RESULTS AND DISCUSSION

1. Chemical Properties and Morphological Properties of Rice Flour and Rice Starch

1.1 Chemical analysis of dry- and wet-milled rice flour and rice starch

Chemical compositions of dry- and wet-milled rice flour and rice starch from three rice varieties (Pathum Thani 1, RD 7 and Leuang 11) are shown in Table 3. Rice flour samples contained 11.85-13.41% moisture, 5.49-7.69% protein, 0.38-1.05% fat and 0.26-0.72 % ash, whereas rice starch contained 10.59-11.50% moisture, 0.55-1.64% protein, 0.09-0.14% fat and 0.16-0.34% ash. Theoretically, high purity rice starch should contain a low amount of protein, lipid and ash contaminations, In general, lipids and ash exist in rice at much lower amounts. Therefore, isolation of rice starch is generally less than 0.5%. Compared to maize and wheat starch, isolation of rice starch from proteinaceous material is very difficult. However, the purification of rice starch is involving to the reagents and methods used (Lumdubwong and Seib, 2000).

Milling processes are found to affect chemical compositions of both rice flour and starch. In comparison, dry-milled rice flour from all three rice varieties contained significantly (p<0.05) higher amounts of protein (6.92-7.69 %), fat (0.88-1.05 %) and ash (0.59-0.72 %) than those of wet-milled rice flour, which contain 5.49-6.72 % protein, 0.38-0.58 % fat and 0.26-0.33 % ash. However, in the case of rice starch only protein content of dry-milled rice starch from all three rice varieties are found significantly (p<0.05) higher (1.50-1.64% protein) than those of wet-milled rice starch (0.55-0.85 % protein), whereas fat and ash content between dry- and wetmilled rice starch was not significantly different.

Sample	Moisture	Protein	Fat	Ash	Amylose	Starch damage
	(%)	(%db)	(%db)	(%db)	(%db)	(%db)
Pathum Thani 1						
dry-milled flour	13.24 ± 0.12 a	$7.09\pm0.04\ b$	$0.93 \pm 0.02 \ ab$	$0.59\pm0.00\ b$	$13.97\pm0.21~j$	$8.32\pm0.30\ b$
wet-milled flour	$11.85\pm0.04\ bcde$	$5.49\pm0.23~e$	$0.58\pm0.05\;c$	$0.26\pm0.00\;d$	$17.16\pm0.14\ h$	$5.70\pm0.06\;c$
dry-milled starch	$11.50\pm0.11~\text{cdef}$	$1.50\pm0.06\;f$	$0.14\pm0.01\;e$	$0.30\pm0.02\ cd$	$15.28\pm0.07\ i$	$5.20\pm0.24\;d$
wet-milled starch	$10.59\pm0.39~g$	$0.79\pm0.07~gh$	$0.11\pm0.02\;e$	$0.19\pm0.01~e$	$19.25\pm0.42~g$	$4.34\pm0.12\;f$
RD 7						
dry-milled flour	$12.40\pm0.64\ b$	$7.69 \pm 0.16 \text{ a}$	$1.05\pm0.01~a$	$0.62\pm0.00\ b$	$26.37 \pm 0.69 \; f$	$8.83\pm0.22\ b$
wet-milled flour	$13.41 \pm 0.08 \text{ a}$	$6.72\pm0.03\;c$	$0.58\pm0.03\ c$	$0.33\pm0.01~\text{c}$	28.82 ± 1.39 de	$4.73\pm0.06\ e$
dry-milled starch	$11.39\pm0.28~ef$	$1.64\pm0.09~f$	$0.10\pm0.00\;e$	$0.34\pm0.03\ c$	$28.27\pm0.69~e$	$4.42\pm0.07~f$
wet-milled starch	$10.93\pm0.07~fg$	$0.55\pm0.03\ h$	$0.09\pm0.01~\text{e}$	$0.16\pm0.00\;e$	$30.28\pm0.76~d$	$3.72\pm0.07~g$
Leuang 11						
dry-milled flour	$12.16\pm0.08\ bc$	$6.92\pm0.22\ bc$	$0.88\pm0.03~b$	$0.72\pm0.06\ a$	$32.21\pm0.76\ c$	9.11 ± 0.21 a
wet-milled flour	$12.08\pm0.36~bcd$	$6.24\pm0.04~d$	$0.38\pm0.23~\text{d}$	$0.30\pm0.00\ cd$	$37.40\pm0.35\ b$	$3.99\pm0.32~g$
dry-milled starch	$11.42\pm0.37~def$	$1.64\pm0.04~f$	$0.09\pm0.00\;e$	$0.20\pm0.00\;e$	$37.98\pm0.89\ b$	$4.23\pm0.08\;f$
wet-milled starch	11.95 ± 0.01 bcde	$0.85\pm0.62\;g$	$0.11\pm0.01~\text{e}$	$0.18\pm0.01\ e$	40.09 ± 0.62 a	$3.53\pm0.17~g$

Table 3 Chemical composition of dry-milled and wet-milled rice flour and rice starch from three rice varieties.¹

¹ Values are means of duplicate measurements \pm standard deviation. Means for each characteristics followed by the different letter within the same column are significantly different determined by ANOVA and DMRT (*p*<0.05).

Similar results were reported by many researches. Lu and Li (1989) reported that dry-milled rice flour from both Japonica (TNu 70) and Indica (TCS 80) rice varieties contained higher amount of protein, fat, ash, and reducing sugar than the wet-milled flour. Dry-milled TNu 70 rice flour contained 8.02 % protein, 0.41 % fat and 0.45 % ash, whereas wet-milled rice sample contained 6.67 % protein, 0.03 % fat and 0.17 % ash. Likewise, dry-milled TCS 80 rice flour contained 7.91 % protein, 0.27 % fat and 0.57 % ash compared to wet-milled rice sample that contained 5.70 % protein, 0.03 % fat and 0.22 % ash. In similarly, Chen et al. (1999) showed that drymilled flour from both Japonica (Taichung Waxy 70, TCW70) and Indica (Taichung Sen Waxy 1, TCSW1) rices, which prepared from dry-milling processes used turbo-, cyclone- and hammer-mill contained higher level of protein, lipid and ash than those wet-milled rice flour. For instance, the dry-milled short grain TCW70 rice flour contained 6.35-7.05 % protein, 1.23-2.20 % fat and 0.47-0.89 % ash, whereas wetmilled samples contained 5.71 % protein, 0.57 % fat and 0.42 % ash. Likewise, the dry-milled long grain TCSW1 rice flour contained higher amounts of protein (7.40-8.05 %), lipid (0.83-2.54 %) and ash (0.31-0.68 %) than those of wet-milled rice flour, which contained 4.97 % protein, 0.30 % fat and 0.19 % ash. Yoenyongbuddhagal and Noomhorm (2002b) also reported that dry-milling process used to prepare the high amylose rice flour (Sao Hai) retained larger amounts of protein, lipid and ash contents in rice flour samples than wet-milling process did. Drymilled Sao Hai rice flour contained 7.99 % protein, 0.48 % lipid and 0.43 % ash, whereas wet-milled sample contained 7.83% protein, 0.11% lipid and 0.25% ash.

As mention above, dry-milled flour and starch yielded higher amounts of protein, lipid and ash than those of wet-milled samples. This might causes by some water-soluble proteins, sugars, and lipids were washed out during soaking and wet-grinding step in wet-milling process. Chiang and Yeh (2002) Indicated that during soaking in wet-milling process of rice flour, some of protein, lipid, and ash leached out from the rice kernel. The high-amylose Indica rice grain was soaked at 5 °C and 25 °C. At the end of soaking (8 hr at 25 °C and 7 days at 5 °C), the rice grain samples lost 7 % of protein at both soaking temperature. Moreover, the results showed that 50 % and 30 % of both lipid and ash were leached out at 5 °C and 25 °C soaking.

Beside minor constituents, amylose content in rice flour and starch from three rice varieties were also examined. Amylose content is not just the factor used to identify rice into a group, but it also the crucial inherent properties that correlated with physicochemical, cooking and eating properties of rice (Yeh, 2004). Theoretically, rice was divided into 5 types following the amylose content: waxy (0-2%), very low (5-12%), low (12-20%), intermediate (20-25%), and high (25-33%) (Juliano, 1985). From the results in Table 3, Leuang 11 showed the highest amylose content rice flour (32.21-37.40%) following with RD 7 (26.37-28.82%), whereas Pathum Thani 1 yielded the lowest amylose content (13.97-17.16%). Likewise, rice starch prepared from Leuang 11 provided the highest amylose (37.98-40.09%), following with RD 7 (28.27-30.28%), whereas Pathum Thani 1 rice starch yielded the lowest amylose content (15.28-19.25%). From the results, rice starch samples gave higher amylose content than flour samples. This was possible caused by the less amount of minor constituents (protein, fat and ash) of rice starch samples compared to rice flour as shown in Table 3, thus the higher amount of starch and amylose content were consequently increased.

Our presented data showed quite higher amount of amylose content compared to the previous reports. The data from Department of Agriculture (2002) informed that Pathum Thani 1 contained 14-18 % amylose, whereas RD 7 contained 24-28 % amylose. Varavinit *et al.* (2003) reported that Pathum Thani 1 contained 15.45 % amylose, while Leuang 11 contained 21.95 % amylose. The overestimated of amylose content in this experiment might caused by the different method of determination used in this experiment compared to other studies. The iodine-binding method introduced by Juliano *et al.* (1981) was the simple method that frequently used in many researches. However, this method had limitations such as the low solubility of amylose during granule dispersion step (using NaOH solution and/or heating in boiling water) and the influence of lipid (which complex with amylose to reduce its iodine binding capacity), which lead to increase the variation of the results. In this experiment, we used the method developed by Morrison and Laignelet (1983). This method would disperse amylose from starch granule by used dimethysulphoxide (DMSO) plus heating in the boiling water (5-10 min) and 100°C (60-90 min) to

maximize amylose dispersion. Moreover, the total amylose content was acquired by precipitation of starch to minimize the interference of lipid. Morrison and Laignelet (1986) reported that the total amylose content of many cereal starch (wheat, maize and rice) obtained from this method was 4.4-7.7 % higher compared to the apparent amylose content (measure in the presence of lipids). The results showed that the total amylose content was 13.6% (5.9% lower than the total amylose content). Beside the difference in the method used to determined amylose content, Champange (1996) stated that different growth location, management and cultural practice, soil and climate acted as the factor affected to rice amylose content.

Milling process also affected the amylose content of dry-milled rice flour and rice starch. Amylose content of rice flour prepared from all three rice varieties were significantly (p < 0.05) lower for dry-milled samples (13.97-32.21%) than those of wet-milled samples (17.16-37.40%). Likewise, amylose content of rice starch prepared from all three rice varieties were significantly (p < 0.05) lower for dry-milled samples (15.28-37.98%) than those of wet-milled samples (19.25-40.09%). This might be caused the greater disintegration of starch molecule particularly for the case of rice flour as confirm by the amount of starch damage content in the dry-milled rice flour (8.32-9.11%) compared to wet-milled samples (3.99-5.70%) as presented in Table 3. Thus, the amylopectin (high molecular weight molecule) might be disintegrated to smaller molecular weight molecule. In addition, amylose itself may incline to be a shorter molecule. These two types of the starch disintegration products were possible could not complex well with iodine and resulting lower amounts of amylose content for dry-milled rice flour compared to the wet-milled rice flour. On the other hand, dry-milled samples particularly rice flour samples contained higher amount of fat (lipid) which might formed the inclusion complex with amylose caused reduction the degree of amylose-iodine complex formation.

The presented results showed that rice flour and rice starch from different rice varieties contained the different amount of starch damage content. Rice starch samples contained lower amount of starch damage (3.53-5.20%) compared to rice

flour (3.99-9.11%). This was possible due to the loss of starch damage during the starch isolation process. Damaged starch was absorbed water and swelled in the high extent particular in NaOH solution that used in the protein elimination step. Swollen damaged starch granules were gathered with protein at the upper layer after centrifugation step. The swollen damaged starched were possible to be craped off with protein layer. Therefore, rice starch samples contained the lower amount of starch damage than rice flour when compared between the same rice variety.

The presented results showed that milling process significantly effected on starch damage content. The dry-milled rice flour (8.31-9.11%) gave the higher amount of starch damage than those of wet-milled rice flour (2.99-5.70%) in all rice varieties. Likewise, the dry-milled rice starch from all three rice varieties gave the higher amount of damaged starch (4.23-5.20%) than those of wet-milled rice starch (3.53-4.34%). These results Indicated that dry-milling process caused more mechanical damage to the starch granules than wet-milling process. The results were similar to the results of Yoenyongbuddhagal and Noomhorm (2002b), which found that the dry-milled high amylose content rice flour (Sao Hai) contained significantly higher amount of starch damage (12.10%) than those of wet-milled flour (4.20%). Chiang and Yeh (2002) stated that due to the leaching out protein, lipid, and ash and the penetration of water during soaking, water caused the structure of rice endosperm became loosened. Thus, fine flour with less damaged starch was obtained from wetmilled process. This research showed that when the moisture content of rice kernel was increased from 13% to 28%, the starch damage decreased from 8.4% to about 5%.

From all of data (Table1), it can summarized that rice starch contained the lower amount of protein, fat, ash and starch damage compared to the parent rice flour samples. Milling process showed significantly effect on chemical composition particularly in rice flour samples, which dry-milled flour showed the higher amount of protein, fat and ash than wet-milled flour did. The higher amount of starch damage of dry-milled samples implied the larger degree of mechanical disintegration of starch granules compared to wet-milled samples.

1.2 Scanning electron microscopy examination

The scanning electron microscopy (SEM) of normal and α -amylase treated of dry-milled and wet-milled rice flour and rice starch from Pathum Thani 1, RD 7 and Leuang 11 are presented in Figure 11-16. Under the microscopy, the normal dry-milled rice flour samples from all three rice varieties (Figure 11a, 13a and 15a) showed the high variation in flour particles size (10-180 µm), which appeared to pack with numerous of compound rice starch granules, whereas the starch granules from wet-milled rice flour (Figure 11b, 13b and 15b) were mostly separated with the trace of some compound starch granule, which is approximately 10-15 µm in size. For the normal rice starch both from dry- an wet-milled samples (Figure 12a,b, 13a,b and 14a,b) are evidently presented the separately starch granule with polygonal in shape and ranging in size from 3-9 µm. Moreover, it can be seen that many pits were presented on the surface of some individual starch granule particular in the rice starch samples, which might reflex the evident of the protein bodies dislodgment. This might confirm the data about the lower amount of protein content in rice starch (0.79-1.64%) compared to rice flour (5.49-7.09%).

The results showed that for the normal dry-milled rice flour samples the large aggregated of starch granules with smooth fracture surfaces were found as shown in Figure 11a, 13a and 15a. The smooth areas might correspond to fractures within rice endosperm. As a result, this event caused the starch granule partially disruption resulting damaged starch occurred. Inside these clump flour particles, the undamaged starch granules and other constituents i.e. protein bodies, lipid and mineral were existed. These confirmed the results for the higher amount of starch damaged (8.32-9.11%) and other compositions (6.92-7.69% protein, 0.88-1.05% fat and 0.59-0.72% ash) were determined in dry-milled rice flour compared to those of wet-milled flour samples as presented in Table 3.





- (a) Dry-milled Pathum Thani 1 rice flour (1,000X)
- (b) Wet-milled Pathum Thani 1 rice flour (1,000X)



Hour (1,000X)



(c) Dry-milled Pathum Thani 1 rice flour after α -amylase treated (1,000X)



(d) Wet-milled Pathum Thani 1 rice flour after α -amylase treated (1,000X)



- (e) Dry-milled Pathum Thani 1 rice flour after α-amylase treated (3,000X)
- (f) Wet-milled Pathum Thani 1 rice flour after α-amylase treated (3,000X)

Figure 11 SEMs of dry-milled and wet-milled Pathum Thani 1 rice flour with and without α -amylase treatment at magnificent (1,000X) and (3,000X).



(a) Dry-milled Pathum Thani 1 rice starch (b) Wet-milled Pathum Thani 1 rice (1,000X) starch (1,000X)





(c) Dry-milled Pathum Thani 1 rice starch (d) Wet-milled Pathum Thani 1 rice starch after α -amylase treated (1,000X) after α -amylase treated (1,000X)





- (e) Dry-milled Pathum Thani 1 rice starch (f) Wet-milled Pathum Thani 1 rice starch after α-amylase treated (3,000X)
- **Figure 12** SEMs of dry-milled and wet-milled Pathum Thani 1 rice starch with and without α -amylase treatment at magnificent (1,000X) and (3,000X).



(a) Dry-milled RD 7 rice flour (1,000X)

(b) Wet-milled RD 7 rice flour (1,000X)



- 19kU X1, 008 (04m 0000 (11 20 SET
- (c) Dry-milled RD 7 rice flour after α amylase treated (1,000X)



(e) Dry-milled RD 7 rice flour after α amylase treated (3,000X) (d) Wet-milled RD 7 rice flour after α -amylase treated (1,000X)



(f) Wet-milled RD 7 rice flour after α amylase treated (3,000X)

Figure 13 SEMs of dry-milled and wet-milled RD 7 rice flour with and without α amylase treatment at magnificent (1,000X) and (3,000X).



(a) Dry-milled RD 7 rice starch (1,000X) (b) Wet-milled RD 7 rice starch (1,000X)





(c) Dry-milled RD 7 rice starch after αamylase treated (1,000X)



(e) Dry-milled RD 7 rice starch after α -amylase treated (3,000X)

(d) Wet-milled RD 7 rice starch after α amylase treated (1,000X)



(f) Wet-milled RD 7 rice starch after α amylase treated (3,000X)

Figure 14 SEMs of dry-milled and wet-milled RD 7 rice starch with and without α amylase treatment at magnificent (1,000X) and (3,000X).



- (a) Dry-milled Leuang 11 rice flour (1,000X)
- (b) Wet-milled Leuang 11 rice flour (1,000X)





- (c) Dry-milled Leuang 11 rice flour after α-amylase treated (1,000X)
- (d) Wet-milled Leuang 11 rice flour after α -amylase treated (1,000X)



- (e) Dry-milled Leuang 11 rice flour after α -amylase treated (3,000X)
- (f) Wet-milled Leuang 11 rice flour after α -amylase treated (3,000X)
- **Figure 15** SEMs of dry-milled and wet-milled Leuang 11 rice flour with and without α -amylase treatment at magnificent (1,000X) and (3,000X).



(a) Dry-milled Leuang 11 rice starch (1,000X)



(b) Wet-milled Leuang 11 rice starch (1,000X)



- 15kU X1,000 X104m 20.20 SE1
- (c) Dry-milled Leuang 11 rice starch after α-amylase treated (1,000X)



(e) Dry-milled Leuang 11 rice starch after α-amylase treated (3,000X) (d) Wet-milled Leuang 11 rice starch after α -amylase treated (1,000X)



(f) Wet-milled Leuang 11 rice starch after α -amylase treated (3,000X)

Figure 16 SEMs of dry-milled and wet-milled Leuang 11 rice starch with and without α -amylase treatment at magnificent (1,000X) and (3,000X).

In case of using different type of miller, the different morphology of rice starch granules was observed. Chen *et al.*, (2003) reported that after subjected ballmilling, the surface of rice starch granule from both TNUS19 and TCW70 rice starch were lost of smoothness and the granule became flat. The starch samples showed the attachment of starch granule to each other and accumulated to the clumps, especially after long milling time (60 min). The researchers suggested that the clump of rice starch granules might caused by the broken of glycosidic bonds during ball-milling, resulting increase free hydroxyl groups to form hydrogen bonding between starch molecules.

Rice flour and rice starch samples were observed again after subjected to α -amylase in the process of starch damaged determination. The SEM of α -amylase treated samples were shown in Figure 11(c-f), 13(c-f) and 15(c-f) for rice flour and 12(c-f), 14(c-f) and 16(c-f) for rice starch samples. For dry-milled rice flour, the sponge-like structure of the flour particles with many holes at the surface was observed in Figure 11(c,e), 13(c,e) and 15(c,e). This might caused by α -amylase amylolysis of the damaged starch granules, which located at the fracture surface of the flour particles and left the undamaged starch inside. Theoretically, α -amylase was prefer to attacked the amorphous growth rings than the semicrystalline (Eliasson, 2004). As observed in Figure 13(c,e), the growth rings appeared very clear after α -amylase treated due to the hydrolysis of amorphous region.

After α -amylase treatment, the wet-milled rice flour as shown in Figure 11(d,f), 13(d,f) and 15(d,f). and rice starch from both dry- and wet-milled samples as shown in Figure 12(c-f), 14(c-f) and 16(c-f), some fragments of starch granule were occasionally found but less than those of α -amylase treated dry-milled rice flour. This Indicated the damaged starch granule in the wet-milled rice flour and rice starch from both dry- and wet-milled samples were also hydrolyzed, but in a lower extent than dry-milled flour samples. Chiang and Yeh (2002) stated that during soaking in rice flour wet-milling process, protein matrix and other substances were leached out from the surface of starch granules caused the structure of starchy endosperm became

loosen which resulting fine particle with less damaged starch was obtain from wetmilling process.

In summary rice flour particularly dry-milled rice flour presented the larger flour particles with may retain the minor constituents (protein, fat and ash) inside compared to the wet-milled rice flour and rice starch. From the results of α -amylase treatment, the dry-milling process presented the large starch granule disruption particularly at the fracture surface of rice flour particles agree with the results of starch damage content determination.

2. Physicochemical Properties of Rice Flour and Rice Starch

2.1 Gelatinization properties

The gelatinization properties of dry- and wet-milled rice flour and starch from Pathum Thani 1, RD 7 and Leuang 11 were shown in Table 4. The gelatinization temperature (T_o , T_p and T_c) and enthalpies of gelatinization (Δ H) of flour and starch are found significantly (p<0.05) different among rice varieties. For rice flour samples, RD 7 rice flour showed highest gelatinization temperature range (T_o - T_c) (73.14 – 87.03 °C), following by Leuang 11 (69.80- 85.77 °C) and Pathum Thani 1 showed the lowest (T_o - T_c) (65.39- 83.17 °C). In case of rice starch, RD 7 rice starch showed highest gelatinization temperature range (T_o - T_c) (72.80-85.15°C), following by Leuang 11 (69.73-83.20 °C) and Pathum Thani 1 showed the lowest (T_o - T_c) (64.04-81.08 °C).

From the presented results, the gelatinization temperatures were not correlated to amylose content of rice samples. However, the contradictory results from many researches regard to the influence of amylose on gelatinization temperature were reported. Biliaderis *et al.* (1986) found that the gelatinization temperatures of eight waxy and non waxy rice samples (2.1-31.2 % amylose) were independent on amylose content. Similarly, Juliano and Perez (1990) also reported the discorrelation between the amylose content (0.8-33.0 % amylose) and gelatinization

temperatures of thirty-four waxy and non waxy rice samples. In contrast, the research done by Varavinit *et al.* (2003) showed the positive correlation (*r*) between amylose content of the eleven Thai rice varieties (4.47-26.42 % amylose) and T_o, T_p and T_c (*r* = 0.84, 0.88, and 0.85, respectively). The results showed that low amylose rice flour (n = 3, 4.47-5.28 % amylose) showed the lower gelatinization temperature range (T_o-T_c) (60.62-78.85 °C) than those of medium amylose rice flour (n = 2, 14.63-15.45 % amylose) (61.50- 78.60°C) and high amylose rice flour (n=6, 21.95-26.42 % amylose) (68.81-83.58 °C), respectively.

Table 4 Gelatinization properties dry-milled and wet-milled rice flour and rice starch from three rice varieties.¹

Sample	T_{o} (°C)	$T_p (^{o}C)$	T_{c} (°C)	Enthalpy (J/g)	
Pathum Thani1					
dry-milled flour	$67.12 \pm 0.07 \text{ e}$	$74.14\pm0.00\;g$	$83.17 \pm 0.04 \text{ e}$	$6.02\pm0.06~i$	
wet-milled flour	$65.39\pm0.01~g$	$71.89\pm0.02\ h$	$82.87\pm0.06~e$	$9.32\pm0.11~\text{c}$	
dry-milled starch	$64.04\pm0.04~h$	$71.60\pm0.05~h$	$80.24\pm0.41~g$	$8.11 \pm 0.16 \text{ de}$	
wet-milled starch	$65.94\pm0.08~f$	$71.98\pm0.15~h$	$81.08\pm0.33~f$	$12.48\pm0.06~a$	
RD 7					
dry-milled flour	74.00 ± 0.03 a	79.28 ± 0.01 a	87.03 ± 0.04 a	$7.63\pm0.00\;f$	
wet-milled flour	$73.14\pm0.03~b$	$78.24\pm0.01~b$	$86.12\pm0.01~b$	$8.27\pm0.06\;d$	
dry-milled starch	$72.80\pm0.15~\text{b}$	$77.62\pm0.18~\mathrm{c}$	$84.77\pm0.05~c$	$9.53\pm0.04\ c$	
wet-milled starch	$73.02\pm0.64~b$	$78.16\pm0.28~\text{b}$	$85.15\pm0.06\ c$	$10.66\pm0.32~b$	
Leuang 11					
dry-milled flour	$71.52\pm0.06\ c$	$76.87 \pm 0.21 \text{ d}$	$85.77\pm0.18~\text{b}$	$6.67\pm0.03~h$	
wet-milled flour	$69.80 \pm 0.04 \text{ d}$	$75.75\pm0.00~e$	$83.72\pm0.00~d$	$7.87\pm0.18~ef$	
dry-milled starch	$69.73 \pm 0.10 \text{ d}$	$74.58\pm0.18\;f$	$83.10 \pm 0.16 \text{ e}$	$7.08\pm0.06~g$	
wet-milled starch	$70.12\pm0.15~d$	$75.86\pm0.03~e$	$83.20\pm0.49~e$	$9.24\pm0.14~c$	

¹ Values are means of duplicate measurements \pm standard deviations. Means for each characteristics followed by the different letter within the same column are significantly different determined by ANOVA and DMRT (*p*<0.05).

In contradictory, Vandeputte et al. (2003a) accomplished the experiment using five waxy rice and ten normal rice starch. The rice starch samples were divided into four groups: waxy (Tp: 65.2-65.8 °C), normal-low Tp starch (Tp: 62.8-67.0 °C), normal-intermediate T_p (71.7-73.5 °C) and normal-high T_p (76.7-78.5 °C) rice starch. The result showed that absolute (AAM) and free (FAM) amylose contents did not affect To, Tp and Tc of waxy and normal low Tp rice starch, but decreased gelatinization temperatures (T_o, T_p and T_c) (r^2 = 0.84, 0.91 and 0.98, p < 0.05) of normal intermediate and high Tp rice starch, whereas lipid-complexed (LAM) amylose content increased T_o, T_p and T_c (r^2 = 0.71, 0.67 and 0.56, p < 0.05) in all rice starch samples. In the case of waxy rice, the amylose content was slightly (1.9-3.4 % AAM and 0.0-0.4 % FAM), probably caused insufficient to significantly influence gelatinization parameters. The researches also postulated that the two-step of granule swelling in the gelatinization process, only the second step, which occurred at the high temperature was influenced by amylose. For the normal-low T_{p} rice starch, the gelatinization was finished at the low temperature (early in the first step). Thus, amylose were not affected the gelatinization temperature of the normal-low T_p samples

In our presented study, the significant influence of milling processes on the gelatinization parameters was found particularly in the case of rice flour. The results showed that dry-milled rice flour from all rice varieties showed significantly (p<0.05) higher gelatinization temperatures (T_o: 67.12 – 74.00 °C, T_p: 74.14 – 79.28 °C and T_c: 83.17 – 87.03 °C) than those of wet-milled rice flour (T_o: 65.39 – 73.14 °C, T_p: 71.89 – 78.24 °C and T_c: 82.87 – 86.12 °C) as shown in Table 2. This was possible caused by the larger flour particle size of dry-milled flour compared to wet-milled flour as confirmed by scanning electron micrographs (Figure 11-16). Hence, water was more difficult to penetrate into the larger flour particles of dry-milled flour for beginning of gelatinization process. Marshall (1992) reported the influence of particle size of milled Lemont rice on gelatinization properties. The results showed that the larger rice flour particle size exhibited higher value of gelatinization temperature than those of the smaller one. For instance, at the flour particle size range (710-1,400 µm), a increase about 1°C was observed for T_o, and increases of 4.8 and 8.6 °C for T_p and

 T_c , respectively, when compared to gelatinization temperature of the smaller flour particle size range (53-64 µm). The broader and more complex transition gelatinization peaks were observed from the large particle size flour compared to the small particle size flour. The researches stated that the extent to which gelatinization was affected might depend on the degree of expose of the starch granule, which means the ratio of granules easily accessible to water to granule less easily accessible. Moreover, higher amount of protein content found in the dry-milled samples might affect to the delay of starch gelatinization. Hamaker (1994) stated that protein especially starch granule-associated protein could affect the manner in which the starch in the granule gelatinization and the manner in which the granule maintains its shape even when swollen.

The similar results were reported by Chen *et al.* (1999). The results showed that dry-milled waxy rice flour prepared by turbo, cyclone, hammer and grinding mills showed the highest gelatinization temperatures (T_o and T_p) followed with those of semi-dry hammer mill, whereas the wet-milled (stone mill) rice flour showed the lowest gelatinization temperatures. For instance, the dry-milled TCW70 rice flour showed the highest gelatinization temperatures (T_o : 59.83-62.06 °C and T_p : 71.21-73.30 °C) followed with semi-dry-milled rice flour (T_o : 58.81 °C and T_p : 71.71 °C) and wet-milled rice flour (T_o : 58.17 °C and T_p : 69.64 °C). Similarly, the dry-milled TCSW1 rice flour showed the highest gelatinization temperatures (T_o : 62.10-65.09 °C and T_p : 72.53-74.61 °C) followed with semi-dry-milled rice flour (T_o : 58.17 °C and T_p : 69.64 °C). The researchers stated that these possible due to the effect of flour particle size. In comparison with semi-dry milled flour and wet-milled flour, the dry-milled rice flour yielded the higher particle size, thus the higher gelatinization temperature were investigated.

However, the contradictory results were reported by Yoenyongbuddhagal and Noomhorm (2002b). The results showed that T_o of dry-milled high amylose rice flour (Sao Hai) (T_o : 64.26 °C) was significantly (p<0.05) lower than those of wet-milled rice flour (T_o : 69.94 °C), whereas T_p and T_c of these samples were not

significantly different. The researchers stated that these results might caused by the higher amount of starch damage, which affected to the earlier gelatinization of drymilled rice flour. Starch damage content was reported as an important factor, which affected gelatinization properties of wheat and maize starch from the previous researches (Morrison et al., 1994). For maize starch samples, the increasing the ballmilling time from 0 to 4 hr resulted raising amount of starch damage from 1.2 to 44.1 % and decreasing T_0 : from 59.0 to 44.0 °C, T_p : from 70.5 to 63.0 °C and T_c : from 85.0 to 76.0 °C. For the longer time of ball-milling at 8 hr, maize starch contained 66.0 % starch damage and no gelatinization endotherm was found. In the case of wheat starch samples, the increasing the ball-milling time from 0 to 8 hr resulted raising amount of starch damage from 4.6 to 80.2 % and decreasing T_0 : from 47.5 to 44.7 °C, T_p : from 61.6 to 56.8 °C and T_c: from 77.3 to 70.0 °C. For the longer time of ball-milling at 16 hr, wheat starch contained 91.1 % starch damage and gelatinization endotherm was undetectable. The similar results were reported by Chen et al. (2003). The results Indicated that the TNuS19 and TCW70 rice starch showed significantly (p < 0.05) decrease in gelatinization temperature after the increasing of ball-milling time. The researchers also stated that the longer ball-milling time, the higher disruptions of the order of rice starch granule were found.

From the presented data in Table 4, rice starched showed significantly (p<0.05) lower gelatinization temperature compared to the parent rice flour particularly in the case of dry-milled sample. For example, Leuang 11 dry-milled rice starch showed significantly lower gelatinization temperature range (T_0 - T_c : 69.73-83.10 °C) compared to the parent Leuang 11 dry-milled rice flour (T_0 - T_c : 71.52-85.77 °C). This might imply the effect of the larger particle size and minor constitute particularly protein contamination of dry-milled flour over the dry-milled starch. The similar results were reported by Lumdubwong and Seib (2000). The results showed that rice starch prepared by NaOH extraction showed the approximate 2 °C lower gelatinization temperature (T_0 : 67.8 °C, T_p : 73.5 °C and T_c : 79.3 °C). Likewise, Wang *et al.* (2002) reported that rice starch extracted from whole Bengal rice showed the lower gelatinization temperature (T_0 : 64.6 °C and T_p : 70.5 °C) than Bengal rice flour did (T_0 : 66.4 °C and

 T_p : 72.7 °C). Both group of researchers suggested the higher gelatinization temperature of rice flour compared to rice starch was the influence of minor constituents such as protein and lipid, which inhibited swelling of starch and increased the gelatinization temperature. However, it can be seen from the data that wet-milled rice starch showed not significantly different of gelatinization temperature from the parent wet-milled rice flour and dry-milled rice starch, except in the case of Pathum Thani 1. This might caused by the close particle size and nearby amount minor constituents (Table 3) among wet-milled flour, dry-milled starch and wet-milled starch

Gelatinization temperature was said to be an index of the quality of order structures in the starch molecule, while enthalpy was a quantitative parameter regarded as the amount of crystallinity structure of starch granules (Morrison *et al.*, 1994). The presented data in Table 4 showed different gelatinization enthalpy (Δ H) of dry- and wet-milled rice flour and rice starch from different rice varieties. Rice flour showed significantly (p<0.05) lower Δ H than rice starch due to the lower amount of crystallinity structure according to the lower starch content.

The milling process showed significantly effect on gelatinization enthalpy (Δ H). The results showed that the Δ H value measured from dry-milled rice flour from all rice varieties (6.02-7.63 J/g) were lower than those of wet-milled samples (7.87-932 J/g). Likewise, dry-milled rice starch showed lower Δ H (7.08-9.53 j/g) than wet-milled rice starch (9.24-12.48 j/g). These results confirmed the reduction of starch crystallinity structure after subjected to dry-milling process, consequently the increasing of starch damage content as shown in Table 3. The similar results were reported by Yoenyongbuddhagal and Noomhorm (2002b). Dry-milled high amylose rice flour (Sao Hai) exhibited significant lower level of gelatinization enthalpy (7.08 J/g) than those of wet-milled rice flour (12.62 J/g). The researches stated that these evident showed considerable disruption of the native starch structure due to the grinding process of dry-milling.

Dry-milling, especially ball-milling, caused the large extent of starch granule structure disruption as found by the previous study. Morrison et al. (1994) reported that the increasing the ball-milling time from 0 to 4 hr resulted raising amount of starch damage of maize starch from 1.2 to 44.1 % and decreasing ΔH from 12.2 to 3.4 J/g. For the longer time of ball-milling to 8 hr, maize starch contained 66.0 % starch damage and no gelatinization endotherm was detected. In the case of wheat starch samples, the increasing the ball-milling time from 0 to 8 hr resulted raising amount of starch damage from 4.6 to 80.2 % and decreasing Δ H from 10.6 to 1.8 J/g. When the ball-milling time was prolonged to 16 hr, wheat starch contained 91.1 % starch damage and gelatinization endotherm was undetectable. The researchers stated that the diminishing of gelatinization enthalpy of both maize and wheat starch during ball-milling exhibited mechanical damage of large ordered regions in the starch granule into disordered amorphous material. The similar results were reported by Chen et al. (2003). The gelatinization enthalpy of TNuS19 and TCW70 rice starch were decreased after ball-milling treatment. The ΔH showed negatively correlated with ball-milling treatment time (r=-0.84, p<0.01).

In summary, gelatinization properties of rice flour and starch were affected by rice varieties, minor constituents and milling process. Dry-milled rice samples provided higher gelatinization temperature due to the higher particle size and the greater amount of minor constituents compared to the wet-milled sample. The lower amount of starch crystallinity as shown by the lower enthalpy of gelatinization (Δ H) implied the larger degree of starch granule disruption due to dry-milling process compared to wet-milling process.

2.2 Swelling power and solubility

When starch was heated in excess water, the crystalline structure was disrupted due to the break of hydrogen bonds, and water molecules became linked by hydrogen bonding to the exposed hydrogen group of amylose and amylopectin. This caused an increase in granule swelling and solubility (Bao and Bergman, 2004). The swelling power (SP) dry- and wet-milled rice flour and rice starch from three rice

varieties were exhibited in Figure 17(a) and 17(b) and Table 5. For rice flour samples, the presented results showed that when the temperature was raised from 55 to 95 °C, SP of all rice flour samples was also increased incidentally. It can be seen from Figure 4(a) that the swelling power (SP) of all rice flour samples was gradually increased from 1.54-2.77 g/g to 6.59-10.61 g/g during increasing of the temperature from 55 to 75 °C, coinciding with onset temperature to peak temperature ($T_o - T_p$) measured by DSC as shown in Table 2. The SP remained almost constant between 6.59-10.61 g/g to 8.30 -10.54 g/g during the temperature ($T_p - T_c$) as shown in Table 2 and immediately jumped up to the highest value in the range of 11.41 – 15.32 g/g at the 95 °C. Pathum Thani 1 rice flour showed the highest swelling power (2.04-15.32 g/g) in all test temperatures, particularly, at 55 to 75 °C, following with RD 7 rice flour (1.73- 14.12 g/g) and Leuang 11 rice flour (1.54-12.28 g/g).

The influence of milling process on gelatinization was also investigated. The results showed that dry-milled flour from all rice varieties showed slightly higher SP compared to wet-milled flour, except at 75 °C. At 75 °C, dry-milled rice flour from all three rice varieties showed significantly (p<0.05) higher SP than wet-milled flour. For example, Pathum Thani 1 dry-milled rice flour showed the higher SP (10.61 g/g) compared to wet-milled rice flour (7.76 g/g). Likewise, RD 7 dry-milled rice flour showed the higher SP (8.92 g/g) compared to wet-milled rice flour (7.10 g/g). Similarly, Leuang 11 dry-milled rice flour showed the greater SP (8.23 g/g) compared to wet-milled rice flour (6.59 g/g).



Figure 17 Swelling power of rice flour (a) and rice starch (b) (PD= dry-milled Pathum Thani 1, PW=wet-milled Pathum Thani 1, RD = dry-milled RD 7, RW=wet-milled RD 7, LD=dry-milled Leuang 11, LW=wet-milled Leuang 11).

Sample	Swelling Power (g/g)				
	55 °C	65 °C	75 °C	85 °C	95 °C
Pathum Thani 1					
dry-milled flour	$2.77\pm0.01 \; qr$	$5.15\pm0.02\;o$	$10.61\pm0.37~gh$	9.55 ± 0.46 hij	15.25 ± 1.61 de
wet-milled flour	$2.04\pm0.02\ rs$	$4.92\pm0.03\ p$	$7.76\pm0.10~klm$	8.35 ± 1.27 jkl	$15.32 \pm 0.93 \text{ de}$
dry-milled starch	$1.55\pm0.01~s$	$6.17\pm0.43~n$	$8.70\pm0.92~ijk$	$11.37 \pm 0.17 \text{ fg}$	19.28 ± 0.92 a
wet-milled starch	$1.58\pm0.02\ s$	$5.03\pm0.43\ p$	8.47 ±0.28 jkl	$10.58\pm0.18~gh$	$17.51 \pm 0.27 \text{ bc}$
RD 7					
dry-milled flour	$2.31\pm0.06\ r$	$2.89\pm0.09\ qr$	$8.92\pm0.12~ijk$	$9.03\pm0.92~ij$	$12.64\pm1.60\ f$
wet-milled flour	$1.73\pm0.04~s$	$1.90 \pm 0.09 \text{ rs}$	$7.10\pm0.02~lmn$	$8.33\pm0.19~jkl$	$14.12 \pm 0.70 \text{ e}$
dry-milled starch	$1.50\pm0.04\ s$	1.94 ± 0.26 rs	8.27 ± 0.41 jkl	$10.47\pm0.02~gh$	19.30 ± 0.41 a
wet-milled starch	$1.33\pm0.06\ s$	$1.64 \pm 0.15 \text{ s}$	$8.13\pm0.49~jkl$	10.01 ± 0.02 ghi	18.16 ± 0.49 ab
Leuang 11					
dry-milled flour	$2.38\pm0.16\ r$	$3.41\pm0.11\;q$	8.23 ± 0.44 jkl	$8.30 \pm 1.14 \; jkl$	$11.41\pm0.14~fg$
wet-milled flour	$1.54\pm0.00\ s$	$3.35\pm0.62~qr$	$6.59\pm0.08\ mn$	$8.38\pm0.08~jkl$	$12.28\pm0.02~f$
dry-milled starch	$1.54\pm0.03~s$	$2.78\pm0.20\ qr$	8.19 ± 1.25 jkl	$10.05\pm0.03~ghi$	16.75 ± 1.25 bc
wet-milled starch	$1.34\pm0.11\ s$	$2.35\pm0.21~\text{r}$	$7.82 \pm 1.35 \text{ klm}$	9.44 ± 0.15 hij	$16.39\pm1.35~\text{cd}$

Table 5 Swelling power of rice flour and rice starch from three rice varieties.¹

¹ Values are means of duplicate measurements \pm standard deviation. Means for each characteristics followed by the different letter within the same column are significantly different determined by ANOVA and DMRT (*p*<0.05).

In the case of rice starch, the SP of rice starch were gradually increased during the temperature increasing from 55 to 95° C. However, RD 7 and Leuang 11 rice starch showed the slightly difference swelling pattern from Pathum Thani 1. The results showed that SP of RD 7 and Leuang 11 rice starch were slightly increased during heating at 55 and 65 °C of 1.33-1.50 to 1.64-1.94 g/g for RD 7 rice starch and 1.34-1.54 to 2.35-2.78 g/g for Leuang 11 rice starch, when gradually increased after 75 °C and reached to the highest value at 95°C of 18.16-19.30 g/g for RD 7 and 16.39-16.75 g/g for Leuang 11. Unlike, Pathum Thani 1 rice starch, which showed the regularly increase in SP value from the beginning at 55 °C, when gave the highest value at the end of heating at 95 °C.

From our results as shown in Figure 17 (a) and 17(b), the swelling pattern of rice flour and rice starch are found to be two-step process. According to Leach (1965), cereal flour are known to swell in two- stages reflecting the presence of two sets of internal bonds involving linear and branched polymers of amylose and amylopectin. Tester and Morrison (1990) explained about the swelling phenomenon in cereal starch through the association-dissociation of bonding particularly in amylopectin molecule. They postulated that when cereal starch were heated in excess water, the dissociation of bonding between clusters of amylopectin was performed at the first stage of swelling (45-55 °C), when heating starch from 55-60 °C dissociation of amylopectin double-helices was exhibited. After heating above 60 °C, the external chains of amylopectin molecules formed a restrict semirandom conformation. These made amylopectin swelled in highly extent, while the starch granules still existed through intermolecular (might be hydrogen) bonding. From these evident, they concluded that amylopectin would promote starch swelling especially at the early stage of swelling. Amylose was leached out during heating process particularly at the higher temperature (the later stage of swelling). They postulated that amylose itself acted as both a dilutent and swelling inhibitor through complexing with lipid. Likewise, Vanderputte et al. (2003b) reported about the influence amylopectin and amylose during the two-stage swelling of starch in five waxy and 10 normal rice starch. The results showed that at the first swelling step (55-85 °C), molecular structure of amylopectin showed the influence on the swelling power of rice starch.

The short chain amylopectin (DP 6-9) led to increased swelling power, whereas longer chain amylopectin (DP 12-22) had the opposite effect. Only in the second swelling step (at temperature above 95-125 $^{\circ}$ C), amylose decreased the swelling power.

As mention above, amylopectin played an important role in the increasing degree of swelling power of flour, whereas amylose hesitated it. Pathum Thani 1 contained the lowest amount of amylose (11.85-13.24 % for rice flour and 15.28-19.25 % for rice starch) among all rice samples. Thus, it exhibited the higher SP typically at the first-stage of swelling (55 to 75 °C) compared to rice flour and rice starch from RD 7 and Leuang 11, which contained higher amount of amylose. Similar results were reported by Singh *et al.* (2000). The results showed that among three rice flour from Indica flour (28% amylose), Japonica flour (20% amylose) and Japonica waxy flour (0.0% amylose), the highest SP was shown by waxy rice flour (3-18 g/g) and followed by the Japonica (5-12 g/g) and Indica flour (5-12 g/g). Similarly, Sodhi and Singh (2003) showed that among five rice starch, which contained 7.8-18.9% amylose, PR 103 with the lowest amylose content had the highest swelling power (33.2 g/g).

It can be seen from Figure 17(a) and Table 5 that milling process could affect on SP value particularly in rice flour samples. The SP of dry-milled rice flour from all rice varieties were significantly (p<0.05) higher SP compared to wet-milled rice flour particularly in the range of 55 to 75 °C, then SP values became close to each other at the higher temperature of 85 and 95 °C. For instant, at 75 °C dry-milled Pathum Thani 1 rice flour showed significantly (p<0.05) higher SP (10.61 g/g) than wet-milled Pathum Thani 1 rice flour (7.76 g/g). Similarly, SP of dry-milled RD 7 rice flour (8.92 g/g) were significantly (p<0.05) higher than SP of wet-milled RD 7 flour (7.10 g/g). Likewise, dry-milled Leuang 11 rice flour showed significantly (p<0.05) greater SP (8.23 g/g) than those of wet-milled sample (6.59 g/g). After heating to 85 °C, the SP of both dry- and wet-milled rice flour from all three rice varieties became closed together (8.30 – 10.54 g/g). At 95 °C, the SP of all rice samples were jumped to the maximum, but the SP of dry-milled flour of each rice

varieties became non-significantly different with those of wet-milled sample prepared from the same rice varieties. The higher value of SP from dry-milled rice flour in the early stage of heating at 55 to 75 °C might be the influence of the higher starch damage content of dry-milled rice flour compared to the wet-milled flour as shown in Table 3. In the early stage of gelatinization, the damaged granules probably permitted the larger amount water to go into the starch granule caused the granule swell. However, the damaged granules might lose their capability of granule integrity during heating to the higher temperature particularly at the temperature above gelatinization temperature. However, in the case of rice starch, dry-milled rice starch showed non significantly of SP values compared to wet-milled in very test temperature.

However, starch damage content were reported as the factor affected swelling power of starch. Tester and Morrison (1994) reported that the swelling factors of wheat starch increased with the starch damage content particularly during the gelatinization. When starch was heated to below gelatinization temperature, the swelling factor increased gradually from 1.0 to 6.7 at both 20 and 40 °C with the increasing of starch damage content from 4.6 to 93.7%. At 60 °C (approximately the wheat starch sample gelatinization temperature), the swelling factor increased from 5.6 to 8.0 with the increasing of starch damage from 4.6 to 80.6 %, then decreased to 7.7 and 6.7, when the starch damage levels were 91.1 and 93.7 %, respectively. On the other hand at 80°C (above the gelatinization temperature), the swelling factor reached to the highest values, but decreasing from 10.9 to 9.4 with the increasing of starch damage from 4.6 to 9.4 %. Yoenyongbuddhagal and Noomhorm (2003b) presented the similar results. Dry-milled high amylose (Sao Hai) rice flour swelled to higher extent than wet-milled flour during heating from 60 to 80 °C. At the higher temperature (90°C), the SP was lower for dry-milled flour compared to wet-milled flour. They postulated that the higher starch damage that occurred to dry-milled flour since disruption of the crystalline structure in dry-milled flour allowed permeation by water into the granule, but on the other hand the disrupted granule could not hold the swelled structure as good as undisrupted granules in wet-milled rice flour.

In comparison between rice flour and rice starch, the SP values of rice starch were not significantly different from those of rice flour until after 75°C. At the temperature between 85 to 95°C, rice starch from all three rice varieties showed significantly higher SP than rice flour. At 85 °C, Pathum Thani 1 rice starch showed the higher SP (10.58-11.37 g/g) compared to Pathum Thani 1 rice flour (8.35-9.55 g/g). Likewise, RD 7 rice starch showed the higher SP (10.01-10.47 g/g) compared to RD 7 rice flour (8.33-9.03 g/g). Similarly, Leuang 11 rice starch showed the higher SP (9.44-10.05 g/g) compared to Leuang 11 rice flour (8.30-8.31 g/g). At 95 °C, all rice starch showed the highest value of SP. Pathum Thani 1 rice starch showed the higher SP (17.51-19.28g/g) compared to Pathum Thani 1 rice flour (15.25-15.32g/g). Likewise, RD 7 rice starch showed the higher SP (18.16-19.30 g/g) compared to RD 7 rice flour (12.64-14.12 g/g). Similarly, Leuang 11 rice starch showed the higher SP (16.39-16.75 g/g) compared to Leuang 11 rice flour (11.41-12.28 g/g). The higher SP of starch over the flour samples particularly at above gelatinization temperature (85 to 95 °C) might be the effect of less extent of minor constituents typically lipid. After gelatinization, amylose leach out was occurred. The less amount of lipid in rice starch samples might allowed extra swelling of starch granule, which can be exhibited by amylose-lipid complex.

The amount of solubility for rice flour and rice starch are shown in Figure 18(a) and 18(b) and Table 6. The results showed that the solubility of rice flour and rice starch increased during the temperature increased from 55 to 95 °C. For rice flour, the solubility of all rice varieties showed slightly increase during temperature increase from 55 to 75 °C (0.82-3.27%). After 75 °C, the solubility of rice flour were increased approximately two times particularly for dry-milled rice flour (3.81-9.30%) and raised to the highest value (3.81-9.30%) at 95 °C. For the rice starch, the solubility of all rice varieties showed gradually increase during temperature increase from 55 °C (0.42-0.90%), until gave the highest value (6.22-10.59%) at 95 °C.



Figure 18 Solubility of rice flour (a) and rice starch (b) (PD= dry-milled Pathum Thani 1, PW=wet-milled Pathum Thani 1, RD = dry-milled RD 7, RW=wet-milled RD 7, LD=dry-milled Leuang 11, LW=wet-milled Leuang 11).

Sample	Solubility (%)					
	55 °C	65 °C	75 °C	85 °C	95 °C	
Pathum Thani 1						
dry-milled flour	$3.23\pm0.26~gh$	$3.57\pm0.52\ g$	$3.27\pm0.01 \text{gh}$	$3.89\pm0.49~fg$	$6.36\pm0.53~d$	
wet-milled flour	0.82 ± 0.081	$1.42\pm0.07\;k$	$1.92\pm0.09~j$	$1.93\pm0.12\ j$	$3.81\pm0.21~fg$	
dry-milled starch	$0.90\pm0.02l$	$1.50\pm0.18\;k$	2.82 ± 0.21 hi	$4.07\pm0.27~f$	$7.79\pm0.82\ c$	
wet-milled starch	$0.86\pm0.14l$	$1.29\pm0.37\;kl$	$1.81\pm0.05\;jk$	2.61 ± 0.16 i	$6.22\pm0.10~d$	
RD 7						
dry-milled flour	$2.13\pm0.29~j$	$2.27\pm0.14~ij$	$3.03\pm0.16\ h$	$4.26\pm0.69~ef$	$7.74\pm0.34\ c$	
wet-milled flour	$1.06\pm0.04l$	1.19 ± 0.211	$1.58\pm0.12\;k$	2.38 ± 0.05 ij	$4.12\pm0.45~e$	
dry-milled starch	$0.75\pm0.07\ lm$	$0.61\pm0.02\ m$	$2.36\pm0.03~ij$	$4.54 \pm 0.10 \text{ ef}$	$9.59\pm0.46~ab$	
wet-milled starch	$0.42\pm0.06\ m$	$0.54\pm0.06\ m$	$1.90\pm0.13~j$	$3.41\pm0.02~g$	$9.18\pm0.53\ b$	
Leuang 11						
dry-milled flour	$1.66\pm0.01\ k$	$1.89\pm0.02\ j$	$2.49\pm0.00\ i$	$4.72 \pm 0.59 \text{ e}$	$9.30\pm0.95~b$	
wet-milled flour	$1.06\pm0.03\ k$	$1.61\pm0.25\;k$	$2.34\pm0.08~ij$	2.81 ± 0.21 hi	$4.07\pm0.23\;f$	
dry-milled starch	$0.60\pm0.11~lm$	1.00 ± 0.081	$2.96\pm0.07\ h$	$4.83 \pm 0.05 \text{ e}$	10.59 ± 1.33 a	
wet-milled starch	$0.53\pm0.07\ m$	$0.74\pm0.03\ lm$	$2.16\pm0.00\ j$	$3.72\pm0.14~fg$	$8.24\pm0.65\ c$	

Table 6 Solubility of rice flour and rice starch from three rice varieties.¹

¹ Values are means of duplicate measurements \pm standard deviation. Means for each characteristics followed by the different letter within the same column are significantly different determined by ANOVA and DMRT (*p*<0.05).

However, there was the different pattern of solubility are found among the flour and starch from different rice varieties. The results showed that at the temperature below gelatinization temperature (55 and 65 °C), the solubility of Pathum Thani 1 rice flour showed higher level of solubility than those of RD 7 and Leuang 11. For in stance, at 65 °C, the solubility of Pathum Thani 1 was the highest (1.42-3.57 %), followed with RD 7 (1.19-2.27 %) and Leuang 11 (1.61-1.89 %). At the temperature of gelatinization (75°C), the solubility of rice flour from all three rice varieties were close together. But, after heated to above gelatinization temperature (85 and 95°C), the solubility Pathum Thani 1 showed significantly (p < 0.05) the lower solubility compared to those RD 7 and Leuang 11. At 95 °C, Pathum Thani 1 rice flour showed the lowest solubility (3.81-6.36 %), following with RD 7 (4.12-7.74 %) and Leuang 11 showed the highest solubility (4.07-9.30 %). The similar pattern was also found in the case of rice starch. This evident might be explained by the fact that during heating starch in excess water below gelatinization, most of soluble matter leach out from the damaged starch granule was low molecular weight amylopectin (LMWAP) followed the report of Tester and Morrison (1994). Thus, Pathum Thani 1 dry-milled rice flour, which contained the lowest amount of amylose (thus the highest amount of amylopectin) were subjected to produce the highest level of solubility, which mostly composed of LMWAP. On the other hand, after heated starch slurry to above gelatinization temperature, lipid free amylose (FAM) was leached out from the undamaged starch (Tester and Morrison, 1994). Hence, Leuang 11 dry-milled flour, which contained the highest amount of amylose (32.21%) were prone to give the highest amount of solubility, which mostly composed of both LMWAP plus FAM.

The results showed that dry-milled rice flour showed the significantly (p<0.05) higher extent in the solubility compared to wet-milled rice flour at all test temperature (55 to 95 °C). In the case of rice starch, at the temperature below gelatinization (55 to 75°C), the solubility of dry-milled rice starch are found slightly higher than those of wet-milled rice starch. However, when the temperatures were raising to above gelatinization (85 to 95 °C), dry-milled rice starch showed significantly (p<0.05) higher solubility than wet-milled starch. The effects of milling process on the solubility might possible be the influence of higher amount of starch

damage of the dry-milled rice flour than the wet-milled samples as shown in Table 3. It was possible that the substances inside starch granule i.e. amylose (AM) and low molecular weight fragments of amylopectin (LMWAP) from damaged starch granules could leach out in the higher extent compared to those of the undamaged granules particularly when the temperature was rising. The supporting data were reported by Tester and Morrison (1994). The results showed that on the hydration of wheat starch with various levels of starch damage (4.6-93.7%) in excess water at the different temperature (20, 40, 60 and 80 °C), the damaged starch gave soluble material comprising of low molecular weight fragments of amylopectin (LMWP) and a little amount of lipid-free amylose (FAM). The amount of LMWP and FAM were increased by rising of temperature and increasing of starch damage content. The amount of LMWP and FAM ranged from 0.6 to 24.5% and 0 to 2.9%, respectively at 20 °C, and from 0.6 to 41.0% and 6.7 to 8.2%, respectively at 80 °C with the starch damage content increased from 4.6 to 93.7%.

In comparison between rice flour and rice starch, rice flour showed the higher solubility than rice starch particularly below gelatinization temperature (55 to 65°C). For instance, at the temperature 65 °C, Leuang 11 rice flour showed significant (p < 0.05) higher solubility (1.89%, for dry-milled rice flour and 1.61%, for wet-milled rice flour) than those of Leuang 11 rice starch (1.00%, for dry-milled rice starch and 0.74%, for wet-milled rice starch). At gelatinization temperature (75°C), rice starch showed the non significant different of solubility compared to the parent rice flour. When rice starch were heated to above gelatinization temperature (85 and 95°C), rice starch showed higher solubility than the parent rice flour particularly at 95°C. For instance, at 95°C, Leuang 11 rice starch showed significant (p < 0.05) higher solubility (10.59%, for dry-milled rice flour and 8.24%, for wet-milled rice flour) than those of Leuang 11 rice starch (9.30%, for dry-milled rice starch and 4.07%, for wet-milled rice starch). This might be involving the influence of both damage starch and minor constituents. From the fact that, the damaged starch provided high extent amount of the solubility substances, even they were heated at below gelatinization temperature. Thus, rice flour, which contained the higher amount of starch damage would possible to yield the higher solubility compared to rice starch. After starch granules was heated to gelatinization temperature, the substantially swelling of starch granules was occurred simultaneously with the extensively leach out amylose. Amylose-lipid was existed and caused decrease of solubility of starch. Hence, rice starch, which content smaller amount of lipid were possible to exhibit the higher solubility compared to the parent rice flour.

In summary, swelling power and solubility of both rice flour and rice starch increased with the temperature increased. Dry-milled rice flour showed significantly higher degree of swelling and solubility compared to the wet-milled samples, particularly at the temperature below gelatinization temperature, while the negligible difference of swelling power and solubility was found between dry- and wet-milled rice starch samples. This might imply both starch damage and minor constituents such as protein and lipid affected to swelling power and solubility of rice flour and rice starch samples.

2.3 Pasting properties

In this experiment, pasting properties of dry- and wet-milled rice flour and rice starch from three rice varieties (Pathum Thani 1, RD 7 and Leuang 11) were observed using RVA. Typical pasting curves obtained from RVA are shown in Figure 19, and and pasting properties are summarized in Table 7. The results showed that Pathum Thani 1 showed the lowest pasting temperatures at 73.95-78.23 °C (for rice flour) and 71.60-72.43 °C (for rice starch), followed with Leuang 11, which showed the pasting temperatures at 78.38-80.18 °C (for rice flour) and 76.55-76.70 °C (for rice starch), whereas RD 7 showed the highest pasting temperatures at 78.98-82.33 °C (for rice flour) and 77.78-78.18 °C (for rice starch). All pasting temperatures determined by RVA were also coincident with DSC gelatinization temperatures as showed in Table 2. The DSC data showed that RD 7 showed the highest gelatinization temperatures (72.80-87.03 °C), following with Leuang 11 (69.73-85.77 °C) and Pathum Thani 1 (64.04-83.17 °C) exhibited the lower gelatinization temperatures.



Figure 19 RVA viscographs of dry- and wet-milled rice flour and rice starch from three rice varieties (a) Pathum Thani 1 (b) RD 7 and (c) Leuang 11.

Rice flour	Pasting Temperature	Viscosity (RVU)				
	(°C)	Peak Viscosity	Breakdown	Final Viscosity	Setback	
Pathum Thani 1						
dry-milled flour	$78.23 \pm 0.25 \text{ c}$	$338.42 \pm 1.06 \text{ c}$	151.34 ± 3.30 c	$350.25 \pm 2.72 \text{ d}$	$163.17 \pm 0.47 \ e$	
wet-milled flour	$73.95\pm0.00\ f$	363.46 ± 2.30 a	$162.08\pm1.06\ c$	$307.71 \pm 5.78 \text{ e}$	$106.34\pm5.42~g$	
dry-milled starch	$71.60\pm0.05\ g$	$353.80 \pm 0.18 \; b$	$177.63 \pm 0.29 \; b$	$248.64\pm0.39\ h$	57.66 ± 6.43 i	
wet-milled starch	$72.43\pm0.53~g$	$370.03 \pm 4.82 \text{ a}$	$186.97 \pm 6.08 \ a$	$309.20 \pm 3.00 \text{ e}$	$91.58\pm4.72\ h$	
RD 7						
dry-milled flour	82.33 ± 0.32 a	$268.22\pm0.40~fg$	$117.25 \pm 3.30 \; h$	$353.29\pm7.37~d$	$176.64 \pm 1.83 \text{ d}$	
wet-milled flour	$78.98\pm0.46\ c$	$275.71 \pm 1.56 \ ef$	$125.20\pm2.82~g$	$292.08 \pm 1.80 \; f$	$149.05 \pm 3.00 \; f$	
dry-milled starch	$77.78\pm0.21~cd$	$262.50\pm3.07~gh$	$134.42 \pm 2.12 \; f$	$253.22\pm7.60~gh$	$104.22 \pm 7.11 \text{ g}$	
wet-milled starch	$78.18\pm0.32\ c$	$281.11 \pm 5.26 \text{ e}$	$149.00\pm1.46~e$	$260.04\pm4.30\ g$	$112.62 \pm 5.01 \text{ g}$	
Leuang 11						
dry-milled flour	$80.18 \pm 1.03 \ b$	$246.46\pm1.94\ i$	42.00 ± 0.951	$455.80 \pm 0.89 \; a$	251.34 ± 1.89 a	
wet-milled flour	$78.38\pm0.56\ c$	$298.00\pm3.53~\text{d}$	$84.53\pm2.42~j$	390.11 ± 4.54 c	$214.46\pm3.00\ b$	
dry-milled starch	$76.55 \pm 0.28 \text{ e}$	$257.75 \pm 4.24 \; h$	$76.55 \pm 0.53 \; k$	$391.00 \pm 2.47 \text{ c}$	$199.84 \pm 5.42 \ c$	
wet-milled starch	$76.70 \pm 0.99 \text{ e}$	294.71 ± 1.71 d	$96.58\pm0.47~i$	$411.88 \pm 6.57 \text{ b}$	$209.46 \pm 1.94 \text{ b}$	

Table 7 Pasting properties of dry- and wet- milled rice flour and rice starch from three rice varieties.¹

¹ Values are means of duplicate measurements \pm standard deviation. Means for each characteristics followed by the different letter within the same column are significantly different determined by ANOVA and DMRT (*p*<0.05).

Peak viscosity was implied to the intensity of swelling of starch granules after they were subjected to heat in the excess amount of water (Jane *et al.*, 1999). The presented results showed that Pathum Thani 1 showed the highest peak viscosity of 338.42 – 363.46 RVU (for rice flour) and 353.80-370.03 RVU (for rice starch), followed with RD 7, which showed the peak viscosity of 268.22-275.71 RVU (for rice flour) and 262.50-281.11 RVU (for rice starch), whereas Leuang 11 showed the lowest the peak viscosity of 246.46-289.00 RVU (for rice flour) and 257.75-294.71 RVU (for rice starch).

The results showed the negative effect of amylose content in peak viscosity, Pathum Thani 1, which contained the lowest amount of amylose content (13.97-19.25 %) showed the highest peak viscosity, following with RD 7 (26.37-30.28 %), whereas Leuang 11, which showed the highest amylose content (32.21-40.09 %) exhibited the highest peak viscosity. Many researches reported the negative correlation between RVA peak viscosity and amylose content.

Noosuk *et al.* (2003) reported that the RVA peak viscosity showed negatively correlation (R^2 =0.97, p<0.05) with amylose content of rice starch. RD 6 rice starch, which contained the lowest amylose content (8.70 %), showed the highest RVA peak viscosity (4712 mPa.s) (1 RVU = 12 mPa.s), following Jasmine rice starch (25.62 % amylose) and Supanburi 1 (40.73 % amylose), which exhibited lower peak viscosity of 5277 and 3062 mPa.s, respectively. Likewise, Vandeputte *et al.* (2003) found that RVA peak viscosity of five waxy rice starch and ten non-waxy rice starch decreased with increasing of both absolute amylose (AAM) (r^2 =0.93, p<0.05) and free-lipid complexed amylose (FAM) (r^2 =0.94, p<0.05) contents increased. Following the results from our study, it possibled to say that amylopectin played an important role in the increasing degree of swelling of starch granule (consequently increasing of peak viscosity) whereas amylose hesitated it.

Breakdown was the reduction of the viscosity after starch granules undergone the highest swelling and encountered to the disintegration by shear force. The results showed that Pathum Thani 1 showed the highest breakdown of 151.34-
162.08 RVU (for rice flour) and 177.63-186.97 RVU (for rice starch), followed with RD 7, which showed breakdown of 117.25-125.20 RVU (for rice flour) and 134.42-149.00 RVU (for rice starch), whereas Leuang 11 showed the lowest breakdown of 42.00-84.53 RVU (for rice flour) and 76.55-96.58 RVU (for rice starch).

Likewise, Vandeputte *et al.* (2003b) reported that RVA breakdown five waxy rice starch and ten non-waxy rice starch decreased with the increasing of absolute amylose (AAM) and free-lipid complexed amylose (FAM) (r^2 = 0.94 and 0.94, *p*<0.05) contents. The researcher postulated that the breakdown of rice starch granules could be reduced by amylose.

During cooling of starch pastes, the leached amylose formed a three dimensional network, which embedded with starch granule remnants resulted increasing the viscosity (Lii *et al.*, 1995). Leuang 11 showed the highest final viscosity of 390.11-455.80 RVU for rice flour and 391.00-411.88 for rice starch, followed with RD 7, which showed the final viscosity of 292.08-353.29 RVU for rice flour and 253.22-260.04 RVU for rice starch, whereas Pathum Thani 1 showed the lowest final viscosity of 307.71-350.25 RVU for rice flour and 248.64-309.20 RVU for rice starch. The setback value implied the degree of recrystallization of gelatinized starch during cooling. The results showed that Leuang 11 showed the highest setback of 214.46-251.46 RVU for rice flour and 199.84-209.46 for rice starch, followed with RD 7, which showed the setback of 176.64-149.04 RVU for rice flour and 104.22-112.64 RVU for rice starch, whereas Pathum Thani 1 showed the lowest setback of 106.34-163.17 RVU for rice flour and 57.66-91.58 RVU for rice starch.

The results Indicated the positively correlation of both final viscosity and setback to amylose content. Leuang 11, which contained the higher amylose content showed the greater final viscosity and setback, followed by RD 7 and Pathum Thani 1 showed the lowest values. Vandeputte *et al.* (2003b) reported the similar results. The results showed that setback values of five waxy rice starch and ten non-waxy rice starch decreased with the increasing of absolute amylose (AAM) and free-lipid complexed amylose (FAM) contents ($r^2 = 0.80$ and 0.84, *p*<0.05, respectively). The

final viscosities were also reported as the function AAM and FAM contents, similar to final viscosity.

For the presented results, the influence of milling process on pasting temperatures was exhibited. In the case of rice flour, dry-milled rice flour from all three rice varieties showed significantly (p < 0.05) higher pasting temperatures (78.23-82.33 °C) than those of wet-milled rice flour (73.95-78.98 °C). These results agreed with gelatinization temperatures determined by DSC as shown in Table 2. Chiang and Yeh, 2002 stated that the larger particle rice flour tended to exhibit higher pasting temperature compared to the smaller particle rice flour. It took longer time for water to penetrate into the larger particles for complete swelling, which resulted in low pasting temperatures. For our presented results, dry-milled rice flour, which exhibited the coarser flour particles compared to wet-milled flour as confirmed by SEM in Figure 1-3 would showed the higher pasting temperature than wet-milled rice flour did. Moreover, higher amount of protein found in dry-milled flour might inhibit swelling of starch granule during heating. For these reason, a higher degree of heat was required for creating viscosity. In comparison, rice flour from all rice varieties and milling processes showed higher pasting temperature than those of rice starch. Dry-milled rice flour showed 4-7 °C higher pasting temperatures than dry-milled starch, whereas wet-milled rice flour showed only 1-2 °C higher pasting temperatures than those of wet-milled rice starch. There might strengthen the influence of flour particle size on the pasting properties. The greater particle size caused the higher pasting temperature.

Milling processes also showed the influences on the peak viscosity. For the rice flour samples, dry-milled rice flour from all three rice varieties showed significantly (p<0.05) lower peak viscosity (246.46-338.42 RVU) than those of wetmilled flour (275.71-363.46 RVU). As mention before, dry-milling process yielded coarser flour particle than wet-milling did. The coarser flour particles could not hydrate and swelling well compared to finer flour particles. The similar results were reported by Chen *et al.* (1999). The results showed that the dry milled (hammermilled) waxy-rice flour (TCW70 and TCSW1), which showed the largest flour particles showed the lowest peak viscosity, following with semi-dry milled flour, which showed the medium flour particle size and wet-milled (stone-milled) rice flour, which yield the finest flour particles. Nishita and Bean (1982) hypothesized that the lower of peak viscosity of rice flour was probably due to delayed swelling of granules that were embedded in the relatively large endosperm chunks of coarse flour. Beside the influence of flour particle size, the amount of starch damage was possible a cause of decreasing of peak viscosity. Dry-milled flour, which contained the higher amount of starch damage showed the lower peak viscosity than those of wet-milled rice flour, which yielded the lower amount of damaged starch. It was possible that damaged starch granules could not swell in the greater extent compared to damaged granules. Chen *et al.* (2003) reported that peak viscosity of the rice starch (TNuS19 and TCW70) was decreased by the increasing of starch damage content due to the increasing of ball-milling time.

The presented results showed that dry-milled rice flour showed significantly (p<0.05) lower breakdown (42.00-151.34 RVU) than those of wet-milled flour (84.53-162.08 RVU). The similar results were reported rice by Yoenyongbuddha and Noomhorm, (2002b). The results showed that dry-milled high amylose (Sao Hai) rice flour showed significantly lower breakdown (45.88 RVU) than those of wet-milled flour (84.92 RVU). This results might be the result of lower number of swollen granules (lower peak viscosity) of dry-milled flour. On the other hand, the higher minor constituents particularly protein might play an important role on the decrease of breakdown. Fitzgerald et al. (2003) reported that after protein were removed from rice flour samples by subjected to Protease, the breakdown was increased. The researcher stated that the denatured proteins could support the structure of the starch granules and inhibit the shear thinning nature of starch. In these presented study, dry-milled rice starch showed the similar results in higher breakdown than those of wet-milled rice starch but in the lower extent compared to the case rice flour as mention above. Moreover, the results Indicated that rice starch showed the higher breakdown than the parent rice flour. This might confirm the effect of protein to protect the starch granule from the rupture during shear force was applied. Since,

the increasing protein content from wet-milled starch < dry-milled starch <wet-milled flour < dry-milled flour showed consequently decreasing of breakdown.

Dry-milled rice flour presented significantly (p < 0.05) higher final viscosity and setback (350.25-455.80 RVU and 163.17-251.34 RVU, respectively) than those of wet-milled rice flour (307.71-390.11 RVU and 106.34-214.46, espectively). The similar results were showed by Yoenyongbuddha and Noomhorm, (2002b), particularly in the case of setback values. The results showed that dry-milled high amylose (Sao Hai) rice flour showed significantly higher (123.79 RVU) than those of wet-milled flour (62.21 RVU). The higher of final viscosity and setback of dry-milled rice flour compared to wet-milled rice flour might be the influence of lipid and protein, which retained starch granule integrity during heating and shear force were applied. After cooling, the rigid (less ruptured) starch granules were embedded in the amylose matrix to from the gel. Certainly, this condition would create higher viscosity (higher final viscosity and setback) compared to the gelation of ruptured starch granules. Thus, the flour samples, which contained the higher amount of lipid and protein, would incline to exhibit the higher final viscosity than the other that had the lower amount of lipid and protein. This hypothesis would be supported by the evident of higher final viscosity and setback of rice flour compared to rice starch sample, therefore rice flour contained significantly (p < 0.05) higher protein than rice starch. In addition, after subjected to heating and shear force, dry-milled flour and starch showed the higher solubility than those of wet-milled samples. The solubility substance composed of leaching amylose assembly with low molecular weight amylopectin (LMAP) might show the higher extent of viscosity raising after cooling due to the formation of strongly amylose matrix compared to wet-milled rice flour and starch, which provided the lower amount of solubility as shown in Figure 18 and Table 6. Thus, the dry-milled samples showed the higher final viscosity and setback over the wet-milled samples might be assumed as the influence of the higher amount of amylose (might be together with LMAP) matrix formation. The supporting data were showed by Tsai and Lii (2000). The results showed that the addition of 2% hotwater-soluble components suspension (prepared at 70, 80 and 90 °C) of three rice starch with different amylose content: TCS17 (29.7 %AM), KSS7 (28.2 %AM) and

TNu67 (19.8 %AM) into cross-linked waxy TCW70 rice starch caused the higher storage modulus (G') during cooling the starch paste from 90 to 20 °C. The researcher stated that the hot-water-soluble components of rice starch, which composed of amylose, intermediate fractions and some small molecular amylopectin, increased G' through reinforcing the elastic properties of starch gel during cooling period. Thus, from our study, it can be assumed that the higher solubility of dry-milled samples might affect on the higher final viscosity and setback compared to wet-milled samples with showed the lower solubility.

From all of results above, it can be concluded that milling process influence pasting viscosity properties in two reasons: (1) the mechanical damaged of starch granules and (2) the interaction of starch and minor substances such as protein and lipid.

3. Starch Molecular Properties of Rice Flour and Rice Starch

3.1 Starch crystallinity

The crystallinity characterization of rice flour and starch was investigated with wide-angle X-ray scanning diffractometry (WAXS). The X-ray diffraction patterns from different rice varieties are shown in Figure 20. All rice flour and rice starch showed the A-type X-ray diffraction pattern with individual peak at 2-theta at 15° and 23° and an unresolved peak at 2-theta at 17° and 18° . The slightly different was observed when compared between rice flour and rice starch. Rice starch exhibited sharper peaks at 2-theta at 15° and 23° . In addition, wet-milled samples (both flour and starch) showed sharper peaks at 2-theta at 15° and 23° compared to dry-milled samples. The unsharp peak might imply the less crystallinity between samples.



Figure 20 X-ray diffraction patterns of rice flour and rice starch from three rice varieties (a) Pathum Thani 1 (b) RD 7 and (c) Leuang 11.

Relative crystallinity (%)
$20.51 \pm 0.33 \; f$
$22.24 \pm 0.02 \text{ de}$
$23.42\pm0.76~b$
24.44 ± 0.12 a
$19.57 \pm 0.31 \text{ g}$
21.91 ± 0.27 e
$22.91\pm0.52~bcd$
$23.65\pm0.24~b$
$19.27 \pm 0.07 \ g$
$20.81 \pm 0.06 \; f$
$22.54\pm0.28~cd$
23.15 ± 0.04 bc

 Table 8 Degree of relative crystallinity (%) of rice flour and rice starch from three rice varieties.¹

¹ Values are means of duplicate measurements \pm standard deviations. Means for each characteristics followed by the different letter within the same column are significantly different determined by ANOVA and DMRT (*p*<0.05).

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The degree of relative crystallines (%) of rice flour and starch from different three rice varieties, which were calculated from the ratio of diffraction peak area and total diffraction area are presented in Table 8. The results showed that rice starch from all three rice varieties showed significantly (p<0.05) higher relative crystallinity (22.54-24.44%) than those of rice flour (19.27-22.24%) possible due to the higher purity of starch samples compared to flour samples.

The relative crystallinity values seem to increase when the amylose content of samples decreased. For instance, Pathum Thani 1, which contained the lowest amylose content (13.97-19.25% AM) showed the highest relative crystallinity of 20.51-22.24% for rice flour and 23.42-24.44% for rice starch, followed with RD 7, which showed 26.37-30.28% amylose content yielded the relative crystallinity of 19.57-21.60% for rice flour and 22.91-23.65% for rice starch, and Leuang 11, which contained the highest amylose content (32.20-40.09%) showed the lowest relative crystallinity of 19.27-20.81% for rice flour and 22.54-23.15% for rice starch. The negative correlation (r=-0.84, p<-0.01) between relative crystallinity and amylose content of rice starch was reported by Patindol and Wang (2003). The results showed that among six rice starch (Gohang, IR65, IR74, Risotto, UPLRi7 and XL6), The results showed that the proportion of amylose determined by HPSEC was negatively correlated to crystallinity (r=-0.84, p<-0.01). They stated that the intensity of X-ray diffractions was largely determined by the total of amylopectin content.

The presented results showed that dry-milled rice flour from all three rice varieties showed significantly (p < 0.05) lower relative crystallinity (19.27-20.51%) than those of wet-milled flour (20.81-22.24%). This might imply the higher degree of decreasing of starch crystallinity structure of dry-milling process compared to wetmilling process, which coincident to the higher amount of starch damage of drymilled rice flour compared to wet-milled flour as showed in Table 3. The amount of starch damage was significantly influence on relative crystallinity as reported by the previous researches. Morrison et al. (1994) showed that when the ball-milling time was increased from 0 to 8 hr, the starch damage of wheat starch was increased from 4.6 to 80.2% and the relative crystallinity was decreased from 35.5 to 8.5%. After 16 hr of ball-milling, wheat starch had 91.1 % starch damage and lost all crystallinity. Similar to the case of maize starch, when the ball-milled time was increased from 0 to 4 hr, the starch damage was increased from 1.2 to 44.1% and the relative crystallinity was decreased from 34.3 to 15.1%. The relative crystallinity was reduced to zero after maize starch was subjected to ball-milling for 8 hr. The researchers suggested that the ¹³C-Solid-state NMR spectra data showed the increasing in free hydroxyl groups

during the increasing of ball-milling time implied the disruption of starch molecule at the glycisidic linkage. Chen *et al.* (2003) reported the strongly relation between ballmilling time and the decreasing of relative cryatallinity of rice starch. The results showed that both TNUS19 and TCW70 rice starch showed significantly decreased in X-ray peak intensities after ball-milling time increased. TNuS19 starch almost lost peak intensity after 30 min and completely lost it after 60 min. However, the decreasing of relative crystallinity of our dry-milled (hammer-milled) rice starch was not severe as much as the case of ball-milled samples due to the less starch molecular disintegration as showed by the lower starch damage content compared to those of ball-milling as reported in the previous studies.

3.2 Starch molecular properties

In this study, starch molecular size distributions of total starch fractions (TSF) of rice flour and rice starch and hot-water-soluble fraction (HWSF) from rice flour were determined by size-exclusion chromatography with multi-angle laser light scattering and refractive index detection (SEC-MALLS-RI). The chromatograms of TSF and HWSF are presented in Figure 21-23. The summarized data of molecular size distribution and molecular weight of TSF and HWSF are presented in Table 9.

3.2.1 Starch molecular properties of rice flour and rice starch from the total starch fraction (TSF)

The results obtained from SEC-MALLS-RI determination of TSF of rice flour and rice starch are shown in Figure 21 and 22. The chromatograms from both rice flour and rice starch were separated into two main fractions, one eluted at the void volume at 35-45 mL (fraction I), representing the high-molecular-weight molecule (mainly amylopectin) and the other that was eluted over a wide range at 45-95 mL (fraction II), representing the low-molecular-weight or linear component (mainly amylose). The amount of both fractions (I and II) calculated as the area under peak are shown in Table 9.



Figure 21 Starch molecular size distributions (dots are molar mass, solid line is RI profile) of total starch fraction of dry- and wet-milled rice flour from three rice varieties; (a) Pathum Thani 1 (b) RD 7 and (c) Leuang 11 dry-milled (—) and wet-milled (—) rice flour.



Figure 22 Starch molecular size distributions (dots are molar mass, solid line is RI profile) of total starch fraction of dry- and wet-milled rice starch from three rice varieties; (a) Pathum Thani 1 (b) RD 7 and (c) Leuang 11 dry-milled (—) and wet-milled (—) rice starch.



Figure 23 Starch molecular size distributions (dots are molar mass, solid line is RI profile) of hot-water-soluble fraction (HWSF) of dry- and wet-milled rice flour from three rice varieties; (a) Pathum Thani 1 (b) RD 7 and (c) Leuang 11 dry-milled (—) and wet-milled (—) rice flour.

Sample	Molecular siz	ze distribution	Molecula	r weight
	(9	%)	(g/m	nol)
	Fraction I	Fraction II	Fraction I	Fraction II
Pathum Thani 1				
dry-milled flour	$66.51 \pm 0.75 \; b$	$33.49\pm0.78\ m$	$5.15 \text{ x} 10^7 \text{ abc}$	$2.86 \text{ x} 10^6 \text{ c}$
wet-milled flour	71.33 ± 0.52 a	$28.67\pm0.89\ n$	5.35 x10 ⁷ a	$2.88 \text{ x} 10^6 \text{ bc}$
dry-milled starch	$67.26\pm0.80\ b$	$32.74\pm0.89\ m$	$5.20 \text{ x} 10^7 \text{ ab}$	$2.92 \text{ x} 10^6 \text{ bc}$
wet-milled starch	70.11 ± 0.82 a	$29.89\pm0.40\ o$	$5.42 \text{ x} 10^7 \text{ a}$	$2.98 \text{ x} 10^{6} \text{ abc}$
HWSF-dry milled flour	$46.95\pm0.82\ g$	$53.05\pm0.02~gf$	$4.48 \text{ x} 10^7 \text{ cde}$	$3.33 \text{ x}10^6 \text{ ab}$
HWSF-wet milled flour	$53.47\pm0.67\ h$	$46.53\pm0.14\ i$	$4.76 \text{ x} 10^7 \text{ abcd}$	3.41 x10 ⁶ a
RD 7				
dry-milled flour	$60.90\pm0.09~d$	$39.10\pm0.52~j$	$4.60 \text{ x} 10^7 \text{ bcd}$	2.06 x10 ⁶ d
wet-milled flour	$63.68\pm0.90\ c$	$36.32\pm0.36l$	$4.85 \text{ x}10^7 \text{ abcd}$	$2.16 \text{ x} 10^6 \text{ d}$
dry-milled starch	$62.53\pm0.98~c$	$37.47\pm0.54\ k$	$4.62 \text{ x} 10^7 \text{ bcd}$	$2.10 \text{ x} 10^6 \text{ d}$
wet-milled starch	$67.07\pm0.52\ b$	$32.92\pm0.82\ m$	$5.00 \text{ x} 10^7 \text{ abcd}$	2.16 x10 ⁶ d
HWSF-dry milled flour	$39.83\pm0.89~i$	$60.17 \pm 0.89 \text{ d}$	$3.51 \text{ x} 10^7 \text{ f}$	$3.08 \text{ x} 10^6 \text{ abc}$
HWSF-wet milled flour	$47.23\pm0.74~g$	$52.77\pm0.50~g$	$3.84 \text{ x} 10^7 \text{ ef}$	$3.27 \text{ x} 10^6 \text{ abc}$
Leuang 11				
dry-milled flour	$33.67\pm0.67\ k$	$66.33\pm0.98~b$	$4.42 \text{ x} 10^7 \text{ de}$	2.08 x10 ⁶ d
wet-milled flour	$46.15\pm0.54~g$	$53.85 \pm 0.25 \; f$	$4.57 \text{ x} 10^7 \text{ bcd}$	2.11 x10 ⁶ d
dry-milled starch	$41.45\pm0.81~i$	$58.55 \pm 0.75 \text{ e}$	$4.45 \text{ x} 10^7 \text{ de}$	$2.10 \text{ x} 10^6 \text{ d}$
wet-milled starch	$50.41 \pm 0.78 \; f$	$49.59\pm0.64\ h$	$4.64 \text{ x} 10^7 \text{ bcd}$	$2.12 \text{ x} 10^6 \text{ d}$
HWSF-dry milled flour	23.88 ± 0.451	$76.12 \pm 0.98 \text{ a}$	$3.42 \text{ x} 10^7 \text{ f}$	$3.01 \text{ x} 10^6 \text{ abc}$
HWSF-wet milled flour	$35.94\pm0.94~j$	$64.06\pm0.74\ c$	$3.67 \text{ x} 10^7 \text{ f}$	$2.96 \text{ x} 10^6 \text{ bc}$

Table 9 Molecular size distribution^{1,2} and average molecular weight² from totalstarch fraction (TSF) of rice flour and rice starch and hot-water-solublefraction (HWSF) of rice flour from three rice varieties.

¹ Calculate from peak area under high-molecular-weight fraction (fraction I) and lowmolecular-weight fraction (fraction II)

² Values are means of duplicate measurements. Means for each characteristics followed by the different letter within the same column are significantly different determined by ANOVA and DMRT (p<0.05).

In considered of rice varieties, the results showed that both flour and starch from Pathum Thani 1 presented the highest proportion of high-molecularweight fraction (fraction I) of 66.51-71.33% for rice flour and 67.26-70.11% for rice starch, followed with rice flour and starch from RD7, which contained 60.90-63.68 % for rice flour and 62.53-67.07% for rice starch, whereas rice flour and starch from Leuang 11 contained the lowest proportion of fraction I of 33.67-46.15% for rice flour and 41.45-50.41% for rice starch. In reversely, rice flour and starch from Leuang 11 contained the highest proportion of fraction II of 53.85-66.33% for rice flour and 32.92-37.47% for rice starch, followed those with rice flour and starch from RD 7, which contained 36.32-39.10 % for rice flour and 32.92-37.47% for rice starch, whereas Pathum Thani 1 presented the lowest proportion of fraction II of 28.67-33.49 % for rice flour and 29.89-32.74% for rice starch. The ranking of the proportion of fraction II of rice flour and rice starch in the presented results (Leuang 11 > RD7 >Pathum Thani 1) is concomitant to the amount of amylose content shown in Table 3. Leuang 11 presented the highest amylose content of 32.21-37.40% for rice flour and 37.98-40.09% for rice starch, followed with RD 7, which contained 26.37-28.82% for rice flour and 28.27-30.28% for rice starch and Pathum Thani 1 contained the lowest amylose content of 13.97-17.16% for rice flour and 15.28-19.25% for rice starch.

However, the amylose contents calculated from peak area under low-molecular weight fraction (fraction II) (28.67-66.33 % for rice flour and 29.89-58.55% for rice starch) as presented in Table 9 were higher than the amylose contents determined by iodine-binding method (13.97-37.40 % for rice flour and 15.28-40.09 % for rice starch) as shown in Table 3. These might be the effect from an inclusion of intermediate materials (IM) within the elusion of amylose in the fraction II. The intermediate materials were found in many starches such as normal maize, oats, wheat, rye, barley, rice and potato, and notably in the high-amylose type starches i.e. maize, barley, and potato. The intermediate materials were isolated together with either the amylose or the amylopectin fraction which might influence the structural analysis of the other starch components (Eliasson, 2004). Patindol and Wang (2002) reported that three varieties of long-grain rice cultivars, Cypress, Drew and Wells, which exhibited the different apparent amylose contents (21.3-23.1%) determined by iodine-binding method contained different amount of an intermediate materials (10.9-13.5 %). The results from the starch structure determination by HPSEC showed that Drew had the lowest amylose content and lowest intermediate materials (AM 21.3%, IM 10.9%) and the reverse was found for Cypress (AM 23.1%, IM 13.5%) and Wells which contained 23.1% AM and 11.6% IM.

Milling process showed significantly influence on the proportion of fraction I and II. In comparison, dry-milled rice flour and starch from all three rice varieties showed the lower proportion of fraction I, but higher proportion of fraction II compared to wet-milled samples. The results showed that dry-milled samples from all rice varieties showed significantly (p < 0.05) lower proportion of fraction I (33.67-66.51% for rice flour and 41.45-67.26% for rice starch) compared to those of wetmilled samples (46.15-71.33% for rice flour and 50.41-70.11% for rice starch). For the fraction II, dry-milled samples from all rice varieties showed significantly (p<0.05) higher proportion of fraction II (33.49-66.33% for rice flour and 32.74-58.55% for rice starch) compared to those of wet-milled samples (28.67-53.85% for rice flour and 29.89-49.59% for rice starch). The decreasing of proportion of highmolecular-weight molecule (fraction I) coupled with the increasing of proportion of low-molecular-weight molecule (fraction II) of dry-milled samples might imply the higher degree of molecular disintegration of high-molecular-weight molecule to be the low-molecular-weight molecule resulting from dry-milling process compared to wet-milling process.

The average molecular weight (Mw) of fraction I and fraction II of three rice varieties was $4.42-5.42 \times 10^7$ g/mol and $2.06-2.98 \times 10^6$ g/mol, respectively. The results showed that Mw of both fractions I and II of rice starch ($4.45-5.42 \times 10^7$ and $2.12-2.98 \times 10^6$, respectively) were not significantly different from those of parent rice flour ($4.42-5.35 \times 10^7$ and $2.06-2.88 \times 10^6$, respectively). However, there was slightly different in Mw of fraction I and fraction II among rice varieties. The results showed that Pathum Thani 1 showed slightly higher Mw of fraction I ($5.15-5.42 \times 10^7$ g/mol) compared to RD 7 and Leuang 11, which showed Mw of fraction I ($4.42-5.00 \times 10^7$ g/mol). Similar to the case of Mw of fraction II, Pathum Thani 1 showed

slightly higher Mw of fraction II (2.86-2.98 x 10^6 g/mol) compared to RD 7 and Leuang 11, which showed Mw of fraction I (2.06-2.16 x 10^6 g/mol).

The Mw of amylopectin (fraction I) reported in our presented study $(4.42-5.42 \times 10^7 \text{ g/mol})$ are within the range of values reported by other researchers $(4.01 \times 10^7 - 56.8 \times 10^8)$. Yoo and Jane (2002) showed the significantly higher Mw of amylopectin of three rice starch (normal rice, waxy rice and sweet rice) in the range of 13.6-56.8 x 10^8 compared to our results (4.42-5.42 x 10^7). The similar results in the Mw of amylopectin presented in our study were reported by a study done by Zhong et al. (2006). The Mw of amylopectin from three rice starch: low amylose (BL-1), medium-grain (M202) and long-grain (Cocodrie, CCD) was in the range of 4.01-5.52 $x 10^7$ close to the results from our presented study. This research also found that rice starch, which contained the lowest amylose content showed the largest Mw amylopectin. BL-1, which contained the lowest amylose content of 7.48%, presented the largest Mw amylopectin of 5.52 x 10^7 , followed with 4.64 x 10^7 of M202, which showed the amylose content of 14.20%, whereas CCD, which contained the higher amylose content of 20.12%, showed the smallest Mw amylopectin of 4.01×10^7 . More recently, the Mw of amylopectin of long-grain specialty rice cultivars for canning (SRC): Bolivar, Cheniere, Dixiebelle, and L-205 and regular long-grain Well, which determined by HPSEC-MALLS-RI was reported by Patindol et al. (2007). The results showed the five rice samples showed the Mw of amylopectin in the range of $1.2-2.3 \ge 10^8 \text{ g/mol.}$

The difference of the Mw of amylopectin between our results and previous study might be attributed to the difference in system of HPSEC and methods of preparing starch dispersion (based on solvent used and preparation method). For example, in the method of Yoo and Jane (2002), which reported very large number of Mw of amylopectin, after starch was dispersed in 10% DMSO and precipitated in ethanol, the starch pellet was boiled and injected to HPSEC system immediately. But for our study, after starch was dispersed in 10% DMSO and precipitated in ethanol, the starch pellet was dried at the room temperature before it was redissolved in the boiling water. The drying step in our study might reduce the amylopectin dispersion especially the large-molecular weight amylopectin, which was likely to aggregate together during the drying step. Thus the lower average molecular weight of amylopectin was found in our study compared to those from the previous research. In addition, Zhong *et al.* (2006) found the aggregates between amylopectin and amylose and amylopectin itself upon rice dispersion preparation may cause of the difficulty in obtaining true molecular dispersion of starch molecules, which made many previously reported of the greater Mw of starch than the actual value. Moreover, the difference in the SEC system, which used in each study are possible be the cause of the difference in the presented of the average Mw of amylopectin.

The average Mw of amylose obtained from our presented study $(2.08-2.98 \times 10^{6} \text{g/mol})$ was in the range of previously reported for rice amylose (0.23-3.7 x 10^6 g/mol). The Mw of amylose (0.9-3.7 x 10^6) of eleven cultivars of Indica rice, which were 19.1-29.5 % amylose content, was reported by Ong and Blanshard (1995a). The lower Mw of amylose range of 2.3-2.9 x 10^5 of three rice from Thailand (Jasmine rice, commercial rice and Supan Buri 1 rice) was reported by Noosuk et al. (2005). Zhong et al. (2006) presented the value of Mw of amylose of three rice starch: low amylose (BL-1), medium-grain (M202) and long-grain (Cocodrie, CCD) in the range of 3.12-3.44 x 10^5 g/mol, which was close to the results from our presented study. This research also found that rice starch, which contained the lowest amylose content showed the largest Mw amylose. BL-1, which contained the lowest amylose content of 7.48%, presented the largest Mw amylose of 3.44×10^5 , followed with 3.22x 10^6 of M202, which showed the amylose content of 14.20%, whereas CCD, which contained the higher amylose content of 20.12%, showed the smallest Mw amylopectin of 3.12 x 10^6 . More recently, the reported of Patindol *et al.* (2007) showed that the Mw of amylose from of long-grain specialty rice cultivars for canning (SRC): Bolivar, Cheniere, Dixiebelle, and L-205 and regular long-grain Well were in the range of 3.5-7.5 x 10^5 g/mol. The difference of the Mw of amylose between our results and previous study again might be attributed to the difference in system of HPSEC and methods of preparing starch dispersion (based on solvent used and preparation method). The lowest Mw of amylose were presented by enzyme debranching of separated amylose fraction before SEC-MALLS measurement, where

as the enzyme debranching of the whole starch fraction before applied to SEC-MALLS showed the higher value Mw of amylose. On the other hand, without enzyme debranching before applied to SEC-MALLS caused the highest of Mw of amylose value.

For the effect of milling process on starch molecular properties, the results showed that no significantly different of Mw of both fractions I and II was found between the dry-milled sample (both rice flour and rice starch) from all three varieties compared to wet-milled samples. These might possible that the disintegration of starch molecule from dry-milling process in our presented study was undetectable by MALLS that used in the study.

3.2.2 Starch molecular properties of rice flour from hot-water-soluble fraction (HWSF)

Determination of starch molecular structure through the hot-watersoluble fraction (HWS) is the alternative method to obtain the basic information of starch fine structure and also imply some functional properties of starch (Mizukami et al., 1999). From the chromatograms of HWSF, similar to TSF, two peaks of highmolecular-weight fraction (fraction I) and low-molecular-weight fraction (fraction II) were observed as shown in Figure 23 and Table 9. Among three rice varieties, HMWF from Pathum Thani 1 presented the highest proportion of high-molecular- weight fraction (fraction I) of 46.95-53.47%, followed with those RD7, which contained 39.83-47.23% proportion of fraction I, whereas HWSF from Leuang 11 contained the lowest proportion of fraction I of 23.88-35.94%. In reversely, HWSF from Leuang 11 contained the highest proportion of fraction II of 64.76.12%, followed those from RD 7, which contained 52.77-60.17% proportion of fraction II and HWSF from Pathum Thani 1 presented the lowest proportion of fraction II of 46.53-53.05%. The higher amount of fraction I concomitant with the greater amylose content of the corresponding rice flour. Thus, Leuang 11 which contained the highest amylose content (32.21-37.40%) showed the highest proportion of fraction II, following with

those of RD 7 and Pathum Thani 1, which content the lower amylose content (26.37-28.82% and 13.97-17.16%, respectively).

When the molecular structure of HWSF was resolved, it was clear that HWSF of all rice varieties enriched with the low-molecular-weight molecule due to the high proportion of fraction II (46.53-76.12%), whereas the amount of high-molecular-weight molecule (fraction I) was restricted (23.88-53.47%). HWSF of all rice varieties exhibited the significantly (p<0.05) lower amount of fraction I (23.88-53.47%) compared to parent rice flour (33.67-71.33%) and starch (41.45-70.11%), which were investigated through TSF. On the other hand for the fraction II, HWSF of all rice varieties appeared to give the significantly (p<0.05) higher amount of fraction II (46.53-76.12%) compared to parent rice flour (28.67-66.33%) and starch (29.89-58.55%).

The average molecular weight (Mw) of fraction I and fraction II from HWSF of rice flour from three varieties were $3.42-4.76 \times 10^7$ and $2.96-3.41 \times 10^6$, respectively. The Mw of fraction I from HWSF ($3.42-4.76 \times 10^7$) was significantly (p<0.05) lower as compared to those of corresponding TSF of rice flour ($4.42-5.36 \times 10^7$) and rice starch ($4.42-5.42 \times 10^7$). On the other hand, fraction II from HWSF ($2.96-3.33 \times 10^6$) showed significantly (p<0.05) larger in Mw as compared to those of corresponding TSF of rice flour ($2.08-2.88 \times 10^6$) and rice starch ($2.10-2.98 \times 10^6$). This may imply that after heating, not only the low-molecular-weight molecule (mostly amylose) was released from the swollen starch granules, the other lowmolecular-weight molecules (might be low-molecular-weight amylopectin) were also leached out from starch granule along with amylose. Therefore, the Mw of fraction II of HWSF was found as larger than those of parent rice flour.

The similar result was reported by Ong and Blanshard (1995b). The results showed that the hot-water-soluble fraction from eleven cultivars cooked rice presented the chromatogram with content both fraction of amylose and amylopectin similar to the chromatogram obtained from whole starch fraction, but some multiple components such as long chain amylopectin was absented. This would confirm the hypothesis that the hot-water-soluble fraction was composed of both amylose and amylopectin but mainly composed of low-molecular-weight amylopectin. However, Ong and Blanshard (1995b) reported that the Mw of leached amylose from all the rice samples (3.42-7.22 x 10^5) were lower than those of native samples (0.9-3.7 x 10^6). The researchers stated that the higher molecular weight amylose might interact with other constituents in rice resulting the reduction of them leaching to the hot-water-soluble fraction. However, they presented the similar results, which showed the positively correlation between the proportion of leaching amylose content (9.4-30.5%) from HPSEC method with the amylose content of rice samples (19.1-29.5%) (r = 0.75, p < 0.01).

Similar results were found by Tsai and Lii (2000). The molecular size distribution of the hot-water-soluble fraction (HWSF) from Indica (Taichung Sen 17, TCS17 and Kaohsiung Sen 7, KSS 7), and Japonica (Tainung 67, TNu67) were investigated. The results showed that high-molecular-weight fraction (fraction I) peak of HWSF of showed λ max of 583-613 nm for TCS17, 599 nm for KSS7 and 586 – 604 nm for TNu67. This evident implied that the fraction I molecules belonging to the intermediate-fraction of amylopectin and some low-molecular amylopectin. Moreover, this research pointed out that the ratio of the low-molecular-weight fraction (fraction II) in HWSF was in proportion to the amylose content in the starch. The researchers suggested that during heating linear amylose molecules were leached out preferentially. However, the intermediate fraction and some amylopectin molecules may leach out along with amylopectin.

For the effect of milling process on starch molecular weight properties of starch in HWSF, the results showed that no significantly different of Mw of both fractions I and II was found between the dry-milled sample from all three varieties compared to wet-milled samples. This might imply that disintegration of starch molecule from dry-milling process study was not high enough to detect by MALLS that used in the study similar to the results from TSF as mention above.

4. Correlation between chemical properties, starch molecular properties and physicochemical properties of rice flour and starch.

The Pearson correlation coefficients for the relationship between chemical properties, starch molecular properties and physicochemical properties of rice flour and rice starch are presented in Table 10 and Appendix Table 2.

Amylose content determined by iodine-binding method (AM) showed the relationship with all of physicochemical properties accepted only Δ H, swelling power and solubility at 95°C. Amylose content (AM) showed significant (*p*<0.05) positive correlation with gelatinization temperature T_o, T_p, and T_c at *r* = 0.61, 0.54 and 0.41, respectively. Amylose content was negatively correlated to swelling power (SP55) (*r* = -0.46, *p*<0.05) and solubility at 55°C (S 55) (*r* = -0.45, *p*<0.05), whereas it did not show correlation with both swelling power and solubility at 95°C. The amylose content (AM) showed strongly negative correlation with RVA peak viscosity (PV) (*r* = -0.73, *p* < 0.01) and breakdown (BD) (*r* = -0.83, *p* < 0.01), while it showed the strongly positive correlation with final viscosity (FV) (*r* = 0.58, *p* < 0.01) and setback (SB) and (*r*= 0.64, *p* < 0.01).

Starch damage showed slightly but significant negative correlation with ΔH (r = -0.57, p < 0.05). Starch damage exhibited highly significant (p < 0.01) positive correlation with swelling power (SP55) (r = 0.92) and solubility at 55°C (r = 0.81), but it showed the negative correlation with swelling power at 95°C (r = -0.49, p < 0.05).

 Table 10 Correlation between chemical properties, starch molecular properties and physicochemical properties of rice flour and rice starch.

	To	T_p	T _c	ΔH	SP55	S 55	SP95	S 95	PV	BD	FV	SB
AM	0.61*	0.54	0.41*	-0.01	-0.46*	-0.45*	-0.25	0.38	-0.73**	-0.83**	0.58**	0.64**
SD	0.07	0.14	0.36	-0.57*	0.92**	0.81**	-0.49*	0.03	-0.11	-0.14	0.35	0.39
Protein	0.21	0.28	0.53**	-0.61**	0.78**	0.71**	-0.82**	-0.51*	-0.16	-0.26	0.41*	0.42*
AP_{T}	-0.31	-0.28	-0.28	0.51*	-0.01	0.04	0.49*	-0.39	0.64**	0.92**	-0.86*	-0.83*
AM_{T}	0.32	0.28	0.27	-0.51*	0.02	-0.02	-0.51*	0.40	-0.63*	-0.92**	0.82**	0.83**
MwAP _T	-0.62**	-0.60*	-0.54*	0.47*	0.03	0.04	0.38	-0.42*	0.81**	0.83**	-0.66**	-0.80**
MwAM _T	-0.87*	-0.84*	-0.74*	0.25	0.24	0.19	0.32	-0.42*	0.92	0.80**	-0.49*	-0.69*

** Correlation is significant at p < 0.01, * Correlation is significant at p < 0.05; AM=Amylose content, SD=Starch damage content, Protein=Protein content, AP_T=Proportion of amylopectin from total starch fraction, AM_T= Proportion of amylose from total starch fraction, MwAP_T=Molecular weight of amylopectin from total starch fraction, MwAM_T=Molecular weight of amylose from total starch fraction, T_o, T_p, T_c=onset, peak, conclusion gelatinization temperature, Δ H=gelatinization enthalpy, SP 55=Swelling power at 55°C, S 55=Solubility at 55°C, SP 95=Swelling power at 95°C, S 95=Solubility at 95°C, PV=Peak viscosity, BD=Breakdown, FV=Final viscosity, SB=Setback. Protein content showed positive correlation with T_c (r = 0.53, p<0.01), but showed negative correlation with ΔH (r =-0.64, p<0.01). The correlation between protein and swelling power and solubility are presented. Protein showed strongly positive correlation (p<0.01) with swelling power (r = 0.78) and solubility at 55°C and (r = 0.71), whereas it showed negative correlation with swelling power (r = -0.82, p<0.01) and solubility at 95°C (r = -0.51, p<0.05). Protein content presented the slightly but significantly (p<0.05) positive correlation with RVA final viscosity (PV) (r = 0.41) and setback (SB) (r = 0.42).

The relationships among starch molecular properties (investigated by SEC-MALLS-RI) themselves and between the other physicochemical properties are found. The proportion of amylopectin (AP_T) showed positive correlation with Δ H (r = 0.51, p<0.05). Moreover, the proportion of amylopectin (AP_T) showed positive correlation with swelling power at 95°C (r = 0.49, p<0.05). The proportion of amylopectin (AP_T) was positively correlated with RVA peak viscosity (PV) (r = 0.64, p<0.01) and breakdown (BD) (r = 0.92, p<0.01), while it showed negatively correlation with final viscosity (FV) (r = -0.86, p<0.01) and setback (SB) (r = -0.83, p<0.01). In the opposite results with the proportion of amylopectin (AP_T) showed slightly negative correlation with Δ H (r = -0.51, p<0.05). Moreover, the proportion of amylopectin (AP_T), the proportion of amylose calculated from peak area of fraction II (AM_T) showed slightly negative correlation with Δ H (r = -0.51, p<0.05). Moreover, the proportion of amylose (AM_T) showed negatively correlation with swelling power at 95°C (r = -0.51, p<0.05). The proportion of amylose (AM_T) showed negative correlation with swelling power at 95°C (r = -0.51, p<0.05). The proportion of amylose (AM_T) was negatively correlated with RVA peak viscosity (PV) (r = -0.63, p<0.01) and breakdown (BD) (r=-0.92, p<0.01), while it showed positive correlation with final viscosity (FV) (r = 0.86, p<0.01) and setback (SB) (r = -0.83, p<0.01).

The average molecular weight of amylopectin (MwAP_T) exhibited negative correlation with T_o (r = -0.62, p < 0.01), T_p (r = -0.60, p < 0.05) and T_c (r = -0.54, p < 0.05), but it showed positive correlation with Δ H (r = 0.47, p < 0.05). The average molecular weight of amylopectin (MwAP_T) showed negative correlation with solubility at 95°C (r = -0.42, p < 0.05). The average molecular weight of amylopectin (MwAP_T) was positively correlated with RVA peak viscosity (r = 0.81, p < 0.01) and breakdown (r = 0.83, p < 0.01), while it showed negative correlation with final viscosity (r = -0.66, p<0.01) and setback (r = -0.80, p<0.01). Similarly to the average molecular weight of amylopectin (MwAP_T), the average molecular weight of amylose (MwAM_T) exhibited negative correlation with T_o (r = -0.87, p<0.05), T_p (r = -0.84, p<0.05) and Tc, (r = -0.74, p<0.05), however it did not show correlation with Δ H. The average molecular weight of amylose (MwAM_T) showed negative correlation with solubility at 95°C (S 95) (r=-0.42, p<0.05). The average molecular weight of amylose (MwAM_T) was positively correlated with RVA peak viscosity (PV) (r = 0.92, p<0.01) and breakdown (BD) (r = 0.83, p<0.01), while it showed negative correlation with final viscosity (FV) (r = -0.49, p<0.01) and setback (SB) (r=-0.69, p<0.01).

In summary, the relationship among chemical properties, starch molecular properties and physicochemical properties of rice flour and rice starch are found. Amylose content, the basic chemical property of rice flour and rice starch, showed the relationship with all of physicochemical properties; gelatinization temperature, swelling and solubility at 55°C and RVA pasting viscosities. Molecular weight of amylose and amylopectin also showed the relationship with gelatinization temperature and all RVA pasting viscosities. On the other hand, the amount of starch damage, which presented the intensity of starch granule disruption of dry-milled and wet-milled samples, showed the relationship with only swelling and solubility at 55°C. Similar to protein content that showed the relationship with swelling and solubility at 55°C. In addition, the relationship between gelatinization temperature and RVA pasting viscosities were also presented.

5. Comparison of cooking properties, textural properties and sensory evaluation between dry- and wet-rice noodles.

5.1 Cooking properties of rice noodle made from dry- and wet-milled rice flour.

Cooking properties of rice noodle prepared from dry- and wet-milled rice flour based on the amount of water absorption as water absorption index (WAI) and cooking loss were compared as shown in Table 11.

Rice noodle sample	Cooking properties						
-	Water Absorption Index (%)	Cooking Loss (%)					
Pathum Thani 1							
dry-milled	277.19 ± 0.46 a	7.02 ± 0.34 a					
wet-milled	$248.28\pm0.93~b$	6.66 ± 0.33 a					
RD 7							
dry-milled	$225.57 \pm 0.12 \text{ c}$	5.87 ± 0.12 ab					
wet-milled	200.83 ± 0.43 e	$3.46\pm0.42\ c$					
Leuang 11							
dry-milled	$218.19\pm0.82~d$	$4.91\pm0.24\ b$					
wet-milled	$192.28 \pm 0.47 \; f$	$2.35\pm0.21c$					

 Table 11 Cooking properties of rice noodle prepared from dry- and wet-milled rice

 flour from three rice varieties.¹

¹ Values are means of duplicate measurements \pm standard deviations. Means for each characteristics followed by the different letter within the same column are significantly different determined by ANOVA and DMRT (*p*<0.05).

Among three rice varieties, rice noodle from Pathum Thani 1 showed significantly (p<0.05) the highest of WAI (248.28-277.19%), followed RD 7, which showed the WAI of 200.83-225.57%, whereas Leuang 11 presented the lowest of WAI (192.28-218.19%). This is coincident with the highest swelling power of Pathum Thani 1 rice flour compared to RD7 and Leuang 11 rice flour. This is possible due to the amount of amylose/amylopectin of rice flour samples. It has been known that amylopectin can swell in the higher extent during boiling compared to amylose. Therefore, Pathum Thani 1 rice flour, which contained the highest amount of amylose content of 13.97-17.16%), provided the rice noodle that showed the highest water absorption compared to the rice noodle prepared from RD 7 and Leuang 11 rice flour.

Rice noodle prepared from Pathum Thani 1 provided the highest cooking loss (6.66-7.02%), followed with those from RD 7 (3.46-5.87%), whereas Leuang 11 presented the lowest cooking loss (2.35-4.91%). This result implied that Leuang 11 rice flour may provided stronger and more resistance to loss starch gel during cooking than RD 7 and Pathum Thani 1. As known before, starch gel is composed of amylose matrix embedded with the swollen starch granule. Thus, the strength of starch gel is reported as the function of amylose content as discussed by Mestres *et al.* (1988). Thus, Leuang 11, which contained the highest amylose content, tend to show the lowest loss after cooked. In comparison, Pathum Thani 1, which contained the lowest amylose, inclined to form the weaker gel, which was easier to break and loss to the cooking water compared to rice noodle from the other two rice flour.

Due to the influence of milling process, rice noodle prepared from drymilled rice flour showed significantly (p<0.05) higher WSI (218.19-277.19%) compared to those of rice noodle prepared from wet-milled rice flour (192.28-248.24%). WSI is considered agree with the swelling properties of rice flour as shown in Figure 17. Due to the role of higher starch damage content, the noodle prepared from dry-noodle was understandable to yield the higher WSI in consequently. Moreover, the higher amount of protein retained in dry-milled flour are possible caused the higher WSI, due to the larger water absorption of protein.

Dry-milled rice noodle presented significantly (p<0.05) higher cooking loss (4.91-7.02%) compared to rice noodle prepared from wet-milled rice flour (2.35-6.66%). This is possible the role of the higher starch content of dry-milled rice flour. The similar result was reported by Yoenyongbuddhagal and Noomhorm (2002b). The results showed that rice noodle (vermicelli) prepared from high amylose (Sao Hai) dry-milled rice flour exhibited significantly higher amount of cooking loss (total) of 5.00 % compared to rice noodle prepared from wet-milled rice flour, which showed 4.40% of cooking loss. The researcher stated that this was the effect of higher imperfection of starch network of rice noodle from dry-milled flour due to the existence of starch damage. 5.2 Textural properties of rice noodle made from dry- and wet-milled rice flour.

Textural properties as the cutting force (g) and tensile strength (g) of rice noodle prepared from Pathum Thani 1, RD 7 and Leuang 11 dry- and wet-milled rice flour were reported in Table 12. The results showed that rice noodle prepared from Leuang 11 showed the greatest firmness and elasticity as presented by the highest cutting force (98.93-126.99 g) and the greatest tensile strength (30.29-40.61 g), followed with rice noodle from RD 7, which provided the cutting force of 59.50-89.53 g and tensile strength of 15.41-29.53 g. Pathum Thani 1 rice noodle presented the softest with cutting force of 38.58-70.45 g and tensile strength of 10.82-25.59g.

Rice noodle sample	Cutting Force	Tensile Strength
-	-	-
	(g)	(g)
Pathum Thani 1		
dry-milled	$38.58\pm5.84~f$	$10.82 \pm 1.59 \text{ e}$
wet-milled	$79.45 \pm 4.45 \ d$	25.59 ± 4.24 c
RD 7		
dry-milled	$59.50 \pm 5.31 \text{ e}$	15.41 ± 3.75 d
wet-milled	$89.53\pm5.06\ c$	$29.53\pm5.74~b$
Leuang 11		
dry-milled	$98.93\pm5.05~b$	$30.29\pm4.05~b$
wet-milled	126.99 ± 5.51 a	40.61 ± 5.48 a

 Table 12 Textural properties of rice noodle prepared from dry- and wet-milled rice

 flour from three rice varieties.¹

¹ Values are means of duplicate measurements \pm standard deviations. Means for each characteristics followed by the different letter within the same column are significantly different determined by ANOVA and DMRT (*p*<0.05).

Amylose content was reported as an important factor that affect rice noodle properties. Ruamchit (1979) showed that rice noodle made from Leuang Pra Tew123, RD1 and Khao500 attained the preferable quality noodle while RD5 and RD7 gave the poor quality noodle and Khao Dawk Mali105 could not be utilized in noodle production. Amylose content was reported as the major factors affecting rice noodle quality. He noted that rice varieties with high amylose (above 27%) were best suited for making noodles. Bhattacharya *et al.* (1999) reported that amylose content showed significantly positive correlation with texture attribute of cooked rice noodle as determined by texture analysis. Amylose content (11.9-25.6%) of rice flour was positively correlated with hardness (r=0.74, p<0.05), gumminess (r =0.82, p<0.05), chewiness (r = 0.74, p<0.05) and tensile strength (r=0.72, p<0.05).

The milling process was found to affect rice noodle texture as shown in this study. Rice noodle prepared from dry-milled rice flour showed significant (p<0.05) less firmness and less elasticity compared to rice noodle from wet-milled rice flour. Rice noodle from dry-milled flour showed the lower cutting force (38.58-98.93 g) and smaller tensile strength (10.82-30.29 g) than rice noodle from wet-milled rice flour, which provide higher cutting force (79.45-126.99 g) and greater tensile strength (25.59-40.61 g).

This is possible attributed to the less proportion of flour and water (32-35% db flour) used to prepared the dry-milled rice noodle compared to the case of rice noodle prepared from wet-milled flour that used 40% db flour. Effect of amount of starch concentration on the properties of starch gel was reported by Lii *et al.* (1995). The results showed the linear relationship (r^2 >0.94-0.98) between rice starch concentrations (5-30%) with G'of starch gel. They stated that during heating, the increasing of volume of swollen granules made a close pack system and had a positive effect on the increasing of G'. Moreover, the higher amount of starch damage may decrease the strength of starch gel resulted the fluffy texture of dry-milled rice noodle compared to wetmilled rice noodle. The similar result was reported by Tungtrakul (1997). Rice noodle prepared from dry-milled rice flour from three different rice varieties (imported rice, Taheng and Sao Hai) showed softer texture compared to rice noodle prepared from wet-milled flour. Rice noodle from wet-milled flour showed higher hardness of 7.32-12.7x10⁴dyn/cm² and greater tensile strength of 4.22-6.74x10⁴dyn/cm² compared to rice noodle from dry-milled flour, which showed lower hardness of 6.61-11.674 x10⁴dyn/cm² and smaller tensile strength 4.07-6.1174x10⁴dyn/cm². Likewise the report by Yoenyongbuddhagal and Noomhorm (2002b), rice noodle prepared from wet-milled (Sao Hai) rice flour showed the firmer texture with the greater hardness (489.24 g) compared to the lower hardness of rice noodle from dry-milled rice flour showed the firmer texture of wet-milled rice flour (362.90 g). The researchers stated that the firmer texture of wet-milled rice noodle was attributed to the lower amount of starch damage.

5.3 Sensory evaluation

The sensory attributed of rice noodle prepared from dry- and wet-milled rice flour were established and evaluated by 10 trained panelists. Perceived intensities were scored on a 15-cm-interval scale using qualitative data analysis (QDA). Acceptance for each perceived intensity and overall acceptance were also evaluated using a 1 to 9 hedonic scale. The sensory evaluation data was presented in Table 13.

Rice noodle	QDA (15 cm scale) Hedonic (1-9 scale)								
sample	Turbidity	Firmness	Elasticity	Adhesiveness	Turbidity	Firmness	Elasticity	Adhesiveness	Overall
									acceptance
Pathum Thani 1	-								
dry-milled	12.30±1.15a	3.17±0.84e	2.64±0.68e	11.54±1.56a	4.50±1.96 c	2.70±1.42b	2.70±0.85d	2.90±0.86e	2.90±0.75e
wet-milled	10.87±0.41bc	4.16±0.70e	3.82±0.42d	10.15±1.18b	5.20±1.50bc	3.50±1.33b	3.40±0.92c	3.60±1.56d	4.10±0.85d
RD 7									
dry-milled	11.74±1.02ab	6.09±0.44d	5.31±0.47c	9.43±1.64b	5.30±1.50bc	4.00±1.01b	4.60±0.90b	4.10±1.50cd	5.30±1.10c
wet-milled	9.52±0.53d	7.13±1.45c	8.34±0.63b	9.08±1.96b	6.50±1.08ab	5.80±1.50ab	5.70±1.50ab	5.30±1.20bc	6.10±1.75b
Leuang 11									
dry-milled	9.35±1.53d	7.65±1.47c	8.10±1.05b	5.87±0.88c	6.76±1.41ab	6.40±1.42a	5.90±1.50ab	6.20±0.92ab	6.40±1.05ab
wet-milled	9.31±0.53d	8.69±1.01b	9.97±0.91a	5.46±0.96c	7.40±1.01a	7.00±1.36a	6.90±1.32a	7.00±1.20a	7.10±1.20a
Commercial	10.61±0.90c	10.03±0.06a	10.29±0.94a	5.81±0.73c	7.40±1.07a	6.80±1.50a	7.20±0.90a	7.00±1.45a	7.20±1.23a

Table 13 Sensory evaluation of rice noodle prepared from dry- and wet-milled rice flour from three rice varieties.¹

¹ Results are expressed as an average of the obtain sensory scores evaluated by 10 trained panelists. Means for each characteristics followed by the different letter within the same column are significantly different determined by ANOVA and DMRT (p<0.05).

The result from QDA determination showed that among rice noodle from three rice varieties, rice noodle made from Leuang 11 gave the lowest turbidity and adhesiveness, but the highest firmness and elasticity compared to rice noodle made from RD 7 and Pathum Thani 1. Leuang 11 rice noodle give the clearer appearance with lower turbidity (9.31-9.35), followed with RD 7 rice noodle (9.52-11.74) and Pathum Thani 1 rice noodle (10.87-12.30). Leuang 11 rice noodle provide the firmer texture with the higher firmness (7.65-8.69), followed with RD 7 rice noodle (6.09-7.13) and Pathum Thani 1 rice noodle (3.17-4.16). Again, Leuang 11 rice noodle exhibited the higher elasticity texture (8.10-9.97), followed with RD 7 rice noodle (5.31-8.34) and Pathum Thani 1 rice noodle (2.62-3.82). In the term of adhesiveness, Leuang 11 rice noodle presented the lowest adhesiveness (5.46-5.87), followed with those of RD 7 rice noodle (9.08-9.43) and those of Pathum Thani 1 rice noodle (11.15-11.54). Moreover, when compared to the commercial rice noodle, Leuang 11 rice noodle showed the closest characteristic with the commercial rice noodle than rice noodle made from the other two rice varieties. This implied that among three rice varieties used in this study, Leuang 11 is the most suitable for rice noodle production when compared to the commercial product.

The milling process showed the significantly effect on the intensively of some sensory characteristics. There are the significantly difference of turbidity between dry-milled and wet-milled rice noodles from both RD 7 and Pathum Thani 1, whereas, rice noodle made from dry- and wet-milled Leuang 11 showed non significantly difference in this attribute. About the textural attributes, dry-milled rice noodle from all three rice varieties showed significantly (p<0.05) lower of firmness and elasticity compared to wet-milled rice noodle in the same rice varieties. Whereas, there were no significant different found between adhesiveness of dry-milled rice noodle and wet-milled rice noodle in the same rice varieties. It can be stated that effect of using different rice flour from difference milling processes (dry- and wet-milled rice flour) are predominant on the textural attribute of rice noodle.

Among the six rice noodles prepared in this study, we found that rice noodle made from dry-milled Leuang and wet-milled RD 7 rice flour showed the closer of sensory characteristics with rice noodle made from wet-milled Leuang 11 compared to rice noodle from dry-milled RD 7 rice flour and rice noodle made from both dry- and wet-milled Pathum Thani 1. However, the presented results showed that Leuang 11 rice noodle, particularly wet-milled Leuang 11 rice noodle presented non significantly different characteristic compared to commercial product in firmness, elasticity and adhesiveness, except only turbidity.

From the acceptance data (1-9 hedonic scale), among rice noodle from three rice varieties, rice noodle from Leuang 11 rice flour showed the highest acceptance score in all attributes (turbidity, firmness, elasticity and adhesiveness) including overall acceptance, followed with rice noodle from RD 7, whereas rice noodle from Pathum Thani 1 showed the lowest acceptance score in all attributes. Rice noodle from Pathum Thani 1 showed dislike slightly to dislike very much for turbidity (4.50-5.20), firmness (2.70-3.50), elasticity (2.70-3.40), adhesiveness (2.90-3.60) and overall acceptance (2.90-4.10). Whereas rice noodle from Leuang 11 showed like slightly to like moderately for turbidity (6.76-7.40), firmness (6.40-7.00), elasticity (5.90-6.90), adhesiveness (6.20-7.00) and overall acceptance (6.40-7.10). Moreover, rice noodle from Leuang 11 showed none significantly difference in all attributes compared to commercial rice noodle, which presented like slightly to like moderately for turbidity (7.40), firmness (6.80), elasticity (7.20), adhesiveness (7.00) and overall acceptance (7.20).

The acceptance in the sensory attributes and overall acceptance of rice noodle produced from dry- and wet-milled rice flour was compared. The results showed that rice noodle from dry-milled rice flour from all three rice varieties give non significantly different of acceptance in turbidity and firmness compared to rice noodle from wet-milled flour. For the acceptance of elasticity, rice noodle from wetmilled Pathum Thani 1 rice flour showed the significantly higher acceptance score (3.40) compared to rice noodle from dry-milled flour (2.70), where as rice noodle from dry-milled flour from RD 7 and Leuang 11 showed non significantly difference in elasticity compared to rice noodle from wet-milled rice flour of the same rice varieties. Similar to the acceptance of elasticity, wet-milled Pathum Thani 1 rice flour showed significantly higher acceptance in adhesiveness (2.90) compared to rice noodle from dry-milled flour (3.60), whereas rice noodle from dry-milled flour from RD 7 and Leuang 11 showed non significantly difference in adhesiveness compared to rice noodle from wet-milled rice flour of the same rice varieties. The results showed that using of dry-milled rice flour to produce rice noodle presented the lower overall acceptance compared to using of wet-milled flour found in case of Pathum Thani 1 and RD 7 rice noodle. However, non significant difference of overall acceptance was found between using of dry- or wet-milled flour to prepared rice noodle in the case of Leuang 11.

Among the six rice noodles prepared in this study, we found that Leuang 11 rice noodle, both made from dry- and wet-milled Leuang 11 rice flour presented non significant different acceptance (turbidity, firmness, elasticity and adhesiveness), including overall acceptance compared to commercial product. From the results, it is possible that we can prepared rice noodle from both of dry- and wet-milled Leuang 11 rice flour, which could provide the similar sensory characteristics to the commercial rice noodles.

6. Correlation between rice noodle properties and chemical properties, starch molecular properties and physicochemical properties of rice flour.

6.1 Correlation between rice noodle properties and chemical properties and starch molecular properties of rice flour.

The Pearson correlation coefficients between rice noodle properties and chemical properties and starch molecular properties of rice flour are presented in Table 14.

	AM	Protein	SD	AP _T	AM_T	MwAP _T	MwAM _T	AP_{H}	AM_{H}	$MwAP_{H}$	MwAM _H
WAI	-0.93**	0.01	0.55	0.52	-0.53	0.65*	0.83**	0.42	-0.42	0.63*	0.45
Loss	-0.87**	0.07	0.67*	0.52	-0.48	0.55	0.70*	0.39	-0.37	0.45	0.47
Cutting	0.77**	-0.28	-0.50	-0.62*	0.56	-0.51	-0.54	-0.49	0.44	-0.27	-0.51
Tensile	0.85**	-0.42	-0.64*	-0.61*	0.61*	-0.48	-0.53	-0.44	0.43	-0.39	-0.39
Turb Q	-0.60*	0.21	0.74*	0.11	-0.11	0.24	0.47	-0.04	0.06	0.24	0.16
Firm Q	0.96*	-0.01	-0.42	-0.79**	0.80**	-0,76*	-0.75**	-0.69*	0.65*	-0.64*	-0.52
Elast Q	0.78**	-0.27	-0.68*	-0.42	0.42	-0.41	-0.59*	-0.25	0.24	-0.38	-0.29
Adh Q	-0.88**	0.09	0.29	0.76**	-0.75**	0.72*	0.72**	0.68*	-0.63*	0.51	0.57
Turb A	0.88**	-0.19	-0.55	-0.65*	0.65*	-0.60*	-0.60*	-0.45	0.47	-0.55	-0.52
Firm A	0.92**	-0.11	-0.36	-0.85*	0.82**	-0.74**	-0.68*	-0.71**	0.68*	-0.58	-0.58*
Elast A	0.89**	-0.19	-0.43	-0.78**	0.77**	-0.69*	-0.59*	-0.63*	0.58*	-0.55	-0.51
Adh A	0.84**	-0.32	-0.45	-0.76**	0.76**	-0.60*	-0.52	-0.58*	0.55	-0.46	-0.48
Overall A	0.91**	-0.24	-0.46	-0.77**	0.76**	-0.66*	-0.62*	-0.61*	0.58*	-0.54	-0.49

Table 14 Correlation between rice noodle properties and some chemical properties and starch molecular properties of rice flour.

** Correlation is significant at p < 0.01, * Correlation is significant at p < 0.05; AM=Amylose content, Protein=Protein content, SD=Starch damage content, AP_T=Proportion of amylopectin from total starch fraction, AM_T= Proportion of amylose from total starch fraction, MwAP_T=Molecular weight of amylopectin from total starch fraction, MwAM_T=Molecular weight of amylose from total starch fraction, AP_H=Proportion of amylopectin from hot-water-soluble fraction, AM_H= Proportion of amylose from hot-water-soluble fraction, MwAP_H=Molecular weight of amylopectin from hot-water-soluble fraction, MwAM_H=Molecular weight of amylose from hot-water-soluble fraction, WAI=Water absorption index, Loss=Cooking loss, Cutting=Cutting force, Tensile=Tensile strength, Turb Q=QDA turbidity, Firm Q=QDA firmness, Elast Q=ODA elasticity, Adh Q=QDA adhesiveness, Turb A= Turbidity acceptance, Firm A=Firmness acceptance, Elast A=Elasticity acceptance, Adh A=Adhesiveness acceptance,Overall A=Overall acceptance Water absorption index (WAI) of rice noodle showed strongly negative correlation with amylose content determined by iodine-binding method (AM) (r = -0.93, p<0.01), whereas it showed positive correlation with both average molecular weight of amylopectin (MwAP_T) (r = 0.65, p<0.05) and amylose (MwAM_T) (r = 0.83, p<0.01) from total starch fraction determined by SEC-MALLS-RI and average molecular weight of amylose from hot-water-soluble fraction determined by SEC-MALLS-RI (MwAM_H), (r = 0.63, p<0.01). Cooking loss of rice noodle showed strongly negative correlation with amylose content (AM) (r = -0.87, p<0.01). Cooking loss was observed to be significantly correlated with starch damage content (SD) (r = 0.67, p<0.01). The cooking loss exhibited positive correlation with average molecular weight of amylose (MwAM_T) from total starch fraction determined by SEC-MALLS-RI (r = 0.70, p<0.05).

Cutting force determined by Texture Analyser, which implied the firmness of rice noodle, showed positive correlation with amylose content (AM) (r = 0.77, p < 0.01). On the other hand, it exhibited negative correlation with the proportion of amylopectin calculated from peak area of fraction I from total starch fraction (AP_T) determined by SEC-MALLS-RI (r = -0.62, p < 0.05). Tensile strength, which Indicated the elasticity of rice noodle products, showed strongly positive correlation with amylose content (AM) (r = 0.85, p < 0.01). Tensile strength was negatively related to starch damaged content (SD) (r = -0.64, p < 0.05). A negative correlation between tensile strength (r = -0.61, p < 0.05) and proportion of amylopectin (AP_T) calculated from peak area of fraction I from total starch fraction between tensile strength (r = 0.61, p < 0.05) and proportion of amylopectin (AM_T) calculated from peak area of fraction I and (r = -0.61, p < 0.05) was presented.

The relationship between intensity of rice noodle sensory attributes determined by QDA and chemical properties, starch molecular properties were found. Turbidity of rice noodle strand evaluated by QDA (Turb Q) was showed negative correlation with amylose content (AM) (r = -0.60, p < 0.05). On the other hand, the

positive correlation between turbidity evaluated by QDA and starch damage content (r = 0.74, p < 0.05) was found.

Firmness of rice noodle strand evaluated by QDA (Firm Q) was showed strongly positive correlation with amylose content (AM) (r = 0.96, p < 0.05). The molecular properties determined from both total starch fraction and hot-water-soluble fraction showed significantly correlation with firmness evaluated by QDA. Firmness showed positive correlation with proportion of amylose from total starch fraction (AM_T) (r = 0.80, p < 0.01), whereas it showed negative correlation with proportion of amylopectin (AP_T) (r = -0.79, p < 0.01), average molecular weight of amylopectin (MwAP_T) (r = -0.76, p < 0.05) and molecular weight of amylose (MwAM_T) (r = -0.75, p < 0.01). The correlation between firmness and starch molecular structure from hotwater-soluble fraction were also present. Firmness showed positive correlation with proportion of amylose (AM_H) (r = 0.65, p < 0.05), while it presented negative correlation with proportion of amylopectin (AP_H) (r = -0.69, p < 0.05) and average molecular weight of amylopectin (MwAP_H) (r = -0.64, p < 0.05).

The intensity of elasticity determined by QDA (Elast Q) was positively correlated with amylose content (AM) (r = 0.78, p < 0.01), while it showed negative correlation with starch damage content (SD) (r = -0.68, p < 0.05) and average molecular weight of amylose from total starch fraction (MwAM_T) (r = -0.59, p < 0.05). Adhesiveness determined by QDA (Adh Q), which presented the surface stickiness between rice noodle strands, was negatively correlation with amylose content (AM) (r = -0.88, p < 0.01) similar to proportion of amylose from total starch fraction (AM_T) (r = -0.75, p < 0.01). The results showed that adhesiveness showed positive correlation with proportion of amylopectin from total starch fraction (AP_T) (r = 0.76, p < 0.01) and average molecular weight of both amylopectin (MwAP_T) (r = 0.72, p < 0.05) and amylose (MWAM_T) from total starch fraction (r = 0.72, p < 0.01). Adhesiveness showed positive correlation with proportion of amylopectin from total starch fraction (AP_H) (r = 0.68, p < 0.05), but it presented negative correlation with proportion of amylopectin from hot-water-soluble fraction (AP_H) (r = 0.68, p < 0.05), but it presented negative correlation with proportion of amylopectin from hot-water-soluble fraction (AP_H) (r = 0.68, p < 0.05), but it presented negative correlation with proportion of amylopectin from hot-water-soluble fraction (AP_H) (r = 0.68, p < 0.05), but it presented negative correlation with proportion of amylopectin from hot-water-soluble fraction (AM_H) (r = 0.63, p < 0.05).
The correction between acceptance of rice noodle determined by 1-9 point hedonic scale and some chemical and starch molecular structure are presented. The results showed that the acceptance in turbidity of rice noodle (Turb A) was positively correlation with amylose content (AM) (r = 0.88, p < 0.01), similar to the proportion of amylose from total starch fraction (AM_T) (r = 0.65, p < 0.05). The results showed that the acceptance in turbidity showed negative correlation with proportion of amylopectin from total starch fraction (AP_T) (r = -0.65, p < 0.05) and average molecular weight of both amylopectin (MwAP_T) (r = -0.60, p < 0.05) and amylose (MWAM_T) from total starch fraction and (r = -0.60, p < 0.05). According to the presented results, the acceptance in firmness of rice noodle (Firm A) was strongly positively correlation with amylose content (AM) (r = 0.92, p < 0.01), similar to proportion of amylose from total starch fraction (AM_T) (r=0.82, p<0.01). The results showed that the acceptance in firmness showed negative correlation with proportion of amylopectin from total starch fraction (AP_T) (r = -0.85, p < 0.05) and average molecular weight of both amylopectin (MwAP_T) (r = -0.74, p < 0.05) and amylose (MWAM_T) from total starch fraction (r = -0.68, p < 0.05).

The acceptance in firmness showed negative correlation with proportion of amylopectin from hot-water-soluble fraction (AP_H) (r = -0.71, p<0.01), but it presented positive correlation with proportion of amylose from hot-water-soluble fraction (AM_H) (r = 0.68, p<0.05). The negative correlation between the acceptance in firmness and average molecular weight of amylose from hot-water-soluble fraction (MwAP_H) (r = -0.58, p<0.05) was also exhibited.

The acceptance in elasticity of rice noodle (Elast A) showed strongly positively correlation with amylose content (AM) (r = 0.89, p < 0.01), similar to proportion of amylose from total starch fraction (AM_T) (r = 0.77, p < 0.01). The presented results showed that the acceptance in elasticity showed negative correlation with proportion of amylopectin from total starch fraction (AP_T) (r = -0.78, p < 0.01) and average molecular weight of both amylopectin (MwAP_T) (r = -0.69, p < 0.05) and amylose (MWAM_T) from total starch fraction (r = -0.69, p < 0.05). The acceptance in elasticity showed negative correlation with proportion of amylopectin from hot-watersoluble fraction (AP_H) (r = -0.63, p < 0.05). On the other hand, it presented positive correlation with proportion of amylose from hot-water-soluble fraction (AM_H) (r = 0.58, p < 0.05).

The results showed that the acceptance in adhesiveness of rice noodle (Adh A) showed strongly positively correlation with amylose content (AM) (r = 0.84, p<0.01), similar to proportion of amylose from total starch fraction (AM_T) (r = 0.76, p<0.01). The acceptance in adhesiveness showed negative correlation with proportion of amylopectin from total starch fraction (AP_T) (r = -0.76, p<0.01) and average molecular weight of amylopectin from total starch fraction (MwAP_T) (r = -0.60, p<0.05), but not correlated to average molecular weight amylose from total starch fraction (MWAM_T). The acceptance in elasticity showed negative correlation with proportion of amylopectin from hot-water-soluble fraction (AP_H) (r = -0.58, p<0.05), but not correlated with amylose content from hot-water-soluble fraction (AM_H).

The overall acceptance of rice noodle (Overall A) was correlated with many starch molecular aspects. The results showed that the overall acceptance of rice noodle showed strongly positively correlation with amylose content (AM) (r = 0.91, p<0.01) similar to the proportion of amylose from total starch fraction (AM_T) (r = 0.76, p<0.01). The presented results showed that the overall acceptance showed negative correlation with proportion of amylopectin from total starch fraction (AP_T) (r = -0.77, p<0.01) and average molecular weight of both amylopectin (MwAP_T) (r = -0.66, p<0.05) and amylose (MWAM_T) from total starch fraction (r = -0.62, p<0.05). The overall acceptance presented negative correlation with proportion of amylopectin multiple fraction (AP_H) (r = -0.61, p<0.05), but it showed positive correlation with proportion of amylose from hot-water-soluble fraction (AM_H) (r = 0.58, p<0.05).

It could be summarized that rice noodle quality both cooking properties (water adsorption index and cooking loss) and textural properties (firmness and tensile strength) were strongly correlated with amount of amylose content, where as some properties were attributed to starch damage content. Both the intensity of product characters investigated by QDA (turbidity, firmness, elasticity and adhesiveness) and the acceptance of rice noodle were also strongly correlated with amylose content and starch molecular structure from both total starch fraction and hot-water-soluble fraction determine by SEC-MALLS-RI.

Similar to the study of Bhattacharya *et al.* (1999), amylose content was presented as significantly factor which affected to extruded rice noodle. Textural properties of extruded rice noodle made from 11 rice flour samples, which contained 11.9-25.6% amylose content, showed positive correlation with amylose content of rice flour. Hardness (r= 0.74), gumminess (r= 0.82), chewiness (r= 0.74) and tensile strength (r= 0.72.) determined by texture profile analysis TPA measurement were significant (p <0.05) positively related to amylose content.

6.3 Correlation between rice noodle properties and physicochemical properties of rice flour.

The relationship between rice noodle properties and physicochemical properties of rice flour was investigated and summarized in Table 15.

The results showed that water absorption index (WAI) was negatively correlated to T_o (r = -0.63, p<0.05). WAI showed positive correlation with swelling power at both 55°C (SP55) (r = 0.82, p<0.01) and 95°C (SP95) (r = 0.60, p<0.05), while it showed negative correlation with solubility at 55°C (S 55) (r = -0.67, p<0.05). WAI was correlated to RVA peak viscosity (PV) (r = 0.65, p<0.05), and breakdown (BD) (r=0.61, p<0.05). Cooking loss was not significantly correlated with gelatinization properties (T_o, T_p, T_c and Δ H), but it present positive correlation with swelling power at 55°C (SP55) (r = 0.81, p<0.01).

	To	T _p	T _c	ΔH	SP55	S 55	SP95	S 95	PV	BD	FV	SB
WAI	-0.63*	-0.57	-0.48	-0.29	0.82**	-0.67*	0.60*	-0.10	0.65*	0.61*	-0.19	-0.28
Loss	-0.45	-0.41	-0.23	-0.16	0.81**	0.57	0.50	0.14	0.50	0.53	-0.17	-0.19
Cutting	0.15	0.09	0.03	0.30	-0.68*	-0.66*	-0.60*	0.06	-0.26	-0.58*	0.40	0.20
Tensile	0.16	0.08	0.01	0.33	-0.81**	-0.77**	-0.50	-0.12	-0.33	-0.62*	0.35	0.17
Turb Q	-0.39	-0.34	-0.22	-0.38	0.83**	0.61*	0.12	0.45	0.36	0.17	0.27	0.16
Firm Q	0.45	0.41	0.26	-0.06	-0.62*	-0.45	-0.71*	0.14	-0.62*	-0.82**	0.55	0.50
Elast Q	0.38	0.31	0.22	0.31	-0.84*	-0.71**	-0.36	-0.24	-0.47	-0.47	0.05	0.07
Adh Q	-0.38	-0.32	-0.29	-0.17	0.59*	0.57	0.81**	-0.29	0.52	0.78**	-0.58*	-0.48
Turb A	0.28	0.23	0.11	0.20	-0.72**	-0.59*	-0.47	-0.04	-0.41	-0.64*	0.39	0.27
Firm A	0.32	0.26	0.17	0.01	-0.58	-0.51	-0.67*	0.21	-0.53	-0.83**	0.62*	0.49
Elast A	0.24	0.19	0.07	0.03	-0.61*	-0.51	-0.57	0.08	-0.45	-0.77**	0.57	0.41
Adh A	0.12	0.07	-0.03	0.10	-0.62*	-0.56	-0.55	0.02	-0.35	-0.74**	0.57	0.35
Overall A	0.27	0.21	0.13	0.14	-0.67*	-0.63*	-0.60*	0.09	-0.48	-0.77**	0.52	0.38

 Table 15
 Correlation between rice noodle properties and some physical properties of rice flour.

** Correlation is significant at p < 0.01, * Correlation is significant at p < 0.05; T_o, T_p, T_c=onset, peak, conclusion gelatinization temperature, Δ H=gelatinization enthalpy, SP 55=Swelling power at 55°C, S 55=Solubility at 55°C, SP 95=Swelling power at 95°C, S 95=Solubility at 95°C, PV=Peak viscosity, BD=Breakdown, FV=Final viscosity, SB=Setback, WAI=Water absorption index, Loss=Cooking loss, Cutting=Cutting force, Tensile=Tensile strength, Turb Q=QDA turbidity, Firm Q=QDA firmness, Elast Q=ODA elasticity, Adh Q=QDA adhesiveness, Turb A= Turbidity acceptance, Firm A=Firmness acceptance, Elast A=Elasticity acceptance, Adh A=Adhesiveness acceptance, Overall A=Overall acceptance

The relationship between textural properties of rice noodle and physicochemical properties of rice flour was determined. Firmness of rice noodle, which Indicated by cutting force was negatively correlated with swelling power at both 55°C (SP55) (r = -0.68, p < 0.05) and 95°C (SP95) (r=-0.60, p < 0.05) and solubility at 55°C (S 55) (r = -0.66, p < 0.05). The cutting force also showed negative correlation with RVA breakdown (BD) (r = -0.58, p < 0.05). Similarly to cutting force, tensile strength of rice noodle strand showed negative correlation with swelling power at both 55°C (SP55) (r = -0.81, p < 0.01) and 95°C (SP95) and (r = -0.77, p < 0.01) and RVA breakdown (BD) (r = -0.62, p < 0.05).

The relationship between intensity of rice noodle sensory attributes determined by QDA and some physicochemical properties were found. The intensity in turbidity of rice noodle evaluated by QDA (Turb Q) was positively correlated with swelling power at 55 °C (SP55) (r = 0.83, p < 0.01) and solubility at 55 °C (S 55) (r =0.61, p<0.05). No correlation between turbidity (Turb Q) and gelatinization and RVA pasting viscosity was found. Like the firmness determined by texture analyzer as presented by cutting force, the firmness determine by QDA showed negative correlation with swelling power at 55°C (SP55) (r = -0.62, p < 0.05), swelling power at 95° C (SP95) (r =-0.95, p<0.05). Moreover, the firmness of rice noodle was negatively correlated both RVA peak viscosity (PV) (r = -0.62, p < 0.05) and breakdown (BD) (r = -0.95, p < 0.01). Similarly to the elasticity determine by texture analyzer as shown by tensile strength, the elasticity determined by QDA showed negative correlation with swelling power at both 55°C (SP55) (r = -0.84, p < 0.05) and 95°C (SP95) (r =-0.71, p < 0.01). Adhesiveness of rice noodle was positively correlation with swelling power at both 55°C (SP55) (r = 0.59, p < 0.05) and 95°C (SP95) (r = -0.81, p < 0.01). In addition it showed negative correlation with RVA breakdown (BD) (r = 0.78, p < 0.01), but exhibited negative correlation with final viscosity (FV) (r = 0.58, *p*<0.05).

The correction between acceptances of rice noodle determined by 1-9 point hedonic scale and some physicochemical were found. The acceptance in turbidity of rice noodle showed negative correlation with swelling power at 55°C

(SP55) (r = -0.72, p < 0.01) and solubility at 55°C (S 55) (r = -0.59, p < 0.05). Moreover, it showed negative correlation with RVA breakdown (BD) (r = -0.64, p < 0.05). The acceptance in firmness of rice noodle showed negative correlation with swelling power at 95°C (SP95) (r = -0.67, p < 0.05). The results showed that the acceptance in firmness showed negative correlation with RVA breakdown (BD) (r =-0.83, p < 0.01), while it presented positive correlation with final viscosity (FV) (r = 0.62, p < 0.05). The acceptance in elasticity of rice noodle showed negative correlation with swelling power at 55°C (SP55) (r = -0.61, p < 0.05). Moreover it presented strongly negative correlation with RVA breakdown (BD) (r = -0.77, p < 0.01). Like the acceptance in elasticity, the acceptance in adhesiveness of rice noodle showed negative correlation with swelling power at 55°C (SP55) (r = -0.62, p < 0.05) and RVA breakdown (BD) (r = -0.74, p < 0.01). The overall acceptance of rice noodle showed negative correlation with swelling power at both 55°C (SP55) (r =-0.67, p < 0.05) and 95°C (SP95) (r = -0.60, p < 0.05) and solubility at 55°C (S 55) (r =-0.63, p < 0.05). The cutting force also showed negative correlation with RVA breakdown (BD) (r = -0.77, p < 0.01).

It can be summarized from the presented results that rice noodle properties were related to some physicochemical properties of rice flour. The results showed that, except for WAI, there was not correlation between rice noodle properties and gelatinization properties. On the other hand, the swelling power at 55°C showed correlation with all of rice noodle properties, except only the acceptance in firmness of rice noodle. The swelling power at 55°C was positively correlated with WAI, cooking loss and turbidity and adhesiveness determined by QDA, whereas it presented negative correlation with cutting force, tensile strength, firmness and elasticity determined by QDA and the acceptance of turbidity, elasticity, adhesiveness and overall acceptance. For the pasting properties, breakdown was related to the almost rice noodle properties, except only cooking loss, turbidity and elasticity determined by QDA. Similar to the swelling at 55°C, RVA breakdown showed positive correlation with WAI and adhesiveness determined by QDA, while it presented the negative correlation with textural properties (cutting force and tensile strength), rice noodle characteristics from both QDA determination and the acceptance test. This was possible that we might predict rice noodle properties from the value of swelling power at 55° C and breakdown determined by RVA.

Similar to the previous research done by Bhattacharya et al. (1999), swelling power and some pasting properties determined by RVA were related to extruded rice noodle properties particularly textural properties determined by texture profile analysis. The results showed that all textural properties (hardness, springiness and gumminess) of eleven extruded rice noodles showed a significantly negative relation with the swelling power. The hardness (r=-0.81, p<0.01), springiness (r=-0.72, p < 0.05) and gumminess (r=-0.81, p < 0.01) showed negative correlation with swelling power. Moreover, some pasting properties from RVA determination particularly breakdown were related with the TPA textural properties of extruded rice noodle. The peak viscosity exhibited negative correlation with hardness (r=-0.83, p < 0.01), springiness (r=-0.61, p < 0.05) and gumminess (r=-0.73, p < 0.05). Similar to the case of breakdown, it presented negative correlation with hardness (r=-0.60, p < 0.05), springiness (r = -0.65, p < 0.05) and gumminess (r = -0.61, p < 0.05). However, Yoenyoungbuddhagal and Noomhorm (2002a) presented the different results. They found that both swelling power and RVA pasting parameters were not well correlated with properties of rice noodle (vermicelli) made from the five high-amylose (32.9-36.7%) Thai rice flour samples. However, there was the relationship between gel hardness and some noodle properties. Gel hardness was negatively correlated with soluble loss (r = -0.82, p < 0.01) and total loss and (r = -0.98, p < 0.01), whereas it showed positive correlation with hardness of rice vermicelli (r=0.90, p < 0.05).