes in the starch on heating were analyzed using a Rapid Visco analyzer (RVA-3D; Newport Scientific, Narrabeen, Australia). Changes in starch viscosity were measured as the temperature was increased at a rate of 12°C/min from 50 to 95°C, which was maintained at 95°C for 2 min and then decreased at the rate of 12°C/min to 50°C. Results from RVA demonstrated the pasting temperature and peak viscosity 15 s after 95°C (trough), final viscosity at 50°C, calculated setback viscosity (final viscosity (trough)), and breakdown viscosity (peak viscosity (trough)).

Differential Scanning Calorimetry (DSC) and viscoelasticity of rice flour To determine the gelatinization of each rice flour sample, differential scanning calorimetry (DSC-4000; Perkin Elmer, Waltham, MA, USA) was used. Each rice powder sample was changed into a suspension solution at a ratio of 3:7 (distilled water:rice powder), and 10 mg of each sample was placed in an aluminum pan; an empty aluminum pan was used for the control. The temperature range for the DSC was 30–120°C with 10°C/min increments for both wet-milled and dry-milled rice powders.

To measure the dynamic viscoelasticity, a dynamic rheometer (Discovery Hybrid Rheometer HR-3; TA Instruments, New Castle, DE, USA) was used. To set the range of the linear viscoelastic range, frequency and stress sweep were done, and the setting for linearity was set as 10 rad/sec at 1 Pa stress. Dynamic testing was conducted using a plate–plate system (diameter: 4 cm, gap: 3,000 µm), which measured the storage modulus (*G'*) and loss modulus (*G''*) of the citric-acid-treated rice powder paste during heating from 35 to 95°C.

Preparation and texture analysis of *Baekseolgi* (Korean rice cake) *Baekseolgi* was prepared using methods described by Lee *et al.* (16) and Park (17). Briefly, acid-treated rice powder without any lumps

was mixed with water and sifted using a 20 mesh sieve. A mold (diameter: 6 cm height: 9 cm) was placed on a steam cooker (SSM-1100S; Shinil, Seoul, Korea) and then the rice powder was placed in the mold. The leveled rice powder was steamed for 20 min and allowed to sit for 15 min. The formed rice cake was allowed to sit for 10 min at room temperature and was stored for 24 h before use. After 24 h at room temperature, the *Baekseolgi* was evenly sliced into cylinders (diameter: 2 cm; height: 2 cm) and a texture profile analysis (TPA) was performed using a rheometer (CR-200D; Sun Scientific Co., Tokyo, Japan). Each experiment was repeated three times and measurements were taken with a fixed crosshead speed of 300 mm/min, chart speed of 300 mm/min, and strain of 0.55.

Statistical analysis All experiments were conducted three times for the purpose of measurement, and the statistical process of the experimental results was analyzed using SPSS 23.0 (SPSS Inc, Chicago, IL, USA) program, indicating the mean±standard deviation. Comparative analysis using the milling method was performed on an independent sample *t*-test. The other results from acid treatment were analyzed with ANOVA using SPSS 23.0 (SPSS Inc., Chicago, IL, USA), and the significance of the average values (*p*<0.05) was determined using Duncan's multiple range test.

Results and Discussion

Change in viscosity of rice flour because of milling method Wet- and dry-milled rice powders were analyzed through particle-size distribution at 10, 50, and 90%, respectively. The average particle size of dry-milled rice flour (17.76 µm) was larger than that of wet-milled rice flour (16.21 µm) (data were not shown).

Viscosity changes during heating for both dry- and wet-milled rice flours are shown in Table 1. Dry-milled and wet-milled rice flours showed significant differences for all results, including peak viscosity, trough and pasting temperature (*p*<0.05). The gelatinization characteristics analyzed using RVA showed that the pasting temperature of dry-milled rice flour was 78.1°C, whereas the pasting temperature of wet-milled rice flour was 72.2°C. Different gelatinization temperatures obtained depending on the particle size, are similar to those reported in a previous research, wherein the pasting temperature decreased as the size of the particle decreased (18), and the particle-size characteristics of glutinous rice flour also showed that the

Table 1. RVA pasting properties of dry- and wet-milled rice flours

Rice flour	Viscosity (RVU ¹⁾)					Peak time (min)	Pasting temperature (°C)
	Peak viscosity	Trough	Final viscosity	Break down	Setback		
Dry-milled	249.5±1.7 ²⁾ * ³⁾	170.7±8.7*	285.4±6.2*	78.8±6.9*	114.7±2.4*	6.2±0.1*	78.1±0.5*
Wet-milled	197.6±2.5	130.4±4.4	254.6±7.2	67.2±1.8	124.2±2.9	6.1±0.1	72.2±1.1

¹⁾RVU units (1 RVU=12 cP)

²⁾Mean of triplication±standard deviation.

³⁾*Significant difference indicate at *p*<0.05 by two-independent samples *t*-test.

Table 2. DSC thermal characteristics of dry- and wet-milled rice flours

Rice flour	T_o (°C) ¹⁾	T_p (°C)	T_c (°C)	ΔH
Dry-milled	59.6±0.3 ^{2)*3)}	66.3±0.6*	74.0±0.3*	9.5±0.8*
Wet-milled	56.9±0.1	65.1±0.3	72.5±0.2	7.3±0.3

¹⁾ T_o , opening temp.; T_p , peak temp.; T_c , closing temp.; ΔH , gelatinization enthalpy

²⁾Mean of triplication±standard deviations.

³⁾*Significant difference indicates at $p<0.05$ by two-independent samples t -test.

pasting temperature decreased as particle size decreased (19).

The peak viscosity of the dry-milled rice flour was 249.5 RVU, which was significantly higher than the 197.6 RVU of the wet-milled rice flour ($p<0.05$). Viscosity after 15 s at 95°C (trough) and final viscosity of the wet-milled rice flour (130.4 RVU and 254.6 RVU, respectively) were also much lower than those of the dry-milled rice flour (170.7 RVU and 285.4 RVU, respectively). The breakdown value represents the stability of the starch paste and the degree of rupture for swollen starch. For wet-milled rice flour, the breakdown value was 67.2 RVU, whereas that for dry-milled rice flour was 78.8 RVU. The setback value representing the degree of retrogradation for wet-milled rice flour was 124.2 RVU and that of dry-milled flour was

114.7 RVU. Previously, dry-milled black rice flour was shown to have a higher peak viscosity, trough, and final viscosity than those of wet-milled black rice flour (13). On the basis of the particle size and viscosity results, we conclude that differences in milling conditions may lead to changes in particle size, which ultimately influences the RVA results.

Thermostability of rice flour The thermostability results of the wet-milled and dry-milled rice flours using DSC are shown in Table 2. Wet-milled rice flour showed an opening temperature (T_o) of 56.95°C, a peak temperature (T_p) of 65.08°C, and a closing temperature (T_c) of 72.46°C. Dry-milled rice flour showed an opening temperature (T_o) of

Fig. 1. Pasting properties of wet-milled rice flour treated with citric acid (A) and acetic acid (B)

Table 3. RVA pasting properties of wet-milled rice flour treated with different citric and acetic acid concentrations

Rice flour		Viscosity (RVU)					Peak time (min)	Pasting temperature (°C)
		Peak viscosity	Trough	Final viscosity	Break down	Setback		
Control		400.0±7.2 ^{a1)}	246.7±5.1 ^c	358±6.6 ^e	153.3±3.5 ^a	111.3±1.5 ^e	6.4±0.0 ^e	76.9±0.3 ^c
Rice flour treated with citric acid	0.5%	376.7±2.5 ^d	175.7±4.2 ^d	246.3±4.7 ^d	201.0±5.6 ^c	70.7±0.6 ^d	6.1±0.0 ^c	71.4±0.5 ^b
	1.0%	366.7±4.7 ^c	160.7±9.0 ^c	227.3±8.4 ^c	206.0±4.6 ^c	66.7±1.2 ^c	6.1±0.1 ^{bc}	71.3±0.2 ^b
	1.5%	349.3±3.8 ^b	133.0±8.7 ^b	186.3±6.7 ^b	216.3±5.1 ^d	53.3±2.5 ^b	6.1±0.1 ^b	71.0±0.4 ^b
	2.0%	252.0±1.0 ^a	66.0±0.0 ^a	104.3±0.6 ^a	186.0±1.0 ^b	38.3±0.6 ^a	5.8±0.0 ^a	69.7±0.3 ^a
Rice flour treated with acetic acid	0.5%	403.0±4.6 ^b	252.0±1.0 ^c	361.0±3.6 ^b	151.0±4.4 ^a	109.0±4.0 ^a	6.5±0.1 ^b	71.3±0.2 ^b
	1.0%	408.3±1.2 ^c	225.0±3.2 ^a	333.3±4.7 ^a	182.7±2.1 ^b	107.7±1.5 ^a	6.3±0.0 ^a	73.4±0.4 ^c
	1.5%	397.0±2.7 ^a	239.0±6.0 ^b	344.0±7.2 ^a	157.7±6.3 ^a	104.7±5.9 ^a	6.3±0.1 ^a	70.4±0.4 ^a
	2.0%	428.7±0.6 ^d	230.0±5.7 ^a	334.7±9.6 ^a	198.3±5.1 ^c	104.3±4.9 ^a	6.3±0.0 ^a	71.3±0.3 ^b

¹⁾Means with each column followed by different superscripts are significantly different (Duncan's multiple range test, $p < 0.05$).

59.58°C, a peak temperature (T_p) of 66.26°C, and a closing temperature (T_c) of 74.02°C. All values of wet-milled rice flour were slightly less than those of dry-milled rice flour. DSC gelatinization enthalpy of wet-milled rice flour was 7.26 kJ/g and that of dry-milled rice flour was 9.49 kJ/g. The smaller particle size due to wet-milling showed lower gelatinization enthalpy than that due to dry-milling. This result supports previous research on brown rice flour based on the manufacturing condition, which determined that smaller particle size results in lower gelatinization enthalpy (20).

Change in RVA pasting properties with acid treatment Viscosity changes during the heating of rice flour treated with citric and acetic acids are shown in Fig. 1 and Table 3. Rice flour treated with 0.5% citric acid had a pasting temperature of 71.4°C, which was lower than that of the control (76.9°C). The peak viscosity of control rice flour was 400.0 RVU, which was higher than the 376.7 RVU of rice flour treated with 0.5% citric acid. As the concentration of citric acid increased, the peak viscosity decreased. A similar result was reported earlier, wherein as the concentration of citric acid increased, the viscosity decreased for a rice paste treated with citric acid (21). Moreover, the apparent viscosity of thermoplastic corn starch was lower with the citric acid treatment, which may result from the weakening of the structural integrity of the corn starch by citric acid (22). Compared with the citric-acid-treated rice flour, addition of acetic acid to the wet-milled rice flour did not influence the peak and pasting temperature (Fig. 1).

The viscosity after 15 s at 95°C (trough) and the final viscosity at 50°C cooling temperature showed that the viscosity decreased with increasing concentration of citric acid, similar to the peak viscosity. This was significantly different from the treatment with acetic acid, which did not show significant changes in those values with acetic acid treatment. The breakdown values represent the overall stability of the starch paste and the degree of rupture of the swollen starch; the control showed 153.3 RVU, 0.5% citric acid showed 201.0 RVU, 1.0% citric acid showed 206 RVU, 1.5% citric acid showed 216.3 RVU, and 2.0% citric acid showed 186.0 RVU (Table 3). Significant changes were seen among the rice flours treated with acetic acid. The setback

Fig. 2. Storage and loss moduli of wet-milled rice flour treated with citric acid (A) and acetic acid (B)

value represents the degree of retrogradation. Compared with the setback value of the control (111.3), the addition of citric acid with higher concentration lowered the setback value from 70.7 to 38.3 RVU. Acetic-acid-treated rice flour did not show concentration-dependent significant changes in RVA values, indicating that only the

Fig. 3. Dynamic storage modulus (A) and loss modulus (B) changes of wet-milled rice flour treated with citric acid

citric acid concentration had a significant impact on RVA values ($p < 0.05$).

Viscoelastic characteristics of citric acid treated wet-milled rice flour Differences in the storage modulus (G') and loss modulus (G'') of heated rice-flour paste at 1 Hz for different citric acid and acetic acid concentrations are shown in Fig. 2. The control showed 376.97 kPa G' value, but G' decreased to 58.14 kPa for 0.5% citric acid and continuously decreased as the concentration of acid increased. The G' of acetic-acid-treated rice flour showed, however, less change than that of citric acid. Thus, citric-acid-treated rice flour showed more significant change in G' than acetic-acid-treated rice flour, as reported like a RVA previous study.

The G'' of the control was 61.46 kPa and decreased to 23.14 kPa for 0.5% citric acid, but slightly decreased to 51.8 kPa for 0.5% acetic acid. The difference between the G' and G'' values showed a significant decrease when treated with citric acid. Previous research on the elasticity of corn starch after citric acid treatment showed that when starch particles were treated with citric acid, the starch particles were destroyed, thus decreasing elasticity (14).

Changes in the G' and G'' during heating for different concentrations of citric acid are shown in Fig. 3. The G' value after

Fig. 4. Hardness and cohesiveness of *Baekseolgi* (rice cake) made from wet-milled rice flour treated with citric acid

60°C decreased as the concentration of citric acid increased from 0.5 to 2%, and the loss modulus showed a similar trend. But acetic-acid-treated rice flour did not show significant concentration-dependent impact on G' and G'' (data not shown). These results are similar to those of the RVA values, which showed significant differences depending on the concentration of the citric acid. Therefore, citric-acid-treated rice flour can be used to improve the process suitability and may show similar results for the texture of the rice cake made from citric-acid-treated rice flour as follows.

Texture profile analysis (TPA) of *Baekseolgi* (rice cake) from citric acid treated rice flour

The hardness and cohesiveness results of TPA for *Baekseolgi* prepared from wet-milled rice flour treated with different concentrations of citric acid are shown in Fig. 4. The hardness value of *Baekseolgi* made from rice flour without citric acid was 35.03 N, which is similar to the 35.12 N of the 0.5% citric-acid-treated flour. The hardness values of *Baekseolgi* prepared with rice flour treated with 1.0, 1.5, and 2.0% citric acids were 26.79, 26.62, and 25.73 N, respectively, showing a rapid decreasing trend as the citric acid concentration increased. The cohesiveness value of *Baekseolgi* prepared with rice flour without acid treatment was 0.39,

which increased from 0.51 to 0.71 as the concentration of citric acid increased from 0.5 to 2%. As the concentration of citric acid resulted in significant differences in the texture of *Baekseolgi*, the citric acid concentration can be fine-tuned to be used as a pre-treatment to manufacture highly processible rice flour.

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