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Changes in Pasting and Fluid Properties of Corn and Rice Starches after Physical Modification by Planetary Mill

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Abstract Corn and rice starches were physically modified by planetary mill. While native starches showed high peak viscosities (1,001 and 563 cp), it decreased largely (42 and 20 cp for rice and corn starch, respectively) after 2 hr of physical modification. When two starches were co-ground, peak viscosities decreased more largely than single ground one only in 30 min, indicating the pasting properties could be easily changed by co-grinding. Especially, the higher the amount of corn starch, the viscosity decreased more largely, which means that paste stability could be controlled also by changing the ratio of corn and rice starch. Mean particle size increased with physical modification time since particles became spread because of shear force. There were also changes in surface morphology after physical modification. Fluid property, such as mean time to avalanche (MTA), was improved (from 6.16±0.47 and 8.37±1.23 sec to 5.47±0.78 and 5.26±1.37 sec for rice and corn starch, respectively) by physical modification. Pasting property, such as swelling power, was also improved by physical modification. These mean that native starches can be applied to both conventional powder and new paste-food industry more efficiently by physical modification.

Key words: starch, planetary mill, physical modification, swelling power, viscosity

Introduction

Starch is the most abundant storage reserve carbohydrate in plants. Therefore, it has been utilized for its various functionalities in thickening, stabilizing, texturizing, gelling, film forming, encapsulation, moisture retention, and shelf life extension (1-3).

However, native starches represent low water solubility, thus limiting their wide application and industrial use. Functional properties of starches available on the commercial market, normally obtained from corn or other cereals, are often submitted for physical modification (mainly gelatinization) or for slight and relatively simple chemical modifications to fulfill needs of food and other industries (1,2). Modified food starches generally show better properties, than native ones, such as paste clarity and stability, increased resistance to retrogradation, and freeze-thaw stability (1,4-7).

Grinding or comminution has been one of the most important unit operations in many fields such as chemical, pharmaceutical, and material industries (8,9). In recent years, much attention has been paid on fine grinding due to its importance for nanotechnology and nanomaterials. As a result, many different types of mills for producing a fine powder have been developed. A planetary ball mill, in which rotating pots are installed on the revolving disk, has the potential to generate a high energy to the powder, therefore, it is used for mechanochemistry (10,11), mechanical alloying (12,13), and the mechanical milling (14,15). In addition, there have been many reports for producing composite materials (16,17) and alloys (18,19).

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Physical modification can be divided into two types. The first one is the reaction between starch macromolecules not bringing out changes in shape, and the other one is destruction process by pressure, microparticulation, and extrusion, etc (20). In contrast to physical one, chemical modification cannot be directly used to food materials due to low stability (5-7).

Physical modification has several advantages of not only improving food texture by decrease in particle size and but also separating and concentrating specific components such as protein and dietary fiber by air classification. Therefore, it has been utilized broadly to food industry (21,22).

The objective of this research paper was to physically modify starch by shear force-induced planetary mill in order to prepare new functional starch materials.

Materials and Methods

Materials Rice starch (S-7260; Sigma-Aldrich, St. Louis, MO, USA) and corn starch (S-4126; Sigma-Aldrich) were purchased and used without further purification.

Shear force-induced physical modification of starch by planetary mill Planetary mill (Pulverisette 4; Fritsch GmbH Idar-Oberstein, Germany) was used in order to modify starch by shear force. The principle of planetary mill is same to that described by Mio *et al.* (9). Each mill consists of a pair of pots and grinding balls, in which the pots with 200 mL space were made of zirconia installed on a revolving disk, and the balls with a diameter of 10 mm was also made of the same material. The total weight of balls and samples were 30 and 10 g, respectively. The milling time was 30 to 120 min at 250 rpm, in which the resting time was 30 min every 30 min of milling time in order not to induce thermal change.

Scanning electron microscope (SEM) The microstructure of formulated powder was examined using a SEM (S-2380N; Hitachi, Ltd., Tokyo, Japan). Small amounts of powder (<0.1 g) were applied onto double-face tape (Toyo Ink Inc., Tokyo, Japan) attached to the top of a stub (12 mm dia). Excess sample particles were removed from the stub by a jet of air using an air blower (Hansa Inc., Tokyo, Japan) and coated for 60 sec with gold-palladium in an E-1010 ion sputter coater (Hitachi Ltd., Tokyo, Japan). The surface of the particle was observed at 15 kV, and a representative image on a screen was printed.

Starch viscosity determination A rapid visco-analyser (RVA, Model-3D; Newport Scientific Pty, Ltd., Narrabeen, Australia) was used to investigate the pasting characteristics of the starches. Viscosity profiles were recorded using starch suspensions (7%, w/w; 30 g total weight). A programmed heating and cooling cycle was used, where the samples were held at 50°C for up to 2 min, and then heated to 95°C over 8 min and held at 95°C 2 min, and finally cooled to 50°C over 8 min. Parameters recorded were pasting temperature, peak viscosity, trough viscosity (minimum viscosity at 95°C), final viscosity (viscosity at 50°C), breakdown viscosity (peak-trough viscosity), and setback viscosity (final-trough viscosity).

Mean particle size analysis Particles were analyzed for their size distribution using a laser diffraction particle size analyzer (CILAS 1064; Compagnie Industrielle Des Lasers, Orleans, France). Particle size was expressed as the equivalent volume diameter and triplicate measurements were made for each batch. All samples were analyzed in triplicates.

Mean time to avalanche (MTA) MTA was determined using a commercial powder avalanche tester (Aero-Flow™ Automated Powder Flowability Analyzer, Model 3250; Shoreview, MN, USA), which was determined from the measured frequency distribution of avalanches. All samples were analyzed in triplicates. Powders that demonstrated a high MTA were considered to be more cohesive and non-flowable (Fig. 1).

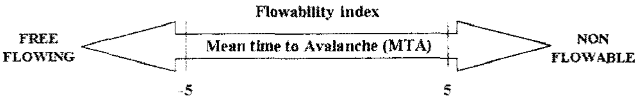

Fig. 1. Analytical index of flowability.

Swelling power Swelling power was determined by modifying the method of Tsai *et al.* (23). Starch was weighed into a centrifuge tube with coated screw cap to which 10 mL distilled water was added. The tube was heated at 50, 60, 70, and 80°C in a shaking water bath for 1 hr. The tube was cooled to room temperature in an iced water bath and centrifuged (8,000×g) for 20 min. All samples were analyzed in triplicates.

Results and Discussion

Physical modification of starch by planetary mill In order to prepare physically modified starch by shear force, planetary mill was used, and changes in viscosity, mean particle size, and surface morphology were investigated.

The RVA parameters of corn and rice starch are shown in Table 1.

Both starches without physical modification showed gradual increase in viscosity with increase in temperature. The increase in viscosity with temperature may be attributed to the removal of water from the exuded amylose by the granules as they swell (24,25). The peak viscosity of corn starch (1,001 cp) was much higher than that of rice starch (563 cp). Differences in peak viscosity suggest that they would behave differently during cooking and processing. However, for physically modified starches, as milling time increased, the peak viscosity decreased and there were few viscosities after 2 hr, in both starches (Table 1).

During the holding period of the viscosity test, the slurries are subjected to high temperature and mechanical shear stress which further disrupt starch granules in the grains, resulting in amylose leaching out and alignment. This period is commonly associated with a breakdown viscosity (26). The ability of starches to withstand heating

Table 1. Effect of planetary milling on the pasting characteristics of starches[1)]

Treatment	Sample	Ratio	Time (min)	PV (cp)	TV (cp)	FV (cp)	BV (cp)	SV (cp)	P_{Time} (min)	P_{Temp} (°C)
Planetary milling[2)]	Rice starch		0	563.00	487.00	991.00	76.00	504.00	7.00	63.35
			30	319.00	113.00	426.00	206.00	313.00	6.80	63.50
			60	76.00	4.00	82.00	72.00	78.00	6.47	58.65
			120	42.00	36.00	60.00	6.00	24.00	6.87	69.45
	Corn starch		0	1,001.00	656.00	1,083.00	345.00	427.00	6.80	58.80
			30	479.00	214.00	369.00	265.00	155.00	6.53	67.00
			60	85.00	21.00	97.00	64.00	76.00	6.47	59.30
			120	20.00	4.00	7.00	16.00	0.00	3.07	58.10
	Rice starch : Corn starch	2:1	30	44.00	10.00	46.00	34.00	36.00	7.07	61.00
		1:1		6.00	-[3)]	8.00	-	-	7.00	61.50
		1:2		-	-	-	-	-	-	-

[1)]PV, Peak viscosity; TV, trough viscosity; FV, final viscosity; BV, breakdown viscosity; SV, setback viscosity; P_{Time}, peak time; P_{Temp}, peak temperature.
[2)]Milling speed was 250 rpm.
[3)]Means almost zero.

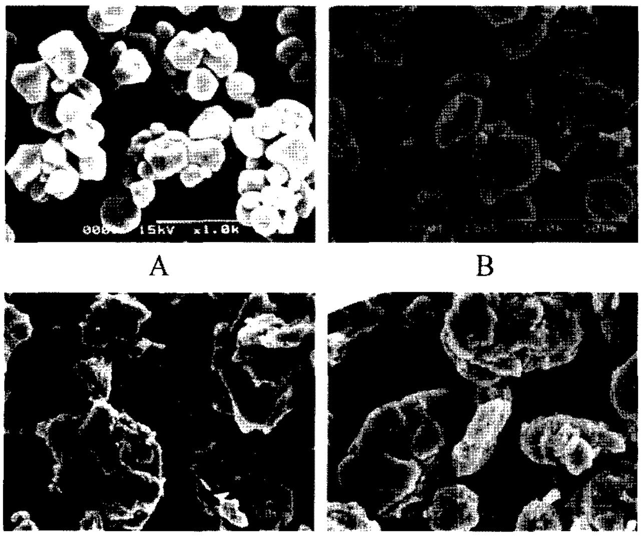

Fig. 2. Morphological changes of corn starch with planetary milling time. (A) Control; (B) 30 min; (C) 1 hr; (D) 2 hr. The milling speed was 250 rpm.

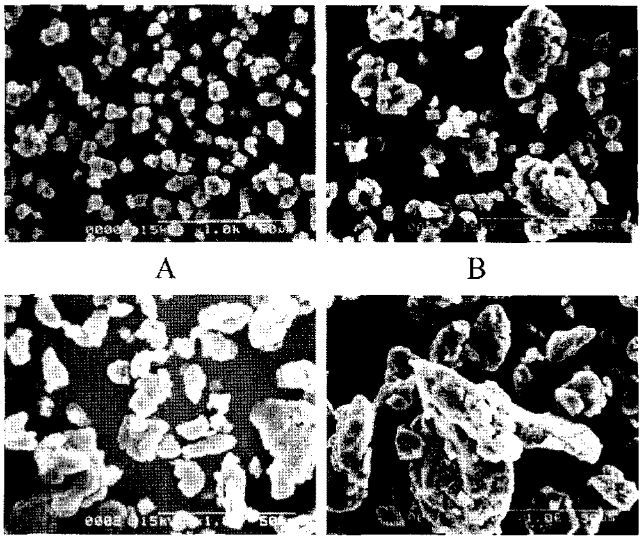

Fig. 3. Morphological changes of rice starch with planetary milling time. (A) Control; (B) 30 min; (C) 1 hr; (D) 2 hr. The milling speed was 250 rpm.

at high temperature and shear stress is an important factor in many processes (26). Breakdown viscosity of rice starch (76 cp) was much lower than that of corn starch (345 cp), indicating that rice starch has higher paste stability than corn starch.

Since differences in the properties of individual starches after physical modification can affect the properties of co-grinding, rice and corn starches were co-ground. When two starches were co-ground, peak viscosities decreased more largely than single ground one only in 30 min (below 44 cp), indicating the pasting properties could be easily changed by co-grinding. Especially, the higher the amount of corn starch, the viscosity decreased more largely and when the ratio was 2:1, no viscosities were observed, which means that paste stability could be controlled also by changing the ratio of rice and corn starch.

Table 2 shows the changes in mean particle size of rice and corn starch after planetary milling. Mean sizes of native corn and rice starch were 12.43±2.47 and 6.39±2.45 μm, respectively. However, the mean sizes of both starches increased to 24.85±3.01 and 14.33±2.11 μm, respectively, after 120 min of planetary milling. Generally, while the driving force of ball mill is shock force, in case of planetary mill, not only shock force but also shear force are induced. Therefore, particles were spread by balls because of shear force and became disk shaped ones, indicating the reason of increase in mean size after physical modification by planetary mill (Fig. 2 and 3). Same phenomenon was also shown when rice and corn starch were co-ground (Table 2).

Setback viscosities of corn starch at all milling time were lower than those of rice starch (Table 1). In general, during cooling, re-association between starch molecules, especially amylose, will result in the formation of a gel structure and, therefore, viscosity will increase to a final viscosity. This phase is commonly described as the setback region and is related to retrogradation and reordering of starch molecules. The setback viscosities of rice and corn starch were 504 and 427 cp, respectively (Table 1). The low setback viscosity values of corn starch indicate the low rate of starch retrogradation and syneresis (26). It means that corn starch is more stable to retrogradation than rice starch.

Table 2. Changes in mean particle size of starches after planetary milling

Treatment	Sample	Ratio	Time (min)	Mean particle size (μm)
Planetary milling[1)]	Corn starch		0[2)]	12.43±2.47
			30	13.94±4.32
			60	20.73±3.10
			120	24.85±3.01
	Rice starch		0[2)]	6.39±2.45
			30	10.96±1.90
			60	11.53±2.56
			120	14.33±2.11
	Corn starch : Rice starch	1:2	30	16.14±2.55
		1:1		16.69±1.89
		2:1		19.08±1.99

[1)]Milling speed was 250 rpm.
[2)]Native starch.

Fluid properties of starches In order to investigate the fluid properties of physically modified starch, MTA value was measured (Fig. 4).

MTA values of native rice and corn starch decreased as the milling time increased to 120 min (from 8.37±1.23 and 6.16±0.47 sec to 5.26±1.37 and 5.47±0.78 sec, respectively), indicating improvement in fluid property by physical modification (Fig. 4).

Generally, grinding techniques have been used to physically modify the surface of large materials with small functional materials and to change physical properties of

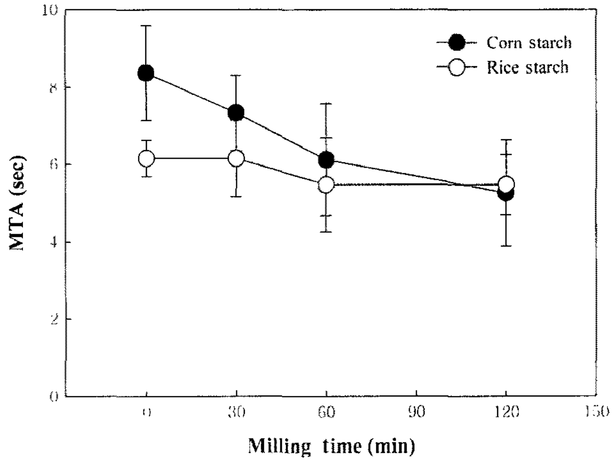

Fig. 4. Changes in mean time to avalanche (MTA) of corn and rice starch with planetary milling time. Milling speed was 250 rpm; mean±SD, n=3.

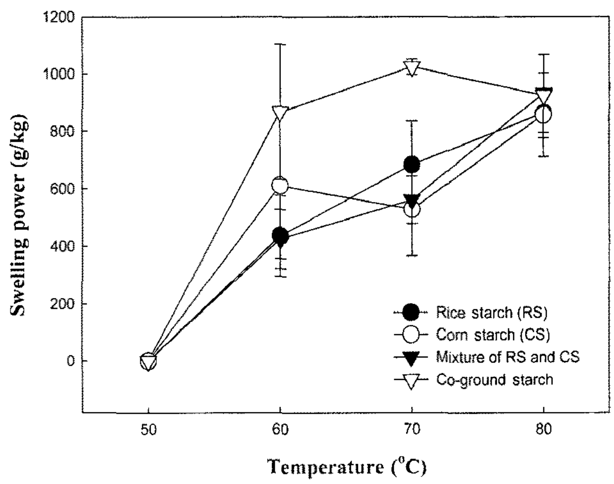

Fig. 5. Changes in swelling power of rice and corn starch after co-grinding. Rice starch:corn starch=1:2; mean±SD, n=3.

these materials (27-29). Especially, co-grinding has been extensively utilized not only to induce regular dispersion but also to improve hygroscopicity and stability of microparticles in pharmaceutical industry (28-30).

These results show that starch can be applied to much broader area by changing the fluid properties, and that rheological property of native starch can be improved by physical modification without changing the components in it.

Paste properties of starches In order to investigate the paste properties of physically modified starch, swelling powers were measured (Fig. 5).

The swelling powers of native and physically modified starch were measured at 10 intervals from 50 to 80°C and increased with temperature.

The swelling powers of rice and corn starch at 60°C, gelatinization starting temperature, were 436 and 611 g/kg, respectively, and co-ground one showed higher values than those of native ones (Fig. 5).

Swelling power indicates the ability of starch to hydrate under specific cooking conditions. Generally, differences in swelling power may be attributed to the differences in

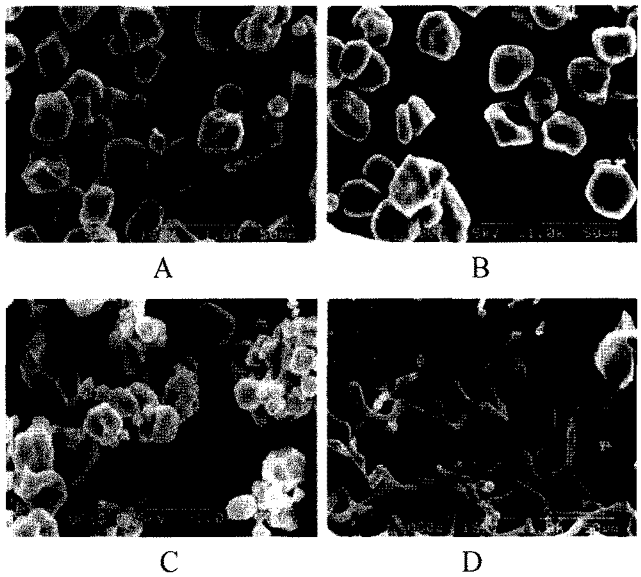

Fig. 6. Morphological changes of starches after 30 min of swelling at 60°C. (A) Rice starch (RS); (B) corn starch (CS); (C) mixture of RS and CS; (D) co-ground RS and CS (250 rpm, 30 min). (rice starch:corn starch=1:2).

amylose content, viscosity patterns, and internal organization (30,31). Amylopectin contributes to swelling of starch granules and pasting, while amylose and lipids inhibit the swelling (32).

Figure 6 shows the surface morphology of rice and corn starch after planetary milling. Although there were few changes in surface morphology for native starch and mixture of rice and corn starch, co-ground starch showed rod-like structure (Fig. 6D), which might be the reason of higher swelling power.

Therefore, physically modified starches could be applied into materials for pasting and cooling food by considering these structural change and swelling phenomenon.

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