EFFECT OF DRY- AND WET-MILLING PROCESSES ON RICE FLOUR, RICE STARCH AND RICE NOODLE PROPERTIES

INTRODUCTION

Rice (*Oryza sativa* L.) is one of the leading food crops in the world and the staple food for more than half of the world populations. Brown-, milled- or broken rice from low to high amylose and waxy rice varieties are used to produce rice flour of different granulations and functionalities. Rice flour are used to produce many kind of food such as baby foods, breakfast cereals, crackers, candy, noodles, unleavened breads and snack foods (Bao and Bergman, 2004). Thailand is a major exporter of rice flour. In January-July 2006, 15,759 tonnes of nonwaxy rice flour and 39,917 tonnes of waxy rice flour were exported and earned 12,000 million baht (Ministry of Commerce [MOC], 2006).

There are three methods (wet-, semidry-, and dry-milling) used to prepare rice flour. However, wet-milling is the traditional method to prepare rice flour. Soaking, adding excess water during grinding, and drying to remove the excess water are the three steps that differentiates wet-milling from dry-milling. The additional cost associated with redrying, regrinding, and wastewater treatment encouraged the seeking of alternative method. Many researchers try to compare chemical composition and physicochemical properties of wet-milled rice flour with dry-milled flour (Chen *et al.*, 1999, Chiang and Yeh, 2002, Yoenyongbuddhagal and Noomhorm, 2002b). However, the information about the effect of both dry-milling and wet-milling on rice flour, rice starch and rice products properties are still required.

Traditionally, rice noodle are made from wet-milled flour. However, the wet-milling process requires a large amount of water, which in turn created a lot of wastewater. Many attempts have been made to prepare the products from dry-milled flour instead of wet-milled flour to minimized wastewater and energy consumption (Tungtrakul, 1997; Yoenyongbuddhagal and Noomhorm, 2002b). The attempt to prepare the rice noodle from dry-milled flour instead of wet-milled flour should be accomplished. Thus, this study was aimed to examine effects of dry- and wet-milling processes on chemical properties, physicochemical properties, and starch molecular structure of rice flour and starch. In addition, the relationship between rice flour and rice starch properties, and rice noodle properties was also investigated.

OBJECTIVES

1. To prepare dry- and wet-milled rice flour and rice starch and investigate chemical properties and morphological structure of rice flour and rice starch with scanning electron microscope (SEM).

2. To characterize physicochemical properties of dry-milled and wet-milled rice flour and rice starch including gelatinization properties with a differential scanning calorimeter (DSC), swelling and solubility properties and pasting properties with a rapid visco analyzer (RVA).

3. To investigate starch molecular structure of dry- and wet-milled rice flour and rice starch with X-ray diffractometry and size-exclusion chromatography with multi-angle laser light scattering and refractive index detection (SEC-MALLS-RI).

4. To investigate the relationship between chemical properties, physicochemical properties and starch molecular properties of dry- and wet-milled rice flour and rice starch.

5. To prepare rice noodle from dry- and wet-milled rice flour and evaluate cooking properties, textural properties with the texture analyzer, and sensory tests.

6. To investigate the relationship between rice noodle properties and chemical properties, physicochemical properties and starch molecular properties of dry- and wet-milled rice flour.

LITERATURE REVIEW

Rice (*Oryza sativa* L.) is one of the leading food crops in the world and the staple food for more than half of the world populations. It is generally considered a semiaquatic, annual grass plant. Cultivars of the two cultivated species, *O.sativa* L. and *O.glaberrima* Steud., can grow in a wide range of water-soil regimes, from deeply flooded land to dry, hilly slopes. However *O.glaberrima* is grown only in Africa and only on a limited scale (Marshall and Wadsworth, 1992).

1. Composition and Properties of Rice Starch

1.1 Rice Starch Granule Structures

Rice starch granules were one of the smallest granules among the cereal grains, ranging in size from 3 to 5 μm in the mature grain (Figure 1). These granules are polyhedral and constitute approximately 90% of milled rice (dry weight). Most starch granules grow as a single entity inside an amyloplast or chloroplast of cell. Rice, however, contains only compound granules in which many granules have developed within a single amyloplast. The amyloplast contains 20-60 of the small granules forming a spherical to ellipsoidal cluster, varying from 7 to 39 μm in diameter (Champagne, 1996).

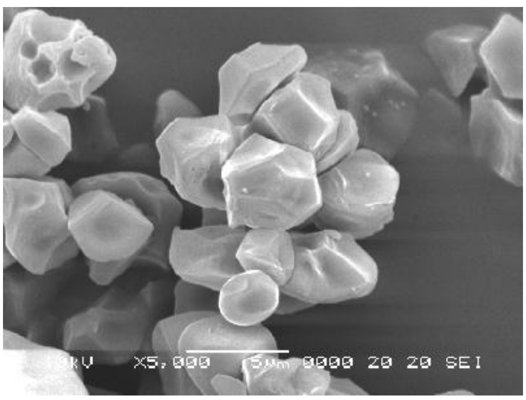


Figure 1 Rice starch granules magnified x5,000 at 5 μm by a scanning electron microscope.

Source: Naivikul (2004)

Rice starch, as other starch, is composed of two polymeric forms of glucose: amylose and amylopectin. There two molecules are organized into semi-crystalline structure in the starch granule (Champagne, 1996). A model of the starch granule is schematically shown in Figure 2. The more or less concentric layers (Figure 2a) show alternating high and low refractive indices, densities, crystallinities, and resistance to acid and enzymatic hydrolysis and presumably represent growth rings. These growth rings arise from a periodicity in the biosynthesis. The dense layer in a growth ring consists of ~16 repeats of alternating crystalline (5-6 nm) and amorphous (2-5 nm) lamellae (semicrystalline layer, Figure 2b). It has a thickness between 120 and 400 nm. The less dense layer is largely amorphous, contains more water and at least as thick as the dense layer. Starch granules are thus partially crystalline with a degree of crystallinity of 20-40%. The crystalline lamellar are made up by amylopectin double helices, which are packed in a parallel fashion, whereas the amylopectin branch points are in amorphous zones (Figure 2c) (Jacobs and Delcour, 1998).

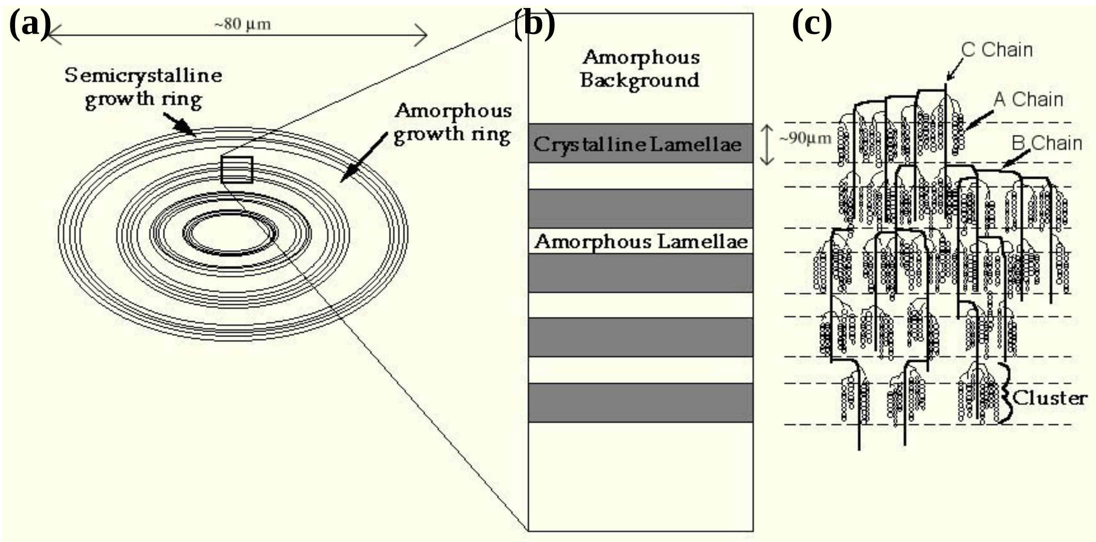


Figure 2 Schematic representation of starch granule structure: (a) a single granule with alternating amorphous and semicrystalline layers, representing growth ring; (b) expanded view of the semicrystalline layer of a growth ring, consisting of alternating crystalline and amorphous lamellae; (c) the cluster structure of amylopectin within the semicrystalline layer of the growth ring.

Source**:** Jacobs and Delcour (1998)

The crystallinity of the granule is thus mainly ascribed to double helices formed by amylopectin branches. Wide-angle X-ray scattering (WAXS) has revealed three forms of packing of amylopectin double helices, A-, B-, and C-crystal types. The exact location of amylose in the granule remains unknown. However, these linear molecules are believed to be interspersed between amylopectin, rather than being located in bundles. Most of the amylose is located in the largely amorphous layers of the growth rings. Recent research has indicated that in cereal starch two amorphous forms of amylose are present: lipid-free amylose and lipid-complexed amylose (Jacobs and Delcour, 1998).

Amylose was recent years known as a linear and branch glucose polymer. Rice amyloses have a β-amylolysis limit of 73-81%, indicating them to be slightly branched molecules with three to four chains on average. This β-amylolysis limit is considerably higher than that of amylopectin (55-60%). Rice starch amyloses have degree of polymerization (DP) values of 1,000-1,100 and average chain-lengths of 250-320. The amylose content of rice is specified as waxy, 0-2%; very low, 5-12%; low, 12-20%; intermediate, 20-25%; and high, 25-33%. The structural properties of amylose from rice are shown in Table 1 (Champange, 1996).

Table 1 Structural properties of amylose from rice.

Source	β-amylolysis limit (%)	Avg. Degree of Polymerization (glucose units)	Avg. Number Chains	Avg. Chain Length (glucose units)	Branched Molecule (%)
Normal rice					
- Indica	73	1,000	4.0	250	49
- Japonica	81	1,100	3.4	320	31

Source: Champagne (1996)

The molecular structure of rice amylose is now elucidated by mean of size-exclusion chromatography with multi-angle laser light scattering and refractive index (SEC-MALLS-RI). Ong and Blanshard (1995a) investigated the molecular structure of eleven cultivars of indica, which were amylose content of 18.4-29.5 % by using SEC-MALLS-RI. The rice starch was debranched with *Pseudimonas amyloderamosa* isoamylase after subjected to the series of SEC-MALLS-RI. The results showed tha the molecular weight (Mw) of amylose was in the range of 0.9-3.7 x 10^6 g/mol. The lower value of Mw of amylose was reported by Ramesh *et al.* (1999). Rice starch samples from four rice varieties (Taichung 1, Jhona-20, Sukanandi and Changlei T65), which was amylose content of 17.6-29.4% were debranched with *Pseudimonas amyloderamosa* isoamylase and fractionation on SEC-MALLS-RI. The results showed that amylose of the rice starch samples presented the Mw of amylose in the range of 0.12-3.80 x 10^5 g/mol. By using the same technique as the previous research done by Ramesh *et al.* (1999), Noosuk *et al.* (2005) presented the similar results of the Mw of amylose from three Thai rice varieties. The jasmine rice, commercial rice and Supan Buri 1, which were amylose content of 15.14, 21.21 and 22.43 %, exhibited the Mw of 2.3 x 10^5, 2.8 x 10^5 and 2.9 x 10^5 g/mol, respectively. Zhong *et al.* (2006) presented the larger Mw of amylose compared with results from the previous study. Amylose was first separated from the aqueous leaching of starch by the physically fractionation (*n*-butanol precipitation) before it subjected to SEC-MALLS-RI. The results showed that the Mw of amylose from BL-1, M202 and CCD rice starch samples were 3.44 x 10^6, 3.22 x 10^6 and 3.12 x 10^6 g/mol, respectively. Recently as the study of Patindol *et al.* (2007), the Mw of amylose from four special rice cultivars for canning (Bolivar, Cheniere, Dixiebelle and L205) and a regular long-grain Wells were reported. After isoamylase-debranching, the Mw of amylose was investigated by HPSEC-MALLS-RI. The results showed that the amylose of Wells presented the lower Mw of 3.5 x 10^5 g/mole, followed by Bolivar (5.2 x 10^5 g/mole), Dixiebelle (6.3 x 10^5 g/mole), L205 (6.8 x 10^5 g/mole) and Cheniere (7.5 x 10^5 g/mole).

Amylopectin is a highly branched polymer having on the average 96% α-1,4 bonds and 4% α-1,6 bonds. Enzymatic techniques have been used to obtain structure information and develop models of amylopectin. The currently accepted structural models are derived from the cluster models proposed by Hizukuri (1985) is depicted in Figure 3. The molecules have 10^4-10^5 individual chains, and the ratio of unbranched to branch chain is about 1.0. Approximately 22-25 chains form each cluster, comprising the crystalline regions of starch granules. In waxy rice, 80-90% of the amylopectin chains probably constitute a single cluster, while the remaining 10-20% forms intercluster connections, which are mainly between adjacent clusters (Champagne, 1996).

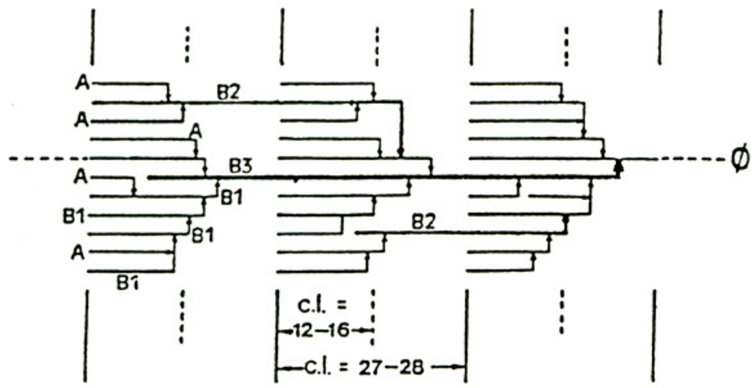


Figure 3 Cluster model of amylopectin. ∅ = Reducing chain-end. Solid lines indicate (1→4)- α-D-glucan chain; arrows indicated α-(1→6) linkage.

Source: Hizukuri (1985)

The structural properties of rice amylopectin are presented in Table 2. Rice amylopectins have β-amylolysis limits of 56-59%, chain lengths of 18-21, and widely different DP and linear chain distribution values. Low average DP values are observed for Indica rice (4,700), as compared to those for Japonica rice (12,800) and waxy rice (18,500) amylopectins (Champagne, 1996).

Table 2 Structural properties of amylopectin from rice.

Source	Avg. Degree of Polymerization (glucose units)	Avg. Chain Length (glucose units)	Avg. Number Chains	Avg. External Chain Length (glucose units)	Avg. Internal Chain Length (glucose units)
Normal rice					
- Indica	4,700	21	220	14	6
- Japonica	12,000	19	670	13	5
Waxy rice	18,500	18	1,000	12	5

Source: Champagne (1996)

The molecular structure of rice amylopectin investigated by mean of size-exclusion chromatography with multi-angle laser light scattering and refractive index detection (SEC-MALLS-RI) is reported by many studies. Yoo and Jane (2002) reported that among the amylopectin of the other A-type cereal starch (normal- , waxy- and *du wx* maize, normal- and waxy wheat, normal and waxy-barley, cattail millet, mung bean, Chinese taro and tapioca), B-type starch (*ae wx* maize, amylomaize V, amylomaize VII, potato and waxy-potato and green leaf canna) and C-type starch (lotus root, water chestnut and green banana), the amylopectin from normal rice, waxy rice and sweet rice presented the largest of amylopectin with the Mw of 2.68 x 10^9, 5.68 x 10^9 and 1.39 x 10^9 g/mol, respectively, while the others A-type starch presented 0.07-1.26 x 10^9 g/mol, B-type starch presented 1.7-3.4 x 10^9 g/mol and C-type starch exhibited presented 1.5-7.1 x 10^9 g/mol. Zhong *et al.* (2006) presented the smaller of the Mw of amylopectin compared with results from the previous study. Amylopectin was separated from the aqueous leaching of starch by the methanol precipitation before it subjected to SEC-MALLS-RI. The results showed that the Mw of amylopectin from BL-1, M202 and CCD rice starch samples were 5.52 x 10^7, 4.64 x 10^7 and 4.01 x 10^7 g/mol, respectively. Recently, the Mw of amylose from four special rice cultivars for canning (Bolivar, Cheniere, Dixiebelle and L205) and a regular long-grain Wells were reported by Patindol *et al*. (2007). After subjected to methanol precipitation, the Mw of amylopectin was investigated by HPSEC-MALLS-RI. The results showed that the amylopectin of Cheniere presented the lower Mw of 1.2 x 10^8 g/mole, followed by Wells (1.4 x 10^8 g/mole), Dixiebelle (1.9 x 10^8 g/mole), L205 (2.1 x 10^8 g/mole) and Bolivar (2.3 x 10^8 g/mole).

1.2 Starch structural properties and physicochemical properties of rice starch

The fine structures of rice starch both amylose and amylopectin chain length distribution is found as an important factor that affect on many starch properties including starch physicochemical properties.

1.2.1 Gelatinization

Gelatinization is the process that takes place when starch is heated in the presence of water, resulting in the irreversible disruption of molecular order with a starch granule. Evidence of this loss of order can be seen by irreversible granule swelling, loss of birefringence, loss of crystallinity and leaching of amylose from starch granules (Whistler and BeMiller, 1999). Gelatinization, an energy-absorbing process can be examined by differential scanning calorimetry (DSC), which measured both the temperature and the enthalpy of gelatinization. Thermal curves generated by the calorimeter depicting rice starch gelatinization are characterized by three temperatures; onset (T_o), peak (T_p), and conclusion (T_c) and by the gelatinization enthalpy (ΔH), which is expressed as J/g, which obtained by integrating the area under the curve (Marshall and Wadsworth, 1992).

Rice starch gelatinization is affected by several factors including starch molecular structure aspects such as amylose content and amylopectin chain length distribution. Biliaderis *et al.* (1986) reported that gelatinization enthalpies (ΔH) of eight waxy and non-waxy rice starch were affected by amylose content. The results showed that ΔH was decreased from 17.1 to 8.6 J/g when amylose content increased from 2.1 to 31.2%. However, there was no evidence that gelatinization temperatures were dependent on amylose content. In contradictory, Varavinit *et al.*

(2003) reported that there is the positive correlation between amylose content and gelatinization temperature: onset (T_o), peak (T_p) and conclusion (T_c) temperatures (r = 0.84, 0.88, and 0.85, respectively) of the eleven different cultivates of Thai rice flour, which varied amylose content (4.46 to 26.42%), but no correlation between amylose content and melting enthalpy of gelatinization (ΔH).

Patindol and Wang (2002) investigated the effect of the other structure aspect of rice starch, apart from amylose content on the gelatinization properties of three rice cultivars contained short range of amylose content (21.3-23.1 %). The results showed that the increasing amounts of long chain amylopectin (DP 37-60) of the three rice samples increased gelatinization temperature and enthalpies. The authors stated that the very long-branch chains of amylopectin could mimic the tendency of amylose to form helical complexes and intertwine with other branch chains, holding the integrity of starch granules during heating and may consequently result in higher gelatinization temperature. 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 (T_p: 65.2-65.8 ^oC), normal-low T_p starch (T_p: 62.8-67.0 ^oC), normal-intermediate T_p (71.7-73.5 ^oC) and normal-high T_p (76.7-78.5 ^oC) rice starch. The result showed that absolute amylose contents did not affect T_o, T_p and T_c of waxy and normal low T_p rice starch, but decreased T_o, T_p and T_c (r^2= 0.84, 0.91 and 0.98, p<0.05), and increased T_c-T_o (r^2= 0.95, 0.97, respectively), of normal intermediate and high T_p rice starch. The correlation between amylopectin molecular structure and gelatinization behavior were found. The higher levels of long chain amylopectin (and thus lower levels of short chains) delayed gelatinization, whereas short chain amylopectin facilitated it. The results showed that the short chain amylopectin (DP 6-9) showed negatively correlation with T_o, T_p, and T_c (r^2= 0.77, 0.74 and 0.59, p<0.05), while the long chain amylopectin (DP12-22) showed positively correlation (r^2= 0.83, 0.83 and 0.77, p<0.05).

From the data above, there is no clear understanding about the relationship between rice starch structure and thermal properties. Thus, the researches about this contradictory data are still succeeding.

1.2.2 Pasting properties

When the starch granule is heated in excess water up to gelatinization temperature, heat transfer and moisture transfer phenomena occur. The granule swelled to several times its initial size as a result of the loss of the crystalline order and absorption of water inside the granular structure. The pasting viscosity during swelling and gelatinization can be recorded using a Brabender Visco Amylograph, Rapid Visco Analyzer (RVA), or other viscometer, which record the viscosity continuously as the temperature is increased, held constant for a time, and then decreased. At the initial step, the viscosity increased rapidly with the increase of temperature as the granule swells. The peak viscosity is reached when granules swelling have been balanced with the granules broken by stirring. With continues stirring, more granules rupture and fragment, causing the further decrease in viscosity. On cooling, some starch molecules partially reassociated to form a precipitate or gel, in which amylose molecules aggregate into a network, embedding remnants of starch granules (Bao and Bergman, 2004).

Quantitative trait locus (QTL) mapping has found that rice starch pasting properties within a given population are mainly controlled by the waxy gene, which is responsible for amylose synthesis. Thus it is not surprising that rice starch pasting properties have been reported to be correlated with amylose content (Bao and Bergman, 2004). Perez *et al*. (1993) showed that RVA setback and consistency at 30^{o}C values of 10 non-waxy rice flour increased with amylose content (15.4-36.2% amylose), whereas breakdown values decreased with amylose content. Varavinit *et al*. (2003) demonstrated that the data obtained from RVA viscogram (peak viscosity, breakdown, setback and pasting temperature) can be used for differentiation of low amylose or waxy rices (4.47 to 5.28%) from medium (14.63 to 15.45%) and high (21.95 to 26.42%) amylose Thai rices. Low amylose rice starch provided the highest peak viscosity and breakdown and the lowest setback and pasting temperature among the groups.

However, there are many evidences that rice starch which has the same amylose content showed the variation of pasting properties. Thus the differences in amylopectin structure would be the answer. Studying ten rice starch with narrow ranges of amylose content (15.1-17.9% amylose), Han and Hamaker (2001) found that RVA paste breakdown were negatively correlated with long amylopectin chains (DP>100), while short chain amylopectin (average DP 7) showed the positively correlation. They proposed that an amylopectin, which composed of higher long chains amylopectin were involved in more than one cluster and hence had less tendency to be dispersed because of entanglement with other amylopectin molecules; and a higher proportion of long chains increased the radius of amylopectin molecules and, hence the viscosity increased. Thus, because of possible decreased breakdown of gelatinized starch granules and/or increased viscosity after the gelatinized starch granule structure were disrupted, increased long chains amylopectin may decrease starch paste breakdown. However, Vandeputte *et al*. (2003b) using a more diverse set of rice starch including five waxy and ten non-waxy starch, found no correlation between RVA paste viscosity and amylopectin chain length distribution. The pasting viscosity of rice flour or starch is affected by environment and post-harvest treatments. Recently, pasting properties of sixteen red rice starch from various locations in US and two cultivated rice starch (medium-grain, Bengel and long-grain, Wells) were investigated as reported by Patindol *et al*. (2006). The results showed that red rice starch from the within or across states provides the varies in paste viscosity profiles and also different in starch molecular structure. The correlation analysis also showed that red rice starch pasting temperature correlated positively with apparent amylose content (r = 0.66, p<0.01). The peak and breakdown viscosities showed positively correlation with the short chain amylopectin (DP6-12) (r = 0.61, p<0.01 for peak viscosity; and r = 0.49, p<0.05 for breakdown) and negatively correlation with amylose content (r = -0.42, p<0.05) and medium chain amylopectin (DP13-24) (r = -0.42, p<0.05) (Patindol *et al*., 2006).

1.2.3 Rheological properties

Rheological properties during rice starch gelatinization have been characterized by many researchers using different rheometers. Lii *et al*. (1995) performed the experiment exhibited the change of rheological properties during rice starch gelatinization and gelation. The rheological properties of 5, 10, 15, 20 and 30% of starch suspension of two kinds of rice starch, indica (Kaoshiung Sen 7, KSS7) and japonicina (Tainung 67, TNu67) were investigated by a small amplitude oscillatory rheometer. The results showed that both G' and G'' of both KSS7 and TNu67 at 5-30% concentration were sudden increased after the temperature was raised to gelatinization temperature (T_o=72.0 and 64.4^{o}C for KSS7 and TNu67). The researchers stated that this was the effect of the increase volume of swollen granules made close packed system. The results showed that the higher starch concentration would assist the earlier rise to G' because of the shorter time to get a close packed system. After continuous heating, the G' and G" reached to the maximum at 76-86^{o}C for 10-30% of starch concentration. The researchers stated that the continuing heating could not only further swell granules and make more amylose to leach out, but could also increase the mobility and collision of swollen granules arranged themselves in a special three-dimensional conformation by entanglement of swollen starch granules. The swollen granules as a filler would also strengthen the networklike structure. These all increased the ability for the formation of networklike structure to display in the growth of G' and G". After maximum G' and G", the further heating reduced the G' to half or one-third of the maximal G' value. The researchers stated that more heat and greater mobility or entropy might loosen the previous interactions and rupturing the structure of swollen starch granules. The strength of networklike structure weakened and G' dropped.

Lii *et al*. (1996) presented the effect of rice variety and amylose on the rheological properties of rice starch during heating. The results indicated that the storage modulus (G') of Kaoshiung Sen 7 (KSS7, indica) starch with sufficient concentration (10-30%) increased dramatically at gelatinization temperature ($T_{G'}$). The addition of 2% amylose inhibited the decreasing of starch gel during heating, but may have reinforced the close-packed swollen granule matrix during the period of aging process at 5^{o}C. The waxy rice starch (Taichung waxy 70, TCW70) with trace amylose content, showed much higher swelling power than that of indica rice starch (KSS7). However, the paste was formed even at high concentration (>20%). The researchers stated that the rigidity of starch granule structure might be in proportion to its amylose content and in inverse proportion to the degree of granule swelling. Thus, the higher G' for KSS7 rice starch than that for TCW70 can be explain by its high inherent amylose content, which could enhance the rigidity of the starch granule structure. Also, the high G' value for the system with the high starch concentration could be attributed to the low swelling and the strong indication among the granules. The researchers concluded that the major influencing factors on the rheological properties of the rice starch during heating were the granular structure and component, followed by the amount of leach out amylose in the process.

Bao and Bergman (2004) summarized that the change in viscoelastic properties of rice starch suspension during gelatinization can be placed into three or four transition stages: starch suspension into sol, sol transition to gel, network destruction and network strengthening. During the early heating of starch granules in water, the increase of storage modulus G' and tan δ is relatively small, which indicates that amylose molecules are dissolved and suspension had been transformed into a 'sol'. Then G' and G" increase to a maximum in which the temperature coincides with the onset temperature, which is attributed to the close-packed network of starch granules. Tan δ decreases simultaneously, which indicated the three-dimensional gel network has been constructed from amylose, reinforced by strong interactions among the swollen starch particles. The G' increases during gelatinization of rice starch are reported to be mainly governed by granule characteristics, which include swollen granule rigidity and the interaction between the close-packed granules. In the third stage, continued heating beyond TG', the G' decreases and tan δ increases, indicated that gel structure has been destroyed during prolong heating. The destruction is likely due to the 'melting' of the crystalline regions remaining in the swollen starch granule or results from the disentanglement of the amylopectin molecules in the swollen particles, which softens the particles.

Another reason the network collapses may be due to the loss of interaction between particles and the network. The fourth stages, G' and G" are reported to increase and tan δ increase even higher after an inflection point (Figure 4). This was attributed the G' increase to the leached low molecular weight amylopectin, which interacted with the amylose matrix to strengthen the continuous phase (network). However, a larger tan δ indicated that the dispersed phase (particles) became softer due to continuing dissolution of amylopectin (Bao and Bergman, 2004).

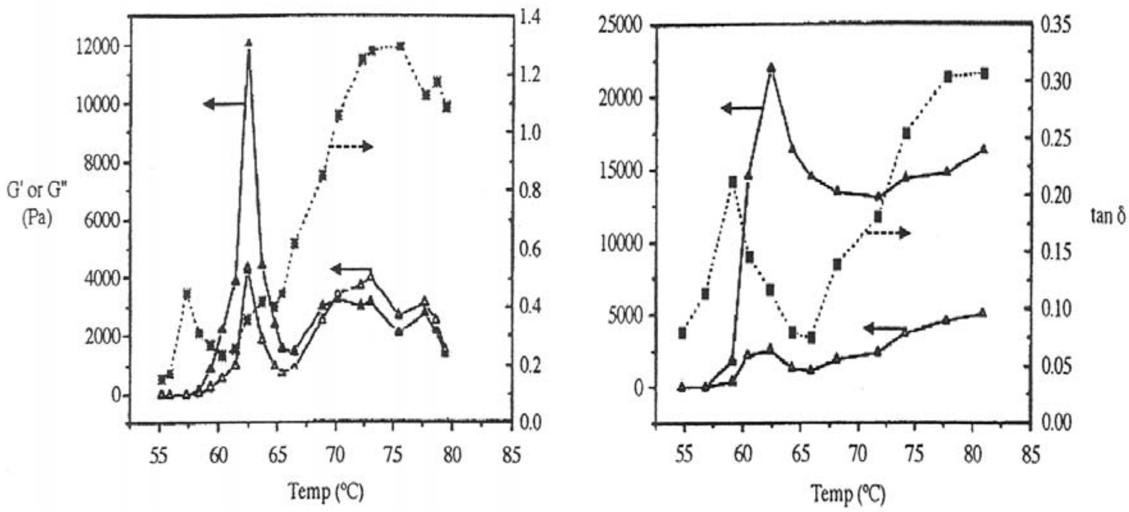


Figure 4 Temperature sweep data for gelatinization of 25% TCW70 (a), waxy rice and TCS10 (b), normal rice with amylose content of 17.1% rice starch suspension. Symbols: G' (-▲-), G" (-Δ-) and tan δ (-*-).

Source: Bao and Bergman (2004)

1.2.4 Retrogradation properties

Retrogradation describes the process in which a heat starch paste cools to below the melting temperature of starch crystallites, and the amylase and amylopectin reassociate and unite with the swollen starch grains in an ordered structure that results in viscosity increase, gel firming, and textural staling of predominantly starch-containing systems. The retrogradation properties can be measured by DSC (Qi *et al,.* 2003; Vandeputte *et al*., 2003c), rheological properties, starch gel hardness (Vandeputte *et al*., 2003c), and NMR (Qi *et al*., 2003).

This phenomenon is generally regarded as a recrystallization (formation and subsequent aggregation of double helices) process of amylose and amylopectin. The rapid initial rate of retrogradation related to the loss of networked amylose, the development of amylose aggregated, and binding of granule remnants into assemblies by amylose and amylose aggregates. Thus, amylose is responsible for short-term (less than one day) changes during retrogradation (Zhou *et al*., 2002). Amylopectin forms shorter double helices which can be attributed to restrictions imposed by the branching structure of the amylopectin molecules and the chain lengths of the branches. Thus, amylopectin retrogradation proceeds slowly over several weeks of storage and contributes to the long term rheological and structural changes of starch systems.

The retrogradation kinetics of starch has received wide attention though the underlying mechanism of retrogradation has not been concluded. The Avrami equation is generally accepted as being able to simulate retrogradation kinetics. Lai *et al*. (2000) reported the retrogradation kinetics of pure amylopectin from 13 rice cultivars. Generally, the amylopectin system showed two stages of retrogradation behavior during early ($\leq$ 7 days) and late (> 7 days) storage. Correlation analysis suggested that the kinetics of early stage retrogradation were more correlated than the late stage retrogradation with the number-average molecular weight and chain lengths of the amylopectin molecules. The proportion of short, long and extra long chain fractions appeared to have greater effects on the enthalpy changes and late stage kinetics than the other structural factors (Lai *et al*., 2000).

Tako and Hizukuri (2000) proposed some mechanism for rice starch retrogradation which are based on the formation of hydrogen bonding at various molecular levels. The researchers postulated that intermolecular hydrogen bonding between O-6 of the amylose and OH-2 of amylopectin molecules take place after preparation rice starch in aqueous solution, following with the formation of another intermolecular hydrogen bond between OH-2 of a D-glucose residue of the former molecule and O-6 of a D-glucose residue of a short side chain (A and B1 chains) of the latter molecule. During storage two or more short side chains (A and B1 chains) of amylopectin molecule will associate with an amylose molecule through hydrogen bonding. After saturation of intermolecular hydrogen bonding between amylose and amylopectin molecules, an intermolecular association also takes place between amylopectin through hydrogen bonding. At this stage, side-by-side associations between O-3 and OH-3 of D-glucosyl residues on different amylopectin molecules also take place. The mechanism of retrogradation is complicated because retrogradation rate may vary from one cultivar to another due to differences in the proportion and interaction of amylopectin and amylose, chain length distribution, and molecular size of branched molecules (Hizukuri, 1986; Eliasson, 2004).

Amylose content, gelatinization temperature (GT), and amylopectin structure in relation to rice starch retrogradation has been studies. Fan and Marks (1998) found that during rice gels were stored at 4^{o}C for 7 days, the enthalpy of retrogradation increased with amylose contents. Whereas, Vandeputte *et al*. (2003c) reported that the amount of amylopectin chains with DP 12-22 showed the positive correlation with enthalpy of retrogradation of rice starch gel stored at 6^{o}C for 4 weeks, but amylose contents showed the negative correlation with both T_c and enthalpy of retrogradation. Qi *et al*. (2003) found that retrogradation of the solubilized native high- and low-GT amylopectin molecules confirmed that the high-GT amylopectin molecules form higher dissociation temperatures and enthalpy crystalline domains. This confirms that the higher proportion of short and especially relatively longer chains promotes crystalline formation.

1.2 Minor Constituents

Minor constituents such as lipids and protein are commonly found in isolated rice starch. Both lipid and protein are reported as an important factor that influence many functional properties of rice starch (Champagne, 1996).

Lipids: Non-waxy rice contains 0.3-04% bound lipids; waxy rice starch contains much less bound lipid (0.03%). Lipids may be associated with native starch granules in three ways. On the exterior of the granule are contaminating non-starch lipids that bind to protein adhering to the granular surface; these are removed by suitable clean-up procedures. In the interior of the granule are monoacyl non-starch and true starch lipids. Monoacyl non-starch lipids enter the granule generally during steeping and wet-milling for starch isolation**.** The composition of the true starch lipids in non-waxy rice starch is comparatively constant, averaging 32% free fatty acids and 68% lysophosphatidyl choline. Major fatty acids are linoleic, palmitic, and oleic or myristic acid (Champagne, 1996).

X-ray diffraction and differential scanning calorimetry have shown helical complexes of amylose with lipids after normal cereal starch gelatinize. These complexes are more resistant to enzymatic attack and less soluble in water. The rate of amylose retrogradation in rice starch is also suppressd by lipids. Defatted rice starch reduces the gelatinization temperature and gel viscosity and increases gel consistency and susceptibility to lintnerization. Amylopectin shows little evidence of interaction with lipids. However, the lipids may indirectly affect the behavior of amylopectin toward water through their complex formation with amylose (Champagne, 1996).

Protein: The protein content of rice varies somewhat among cultivars. Studies conducted on rices grown in India, the Philippines, and the United States showed gross protein content of milled rice (dry weight basis) ranging from 6.0-9.0, 6.1-11.4, and 7.7-10.0, respectively. Protein is nonuniformly distributed in the rice grain. There are greater concentrations in the bran and periphery of the endosperm and smaller quantities towards the center of the grain (Hamaker, 1994).

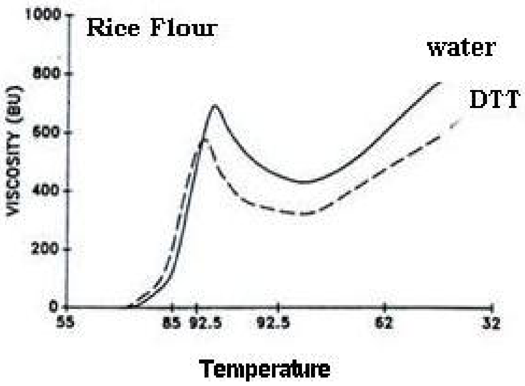
Rice is unique among the cereals in that its storage protein is primarily glutelin (alkali-soluble protein), while in most other cereals it is prolamin. Glutelin proteins are thought to be found exclusively encapsulated in protein bodies distributed throughout the starchy endosperm of the grain. Little or no matrix protein has been found in the rice endosperm. However, possibilities that could form a network in the rice endosperm and would be difficult to detect even with an electron microscope (Hamaker, 1994).

After repeated protein extraction, all rice starch preparations contain residual Kjeldahl nitrogen. Protein may be found on the periphery of the starch or embedded inside the granule. Starch-protein complexes involve primarily amylose and waxy gene protein (60 kDa) or granule-bound starch synthase, which has about 8.6% lysine. Indica, non-waxy rice starch has about three times as much bound protein as japonica rice starch at similar amylose content. It has a lower specific activity of bound starch synthase in the developing grain compared to japonica starch (Champagne, 1996).

The close association of proteins with starch in rice makes isolating the protein to obtain starch with less than 0.5% protein difficult. Alkali extraction appears to be the most effective in solubilizing the protein; as least 80% of the protein alkali-solution glutelin. Commercially, rice is steeped in 0.3-0.5% sodium hydroxide at temperature ranging from room temperatures to 50 ^{o}C for 24 hr to solubilize the proteins. The steeped kernels are then wet-milled in pin-mill, hammer-mills or stone-mill disintegrators in the presence of sodium hydroxide. The starch suspension is stored for 10-24 hr, after which fiber is removed by passing the suspension through screens. Starch is isolated from protein by centrifugation. Protein may also be separated from starch by proteolysis. Commercial proteases, however, have very limited application for solubilizing rice protein; they take days to hydrolyze rice proteins versus hours for other protein. (Champagne, 1996).

There are many works on starch-protein interactions in rice. Hamaker and Griffin (1990) determined the relationship between starch granule-associated protein and starch pasting characteristics of 9 rice varieties commonly grown in Arkansas by disruption of protein structure through cleaving disulfide bonds by adding reducing agents dithiothreitol (DTT) the cooking water. Following this treatment, cooked rice stickiness, as measured using the Instron Universal Tester, were significantly increased in 7 of 9 rice samples. Brabender amylograph curves were lower when a reducing agent was added to the flour-water slurry (Figure 5a) and were like wise lower when treated with proteinases (Figure 5b)

(a)



(b)

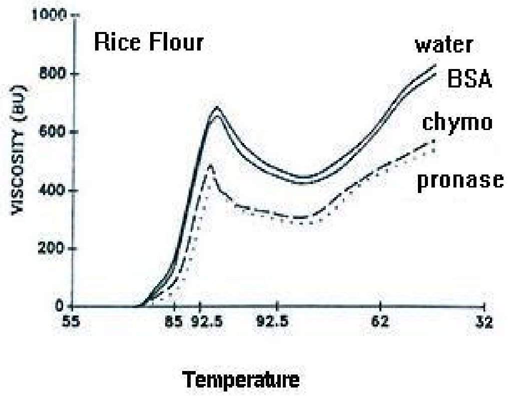


Figure 5 Amylograms of rice flour at 10% solids in water with and without dithiothreitol (DTT) added, (b) incubated 2 hours before analysis in water or a solution containing chymotrypsin, pronase, or bovine serum albumin (BSA)

Source: Hamaker and Griffin (1990)

The similar results were recently reported by Martin and Fitzgerald (2002) and Fitzgerald *et al*. (2003). The result showed that peak viscosity, final viscosity and overall curve were decreased when protein are removed by protease treated. Beside that the addition of DTT to disrupt the disulfide bridges lower the curve similar to effects of protease. The researchers concluded that protein influence viscosity curves in two reasons: (1) through binding water, which caused the concentration of the dispersed and viscous phase of gelatinized starch to increased, and (2) through the agency of a net work link by disulfide bonds.

All information above clarifies that the properties of rice starch are influenced by many factors. The starch molecular structures (amylose and amylopectin chain length distribution are reported as the important aspect that affected on rice starch physical properties. Minor constitutes in rice starch such as lipids and protein can strongly interact with starch and cause many change of rice starch properties.

2. Rice Flour

Thailand is a major exporter of rice flour. In January-July 2006, 15,759 tonnes of nonwaxy rice flour and 39,917 tonnes of waxy rice flour was exported and earned 27.9 million US$ (MOC, 2006). Brown-, milled- or broken rice from high to low amylose and waxy rice varieties are used to produce rice flour of different granulations and functionalities. Rice flour are used to produce many kind of food such as baby foods, breakfast cereals, crackers, candy, noodles, unleavened breads and snack foods. Rice flour is commonly used as an extender in powdered for refrigerated-preformed-unbaked biscuits and pizza, as an extender in powdered cheeses and sugars, as coating for French fried and in mixes for pancakes and waffles. Rice flour in deep fat frying batters adds crispness to the coating, a reduce oil-pick-up, a retarded moisture transmission, and extended holding time. Leavened bread is produced from rice flour with the addition of hydroxylpropyl methylcellulose. Rice flour is also being used as a source of carbohydrate in oral dehydration solutions. A combination of extrusion cooked rice flour and rice syrup is said to mimic fat in texture and flavor. Extrusion cooked, pressure cooked and steam cooked rice kernels are also dried and ground into pregelatinized rice flour with varying functionality. The processing quality of this flour is greatly dependent on each sample's inherent chemical profile and also method of preparation and degree of gelatinization. For example, in the United States baby foods, beer, and breakfast cereals are primarily produced using low amylose rice (12-20%) and an intermediate amylose rice (20-25%) is used for making extruded (dried) pasta. Waxy rice flour is frequently used as a thickening agent for white sauces, gravies, and subsequently thawed. Rice flour is also an important ingredient in a multitude of traditional foods prepared in home across the world. *Puttu,* (rice cake from India), Chinese rice stick noodle, Vietnamese-style salad rolls and deep-fried spring rolls, Japanese-style noodle, cake, crackers and pudding, and *horchata* (rice-flour based beverage from Mexico) are examples of the diversity of traditional rice flour based products from all over the world (Bao and Bergman, 2004).

Rice flour is prepared from three methods (wet-, semidry- and dry-milling) as illustrated in Figure 6. Soaking, milling, drying, and regrinding are involved in wet-milling. Usually rice is soaked in water for more than 4 hr, drained, and ground by a stone mill with water. After milling, excess water is removed by drying, and the flour is then gently reground to prepare the wet-milled flour. In semidry milling, rice is soaked, drained, and ground by using a stamp or pin mill without adding any water. For dry-milling process, cleaned (or tempered) rice can be directly ground to different sized by various mills (including rolling, pounding, shock, stone, and lateral steel). In general, wet-milled rice flour is mostly used to prepared many rice products such as rice noodles, baked products and traditional Asian products. However, the wet-milling process requires a large amount of water, which in turn created a lot of wastewater. Many attempts have been made to prepare the products from dry-milled flour instead of wet-milled flour to minimized wastewater and energy consumption (Yeh, 2004).

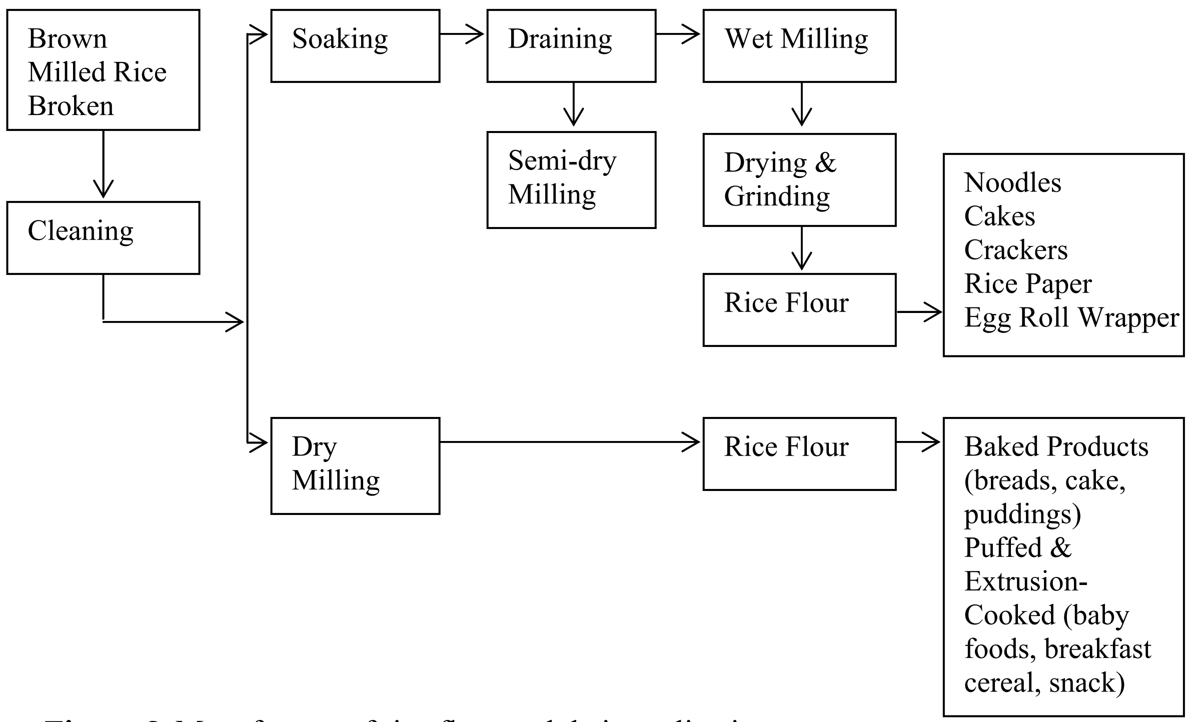


Figure 6 Manufacture of rice flour and their applications.

Source: Yeh (2004)

2.1 Dry-milling

The type of mill or grinder affects the particle size distributions, temperature, and functional properties of flour. Nishita and Bean (1982) reported that pin mills and hammer mills yield fine particles of the PS50 value (estimated sieve size through which 50% of the sample passed) 88 µm and 117 µm. Using three different grinders (turbo-,cyclone-,hammer-,and plate-mills) for dry-milling and analyzing particle size with a laser particle size analyzer. Chen *et al.* (1999) reported that turbo-milling yielded the finest flour, with finer particles than that obtained by Nishita and Bean (1982) PS50 of 62.2 µm vs. 151 µm. Nevertheless, the hammer-milled waxy rice flour (PS50 of 197.2 µm) obtained by Chen *et al.* (1999) was coarser than that (117 µm) reported by Nishita and Bean (1982). Thus it is necessary to know the basic information on the machine before comparing the performance of mills or grinders. When compared with semi-dry and wet-milling processes, dry-milling gave the coarser rice flour than the other two processes. Chen *et al.* (1999) reported that dry-milled waxy rice (TCW70 and TCSW1) showed the coarser particle size of rice flour compared to semi-dry and wet-milled flour. The results showed that the semi-dry hammer milled rice flour (100-200 µm) was finer than dry hammer milled rice flour (100-300 µm) and wet-milling stone milled had more finer rice flour (10-30 µm) than those of dry- and semi-dry milled rice flour.

Beside production of coarser flour, dry-milling process yield the higher degree of starch damaged than other milling processes. As reported by Chen *et al.* (1999), the turbo-mill heated the sample to 50 ^{o}C, the hammer mill also reached to 42 ^{o}C during milling, but the stone wet-milled samples stayed at room temperature. That is a part of reasons they yield flour that had more damaged starch. On the other hand, soaking rice grains before milling in wet-milling process caused the increasing in the softness of the rice grains and reduction in damaged starch. Nishita and Bean (1982) stated that turbo-milled rice flour with median particle size by weight (PS50) of 151 µm had damaged starch of 24.2%, while wet-milled flour in similar size (average particle size of 199.7 µm) as reported by Chiang and Yeh (2002) had the lower amounts of damaged starch of 6.7%. Similar to the results showed by

Yoenyongbuddhagal and Noomhorm (2002a). They found that the dry-milled rice flour from high amylose Thai rice (Saohai) yielded the higher amounts of damaged starch of 12.1% compared with wet-milled rice flour, which had the damaged starch of 4.2%.

Damaged starch has been a concern in flour preparation. The damaged starch granules were first differentiated from intact granules by their aqueous solubility and rapid susceptibility to enzymatic digestion by amylases. Pulkki (1938) showed that physical injuries occurred to starch granules as a result of grinding treatments. Damaged granules are stained with Congo red, while intact granules do not. Jones (1940) showed that the diameter of damaged granules expanded by 50% in cold water, while intact granules only increased in size by 10%. Damage granules fail to exhibit birefringence when hydrated, which suggested a loss of ordered structure (Sandtedt and Schroeder, 1960). As reported by Meuser (1978), after 120 min of ball-milling, starch had a gradual increase in reducing power, and decrease in limiting viscosity, and iodine-binding capacity. This indicated that the molecular size of starch molecules was reduced by milling treatment. Meuser (1978) also concluded that amylopectin molecules were inclined to fragmentation than amylose during ball milling.

Morrison *et al.* (1994) reported that after gradual ball-milling of wheat and maize starch (up to 24 hr), starch granule crystallinity from wide-angle X-ray diffraction patterns, and double helix content from ^{13}C-CP/MAS-NMR spectra were decreased with damaged starch content increased. For maize starch samples, when the ball-milling time was increased from 0 hr to 8 hr, the damaged starch content was increased from 1.2% to 66.0%, while the crystallinity was decreased from 35.2 % to 5.0%, and the double-helix content was decreased from 45% to 15%. In the case of wheat starch, when ball-milling time was increased from 0 hr to 16 hr, the damaged starch content was increased from 4.6% to 91.1%, while the crystallinity and the double-helix content were reduced from 35.5% and 37.2%, respectively to no detectable level. The researchers postulated that the primary event caused by mechanical damaged is the conversion of large order regions (crystalline amylopectin) into essentially disordered amorphous material. This evident is freely the damaged starch be accessible to external agents such as solvent water and amylolytic enzymes. The authors also suggested that the mechanical damaging of the crystalline shells allows the damaged granule to swell spontaneously and leach solubles in cold water.

To elucidate the molecular structure of damaged starch granules, Morrison and Tester (1994) studied the molecular structure of damaged starch granules through the water-soluble-fraction. The water-soluble-fraction extracted from wheat starch ball-milled 24 hr and separated on a size exclusion column (Sepharose CL-2B) showed a breakdown of amylopectin to low-molecular-weight amylopectin that co-eluted with amylose. Small fraction of amylopectin formed as ball-milling time increased. The results showed that the molecular structure of amylopectin from the debranched starch had no A-or B-chains shorter than the native amylopectin A-and B-chains. Moreover, amylose was susceptible to fragmentation only at extreme levels of damage that would not be encountered in normal flour milling procedures. Thus, the researchers hypothesized that low-molecular-weight fragmented amylopectin is a result of glycosidic bond breakage in isolated B_2-B_4 chains near amylopectin branching points, know to be located in the amorphous layers of the granule. Shear force could act on a cluster of double helices and break it from amylopectin. The propose model of mechanical damage of starch are showed in Figure 7.

Tester and Morrison (1994) described the composition of the soluble material of ball-milled wheat starch at various temperatures (20, 40, 60 and 80^{o}C), and their relation to starch swelling properties. Wheat starch was ball-milling to obtain various levels of damaged starch (4.6-93.7%). The results showed that on hydration in excess water below the gelatinization temperature of the original starch (20 and 40 ^{o}C), damaged starch gave soluble matter fraction comprising low molecular weigh fragments of amylopectin (LMWAP) with a little lipid-free amylose (FAM), and a gel fraction derived from disorder (amorphous) amylopectin (AP), LMWAP, FAM, and lipid-complex amylose (LAM).

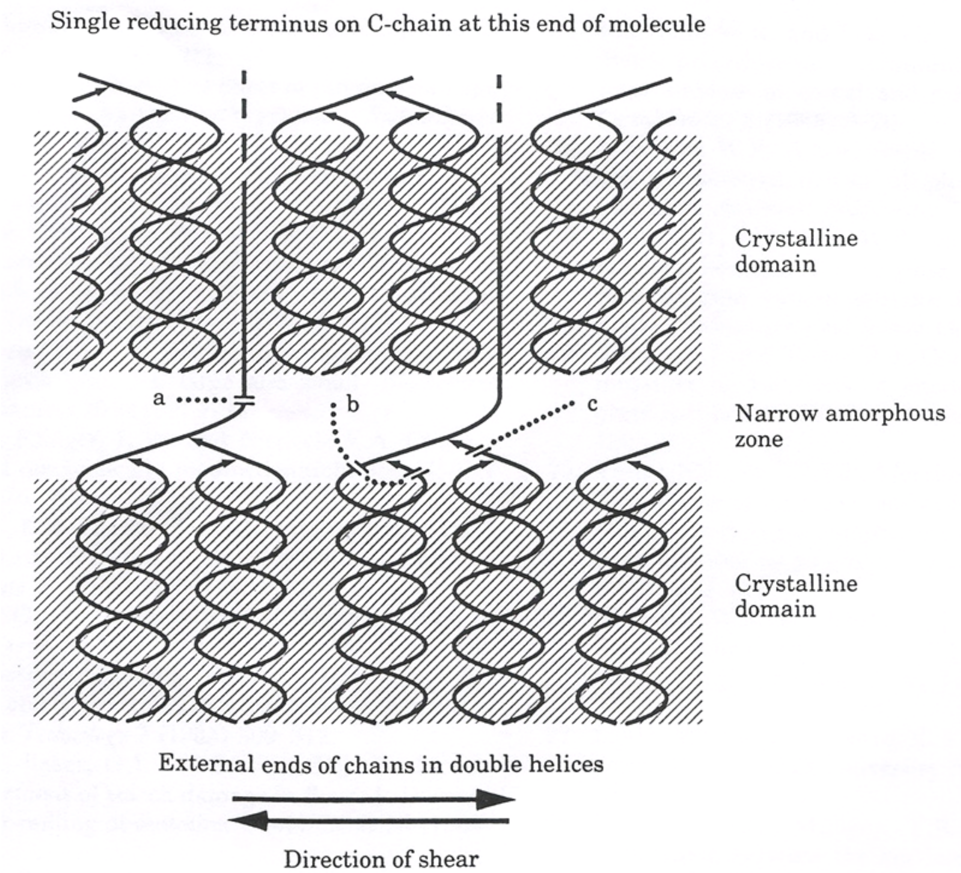


Figure 7 Model of part of an amylopectin molecule showing possible fracture point following mechanical damage: crystalline domains formed by double helices are shaded grey, and α-1, 6-glycosidic branch points are showed by small arrow heads. (a) A single break in a B_2, B_3, or B_4 chain traversing the narrow amorphous zone between two consecutive clusters of helices, giving low molecular weight fragments of amylopectin (LMWAP) of DP 50-80 approximately; (b) breaks in one A-chain and B-chain immediately above the double helix; and (c) a single break in a B-chain that would release LMWAP of DP 20-30.

Source: Morrison and Tester (1994)

The ungelatinized material comprised undamaged granules and some birefringent remnants of partially damaged granules. On the hydration above the gelatinization temperature (60 and 80 ^{o}C), all starch was converted into a gel of AP, FAM and LAM, with little or no LMWAP, or into soluble material. The swelling factors of the starch ranged from 1.0 to 6.7 at 20 ^{o}C, and from 10.9 to 9.4 at 80 ^{o}C with increasing levels of damaged starch from 4.6% to 91.1%. The swelling factor calculated for the gel fraction alone (the main component responsible for swelling and water uptake) ranged from 1 to 10.0 at 20 ^{o}C, and from 11.8 to 18.5 at 80 ^{o}C. There was evidence that the swelling of undamaged granules and remnants was probably inhibited by LAM, while the swelling of damaged starch appeared to be unaffected by its LAM content, but depended greatly on its damaged starch content and on the extent to which structural order in the gel-forming components had been "loosened" during the creation of damaged starch.

Different type of miller and milling method not only affect the degree of damaged starch occur, but also meaning to the variation of physicochemical properties of dry-milled rice flour. Chen *et al*. (1999) reported that the grinding-milled waxy rice flour gave the higher solubility (20-35%) during heating at 65, 75, 85, and 95 ^{o}C compared with the other milling method (turbo, cyclone and hammer mill) due to the higher level of damaged starch. There is the relation between flour particle size and pasting characteristics of waxy rice flour based on RVA measurement. The finest flour showed the lowest initial temperature, while the coarse flour had the highest. The breakdown value decreased as the median of flour particle size (PS50) increased. The results showed that a reduction in particle size of waxy rice flour resulted a decreasing of gelatinization temperature (T_o and T_p) measured by DSC and ΔH due to the decreasing of the native crystalline structure occurred during the grinding process. Similar to the study performed by Chen *et al*. (2003), the results showed that the X-ray peak intensity of the A-type pattern from Tainung Sen 19 (TNuS19) and Taichung Waxy 70 (TCW70) rice starch was significantly decreased as the increasing of ball-milling time from 0 to 60 min. The pasting behavior by RVA measurement was also affected by ball-milling treatment time. The results indicated that both TNuS19 and TCW70 ball-milled starch exhibited lower the onset temperature, peak viscosity, setback and cold-paste viscosity than untreated rice starch samples as showed in Figure 8. After 30 min of treatment, both TNuS19 and TCW70 ball-milled samples showed cold water viscosity. The author pointed that the high proportion of damaged starch probably contributed to their high water retention capacity. The statistical analysis showed that ball-milling treatment time was negatively correlated with the peak temperature (*r* = -0.91, *p*<0.01), peak viscosity (*r* = -0.92, *p*<0.01), hot-paste viscosity (*r* = -0.89, *p*<0.01) and cold-paste viscosity (*r* = -0.83, *p*<0.01). Ball-milling treatment also affected the gelatinization properties of the TNuS19 and TCW70 rice starch. The results indicated that the TNuS19 sample significantly decrease the onset (T_o), peak (T_p), and conclusion (T_c) temperature as well as gelatinization enthalpy (ΔH) after ball-milling treatment. The statistical analysis showed that ΔH was negatively correlated with ball-milling treatment time (*r* = -0.84, *p*<0.01).

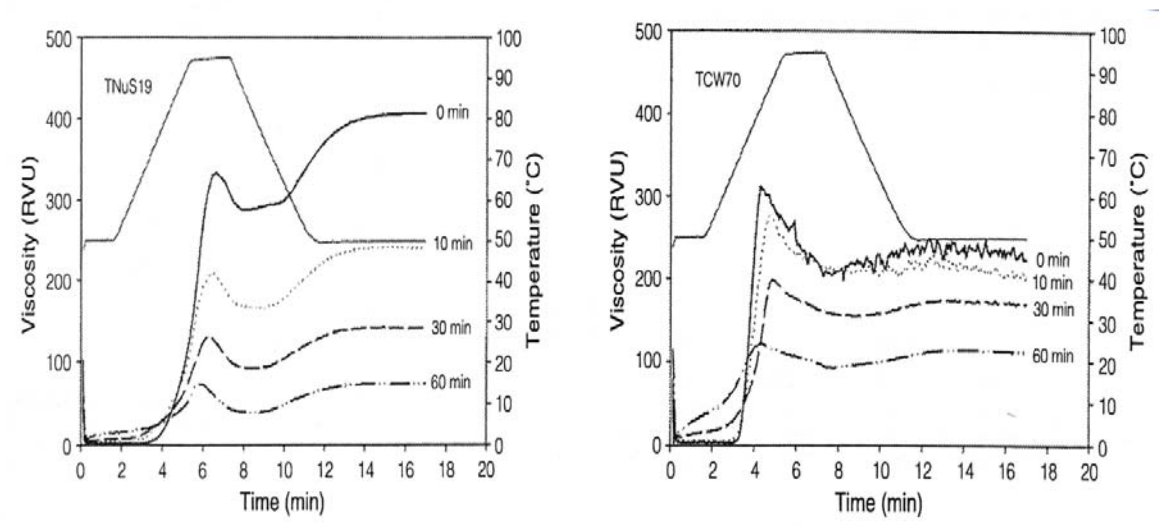


Figure 8 The effect of ball-milling treatment on pasting characteristics of TNuS19 and TCW70 rice starch.

Source: Chen *et al*. (2003)

In conclusion, the type of miller or grinder and the degree of milling are the importance factors that affect degree of starch damaged, flour particle size distribution, and physicochemical properties of dry-milled rice flour. Thus, the information about milling histories and effect on milling process on the properties of rice flour are necessary for evaluation and quality control task in milling processes.

2.3 Wet-milling

Soaking, adding excess water during grinding and removing the excess water are the three steps that differentiate wet-milling from dry-milling. Yeh *et al.* (1992) reported that the absorption of water into the rice kernels was a function of both temperature and time. Using indica rice (TNuS 19) as an example, the water content in the rice kernel increased with time reached to a plateau (a final water content) when the soaking and temperature was lower than 63.5 ^{o}C. The final water content of the rice kernel was 27% at 48 ^{o}C and rose to 32% at 63.5 ^{o}C. The time required to reach the final water content increased with raising of temperature. For minutes was adequate to reach the final water content at 48 ^{o}C, but 80 min was needed at 63.5 ^{o}C. Soaking at a temperature higher than 70 ^{o}C resulted in breakage of the rice kernel due to starch gelatinization. The product became pregelatinization flour after milling. Likewise the research performed by Chiang and Yeh (2002) at lower temperature (5 and 25 ^{o}C), the results indicated that the water uptake by the rice kernel depended upon the temperature and time of soaking. The moisture content in rice kernels (polished high-amylose indica rice) reached to 30.4% in 1 hr and that was close to the plateau moisture content of about 31.6% after 8 hr soaking at 25 ^{o}C. On the other hand, it took one day to have 30.4% moisture content when rice was soaked at 5 ^{o}C which the final moisture content was 32%.

There are many researches showed that part of water-soluble vitamins, proteins sugars, and some lipids are lost during wet-milling process. Lu and Li (1989) showed that dry-milled rice flour was highest in protein, lipid, ash, and reducing sugar compared with wet- and semidry-milled flour from both japonica (TNu 70) and indica (TCS 80) rice varieties. Dry-milled TNu 70 rice flour contained 8.02 % of protein, 0.41 % of fat, 0.45 % of ash and 0.90 % of reducing sugar, whereas wet-milled rice sample contained 6.67 % of protein, 0.03 % of fat, 0.17 % of ash, and 0.15 % of reducing sugar. Likewise, dry-milled TCS 80 rice flour contained 7.91 % of protein, 0.27 % of fat, 0.57 % of ash, and 0.74 % of reducing sugar compared with wet-milled rice sample that contained 5.70 % of protein, 0.03 % of fat, 0.22 % of ash, and 0.15 % of reducing sugar. Similarly, Chen *et al*. (1999) showed that dry-milled maintained a higher level of protein, ash, and lipid than semidry-milled and wet-milled method. Two waxy type rice varieties, japonica type (Taichung Waxy 70, TCW70) and indica type (Taichung Sen Waxy 1, TCSW1) were determined. For dry-milled flour, polished rice kernels were ground with turbo, cyclone, or hammer mills. For semi-dry milled flour, rice samples were steeped in water, centrifuged to remove water, then ground with hammer or plate mill. For wet-milled flour, the rice kernels were steeped and ground with four times its weight in water with a double-disk stone mill. The two waxy rice cultivars, TCW70 and TCSW1, contained 4.97-8.05 % of protein, 0.19-0.89 % of ash, and 0.30-2.54 % of fat. Dry-milling resulted in significantly (p<0.05) higher contents of protein, lipid, and ash than did semi-dry and wet-milling. As reported by Chiang and Yeh (2002), during soaking in wet-milling process of rice flour, protein, lipid, and ash leached out from the rice kernel as the function of temperature and time. With the same moisture content in rice grain (high-amylose indica rice) after being soaked 1 day at 5 ^{o}C and at 1 hr at 25 ^{o}C, the rice lost more crude protein, fat, and ash at 25 ^{o}C than 5 ^{o}C. At the end of soaking, less than 7 % of protein was lost at both soaking temperature. Nevertheless, about 50 % of fat and ash had leached out at 5 ^{o}C and less than 30 % of fat and ash had leached out at 25 ^{o}C for the soaking time of 8 hr due to the longer soaking time of 7 days for 5 ^{o}C soaking.

Wet-milling is reported as the milling method that gains finer rice flour and lower degree of starch damaged compared with dry-milling. Chiang and Yeh, (2002) reported that soaking was the step that caused wet-milling produces the fine and low amount of damaged starch. The soaking temperature and time were reported as the factor affected the particle size distributions of flour. The unsoaked rice kernel yielded 35% of flour with particles larger than 450 μm. After 30 min soaking at 25 ^{o}C, the percentage of particles larger than 450 μm decreased to 4.2% and the percentage of particles smaller than 10.4 μm increased from 17.2% to 36.3%. That extended soaking time reduced particle size was also observed for those soaked at 5 ^{o}C. The percentage of particles smaller than 10.4 μm increased from 21.6% to 28.3% and the percentage of particles larger than 450 μm decreased from 9.6 to 3.7% when soaking time was increased from 3 hr to 1 day. This appeared that the moisture content was a major factor (r^2 = 0.98) affecting the particle size of flour. Amount of damaged starch in wet-milled rice flour are also the effect of the amount of water uptake during soaking process. The increase in moisture content in rice kernel resulted in a decrease in damaged starch. When the moisture content was increased from 13% to 28%, the damaged starch decreased from 8.4% to about 5%. Continued soaking, particularly at 5 ^{o}C, resulted in moisture contents higher than 32% and damaged starch less than 1%. They also found that the effect of soaking on the particle size and damaged starch related by the change in the structure of rice kernels as showed in Figure 9. Before soaking, the SEM of rice endosperm showed a continuous matrix with tightly packed cell contents (Figure 9a). As the surface material leached out and water diffused into the rice kernel after being soaked for 10 min at 25 ^{o}C, large, polygonal, compound starch granules (3-9 μm) and spherical protein bodies were observed (Figure 9b). The continuous matrix was disappeared after 60-min soaking. The compound starch granules were observed clearly. The cavity on the surface of starch granules resulted from the leaching out of protein bodies during soaking (Figure 9c). Extended soaking of 7 days at 5 ^{o}C revealed more individual starch granules (Figure 9d). The authors stated that the leaching out of protein, lipid, and ash and the penetration of water, the loosened of the endosperm structure during soaking caused fine flour and less damaged starch of wet-milled rice flour.

Beside the finer particle size and lower damaged starch content, wet-milled rice flour also exhibited the difference in physicochemical properties compared with dry-milled rice flour. Chen *et al.* (1999) showed that wet-milled waxy rice flour (TCW70 and TCSW1) gave the higher swelling at 75, 85, and 95 ^{o}C than dry-milled (turbo-, cyclone-, and hammer-mill) waxy rice flour. Wet-milled rice flour also showed the higher peak viscosity measured by RVA and enthalpy change (ΔH) than those of dry-milled flour.

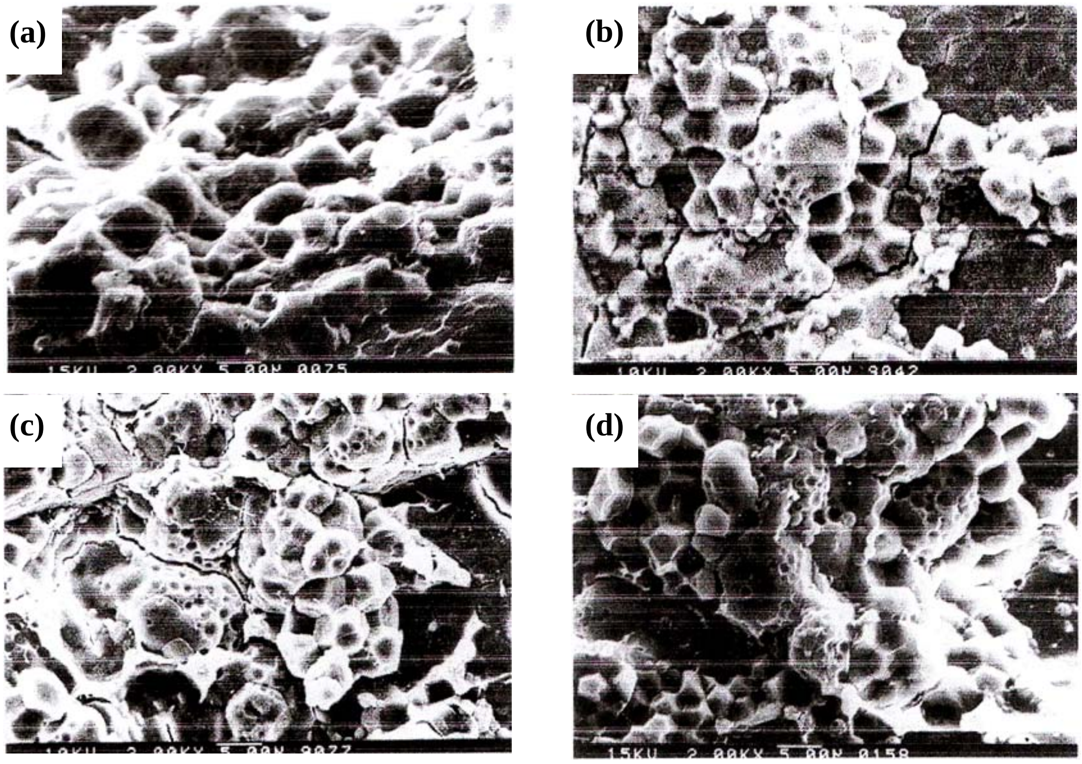


Figure 9 SEM of the outer endosperm of rice kernel. (a) Before soaking, (b) soaked at 25^{o}C for 10 min, (c) soaked at 25^{o}C for 60 min, (d) soaked at 5^{o}C for 7 days.

Source: Chiang and Yeh (2002)

Similar to the results reported by Yoenyongbuddhagal and Noomhorm (2002b), wet-milled rice flour (Sao Hai) showed the higher peak viscosity (P = 309.87 RVU), breakdown (BD = 84.92 RVU), and final viscosity (F = 373.21 RVU) than those of dry-milled flour (P = 202.71 RVU, BD = 45.88 RVU, and F = 326.50 RVU). The onset temperature (T_o = 69.94 ^{o}C) of gelatinization and enthalpy change (ΔH = 12.6 J/g) of the wet-milled rice flour were significantly higher than those of dry-milled rice flour (T_o = 64.26 ^{o}C, and ΔH = 7.08 J/g). Alternatively, Chiang and Yeh (2002) stated that the soaking time (0.5, 2, and 8 hr) did not significantly alter the onset and peak temperature of wet-milled rice flour as measured by DSC due to the low amount of damaged starch (less than 10%) among the samples. However, the finest wet-milled rice flour showed the lowest pasting temperature, and the highest final viscosity. The authors stated that small particles, which were associated with less damaged starch yielded high setback values and final viscosities. The peak viscosity also increased (r^2 = 0.87) as the average particle size decreased.

2.3 Semidry-milling

Rice is soaking for ½ to 1 hr at room temperature and then centrifuged (2,000 rpm) for about 1 min before grinding in the process of semidry milling. After soaking, the moisture content of the rice is approximately 30%, which varies with the rice variety. There is about 5-10% reduction in moisture content after centrifugation. Hammer, plate or pin mills have been used for grinding. After grinding, the flour is redried to about 13% moisture by air at 40 ^{o}C. The contents of protein, fat, ash, and reducing sugar in semidry-milled flour are lower than those in dry-milled flour. The semidry milled flour exhibits low peak viscosity with delayed initial viscosity increase (as shown by the viscoamylograph) and has the highest degree of gelatinization (about 40%) among flour prepared by dry, wet, and semidry milling (Lu and Lii, 1989). During semidry milling, the moisture in rice is not adequate to cool the heat generated by friction force. Instead, the moisture from soaking enhances the gelatinization of starch by lowering the gelatinization temperature. Therefore, semidry-milled flour has a high degree of gelatinization and exhibits low peak viscosity and delayed temperature for the initial viscosity increase (in the viscoamylograph). Compared with wet-milling, no wastewater is generated in semidry-milling, which saves operating costs. Nevertheless, the related literature is limited. Semidry-milled flour are worthy of further studies to investigate their applications (Yeh, 2004).

3. Rice Noodle

Rice noodle is one of the most popular rice products consumed in Thailand and Southeast Asia. There are many kinds of rice noodle type products such as flat or sheeted noodle (big strip, Kuay Tiew and small strip, Sen Lek), rice vermicelli (Sen Mee), Kuay Chap, fermented rice noodle (Kanomjeen) and rice paper. The different types of rice noodle come from size and preparation method. Quality aspects of rice noodle are influenced by many factors including chemical and physicochemical properties of raw materials and production process (Yeh, 2004).

Traditionally, rice noodles are prepared from broken rice. The broken rice should be cleaned, washed and soaked in water for 3 hours. The wet milling of soaked broken rice is done in a stone mill. The rice slurry is placed on a noodle-making machine until the drum is immersed halfway. The smooth drum is then slowly rotated, and flows onto a moving, taut, cotton conveyor belt into a steam tunnel for gelatinization. The gelatinized sheet about 1 mm thick is then passed via conveyor belts through dryer and a cutter. The partially dried rice sheets are placed on frames to further dry and cut to noodle small strip with a cutter, before final drying (Juliano, 1985).

Rice noodles are usually made from long-grain rice with high amylose content (> 27% amylose) (Juliano, 1985). Sanchez (1975) used sensory evaluation to assess the quality of noodles made from different varieties of rice. A highly significant correlation was found between high amylose and general acceptability. Chen and Luh (1980) reported that swelling capacity of starch and amylose-amylopectin ratio are the two major factors affecting rice noodle quality. Li and Luh (1980) noted that rice varieties with high amylose, low gelatinization temperature, and hard gel consistency were best suited for making noodles. Lai (2003) studied the novel method to prepare rice pasta from two commercial rice flour (GTIndica and GTJaponica, with amylose contents of 30.68 and 18.52%, respectively) and their blended flour. The results showed that rice pasta made from high-amylose rice flour had better extrusion properties, better texture, whiter colour, less cooking loss and better eating quality than that made from low-amylose rice flour. The maximum amount of low-amylose rice flour that could be blended in for making an acceptable quality of rice pasta was 1:1. The researcher suggested that steam treatment of extruded rice pasta before drying and emulsifier addition significantly improved the cooking properties for rice pasta.

In Thailand, the influences of rice varieties in rice noodle properties were reported. Ruamchit (1979) showed that rice noodle made from Leuang Pratew 123, RD 1 and Khao 500 attained the preferable quality noodle while RD 5 and RD 7 gave the poor quality noodle and Khao Dawk Mali 105 could not be utilized in noodle production. Amylose content and paste viscosity are reported as the two major factors affecting rice noodle quality. He noted that rice varieties with high amylose (above 27%) and high consistency measured by amylogragh (above 600 BU) were best suited for making noodles. Beside the rice variety, good quality rice noodle must be prepared from aged rice that was stored for more than 4 months after harvest. Tulapongsarug (1995) showed effect of rice varieties and rice aging in the quality of noodles made from 7 varieties of rice with high amylose content (30.62 – 32.42%). The results indicated that the rice noodle made from Khao Gan Tang, Leuang Pratew 123 and Pin Gaew 56 were the most accepted by the panelists. The rice noodles from Koa Gan Tang variety aging for 4-12 month gave the best quality while Leuang Pratew 123 variety and Pin Gaew 56 variety aging for 4-8 month provided good qualities of rice noodles.

Bhattacharya *et al*. (1999) performed the study that aimed to 1) standardized a laboratory-scale method for making rice noodles, 2) study genotypic variation in physicochemical and pasting properties of 11 rice genotypes in relation to noodle quality, 3) assess whether texture analysis of the gel formed after RVA analysis could be used for predicting the eating quality of rice noodles, and 4) identify specific characteristics responsible for producing superior quality rice noodles was performed. The results showed that amylose content ranging from 25.6% in IR46 to 11.9% in IR48 was the major factor affecting pasting and texture properties of rice flour and also rice noodle, which made by laboratory-scale method. Apparent amylose content (AC) was highly correlated with swelling power (r = -0.65, p<0.05), flour swelling volume (FSV) (r = -0.67, p<0.01), noodle hardness (r = 0.74, p< 0.01), gumminess (r = 0.82, p<0.01), chewiness (r = 0.74, p< 0.01), and tensile strength (r = 0.72, p< 0.05). Solubility showed an inverse relationship with the pasting parameters and noodles rehydration, and a positive relationship with cooking loss, noodle hardness, and gumminess. FSV and most of the pasting parameters were negatively correlated with noodle hardness. RVA parameters and textural parameters of gels formed in the RVA canister were well correlated with actual noodle texture. For instance, hardness of cooked noodle was significantly correlated with hardness (r = 0.62), springiness (r = 0.84), gumminess (r = 0.63) and chewiness (r = 0.65) of RVA gel. Therefore, RVA properties can be used as a simple, rapid and accurate tool predicting the textural quality of noodles.

In 2000, Yoenyongbuddhagal and Noomhorm (2000a) investigated the effect of physicochemical properties of rice flour from six different high-amylose Thai rice cultivars: Sao Hai (33.6 %amylose), Suphan Buri 90 (34.9 %amylose), Chai-nat 1 (35.2 %amylose), Prachin Buri 1 (33.3 %amylose), Plai Ngahm Prachain Buri (32.9 %amylose), and Suphan Buri 1 (36.7 %amylose) on vermicelli quality. The results showed rice flour samples had different in onset temperature (T_o = 61 to 72 ^oC), peak temperature (T_p = 65 to 76 ^oC), and the enthalpies of gelatinization (ΔH = 8.6 to 12.6 J/g). The swelling power of rice flour increased with the increasing temperature and furthermore the swelling patterns were different even for samples with similar amylose content implied the difference of molecular structure among rice varieties. Similarly, a wide variation in all pasting parameters among the rice flour samples was also observed. Gel hardness values of rice flour were 23 g to 29 g and they also showed the significantly positively correlated with setback measured by RVA. The cooking quality and texture of the six test rice cultivars and 10 commercial vermicelli products were assessed. The results showed that all rice vermicelli samples were considered acceptable compared with the commercial products in terms of cooking properties, but quite different in textural properties due to differences in the rice cultivars and processing condition. The correlation study indicated that the soluble loss, total loss and hardness of vermicelli samples were significantly correlated to gel hardness of rice flour. The researchers suggested that the gel hardness could be used to predict the vermicelli quality from rice flour.

The wet-milling process used in the traditionally rice noodle making consumes the large amount of water, which in turn creates a lot of wastewater. Thus, many attempts have been made to prepare rice noodle from dry milled flour instead of wet milled flour. In 1997, Tungtrakul conducted the experiment, which aimed to compare the effect of using rice flour from wet-milling and dry-milling process on rice noodle properties. Rice flour samples were prepared from milled three rice varieties (IR, Khao Tah Haeng and Sao Hai) by dry- and wet-milling method. The results showed that rice flour from dry-milling contained higher proportion of large particles (41.2-53.5 μm) than that of wet-milling method (32.8-38.4 μm). The results from texture profile analysis of rice noodles prepared from dry- and wet-milled flour showed that wet-milled rice flour gave harder texture with higher hardness of 7.32, 7.66 and 12.7 (10^4dyn/cm^2) for imported rice, Khao Tah Haeng and Sao Hai rice samples, respectively (Tungtrakul, 1997).

Yoenyongbuddhagal and Noomhorm (2002b) performed the study to investigate the effect of milling method on rice vermicelli quality. The results showed that milling method affected chemical compositions and all physicochemical properties of flour. Dry-milled flour contained significantly higher amount of amylose, protein, fat, ash and starch damage compared to wet milled flour. Dry-milled flour swelled to higher extent than wet milled flour at 60^{o}C. When temperature was raised, swelling power increased in both flour samples. Wet milled flour swelled at a higher rate than dry milled flour after passing 70^{o}C, resulting in a higher swelling power at 90^{o}C. Rice vermicelli made from dry-milled flour had higher cooking losses (total loss = 4.40%) than that made from wet-milled flour (total loss = 5.00%). Wet-milled flour gave significantly firmer texture of vermicelli (hardness = 489.24 g) than that of dry-milled flour (hardness = 362.9 g), whereas no significant difference was found between adhesiveness, springiness and cohesiveness values.