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Research Article
Different Milling Methods: Physicochemical, Pasting and Textural Properties of Rice Flours

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Abstract
Background and Objective: Milling methods had a marked effect on the properties of flour. This study was conducted to investigate the chemical composition and physicochemical properties of rice flour to utilize the suitable rice for product development with desired characteristics. **Materials and Methods:** The effect of three milling methods (wet milling, semi-dry milling and dry milling) was investigated on the physicochemical, pasting and textural properties of rice flour using five varieties with varied amylose content. **Results:** Dry-milled flour had the highest protein, fat, damaged starch, particle size, water absorption index and water solubility index, compared to wet-milled and semi-dry-milled flours. Moreover, these determined parameters of wet-milled flour were rather similar to semi-dry-milled flour. Partial gelatinization occurred during the dry-milled method. The ΔH_{gel} and temperature of gelatinization of wet-milled flour were similar to those of semi-dry-milled samples. There was no effect of milling method on the retrogradation. The physicochemical and textural properties of flour also depended on the amylose content and although this had no clear effect on gelatinization, retrogradation tended to increase with increased amylose content. Stickiness and adhesiveness tended to decrease as the amylose content increased. **Conclusion:** Suitable rice milling depends on the desired food characteristics. Rice cookies should be made from dry milling rice flour because of the high amounts of damaged starch and large particles, resulting in fracturability and porosity in texture. Wet-milled-rice flour is useful for making desserts and foods which require stickiness, smooth texture and oily mouthfeel. Semi-dried rice flour may be attractive ingredients for non-gluten free products.

Key words: Rice flour, milling, physicochemical properties, textural properties, pasting properties

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Rice grains are consumed as staple food in many Asian countries and rice flour is used as a main ingredient in many products for various uses. Consumers prefer rice and rice flour because it is a source of carbohydrate and is highly nutritious and contains non-allergic protein and high amounts of unsaturated fatty acid (>70%) as well as bio-active compounds such as Gamma-oryzanol, vitamin E and phytosterols[1]. Food producers prefer rice and rice flour due to low price, large volume of production and its acceptance by customers. The chemical composition and physicochemical properties of rice and rice flour must be studied to utilize the suitable rice for product development with desired characteristics. The information provided by the current study may encourage rice utilization as an alternative ingredient in various products. The milling method is one of the factors affecting the chemical composition and physicochemical properties of rice flour[2]. There are three milling methods: (1) Dry milling involves cleaning the rice grains using air blowing and then grinding to obtain a powder. This flour has rather low quality because of the coarseness of the powder, the high level of contaminants (dust, husk, stone), its short storage time and high rancidity as well as large amounts being lost to insect damage. The advantages of dry milling are less waste and the low level of loss during the actual milling (2) Wet milling is widely used for rice production especially in Thailand and Asian countries to produce a high quality, fine powder with fewer contaminants. The large volume of wastewater is a disadvantage of wet milling. (3) Semi-dry milling developed from wet and dry milling[3]. The rice grain moisture content is adjusted to about 25% before milling and then the moist flour is dried in a hot-air oven. Milling methods had a marked effect on the properties of flour[2-4]. Both milling method and rice varieties with varying amylose content were studied in this research. The objectives of the current study were to investigate the effect of milling methods and rice varieties with varying amylose content on the chemical composition and the physicochemical, pasting and textural properties of rice flour.

MATERIALS AND METHODS

Materials: The five rice varieties with different amylose content were: RD6 (sticky rice), Pathum Thani 1 (PT1), RD43, Khao Tah Haeng 17 (KTH17), and RD41. All rice varieties were cultivated in 2017.

Rice flour milling

Dry milling: Dry-milled flours were prepared using a pin mill (Alpine 160Z, Augsburg, Germany) and then sealed in polypropylene bags.

Semi-dry milling: Rice grains were soaked in water at room temperature, then drained and the moisture content of the rice grain was adjusted to about 30% (wet basis) by adding water before grinding[3] using a Supper powder mill (SPM-R200, Nishimura Powder Engineering Co., Ltd., Japan) and dried it in a hot-air oven at 40°C for 4 h. Dried flour samples were kept in sealed polypropylene bags.

Wet milling: Rice grains were soaked in water at room temperature for 3 h. Then, the soaked grains were milled using a stone miller with a rice grain-to-water ratio of 1:2[5]. The rice slurry was centrifuged to obtain rice cake. The cake was dried in a hot-air oven overnight at 40°C. The dried rice flour was ground using an Ultra-centrifugal mill (ZM1, Retsch, Germany). Flour samples were kept in sealed polypropylene bags.

The rice flour samples were stored at 4°C before further analysis. Flour was sieved through a 100-mesh sifter for composition analysis and determinations of physicochemical properties, except for the particle size, texture and pasting measurements which were based on unsieved flour.

Proximate analysis of rice flours: The moisture, protein and fat contents of rice flours were determined following the methods of AACC[6].

Amylose content: An amylose/amylopectin assay kit (MegaZyme Pty Ltd., North Rocks, Australia) was used to determine the amylose content.

Physicochemical properties of rice flours

Damaged starch: Damaged starch was determined using a starch damage assay kit (MegaZyme Pty Ltd., North Rocks, Australia).

Water absorption index and water solubility index: The water absorption index (WAI) and water solubility index (WSI) were determined using the modified method of Kadan *et al.*[7]. The WAI indicates the volume occupied by the starch granules after swelling in excess water. A rice flour sample (5 g) was placed in a test tube and suspended in distilled water (30 mL) at room temperature with gentle stirring every 5 min for 30 min, followed by centrifugation at 2,200 rpm for 15 min. The supernatant liquid was poured carefully into a tared Petri dish. The residual gel was weighed and the WAI was calculated using Eq. 1:

$$\text{WAI} = \frac{\text{Weight of sediment}}{\text{Weight of flour}} \quad (1)$$

The WSI determines the amount of polysaccharide released from the starch granules on the addition of excess water. The tared Petri dish containing supernatant liquid from the water absorption index test was dried at 105°C overnight. The dry solids in the supernatant were weighed and the WSI was calculated using Eq. 2:

$$\text{WSI}(\%) = \frac{\text{Weight of dissolved component in supernatant}}{\text{Weight of flour}} \times 100 \quad (2)$$

Color attributes: The color parameters, L*, a* and b*, were measured using a colorimeter (Datacolor international) based on the color system of CIE LAB, where L* = 0 (black) and L* = 100 (white), -a* = greenness and +a* = redness, -b* = blueness and +b = yellowness. White and black calibration tiles were used for calibration.

Average particle size: The particle size of rice flour was expressed as the average particle diameter, being determined using a laser diffraction particle size analyzer (Mastersizer 2000, Malvern Instruments, UK.). The particle size distribution of rice flour was indicated by the relative span factor (RSF), which was calculated using Eq. 3:

$$\text{RSF} = \left(\frac{d[90] - d[10]}{d[50]}\right) \quad (3)$$

where d[10], d[50], and d[90] are the particle size values corresponding to the cumulative distributions at 10%, 50%, and 90%, respectively.

Degree of crystallinity: The crystallinity of the rice flour samples was analyzed using wide angle X-ray diffraction (WAXD). Analysis data were obtained by scanning from 5-35° at a rate of 2.4° min^{-1}. The degree of crystallinity was calculated from the fraction of peak areas at 15°, 17°, 18° and 23° [8].

Microstructure: Scanning electron microscopy: A scanning electron microscope (SEM) (SU3500, Hitachi, Japan) was used to determine the microstructure of the rice flour samples at 10,000× magnification with an accelerating voltage of 5 kV.

Gelatinization and retrogradation: The gelatinization transition enthalpy (ΔH_{gel} expressed as J g^{-1}) and melting temperature of gelatinization (To_{gel}, Tp_{gel} and Tc_{gel}) were determined using differential scanning calorimetry (DSC) (Diamond DSC, Perkin-Elmer, USA). Rice flour samples (2-2.5 mg) were weighed into the DSC pan, then distilled water was added [ratio of flour-to-water of 30:70 (dry basis)]. The DSC pan containing the sample was sealed and heated from 25-100°C at 10°C min^{-1} for gelatinization analysis. Then, the DSC pan containing the gelatinized sample was stored at 4-5°C for 14 days for retrogradation determination. Each sample pan was heated from 25-100°C at 10°C min^{-1}. The retrogradation transition enthalpy (ΔH_{retro} expressed as J g^{-1}) and melting temperature of retrogradation (To_{retro}, Tp_{retro} and Tc_{retro}) were determined. An empty pan was used as the reference[9].

Pasting properties of rice flours: The pasting characterization of rice flour samples (conc. 9.5%), pasting temperature, peak viscosity, final viscosity, breakdown and setback, were determined using a Rapid Visco Analyzer (RVA 4, Newport, Australia)

Textural analysis: For textural measurement the modified method of Charoenrein *et al.*[10] was used. Rice flour slurry 30% (w/w) dry basis was heated in a water bath at 55°C for 15 min. The viscous rice paste was poured into a mold and the mold was placed in boiling water until complete gelatinization had occurred. Then the mold was cooled at room temperature. The resultant rice gel was cut into a cylindrical shape with a diameter of 1.5 cm and a height of 1.5 cm. Textural characteristics were determined using a texture analyzer (TA-XT Plus, UK) with texture profile analysis (TPA). An aluminum cylindrical probe with a diameter of 35 mm was used. The measurement was set with a deformation of 50% and a probe speed of 20 mm min^{-1}. The hardness, stickiness and adhesiveness were analyzed.

Statistical analysis: Data were subjected to one-way analysis of variance (ANOVA) followed by Duncan multiple range test at the 95% confidence level ($p<0.05$) using the SPSS statistical software (IBM, USA).

RESULTS AND DISCUSSION

Influence of milling method on composition of rice flours with various varieties: The moisture contents of all the five varieties (ground using dry, semi-dry and wet milling) of rice flour was in the range of 9-13%, as shown in Table 1. The moisture content of flour should be lower than 13% to inhibit microbial growth. The amylose content of the five rice varieties could be categorized into five groups: (1) Glutinous rice (0-3% amylose), (2) Very low amylose (4-11%), (3) Low amylose (12-20%), (4) Intermediate amylose (21-27%) and (5) High amylose (27-36%). The amylose contents of five rice varieties are expressed in Table 1. RD6 (a glutinous rice)

Table 1: Composition of rice flours with difference of milling methods and varieties

	Amylose (% dry basis)			Moisture (% dry basis)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	3.78±0.41^{dA}	3.43±0.07^{eA}	3.68±0.63^{dA}	10.58±0.12^{abB}	10.45±0.14^{aB}	12.87±0.69^{aA}
PT1	15.96±0.39^{cA}	13.62±0.41^{dB}	14.46±0.01^{cB}	9.95±0.53^{bB}	10.20±0.50^{aB}	11.21±0.28^{bA}
RD43	16.62±0.64^{cA}	16.30±0.04^{cA}	15.25±0.41^{cA}	10.51±0.31^{abA}	10.61±0.40^{aA}	9.90±0.62^{cA}
KTH17	21.23±0.06^{bB}	22.73±0.04^{bA}	19.81±0.01^{bC}	10.56±0.34^{abA}	9.28±0.61^{bB}	8.02±0.67^{dC}
RD41	30.44±0.18^{aA}	29.21±0.11^{aC}	29.89±0.07^{aB}	10.66±0.26^{aA}	9.81±0.46^{abB}	8.67±0.08^{dC}
	Fat (% dry basis)			Protein (% dry basis)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	1.31±0.14^{bA}	0.54±0.07^{aB}	0.44±0.18^{bcB}	8.31±0.44^{bA}	8.59±0.06^{bA}	7.40±0.53^{cA}
PT1	1.46±0.09^{abA}	0.50±0.02^{aB}	0.37±0.02^{cB}	8.65±0.21^{bA}	8.60±0.70^{bA}	8.47±0.15^{bA}
RD43	1.51±0.08^{abA}	0.62±0.15^{aB}	0.77±0.03^{aB}	7.86±0.02^{bA}	7.50±0.11^{cB}	7.70±0.00^{cAB}
KTH17	1.37±0.06^{bA}	0.31±0.09^{bB}	0.41±0.02^{cB}	11.36±0.48^{aA}	10.86±0.05^{aA}	10.46±0.05^{aA}
RD41	1.70±0.02^{aA}	0.69±0.01^{aB}	0.61±0.03^{abC}	11.48±0.21^{aA}	11.33±0.00^{aA}	11.10±0.22^{aA}

*Different small letters (a,b,c) within a same column indicate significantly different at the 95% confidence level. Different capital letters (A,B,C) within a same row indicate significantly different at the 95% confidence level. Means±standard deviation were shown

Table 2: Damaged starch, crystallinity (%), water absorption index (WAI) and water solubility index (WSI) of rice flours with difference of milling methods and varieties

	Damaged starch (%)			Crystallinity (%)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	8.32±0.11^{abA}	4.97±0.12^{aB}	2.73±0.04^{dC}	27.27±1.10^{aB}	35.93±2.44^{aA}	43.16±3.85^{aA}
PT1	7.75±0.85^{abA}	4.06±0.56^{aB}	2.34±0.01^{dB}	23.90±1.23^{abB}	35.21±1.26^{aAB}	42.99±6.30^{aA}
RD43	8.39±0.20^{aA}	2.76±0.47^{bB}	3.34±0.17^{cB}	23.86±1.18^{abB}	37.95±1.63^{aA}	36.40±1.48^{aA}
KTH17	7.29±0.17^{bA}	2.84±0.47^{bC}	4.94±0.33^{bB}	23.27±1.15^{bB}	38.95±4.37^{aA}	39.34±1.87^{aA}
RD41	8.20±0.11^{abA}	2.70±0.01^{bC}	5.78±0.33^{aB}	24.74±1.81^{abB}	39.59±0.87^{aA}	38.38±2.87^{aA}
	Water absorption index (WAI)			Water solubility index (WSI)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	11.52±0.03^{bAB}	11.37±0.20^{aB}	11.79±0.03^{abA}	1.69±0.03^{dA}	1.40±0.04^{bB}	1.72±0.03^{aA}
PT1	12.10±0.06^{aA}	11.27±0.02^{aB}	11.29±0.03^{cB}	4.00±0.35^{aA}	1.76±0.10^{aB}	1.68±0.03^{aB}
RD43	12.37±0.07^{aA}	11.45±0.20^{aB}	11.55±0.11^{bcB}	3.22±0.08^{bcA}	0.85±0.06^{dB}	1.13±0.16^{cB}
KTH17	11.58±0.33^{bA}	11.32±0.14^{aA}	11.31±0.18^{cA}	3.64±0.20^{abA}	1.16±0.06^{cB}	1.42±0.11^{bB}
RD41	12.26±0.11^{aA}	11.41±0.10^{aC}	11.93±0.07^{aB}	3.07±0.00^{cA}	0.84±0.05^{dC}	1.22±0.05^{bcB}

*Different small letters (a,b,c) within a same column indicate significantly different at the 95% confidence level. Different capital letters (A,B,C) within a same row indicate significantly different at the 95% confidence level. Means±standard deviation were shown

contained 3% amylose. PT1 and RD43 were in the low amylose category with amylose contents of 14 and 16%, respectively. KTH17 was categorized as intermedia amylose with amylose contents of 21% and RD41 was in the high amylose group with amylose contents of 30%.

The amylose content of dry-milled flour for KTH17 and RD41 was significantly higher than the semi-milled and wet-milled samples ($p<0.05$). This may be attributed to the fact that dry milling may destroy starch granules and starch molecules resulting in shorter chain molecules due to mechanical force and heat generation during grinding, which increased the amylose content and the amount of highly damaged starch. This result concurred with the results of starch damage (Table 2). The amount of damaged starch in dry-milled flour was significantly higher than semi-dry and wet-milled flour ($p<0.05$). However, there was no significant effect of milling method on the amylose content of RD6 and RD43 ($p\geq 0.05$).

The protein contents of all rice flour samples were in the range of 7-11% (dry basis), as shown in Table 1. Wet-milled and semi-dry-milled flour tended to have lower protein contents than dry-milled flour. This result was in agreement with Asmeda *et al.*[11], who found that some protein and/or contaminated rice bran was removed during washing and soaking in semi-dry and wet milling. KTH17 and RD41 contained the highest protein contents for all milling methods and there was no significant difference between KTH17 and RD41 ($p\geq 0.05$). RD43 contained the lowest protein contents for all milling methods. The fat and ash contents of rice flour with various varieties and using different milling methods were in the ranges of 0.3-1.7% (dry basis) and 0.4-1.4% (dry basis) (data not shown), respectively. The fat and ash contents of wet-milled and semi-dry-milled samples were significantly lower than dry-milled flour ($p<0.05$) perhaps because the dry-milled flour may have been contaminated by rice bran. KTH17 had the lowest fat content and the highest ash content in all milling methods.

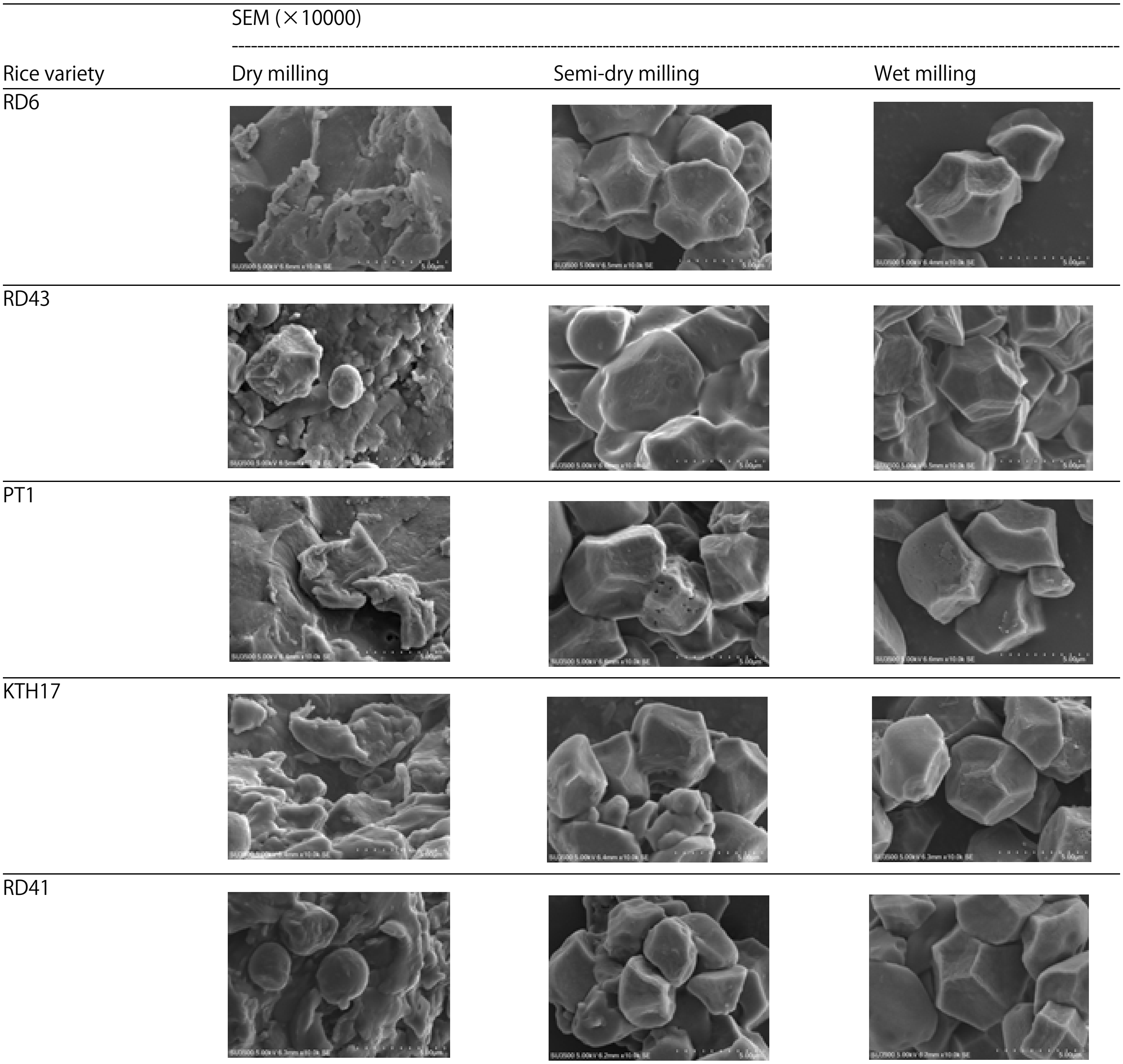

Fig. 1: Scanning electron microscope micrographs of rice flours with different milling methods and varieties (10,000x magnification)

Influence of milling method on physical properties of rice flours of various varieties: The dry-milled flour of all rice varieties, except KTH17, had significantly higher WAI and WSI values than semi-dry-milled and wet-milled samples ($p<0.05$), as shown in Table 2. These results were in accordance with Asmeda *et al.*[11] who stated that the dry milling severely destroying starch granules and thus, water gained easy access into these starch granules and was greatly absorbed, while amylose and amylopectin molecules may have been easily leached out from the damaged areas and dispersed into the aqueous solution, resulting in high WSI values. In addition, the high value of WSI in dry-milled flour might be due to partial gelatinization which occurred after dry milling, leading to increase free molecules of amylose and amylopectin. Partial gelatinization was confirmed by SEM (Fig. 1) and the lower enthalpy of gelatinization (Table 6). The differences in the WAI

Table 3: Whiteness index, L*, a* and b* value of rice flours with difference of milling methods and varieties

	Whiteness index			L*		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	91.18±0.01^{aC}	93.47±0.06^{aB}	94.92±0.16^{aA}	92.72±0.01^{aC}	94.60±0.08^{aB}	95.54±0.12^{aA}
PT1	89.25±0.13^{cC}	92.75±0.06^{cB}	93.37±0.25^{cA}	91.11±0.20^{cB}	93.90±0.04^{dA}	94.41±0.22^{cA}
RD43	89.71±0.14^{bC}	93.24±0.09^{bB}	94.11±0.05^{bA}	91.54±0.18^{bC}	94.13±0.08^{cB}	94.76±0.02^{bcA}
KTH17	88.51±0.02^{dC}	93.33±0.05^{abB}	94.07±0.22^{bA}	90.70±0.00^{dC}	94.29±0.04^{bcB}	94.73±0.19^{bcA}
RD41	89.19±0.02^{cC}	93.40±0.04^{abB}	94.34±0.04^{bA}	91.40±0.02^{bcC}	94.44±0.06^{abB}	94.92±0.01^{bA}

	a*			b*		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	-0.15±0.00^{cB}	-0.24±0.00^{cC}	-0.06±0.02^{bA}	4.97±0.00^{eA}	3.66±0.00^{bB}	2.42±0.11^{bC}
PT1	0.08±0.03^{bA}	-0.16±0.03^{bC}	-0.07±0.01^{bB}	6.05±0.06^{cA}	3.91±0.06^{aB}	3.56±0.11^{aC}
RD43	0.05±0.02^{bA}	-0.21±0.00^{cB}	0.03±0.01^{aA}	5.86±0.01^{dA}	3.35±0.04^{dB}	2.68±0.08^{bC}
KTH17	0.24±0.05^{aA}	-0.09±0.01^{aB}	0.01±0.03^{abB}	6.75±0.04^{aA}	3.43±0.04^{dB}	2.70±0.11^{bC}
RD41	0.08±0.01^{bA}	-0.16±0.01^{bC}	-0.04±0.05^{abB}	6.55±0.00^{bA}	3.55±0.01^{cB}	2.50±0.12^{bC}

* Different small letters (a,b,c,..) within a same column indicate significantly different at the 95% confidence level. Different capital letters (A,B,C,..) within a same row indicate significantly different at the 95% confidence level. Means±standard deviation were show

Table 4: Average particle size and relative span factor (RSF) of rice flours with difference of milling methods and varieties

	Average particle size (μm)			Relative span factor (RSF)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	112.06±0.56^{eA}	53.72±0.37^{aB}	49.09±2.97^{bC}	1.92±0.02^{aB}	1.73±0.00^{cB}	9.21±0.29^{aA}
PT1	118.37±1.19^{dA}	50.41±0.12^{cC}	80.45±1.25^{aB}	1.77±0.01^{aB}	1.87±0.00^{bB}	4.48±0.19^{eA}
RD43	133.55±2.54^{bA}	51.35±0.69^{bB}	52.27±3.03^{bB}	1.81±0.05^{aB}	1.87±0.03^{bB}	7.66±0.49^{cA}
KTH17	130.63±1.85^{cA}	47.24±0.21^{dB}	35.86±3.86^{cC}	1.53±0.45^{aB}	2.14±0.03^{aB}	8.58±0.42^{bA}
RD41	150.33±0.98^{aA}	46.17±0.32^{eB}	37.02±1.67^{cC}	1.58±0.01^{aC}	1.76±0.02^{cB}	5.59±0.14^{dA}

*Different small letters (a,b,c,..) within a same column indicate significantly different at the 95% confidence level. Different capital letters (A,B,C,..) within a same row indicate significantly different at the 95% confidence level. Means±standard deviation were show

values among milling methods for all rice varieties were minimal and PT1 has the highest WSI values in all milling methods.

The degree of crystallinity (%) of dry-milled flour samples was less than that of the wet-milled and semi-dry-milled flour samples for all rice varieties (Table 2). This result might be attributed to the partial gelatinization and/or defragmentation of starch crystalline regions, resulting from the heat and mechanical energy generated during dry milling. The less crystallinity of dry-milled flour was also confirmed by the lower enthalpy of gelatinization (Table 6). The crystallinity of the semi-dry-milled flour and the wet-milled flour samples was similar.

Table 3 shows the L*, a*, b* and whiteness index for all samples. The wet-milled samples had high values of L* and the whiteness index. On the other hand, the lowest values for L* and the whiteness index were observed in the dry-milled samples because enzymatic browning was catalyzed by heat during dry milling. The dry-milled powders were light brown in color due to the highest and positive b* value, compared to the semi-dry and wet-milled flour samples ($p<0.05$). The wet-milled and semi-dry-milled flour samples had better appearance than those of the dry-milled flour due to the former having greater whiteness. The RD6 flour had the highest whiteness, while KTH17 had the lowest for all milling methods.

The average particle size of rice flour for the various varieties and milling methods is shown in Table 4. Particles of dry-milled flour were clearly the largest. The wet-milled flour particle size was a little smaller than that of the semi-dry-milled samples. The particle size of flour markedly affected the textural characteristics and appearance of products. Murakami *et al*.[12] reported that the particle size of rice flour clearly influenced the texture of rice bread. A particle size of 75-106 μm was more efficient at trapping air pockets in the dough; hence the resultant rice bread was spongier, softer and had a greater volume than the rice bread made from particles of 106-150 μm, 45-75 μm and less than 45 μm. The particle size distribution was related to the relative span factor (RSF), as shown in Table 4. The high RSF value of wet-milled flour meant that the wet-milled samples contained wide variation in the particle size, as shown by the size distribution curve (Fig. 2). The RSF of semi-dry-milled flour was quite similar to that of dry-milled samples.

Fig. 1 illustrates the morphology of the flour made from different rice varieties produced using different milling

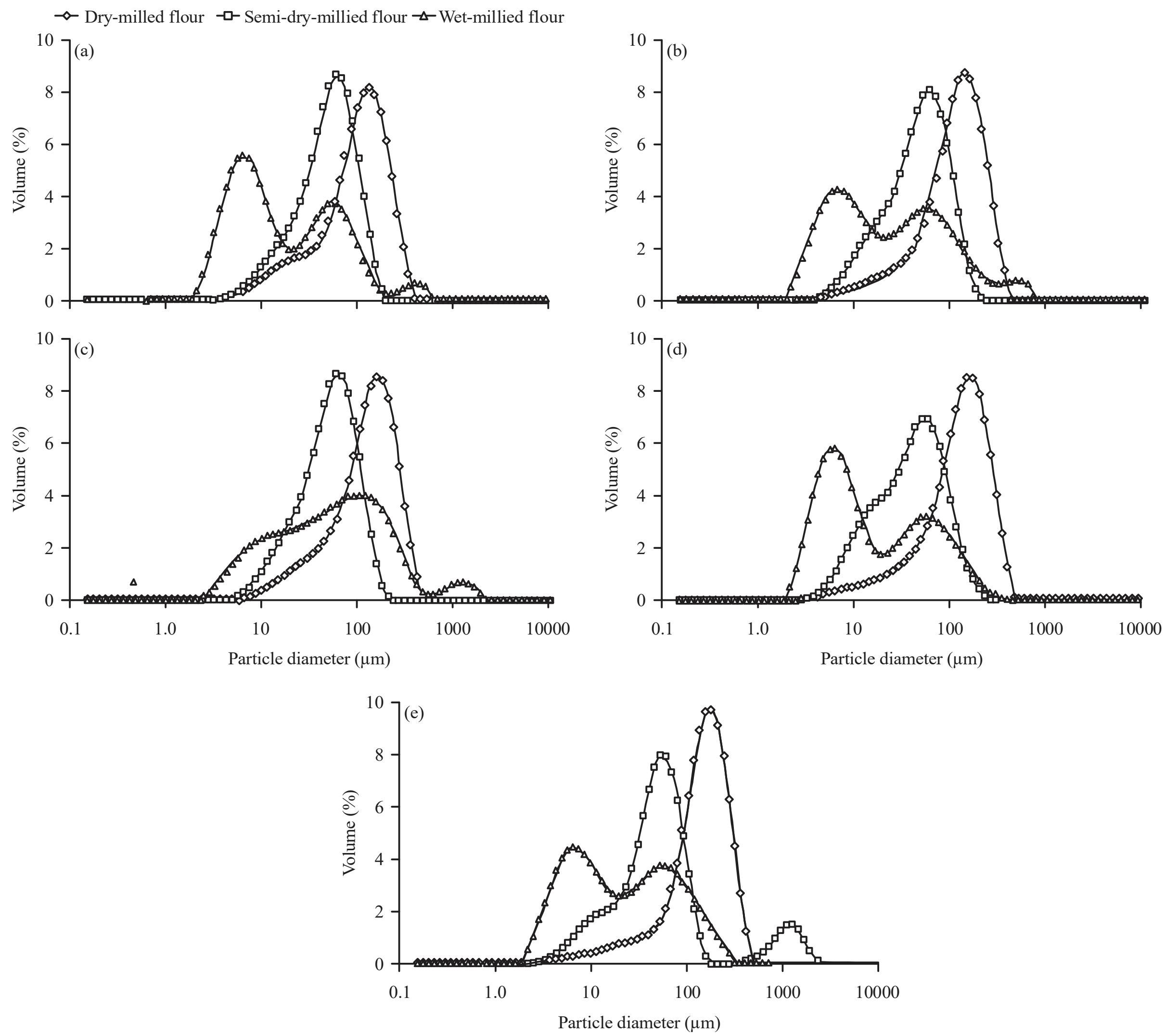

Fig. 2(a-e): Size distribution curve of rice flours with different milling methods and varieties (a), RD6 (b), PT1, (c) RD43, (d) KTH17 and (e) RD41

methods, based on observation using SEM. The rice starch granules of wet-milled flour had a polygonal shape and the edges of granules could be seen clearly. Granules were agglomerated loosely, with some granules being dispersed individually. Semi-dry-milled granules seemed to be more tightly agglomerated than wet-milled samples and had some of the edge detail. Dry milling using the pin mill machine resulted into larger particles and tightly packed granules. The granules on the surface of the large particles had lost their edge and polygonal shape completely. The outer particles were covered with a gelatinized film caused by milling heat generation and the inner part contained the original granules. The mechanical force and heat of dry milling could also enhance the destruction of fragments of particles.

Influence of milling method on pasting properties of rice flours with various varieties: The pasting properties and profiles of rice flours made from different varieties using different milling methods were determined using a Rapid Visco Analyzer (RVA) and the results are shown in Table 5 and Fig. 3, respectively. The pasting temperatures of all samples were in range of 63-71°C and there was no significant effect of milling method on pasting temperature ($p\geq 0.05$), except for the KTH17 variety, where dry-milled KTH17 had a significantly higher pasting temperature than wet-milled and semi-dry-milled KTH17 ($p<0.05$). The differences in pasting temperature were minimal, compared to the influence of rice variety for the same milling method. Semi-dry-milled flour tended to have the highest values of peak viscosity, whereas the lowest values were observed in wet-milled samples. The trend of peak

Table 5: Pasting properties of rice flours with difference of milling methods and varieties

	Peak viscosity (RVU)			Trough (RVU)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	227.75±4.24^{dB}	251.31±4.23^{dA}	200.53±2.03^{dC}	96.21±2.65^{bA}	89.67±0.88^{eB}	80.89±0.99^{dC}
PT1	312.97±2.43^{bA}	296.44±6.39^{bB}	221.61±5.39^{cC}	182.19±3.78^{aB}	199.36±4.46^{cA}	142.61±3.63^{cC}
RD43	354.67±0.23^{aB}	379.50±9.47^{aA}	268.55±1.59^{aC}	188.59±9.07^{aB}	240.00±1.92^{aA}	168.04±1.71^{aC}
KTH17	256.92±2.47^{cB}	285.71±2.65^{cA}	245.17±3.30^{bC}	185.83±19.80^{aB}	225.75±12.02^{bA}	167.58±0.71^{aC}
RD41	95.38±1.12^{eB}	168.00±4.47^{eA}	178.92±6.84^{eA}	93.50±1.41^{bB}	152.47±2.14^{dA}	149.46±6.19^{bA}
	Breakdown (RVU)			Final viscosity (RVU)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	131.55±1.59^{bB}	161.64±3.64^{aA}	119.64±2.44^{aC}	117.75±2.36^{eA}	111.00±0.66^{dB}	97.33±0.66^{eC}
PT1	130.78±3.61^{bA}	97.08±3.03^{cB}	79.00±1.86^{cC}	290.47±3.18^{cA}	295.11±3.78^{bA}	215.81±4.36^{cB}
RD43	166.09±9.31^{aA}	139.50±11.29^{bB}	100.50±0.11^{bC}	344.75±11.31^{bB}	370.45±7.17^{aA}	266.71±0.76^{bC}
KTH17	71.08±17.32^{dA}	59.96±9.37^{dA}	77.59±4.01^{cA}	362.13±16.44^{aA}	358.88±5.24^{aA}	290.38±1.59^{aB}
RD41	1.88±0.29^{cC}	15.53±2.56^{eB}	29.46±0.65^{dA}	149.13±3.95^{dB}	202.75±17.54^{cA}	198.34±4.12^{dA}
	Setback from trough (RVU)			Pasting temperature (°C)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	21.54±0.30^{eA}	21.33±0.55^{dA}	16.44±0.78^{eB}	65.30±0.49^{bA}	63.28±0.68^{aA}	65.67±0.78^{aA}
PT1	108.28±0.71^{cA}	95.75±1.75^{bB}	73.19±0.76^{cC}	65.42±2.33^{bA}	65.75±1.39^{aA}	66.98±1.16^{aA}
RD43	156.17±2.24^{bA}	130.45±6.08^{aB}	98.67±0.94^{bC}	64.38±2.47^{bA}	64.57±0.54^{aA}	66.22±1.07^{aA}
KTH17	176.30±3.36^{aA}	133.13±6.78^{aB}	122.80±2.30^{aC}	74.78±0.60^{aA}	64.50±0.57^{aB}	63.33±1.40^{aB}
RD41	55.63±5.37^{dA}	50.28±15.94^{cA}	48.88±2.06^{dA}	65.42±2.40^{bA}	65.42±1.22^{aA}	66.83±0.49^{aA}

*Different small letters (a,b,c,) within a same column indicate significantly different at the 95% confidence level. Different capital letters (A,B,C,..) within a same row indicate significantly different at the 95% confidence level. Means±standard deviation were shown

Table 6: Thermal properties of gelatinized rice flours with difference of milling methods and varieties

	ΔH_{gel} (J g^{-1} of flour)			To_{gel} (°C)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	3.25±0.39^{aB}	3.52±0.04^{aB}	4.37±0.04^{aA}	60.44±0.30^{dA}	58.10±0.01^{dB}	60.77±0.14^{eA}
PT1	2.85±0.02^{aB}	3.39±0.04^{aA}	3.34±0.07^{bA}	62.03±0.58^{cB}	60.35±0.20^{cC}	63.33±0.09^{cA}
RD43	2.79±0.28^{aA}	3.37±0.22^{aA}	3.42±0.13^{bA}	65.29±0.20^{bA}	64.19±0.12^{bB}	65.38±0.07^{bA}
KTH17	2.88±0.09^{aC}	3.72±0.13^{aA}	3.56±0.06^{bB}	71.12±0.16^{aA}	69.55±0.16^{aB}	70.07±0.37^{aB}
RD41	2.06±0.08^{bB}	2.86±0.17^{bA}	2.34±0.17^{cB}	58.29±1.17^{eB}	56.30±0.41^{eB}	62.27±0.09^{dA}
	Tp_{gel} (°C)			Tc_{gel} (°C)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	69.85±0.36^{cA}	68.27±0.25^{cB}	68.35±0.35^{cB}	78.41±0.59^{bA}	77.72±0.16^{bA}	79.04±0.60^{bA}
PT1	69.26±0.36^{cA}	67.49±0.01^{dB}	68.74±0.11^{cA}	76.02±0.57^{cA}	74.98±0.01^{cA}	75.54±0.11^{dA}
RD43	71.96±0.33^{bA}	70.00±0.25^{bC}	71.07±0.11^{bB}	78.39±0.69^{bA}	77.14±0.30^{bA}	77.69±0.28^{cA}
KTH17	77.22±0.02^{aA}	75.42±0.13^{aB}	75.32±0.24^{aB}	83.33±0.06^{aA}	81.81±0.48^{aB}	81.65±0.20^{aB}
RD41	67.29±0.01^{dA}	64.86±0.36^{eC}	66.34±0.12^{dB}	74.47±0.01^{dA}	72.91±0.05^{dB}	72.15±0.02^{eC}

*Different small letters (a,b,c) within a same column indicate significantly different at the 95% confidence level. Different capital letters (A,B,C) within a same row indicate significantly different at the 95% confidence level. Means±standard deviation were shown

viscosity from the highest to lowest value was RD43, PT1, KTH17, RD6 and RD41, respectively. The breakdown and set back value of dry-milled flour tended to be lowest, compared to wet-milled and semi-dry-milled flour, except for RD41. This may be due to the fact that the dry-milled flour had a higher amylose content (Table 1), which increased retrogradation. In addition, the dry-milled flour contained the highest levels of damaged starch (Table 2); hence, amylose molecules could easily leak out from damaged areas and then interact, resulting in increased setback. Damaged starch may be easily broken and destroyed under a high shear rate and high temperature conditions, resulting in decreased break down of the dry-milled flour.

Influence of milling method on gelatinization and retrogradation of rice flours with various varieties: The enthalpy (ΔH_{gel}) and temperature (To_{gel}, Tp_{gel}, Tc_{gel}) of gelatinization of rice flour samples is shown in Table 6. ΔH_{gel} indicates the quantity and strength of the crystalline structure of starch[13] and also relates to the number of helical chains of

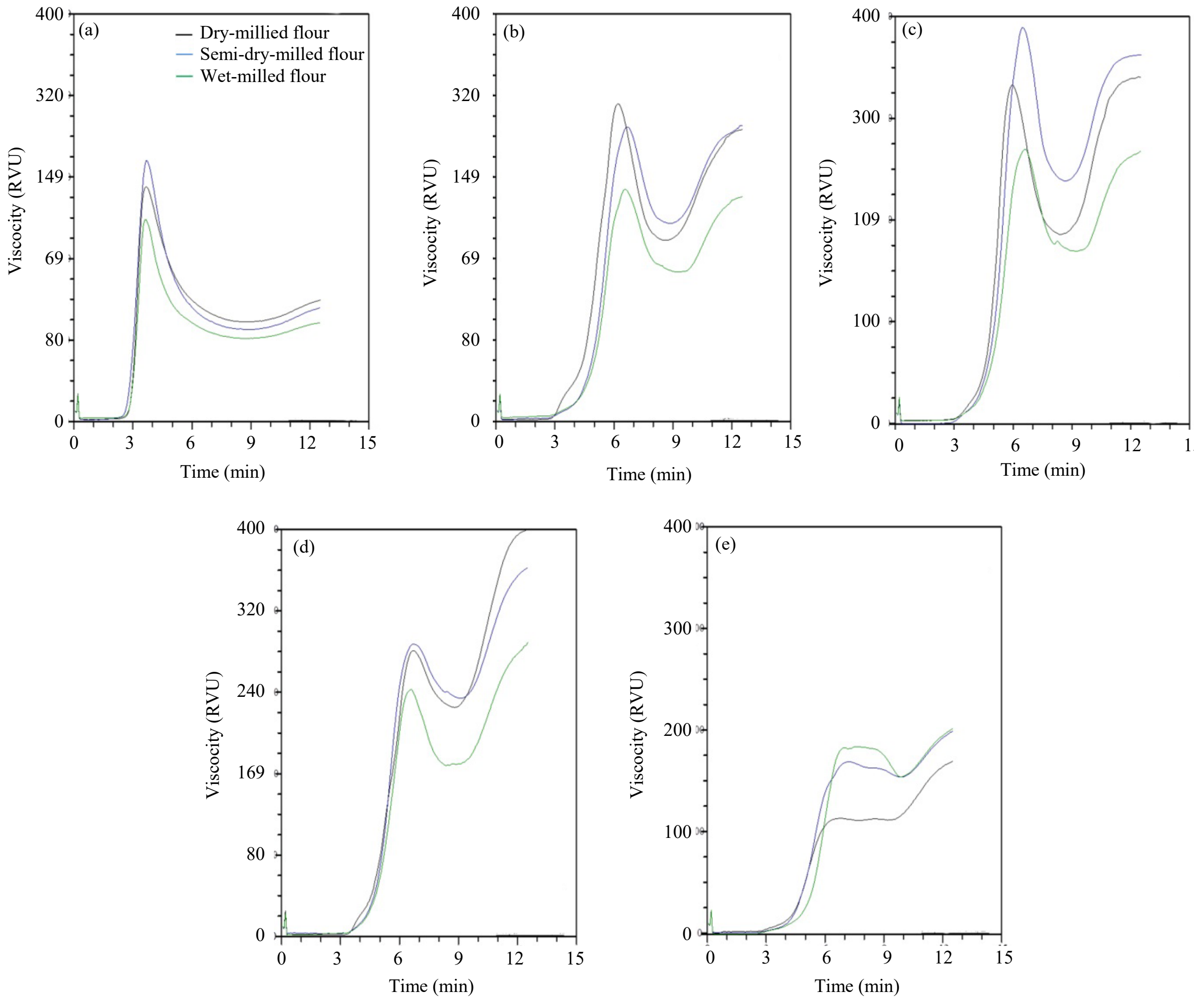

Fig. 3(a-e): RVA pasting profiles of rice flours with different milling methods and varieties (a) RD6, (b) PT1, (c) RD43, (d) KTH17 and (e) RD41

amylopectin and hydrogen bonds[14]. ΔH_{gel} is the total energy required to destroy hydrogen bonding and may include some Van der Waals force in the crystalline structure of starch[15]. The ΔH_{gel} of dry-milled flour was lower than wet-milled and semi-dry-milled flour because of some crystalline structure disruption by the heat and shear force generated during the dry milling process. This result was in agreement with Naivikul and Tungtrakul[3] and Suksomboon and Naivikul[5]. Endothermic thermograms of the gelatinization of the flour from the different rice varieties and milling methods were analyzed using DSC, as shown in Fig. 4. The values of ΔH_{gel} and To_{gel} for RD41 were the lowest, compared to the other rice varieties with the same milling method, which indicated that RD41 was the most easily gelatinized.

To_{gel} (the initial gelatinization temperature) for flour samples from the different rice varieties and milling methods was in the range of 56-71°C and was the lowest for semi-dry-milled flour. Water migration and diffusion into the starch granules was affected by the size of the starch granule. The large starch granules (dry-milled flour) would be slower than small granules; thus, To_{gel} was shifted to a higher temperature. Although the average granule size of wet-milled flour was smaller than semi-dry-milled flour, the particle size distribution of semi-dry-milled flour was narrower than the wet-milled samples (Fig.1). This meant that wet-milled flour contained both much smaller and bigger starch granules than semi-dry-milled flour. The highest To_{gel} was found in KTH17 for all milling methods due to its strong crystalline structure. The gelatinization temperature range was 58-83°C for all samples.

After storing gelatinized gel samples at refrigerated temperature for 14 days, there were no significant differences in retrogradation with the different milling methods ($p \geq 0.05$)

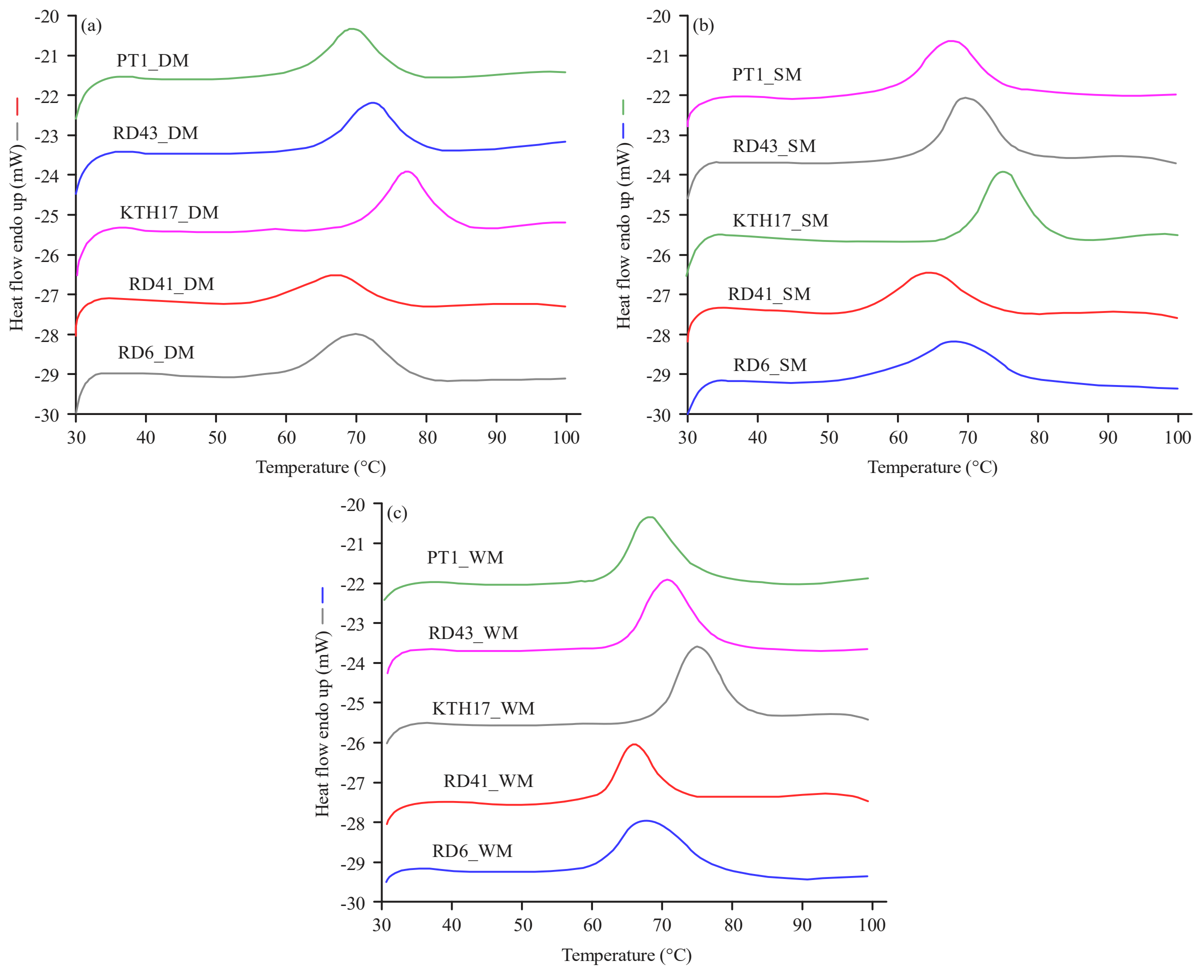

Fig. 4(a-c): DSC endothermic thermogram of gelatinization of rice flours with different milling methods and varieties; (a) Dry-milled flour, (b) Semi-dry-milled flour and (c) Wet-milled flour

in RD6 (glutinous rice), PT1 and RD43 (low amylose content). Moreover, the dry-milled flour of KTH17 (intermediate amylose) and RD41 (high amylose) had less retrogradation compared to wet-milled and semi-dry-milled flour samples. The enthalpy of retrogradation (ΔH_{retro}) of all samples was in the range of 0.1-1.1 $J g^{-1}$ of flour, as shown in Table 7. Ranking of retrogradation in the different rice varieties from high to low was KTH17, RD41, PT17, RD43 and RD6, respectively. Retrogradation of KTH17 was close to that of RD43. Retrogradation tended to increase as the amylose content increased. This result concurred with Chang and Lui[16], who studied glutinous and normal rice starch with high and low amylose contents and the current results also agreed with Vandeputte *et al.*[17], who researched rice starch with varying amylose content. Although KHT17 had a lower amylose content than RD41, retrogradation of KHT17 was higher than for RD41. This may be attributed to the fact that amylopectin molecules of KTH17 may be long chained and have less branched chains, which effectively enhanced retrogradation[10,18] and RD41 may have also formed more amylose-lipid complexes (LAMs) than KTH17 because KTH17 contained the lowest lipid content (Table 1). LAMs could inhibit retrogradation since they interrupted the interaction of retrograded amylopection[19]. There was no clear effect of milling method on To_{retro}. RD41 had the highest To_{retro}, while To_{retro} values for KTH17 and RD6 were the lowest when the same milling method was used. The DSC endothermic thermograms of retrogradation of the rice flour samples of the different rice varieties using the different milling methods are illustrated in Fig. 5. The melting temperatures of retrograded crystals for all samples were in the range of 41-64°C (Table 7). This range of melting temperature indicated retrograded amylopectin, which melts at about 45-60°C[20,21]. Almost all

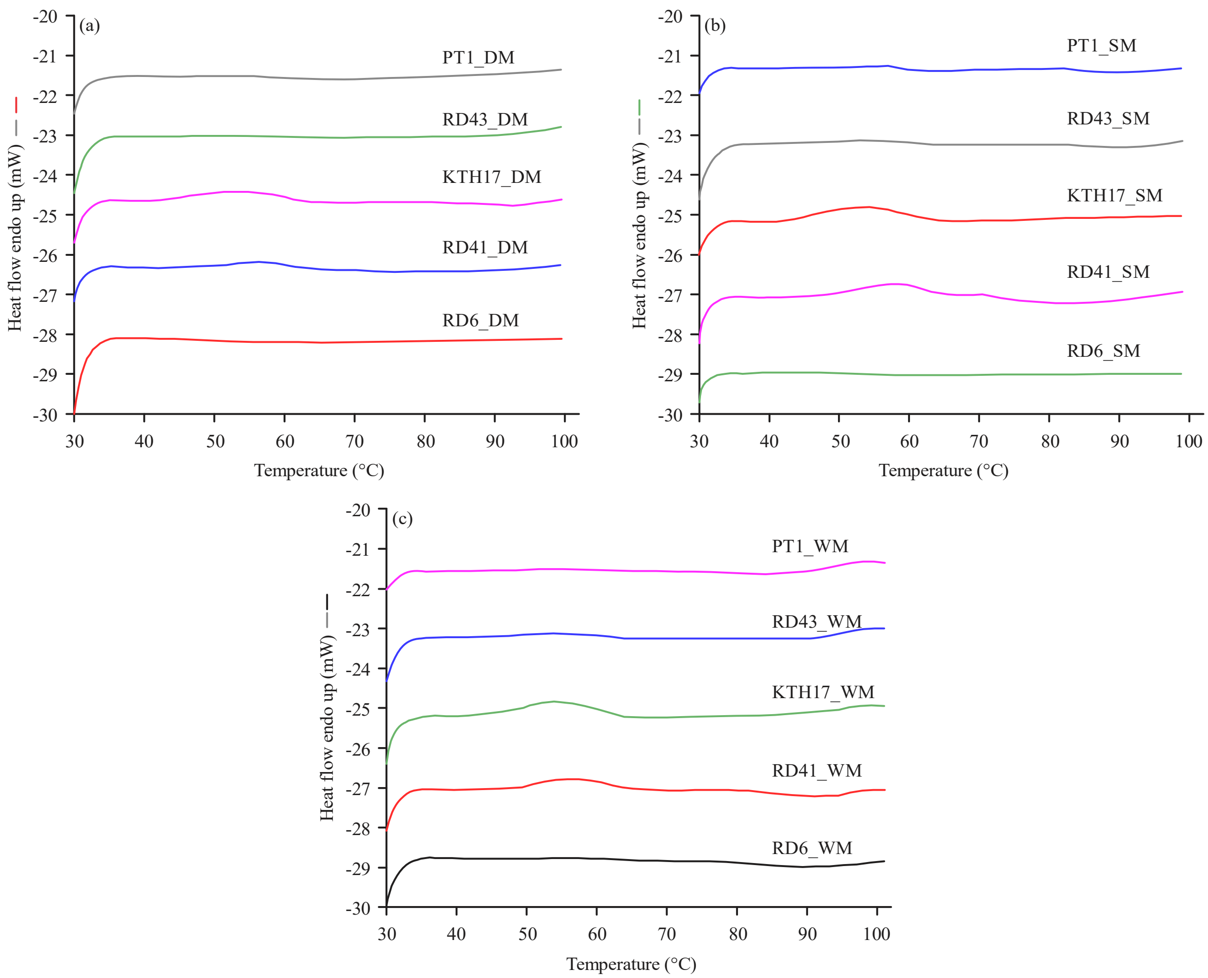

Fig. 5(a-c): DSC endothermic thermogram of retrogradation of rice flour with different milling methods and varieties; (a) Dry-milled flour, (b) Semi-dry-milled flour and (c) Wet-milled flour

Table 7: Thermal properties of retrograded rice flours with difference of milling methods and varieties

	ΔH_{retro} (J g^{-1} of flour)			To_{retro} (°C)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	0.03 ± 0.00^{dA}	0.02 ± 0.01^{eA}	0.01 ± 0.01^{dA}	42.38 ± 1.12^{aA}	41.50 ± 1.51^{cA}	42.16 ± 0.41^{dA}
PT1	0.15 ± 0.00^{cA}	0.16 ± 0.04^{dA}	0.14 ± 0.01^{cA}	43.05 ± 0.52^{aB}	45.36 ± 1.02^{bAB}	46.48 ± 0.88^{bA}
RD43	0.19 ± 0.01^{cA}	0.29 ± 0.08^{cA}	0.17 ± 0.03^{cA}	44.38 ± 1.46^{aA}	44.67 ± 1.12^{bA}	46.99 ± 0.76^{abA}
KTH17	0.69 ± 0.02^{aB}	1.07 ± 0.04^{aA}	1.07 ± 0.02^{aA}	42.78 ± 0.31^{aB}	43.41 ± 0.09^{bcB}	44.45 ± 0.34^{cA}
RD41	0.50 ± 0.08^{bB}	0.73 ± 0.00^{bA}	0.66 ± 0.05^{bAB}	46.35 ± 3.57^{aA}	48.07 ± 0.64^{aA}	48.26 ± 0.57^{aA}
	Tp_{retro} (°C)			Tc_{retro} (°C)		
Rice variety	Dry milling	Semi-dry milling	Wet milling	Dry milling	Semi-dry milling	Wet milling
RD6	44.90 ± 2.12^{bA}	45.15 ± 0.59^{cA}	44.80 ± 0.11^{dA}	49.71 ± 1.55^{cA}	48.20 ± 0.39^{dA}	46.69 ± 0.88^{cA}
PT1	52.67 ± 0.59^{aB}	55.17 ± 0.35^{bA}	55.92 ± 0.01^{bcA}	59.58 ± 0.88^{bA}	59.42 ± 0.18^{cA}	59.72 ± 0.48^{bA}
RD43	53.38 ± 0.58^{aB}	54.03 ± 0.59^{bB}	56.11 ± 0.23^{bA}	59.99 ± 0.63^{bA}	60.33 ± 0.82^{cA}	60.28 ± 0.18^{bA}
KTH17	54.30 ± 0.95^{aA}	54.11 ± 0.71^{bA}	55.52 ± 0.35^{cA}	62.09 ± 0.37^{abA}	62.39 ± 0.07^{Bb}	63.42 ± 0.20^{aA}
RD41	55.20 ± 3.36^{aA}	57.07 ± 0.95^{aA}	56.74 ± 0.23^{aA}	62.78 ± 1.21^{aA}	63.76 ± 0.40^{aA}	63.78 ± 0.49^{aA}

*Different small letters (a,b,c) within a same column indicate significantly different at the 95% confidence level. Different capital letters (A,B,C) within a same row indicate significantly different at the 95% confidence level. Means±standard deviation were shown

retrograded amylopectin crystals were formed by helical intramolecular bonding of the amylopectin molecule and intermolecular interaction among close amylopectin molecules. The melting temperature of retrograded crystals shifted much lower than those for gelatinization (Table 6) due to the weak crystalline structure.

Table 8: Textural characteristics of rice flour gels with difference of milling methods and varieties

	Hardness (g force)			Stickiness (g force)		
Rice variety	Dry milling	Simi-dry milling	Wet milling	Dry milling	Simi-dry milling	Wet milling
RD6	5181.42±567.82^{bcB}	19655.50±8888.03^{abA}	14600.37±1265.76^{bA}	3923.47±328.54^{cB}	7889.81±1166.85^{abA}	7843.33±444.34^{bA}
PT1	6293.04±775.48^{abC}	17577.78±2326.94^{bA}	14344.23±1877.70^{bB}	5785.49±329.88^{aB}	8455.36±182.06^{aA}	8364.45±582.53^{bA}
RD43	3953.88±1420.95^{cC}	19521.12±2987.97^{abB}	30712.54±8139.35^{aA}	4308.14±697.82^{cC}	8014.35±353.75^{abB}	9372.99±1006.55^{aA}
KTH17	5666.77±962.17^{abC}	24445.99±4628.56^{abA}	16369.58±2666.55^{bB}	5011.11±443.01^{bB}	8225.24±2250.74^{abA}	6875.42±471.55^{cA}
RD41	6781.12±1098.39^{aC}	26327.01±3038.11^{aA}	18701.40±1900.96^{bB}	4429.79±47.70^{bcB}	6689.03±529.10^{bA}	6180.34±316.24^{cA}

	Adhesiveness (g s^{-1})		
Rice Variety	Dry milling	Simi-dry milling	Wet milling
RD6	280.63±65.89^{aB}	770.06±150.57^{aA}	702.25±143.96^{aA}
PT1	191.71±23.58^{bB}	223.51±38.72^{bB}	281.37±52.00^{bA}
RD43	167.97±37.29^{bcB}	180.66±13.72^{bAB}	209.26±10.16^{bcA}
KH17	138.12±15.86^{cB}	124.86±20.19^{bcA}	118.65±14.97^{cdB}
RD41	83.74±10.99^{dB}	114.54±12.68^{cA}	94.29±10.40^{dB}

*Different small letters (a,b,c) within a same column indicate significantly different at the 95% confidence level. Different capital letters (A,B,C) within a same row indicate significantly different at the 95% confidence level. Means±standard deviation were shown

Influence of milling method on textural properties of rice flour gel from various varieties: Table 8 shows the textural characteristics of rice gel samples from the different rice varieties and milling methods. Wet-milled and semi-dry-milled rice gels were significantly harder and more adhesive than dry-milled gel for all rice varieties ($p<0.05$). This result may be due to the fact that the dry-milled flour contained many large particles. These large particles may have interrupted the gel network formation by amylose and amylopectin; thus, the set gel was soft and weak. There was no significant difference between the stickiness of the wet-milled and semi-dry-milled flour ($p<0.05$). However, the dry-milled rice gel had the lowest stickiness for all rice varieties since it contained fewer free amylose and amylopectin molecules and this was confirmed by the high setback value (Table 5). The RD41 gel had the lowest stickiness and adhesiveness for all milling methods. Stickiness and adhesiveness tended to decrease as the amylose content increased. Rice flour containing higher levels of amylose may have induced higher retrogradation, thus reducing free amylose molecules and consequently having decreased stickiness. However, the rice gel of PT1 had the highest stickiness for dry and semi-dry milling methods. PT1 may be composed of long chains of amylopectin which enhanced stickiness and may also contain amylose short chains, which interrupted retrogradation.

CONCLUSION

Milling methods (dry, semi-dry and wet milling) and rice varieties (different amylose content, molecular starch structure and composition) influenced the chemical composition, appearance, particle size, physicochemical properties and textural properties of rice flours. Suitable rice milling depends on the desired food characteristics; for example, rice cookies should be made from dry milling rice flour because of the high amounts of damaged starch and large particles, resulting in fracturability and porosity in texture. Moreover, wet-milled-rice flour is useful for making traditional Thai desserts and foods which require stickiness, smooth texture and oily mouth feel. Semi-dried rice flour may be attractive ingredients for non-gluten free products.

SIGNIFICANCE STATEMENT

This study discovered the influence of milling methods on physicochemical properties and textural properties of rice flours that can be beneficial for selection and utilization the proper rice four, providing desired food characteristics.

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