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# DEVELOPMENT OF HIGH-FIBER DRIED RICE NOODLE FROM MODIFIED RICE FLOUR

Miss Pornpimon Kasikitwiwat

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science Program in Food Technology

Department of Food Technology

Faculty of Science

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	FROM MODIFIED RICE FLOUR
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พรพิมล กสิกิจวิวัฒน์: การพัฒนาผลิตภัณฑ์ก๋วยเตี๋ยวเส้นเล็กอบแห้งเส้นใยอาหารสูงจากแป้งข้าวดัด แปร. (DELOPMENT OF HIGH-FIBER DRIED RICE NOODLE FROM MODIFIED RICE FLOUR) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.กัลยา เลาหลงคราม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ.ดร.สายวรุฬ ชัยวานิชศีริ, 99 หน้า.

งานวิจัยนี้มีวัตถประสงค์เพื่อศึกษาผลของการดัดแปรแป้งข้าวด้วยการใช้กรดซิตริกต่อปริมาณแป้งทนย่อยต่อ เอนไซม์และสมบัติเชิงเคมีฟิสิกส์ และพัฒนาผลิตภัณฑ์ก๋วยเตี๋ยวอบแห้งให้มีเส้นใยอาหารสูงด้วยการใช้แป้งข้าวดัดแปรนี้ ์ โดยศึกษาสภาวะในการให้ความร้อนที่เหมาะสมในการดัดแปรแป้งข้าวด้วยกรดซิตริกความเข้มข้น 0.1 M ที่อุณหภูมิ 100, 110 และ 120°C เป็นเวลา 15, 30 และ 45 นาที จากนั้นศึกษาผลของอุณหภูมิที่ใช้ในการบ่มแป้งข้าวดัดแปร โดย แปรที่ 5, 30, 45, 60, 75 และ 90°C วิเคราะห์ปริมาณแป้งทนย่อยต่อเอนไซม์และสมบัติเชิงเคมีฟิสิกส์ของแป้งข้าวและ ้แป้งข้าวดัดแปร จากนั้นผลิตผลิตภัณฑ์ก๋วยเตี๋ยวอบแห้งโดยการแทนที่แป้งข้าวด้วยแป้งข้าวดัดแปรที่ระดับ 10, 20 และ 30% และศึกษาสภาวะที่เหมาะสมในการอบแห้งก๋วยเตี๋ยวที่อุณหภูมิ 50, 60 และ 70⁰C วิเคราะห์ปริมาณแป้งทนย่อยต่อ เอนไซม์ คณภาพหลังการต้ม ลักษณะเนื้อสัมผัสและทดสอบความชอบทางประสาทสัมผัสของเส้นก๋วยเตี๋ยว การศึกษาพบว่า แป้งข้าวที่ผ่านการให้ความร้อนร่วมกับกรดมีปริมาณแป้งทนย่อยต่อเอนไซม์ ปริมาณแอมิโลส ค่าการ ละลายที่ 75ºC และปริมาณสารประกอบเชิงซ้อนของแอมิโลสกับไขมันมากกว่าแป้งข้าวที่ไม่ผ่านกระบวนการ ค่ากำลัง การพองตัวของแป้งข้าวดัดแปรดัดแปรด้วยกรดที่ให้ความร้อน 100°C มีค่าสูงขึ้น แต่เมื่อให้ความร้อนที่สภาวะรุนแรงขึ้น กลับมีแนวโน้มลดลง ส่วนค่าความหนืดสูงสุด ความหนืดสุดท้าย ค่าเบรคดาวน์และค่าเซตแบค รวมทั้งค่าดัชนีความขาว ้และระดับความเป็นผลึกของแป้งข้าวดัดแปรด้วยกรดภายหลังการให้ความร้อนมีแนวโน้มลดลง โดยเมื่อให้อุณหภูมิสูงขึ้น และเวลานานขึ้นจะทำให้สมบัติต่างๆดังกล่าวเปลี่ยนแปลงชัดเจนขึ้น ยกเว้นระดับความเป็นผลึก สภาวะที่เหมาะสมใน การให้ความร้อนแก่แป้งข้าว คือ อุณหภูมิ 120°C เวลา 45 นาที เนื่องจากมีปริมาณแป้งทนย่อยต่อเอนไซม์มากที่สุด (6.51%) สำหรับปริมาณแป้งทนย่อยต่อเอนไซม์ แอมิโลส ค่าการละลาย ปริมาณสารประกอบเชิงซ้อนของแอมิโลสกับ ้ไขมัน และระดับความเป็นผลึกของแป้งข้าวดัดแปรมีค่าสูงขึ้นเมื่ออุณหภูมิในการบ่มสูงขึ้น ซึ่งแป้งข้าวดัดแปรที่บ่มที่ ้อุณหภูมิ 90<sup>0</sup>C มีปริมาณแป้งทนย่อยต่อเอนไซม์สูงที่สุด(12.41%) จากการแทนที่แป้งข้าวด้วยแป้งข้าวดัดแปร พบว่า เมื่อ ระดับการแทนที่มากขึ้นก๋วยเตี๋ยวมีปริมาณแป้งทนย่อยต่อเอนไซม์ ปริมาณของแข็งที่สูญเสียระหว่างการต้ม และการดูด ้น้ำกลับเพิ่มขึ้น แต่ค่าความแข็ง (hardness) ค่าแรงสูงสุดในการดึง และค่าแรงสูงสุดในการตัดลดลง โดยระดับการแทนที่ 20% ให้ก๋วยเตี๋ยวที่ได้รับคะแนนการยอมรับทางประสาทสัมผัสโดยรวมสูงที่สุด โดยอุณหภูมิในการอบแห้งก๋วยเตี๋ยวไม่มี ้ผลต่อปริมาณแป้งทนย่อยต่อเอนไซม์ และปริมาณของแข็งที่สูญเสียระหว่างการต้ม แต่การอบแห้งก๋วยเตี๋ยวที่อุณหภูมิสูง ้ทำให้ค่าการดูดน้ำกลับเพิ่มขึ้น แต่ค่าความแข็ง ค่าแรงสูงสุดในการดึงและค่าแรงสูงสุดในการตัดลดลง ซึ่งอุณหภูมิที่ เหมาะสมในการอบแห้งก๋วยเตี๋ยวคือ 50 <sup>o</sup>C

ภาควิชา	เทคโนโลยีทางอาหาร	ลายมือชื่อนิสิต
สาขาวิชา <u></u>	เทคโนโลยีทางอาหาร	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
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#### # # 5272684723: MAJOR FOOD TECHNOLOGY

# KEYWORDS: Resistant starch / Modified rice flour/ Citric acid modification / Rice noodle PORNPIMON KASIKITWIWAT: DELOPMENT OF HIGH-FIBER DRIED RICE NOODLE FROM MODIFIED RICE FLOUR. ADVISOR: ASSOC. PROF. KALAYA LAOHASONGKRAM, Ph.D., CO-ADVISOR: ASSOC. PROF. SAIWARUN CHAIWANICHSIRI, Ph.D., 99 pp.

This research aims to determine the effect of citric acid modification on resistant starch content and physicochemical properties of rice flour, and to study the application of the modified rice flour in dried rice noodle. Rice flour was modified by 0.1M citric acid at different reaction temperatures (100, 110 and 120°C) and times (15, 30 and 45 min). The acid treated flour was then incubated at 5, 30, 45, 60, 75 and 90°C. The resistant starch content and physicochemical properties of native and modified rice flour were measured. Dried rice noodles were produced with replacing rice flour by modified rice flour at 10, 20 and 30% and drying at 50, 60 and 70°C. Resistant starch content, cooking quality and texture of rice noodle were evaluated. The results showed that the resistant starch content of rice flour increased from 0.65% (native) to 6.51% (acid treated at 120°C, 45 min). Amylose content, solubility and the amylose-lipid complex of modified rice flour were higher than those of the native flour. Treated rice flour at 100°C had higher swelling power, but swelling power decreased at higher condition. The pasting properties of acid treated rice flour showed to decrease in viscosity, breakdown and setback while those treated at the highest condition (120°C, 45 min) exhibited no RVA peak. Whiteness index and relative crystallinity of modified rice flour were lower than the native. The higher reaction temperature and time resulted in greater change in all properties except degree of crystallinity. Rice flour treated at 120°C/45 min was chosen for studying the effect of incubation temperature due to its highest resistant starch content (6.51%). After incubation, the resistant starch content, amylose content, solubility, the amylose-lipid complex, and relative crystallinity of modified rice flour increased with increasing temperature. Modified rice flour incubated at 90°C had the highest resistant starch content (12.41%). Increasing % modified rice flour resulted in higher resistant starch, cooking loss, rehydration, and springiness, but lower in hardness, tensile strength, and cutting force of noodle. The optimum % substitution of modified rice flour at 20% gave noodle having 3.0% resistant starch and the highest sensory score. Drying temperature had no effect on resistant starch content and cooking loss. However, higher drying temperature increased rehydration but decreased tensile strength, cutting force, hardness, and springiness. The suitable drying temperature was 50°C which gave noodle having the highest sensory score.

Department:	Food Technology	Student's Signature
Field of Study:	Food Technology	_ Advisor's Signature
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# CHAPTER I

# INTRODUCTION

Rice noodle is one of the popular staple foods in Thailand as it can be the base of many recipes. Moreover, Thailand exports large amount of this product which can make profit (Prajongwate, 2006). In addition, the growing of the market was increased since it is gluten free. However, it is made from rice that contains high carbohydrate, so it is inappropriate for some group of patients such as diabetes, obesity and health conscious consumer. Improving its nutritional characteristic may provide a choice for these consumers. Addition of dietary fiber in daily intake was reported to lower caloric intake, reduce cholesterol and fat, increase fecal bulk and improve glycemic control, bowel health, and cardiovascular disease risk factors. (Lunn and Buttriss, 2007; Elleuch *et al.*, 2011).

Many studies have indicated that resistant starch is a part of dietary fiber, which is defined as the sum of starch and products from starch degradation not being absorbed in the small intestine of healthy individuals (EURESTA, 1992). These effects may decrease the incidence of colon cancer, atherosclerosis, obesity, type II diabetes (non-insulin dependent) and hypercholesterolemic effect (Haralumpu, 2000; Kim *et al.*, 2003). Unfortunately, rice flour which is the main ingredient in rice noodle contains low resistant starch so native flour must be modified to increase this level. Citric acid modification was found to be one of the modification methods that could increase resistant starch. As it is a polyfunctional carboxylic acid which can esterify hydroxyl groups of starch to form cross-linked starch. (Klaushofer, Berghofer, and Pieber, 1978; Tharanathan, 2005). However, physicochemical properties of the modified flour are also changed.

Therefore, this research aims to modify rice flour by citric acid treatment to increase resistant starch, and to study the application of the modified rice flour in rice noodle. Drying process is also studied to prolong the shelf life of the rice noodle. This can be another choice for consumer and value-added for rice product.

# CHAPTER II

# LITERATURE REVIEWS

#### 2.1 Resistant starch

# 2.1.1 Classification of starch

This classification is based on the nutrition characteristics which expressed starch behavior after being digested with enzymes as digestible starch and resistant starch (Berry, 1986). Digestible starch includes the rapidly digestible starches (RDS) and the slowly digestible starches (SDS) which are completely digested in the small intestine. RDS consists mainly of amorphous and dispersed starch so it is digested quickly in the small intestine which is converted to the glucose molecules in 20 min of enzyme digestion. SDS is found in cereals that consists of physically inaccessible amorphous starch so the rate of digestion is slower than RDS. In vitro testing, SDS is hydrolyzed to glucose between 20 and 110 min. Resistant starch (RS) is a small fraction of starch that resistant to hydrolysis by  $\alpha$ -amylase and pullulanase. It is not hydrolyzed after 120 min of enzyme treatment in vitro (Englyst, Kingman, and Cummings, 1992). Resistant strach is defined as a dietary starch, which is not digested in the small intestine and passes through to the large intestine. It may be fermented by gut microflora.

# 2.1.2 Classification of resistant starch

Resistant starch is defined as the sum of starch and products of starch degradation not absorbed in the small intestine of healthy individuals (European Flair Action Concerted on Resistant Starch (EURESTA), 1992). It is divided into 4 categories

according to the mechanism that prevents enzymatic digestion (Englyst *et al.*, 1992) as follows:

#### - Resistant starch type I

Resistant starch type I (RS1) represents starch that is resistant to enzyme digestion because it is physically inaccessible to digestion due to the entrapment in a non-digestible matrix. RS1 is found in partly milled grains and seeds and in some very dense types of processed starchy foods.

#### - Resistant starch type II

Resistant starch type II (RS2) represents starch that resistant to enzyme digestion due to its certain granular form. In raw starch granules, starch is tightly packed in a radial pattern and is relatively dehydrated. This compact structure limits the accessibility of digestive enzymes. RS2 is found in ungelatinized starches like raw banana.

#### Resistant starch type III

Resistant starch type III (RS3) represents the most resistant starch fraction and is mainly retrograded starch formed during cooling of gelatinized starch. It is found in cooked and cooled starch product and most moist-heated foods.

## - Resistant starch type IV

Resistant starch type IV (RS4) represents the RS which chemical bonds other than  $\alpha$ -(1-4) or  $\alpha$ -(1-6) are formed. The chemical modified starch obtained by many types of chemical treatments such as hydroxypropyl starch, substitution and cross linking starch.

Moreover, Evangelica *et al.* (2011) reported another type of resistant starch (resistant starch type V (RS5)) which is an amylose-lipid complex starch formed from high amylose starches.

# 2.1.3 Benefit of resistant starch on physiological effect

RS is highly resistant to human enzyme and it has physiologically fiber like which can be classified as a part of fiber based on the definitions of dietary fiber (AACC, 2001). RS is not digested in the small intestine but it can be fermented by the microflora in the large intestine. It produces short-chain fatty acids (SCFA) especially butyrate which is a main energy substrate for large intestinal epithelial cells and inhibits the malignant transformation of cells in vitro. So RS fermentable fractions are considered in preventing colonic cancer (Asp and Bjorck, 1992). Moreover, this effect may reduce incidence of atherosclerosis, and obesity-related complications in human (Haralampu, 2000). In food containing RS, the slow digestion of RS has implications for its use in controlled glucose release applications. Long digestion of RS over a 5 to 7 h. period reduces postprandial glycemia and insulinemia and has the potential for increasing the period of satiety (Raben et al., 1994). Higgins et al. (2004) reported that RS3-containing food decreased postprandial blood glucose resulting in improved metabolic control in type II diabetes (noninsulin dependent). Hypocholesterolemic effects of RS were also proved and found that RS can reduce serum cholesterol level and triglycerides by decreasing the production of cholesterol (Haralampu, 2000).

RS in a meal could significantly increase postprandial lipid oxidation, which suggested a reduction in fat accumulation in a long term (Higgins *et al.*, 2004) and it could have a positive effect on intestinal calcium and iron absorption (Morais *et al.*, 1996). Moreover, RS has prebiotic effects on human as it can promote the growth of

probiotics such as *Bifidobacteria* and *Lactobacilli* by supplying food/energy (Charalampopoulos *et al.*, 2002).

# 2.2 Rice flour

Rice (*Oryza sativa* L.) is a staple food and a very important component of worldwide food. However, processed rice product is interesting due to higher profit. So understanding of the physiochemical properties of rice flour is important because the different processed food using rice flour need different functionality.

#### 2.2.1 Rice flour composition

Rice flour is produced from broken rice due to its low cost. Chemical composition of broken rice as raw material for rice flour production is shown in Table 2.1. Rice flour and starch are different due to protein and lipid contents (Kennedy and Burlingame, 2003). Protein attaches to the surface of starch granule so it affects properties of starch such as water absorption, swelling ability, gelatinization and pasting properties. Moreover, protein also has an effect on color due to Maillard reaction (Lamberts *et al.*, 2006). Lipids in rice flour are starch lipids and non starch lipids. Starch lipids can complex with amylose. Lipid affects properties of starch as it reduces swelling, solubility ability and water binding capacity of starch (Tester and Morrison, 1990; Vandeputte *et al.*, 2003b).

Starch granules are composed of two main polymers: a linear polysaccharide called amylose, and a highly branched polysaccharide called amylopectin (Miles *et al.*, 1985). Starch is semi-crystalline, cereal starch such as rice starch has the A-type X-ray diffraction pattern (Wong *et al.*, 2003). The degree of crystallinity of rice was found to be low (Vandeputte *et al.*, 2003b). Ong and Blanshard (1995) reported that the crystallinity of rice starch ranged from 29.2% to 39.3%. Crystallinity is influenced by amylose and amylopectin structure but is not concerned on

amylose and amylopectin ratio (Ong and Blanshard, 1995). Vandeputte *et al.* (2003b) reported that waxy rice starch had more crystalline but lower amylose content than non waxy rice starch and showed lower in gelatinization temperature.

12.0	
79.2	
7.0	
0.4	
0.5	
0.9	
	79.2 7.0 0.4 0.5

 Table 2.1 Chemical composition of broken rice grain

Source: Knight (1969)

Amylose consists of a linear molecule containing ( $\alpha$ -1, 4)-linked glucose units, but may contain a few ( $\alpha$ -1, 6)-linkage branches (Collado and Corke, 2003). The amylose chain has a helical structure. The outer surface is the hydrophilic because of hydroxyl groups while the internal of the helix is hydrophobic. Its structure allowed amylose to form a complex with free fatty acid and iodine (Whistler and BeMiller, 1997). Moreover, amylose can form gel after the starch granule has been cooked due to its linear chains. This is a property of amylose-containing starches (Thomas and Atwell, 1999).

Amylopectin is a highly branched molecule with ( $\alpha$ -1, 4)-linked glucose units in linear chains and ( $\alpha$ -1, 6)-linked branched points (Collado and Corke, 2003). The properties especially gel forming ability of amylopectin differ from amylose because of its highly branch. Pastes from starches that contain only amylopectin are non-gelling but typically have cohesive and gummy texture (Thomas and Atwell, 1999). Rice is divided into 5 categories according to amylose content (Juliano, 1992) as waxy rice (amylose content below 2%), very low amylose rice (amylose content 2-9%), low amylose rice (amylose content 10-20%), intermediate amylose rice (amylose content 20-25%) and high amylose rice (amylose content 25-30%). Rice with different amount of amylose content has different physical, chemical and physicochemical properties.

#### 2.2.2 Properties of starch

#### 2.2.2.1 Swelling power and solubility

Starch granule is insoluble in cold water but it can swell slightly (Fennema, 1996). When starch is heated in excess water, starch granule is disrupted by breakage of hydrogen bonds and these support water molecule to link with amylose and amylopectin by hydrogen bonds. Starch granule hydrates water at amorphous region before crystalline region because crystalline structure is too strong to allow water molecule to go inside (Ever and Steven, 1985). Starch granule absorbs water and swells to several times of its initial size (Tsai, Li, and Lii, 1997). When starch granules swell, the amylose inside the granules leaches out, these call solubility. The swelling behavior of cereal starch is related to amylopectin structure, while solubility is related to degree of polymerization (DP) but amylose-lipid complex acts as an inhibitor of swelling and solubility (Tester and Morrison, 1990). The large DP molecule has a lower tendency to leach out of the granule during heating so solubility decreases (Vandeputte *et al.*, 2003a). It was also found that the low amylose rice starch had high swelling power and low solubility (Lii, Shao, and Tseng, 1995; Sodhi and Singh, 2003)

# 2.2.2.2 Gelatinization

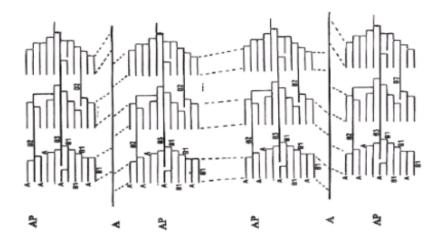
Gelatinization is the process that carries out when starch is heated in excess water. It is an irreversible change which includes disruption of hydrogen bonds between polymer chains and molecular order and also destruction of the crystalline region (Fennema, 1996). These phenomena results in loss of birefringence and loss of crystallinity. Thermal and pasting properties are changed during gelatinization so studying of thermal and pasting properties might be important for understanding starch gelatinization.

Thermal properties is normally measured by Differential Scanning Calorimetry (DSC) which reports in term of onset temperature (To), peak temperature (Tp) and conclusion temperature (Tc) and enthalpy ( $\Delta$ H). DSC parameters correspond to distribution of amylopectin in crystalline regions (Noda *et al.*, 1996).  $\Delta$ H value reflects the loss of double helical order of amylopectin when starch is gelatinized (Cooke and Gidley, 1992; Tester and Morrison, 1990). Gelatinization temperatures correlate with amylopectin structure due to crystalline forming. Comparing rice starch with having similar amylopectin chain length, the low gelatinization temperature rice starch has less perfect crystallite than another (Tester and Morrison, 1990). Effect of amylose content of rice starch and rice starch blend on thermal properties was also studied and found that increasing of amylose content caused increasing in gelatinization temperature (Lu *et al.*, 2009).

When starch is continuously heated to gelatinization temperature, the pasting viscosities are also changed and can be followed by using Brabender Visco Amylograph or Rapid Visco Analyzer (RVA). The pasting viscosity of rice flour is different from its starch due to the presence of protein and fat. The protein associated with starch may cause the decreasing in peak viscosity (Martin and Fitzgerald, 2002). Moreover, the ageing period reduces peak viscosity of rice flour but has no effect on rice starch because a number of disulfide bonds is increased during storage (Teo *et al.*, 2000; Martin and Fitzgerald, 2002). Lipids also affect viscosity of rice flour. Amylose–lipid complex decreases a viscosity because it reduces starch swelling (Zhou *et al.*, 2002). Voravinit *et al.* (2003) reported that high amylose rice starch had lower breakdown and peak viscosity but higher setback and pasting properties.

#### 2.2.2.3 Retrogradation

Retrogradation is the process in which a gelatinized starch is cooled to temperature below melting point of amylose and amylopectin and they can reassociate to form an order structure. As amylose shows a greater tendency to reassociate and form hydrogen bond than the amylopectin molecule, so the rapid initial rate of retrogradation relates to the development of amylose aggregation. Retrogradation of starch/flour caused by amylose may occurred within one day (Zhou *et al.*, 2002). And then, amylose can form hydrogen bond with amylopectin until saturation, after that amylopectin retrogradation is undergone as shown in Figure 2.1 (Tako and Hizukuri, 2000). Amylopectin retrogradation is also important because native starch contain greater amount of amylopectin. Amylopectin has branching structure which can form shorter double helices, thus amylopectin slowly retrogrades over several weeks of storage (Lii *et al.*, 1995; Zhou *et al.*, 2002).



A means amylose and AP means amylopectin

Figure 2.1 Interaction between amylose molecule and amylopectin molecule, and interaction between amylopectin and amylopectin molecule of rice starch (Tako and Hizukuri, 2000).

The retrogradation mechanism of rice is complicated because it may vary due to differences in the proportion and interaction of amylopectin and amylose, chain length distribution and molecular size of branched molecules (Eliasson and Gudmundsson, 1996). The higher proportion of long chains promotes crystalline formation (Qi *et al.*, 2003). Moreover, Vandeputte *et al.* (2003c) indicated that amylose content and amylopectin chain length distribution affect the amylopectin retrogradation. Besides, the amount of amylose-lipid complex reduces the amylopectin crystallization rate of rice starch (Gelders *et al.*, 2004). Retrogradation results in less soluble starch (Fennema, 1996). Moreover, this phenomenon causes an increase in viscosity, texture staling and firming gel that control the texture and quality of starch containing foods (Thomas and Atwell, 1999). Besides, retrograded starch is classified as a type of resistant starch so formation of resistant starch relate to retrogradation process.

#### 2.2.2.4 Resistant starch III formation

RS3 is retrograded starch. Many studies reported that RS3 was interesting because it is thermostable, so study of RS3 formation might be helpful to understand the RS3 in food. For RS 3 formation, the starch granules are disrupted by heating in excess water as known as gelatinization. During starch gelatinization process, the molecular order of crystalline is destroyed and it is irreversibly. Most of amylose is leached out from the granule when it is further heated. Starch granules are disrupted and then partial solubilisation is go on. Upon cooling, starch undergoes a relative slow re-association process commonly called retrogradation. During retrogradation, starch molecules re-associate as double helices and can form a three-dimensional crystalline structure stabilized by hydrogen bonding and dehydration. These tightly packed structures are thermally stable, and can melt at 80 - 150°C, depending upon the extent and nature of the retrogradation and amylose concentrations (Eerlingen and Delcour, 1995). The formation of RS3 depends on degree of amylose polymerization, amylose to amylose ratio, double-helical polymorph, water and lipid content, process and storage condition (Englyst *et al.*, 1992; Thompson, 2000).

The possible model of RS3 formation in aqueous amylose solutions was proposed by Eerlingen, Deceuninck and Delcour (1993): micelle formation and chain folding (lamellar structure as shown in Figure 2.2). Micelles were formed by aggregation of a number of different molecules over particular region of the chain in an ordered structure interspersed with amorphous region. In retrograded amylose, the order regions must be composed of double helices order giving a B-type of X-ray diffraction pattern. Folding of the polymer chain led to two-dimensional structures or lamellar shapes. The regions of the folding were amorphous. The center of the lamella was crystalline while a double helical conformation acted as the barrier to enzyme action.

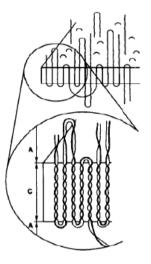


Figure 2.2 Lamella model for the formation of resistant starch in amylose solution. The fold zones are amorphous (A). The center of the lamella is crystalline (C) (Eerlingen *et al.*, 1993).

# 2.3 Starch modification

Starch plays important role in food industry such as improving nutrition, texture, and increasing viscosity, etc. However, the native starches have some disadvantages that would make them restricted for some type of food and application in food processing. The suitable modification can change the properties of starch to desirable character such as wide viscosity range, gel forming at low temperature, more desirable texture and stability, and better nutritionally benefits. These can serve the evolution of new processing technologies and market trends (Light, 1990). Modified starch may be divided by as follows (BeMiller, 1997)

Physical modification: starch can be physically modified using a number of techniques to provide desirable properties. Such techniques include pregelatinization, heat-moisture treatment, annealing etc.

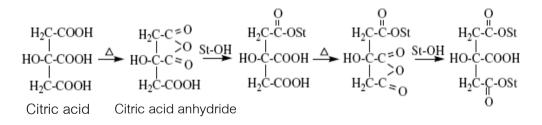
Chemical modification: starch can also be chemically modified such as conversions include acid hydrolysis, oxidation, dextrinization and the addition of unique functional groups called deriverization. Deriverization can be monostarch substitution by esterification and etherification or polystarch substitution by cross-linked starch.

Biotechnological modification: properties of starch are changed by using genetic modification technique to produce various modified starch such as waxy starch and high amylose starch.

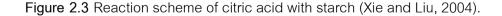
Properties and application of modified starch depend on modification method. Moreover, combination treatments are also commonly used to achieve the desired objective. The most popular are cross-linking, stabilization and pregelatinization. Nowadays, consumers concern their health so some modification is developed to increase slowly digestible starch or resistant starch in starch which is good benefit for health. Example of starch modification that can increase resistant starch are hydrothermal treatment including heat moisture treatment and annealing (Jacobs *et al.*, 1998; Chung, Liu and Hoover, 2009), enzymatic treatment such as debranching (Milasinovic, Radosavljevic, and Dokic, 2010) and chemical treatment such as substitution, cross-linking (Light, 1990). Acid treatment on starch is one of the modification methods that many researchers studied to increase resistant starch content in starch such as acid thinning and partial acid hydrolysis etc. Both organic acid and inorganic acid were used to treat starch, however organic acids should be used to modify starch because of their safety. Many studies of organic acids such as acetic acid, citric acid, lactic acid and maleic acid on starch were reported, but citric acid was the most interesting because it was cheap and had no smell. Moreover, Zhao and Lin (2009) found that retrograded high-amylose maize starch treated with 0.1 M citric acid solution at room temperature for 12 h had resistant starch increase up to 39%, more than those treated with 0.1 M hydrochloric acid or acetic acid at the same condition (29.2 and 30.0%, respectively). So, in this study citric acid was used to modify rice flour.

# 2.4 Citric acid modification

Citric acid treatment on starch can promote esterification between starch and citric acid because citric acid has 3 carboxyl groups which can react with hydroxyl group of starch as shown in Figure 2.3 (Xie and Liu, 2004). The reaction occurs when citric acid is heated to dehydrate under limited water and citric acid anhydride is formed. Citric anhydride esterifies starch to form substituted starch. The bulky substituent groups hinder starch chain from digestive enzyme that resistant to degradation causing the increase in resistant starch (RS4) (Björck, Gunnarsson, and Stergard, 1989). Besides substitution, when citric acid treatment on starch in excess water at higher temperature than its gelatinization temperature, starch is gelatinized and then retrograded during incubation resulting in RS3 formation (Onyango *et al.*, 2006).



 $\bigtriangleup$ means heat and St-OH means starch



Many researchers studied citric acid treatment to increase resistant starch. The methods used can be divided into 2 main methods. First, starch was treated in dry

condition and another was treating starch in solution. Xie and Liu (2004) studied the citric acid modification of corn starch by dry method. They mixed corn starch with citric acid solution at ratio 1:1 to obtain 40% citric acid of starch dry weight and conditioned at room temperature for 16 h to allow citric acid penetrating in starch granule before being dried at 50°C until moisture content below 10%. After that, the sample was kept at different temperature (120-150°C) and time (3-9 h). They reported that resistant starch content of the modified starch from normal corn starch after incubation at 140°C for 7 h increased from 41.1% to 78.8% due to an increase in the degree of substitution from 0.09 to 0.12. While the modified starch from waxy corn starch and high-amylose corn starch incubated at the same temperature and time had 87.5% and 86.4% resistant starch content with degree of substitution of 0.16 and 0.14, respectively. Moreover, Xie, Liu and Cui (2006) reported that the granular structure of citrate corn starch was changed to doughnut-like shape, and ester bonds were found suggesting the increase in resistant starch due to substitution and this resistant starch from corn citrate starch was thermostable.

Besides dry method, many researches were studied on gelatinized starch. Native starch was heated in excess water for gelatinization before incubation at lower temperature to provide time for starch retrogradation process in which RS3 was generated. Formation of RS3 in acid solution was two stages as describe by Onyango *et al.* (2006). Firstly, starch was hydrolyzed during heating and secondly starch chain recrystallized during incubation. Heating temperature and time affected thermochemical reaction as thermal and acid hydrolysis of starch chain. Degree of starch hydrolysis was important as the desirable degree of polymerization was 100-300 glucose units. Too low or too high degree of polymerization was undesirable because RS3 cannot be formed (Eerlingen *et al.*, 1993). Onyango *et at.* (2006) found that autoclaving time (15 to 90 min)

at 121°C affected resistant starch content in modified cassava starch after incubating at 60 °C. Resistant starch content increased as increasing autoclaving time from 15 to 45 min and decreased as autoclaving was longer than 45 min. This was because the formation of resistant starch depended on degree of amylose polymerization.

Besides, temperature and time of incubation was also reported to affect on resistant starch content because they affect the extent of starch retrogradation. Shin et al. (2007) studied the citric acid modified rice starch by gelatinizing rice starch in 0.1 M citric acid solution at 121°C for 30 min and then treated at 4-130°C for 0-24 h. They found that resistant starch content of acid treated rice starch increase which increasing temperature and time. Moreover, resistant starch of modified rice starch resulted from 0.1 M citric acid treatment at 121°C for 30 min and incubation at 128°C for 14 h increased from 23.3% to 40% while degree of substitution was 0.027. Onyango et al. (2006) also studied the effect of incubation temperature (-20 to 100°C) and time (6 to 48 h) on resistant starch when treated cassava starch with 0.1 M lactic acid. They reported that resistant starch content was depended on incubation temperature. The highest resistant starch was formed when incubated at 30°C and decreased with increasing incubation temperature. While, treated cassava starch with 0.1 M lactic acid showed that incubation time did not significantly affect on resistant starch. The result might imply that temperature shows the greater effect of the starch recrystallization than time, the same result was reported by Gonzalez et al., 2007 who studied the effect of storage temperature and time on resistant starch formation. Moreover, Shamai, Bianco-Peled, and Shimoni (2003) studied retrogradation temperature (40 and 95 °C) on RS3 polymorphism and found that different incubation temperature influenced on the different RS3 polymorphism. Incubated starch at 40°C generated the B-type polymorph while incubated starch at 95 °C lead to a mixture of A- and V-type polymorph.

Although, citric acid treatment in dry condition increased higher resistant starch content, this research aimed to modify rice flour by gelatinization starch with mild citric acid concentration because it used less chemical and heating starch slurry in autoclave could reduce process time resulting in lower energy consumption.

# 2.5 Rice noodle

Rice noodle is a processed rice product that is one of the popular Asian noodles. This may be because its process is simple than other starch-base noodle for manufacture (Hou, 2010) and for customer, rice noodle can be made for various menu as snack food or main dish. Moreover, it is an allergen-free product as it contains no gluten. Flat rice noodle is a product made from rice flour mixed with other ingredients such as tapioca starch, salt and sugar, and carried out to be flat. It was steamed until completely gelatinized and cut. Cooked rice noodle shall be white, soft, and sticky but separate from each other and has natural smell (Thai Industrial Standards Institute [TISI.], 1990).

Rice noodle can be divided into 3 groups according to its moisture content (Hou, 2010)

1. Fresh rice noodle has moisture content about 62-64%. It can be kept only 1-2 day.

2. Semi-dried rice noodle is a pre-dried noodle which is moisture content of about 37%. It can be kept for 2-3 days.

3. Dried rice noodle is the cut noodle which is dried until moisture content below 13%. Its shelf life was about 1 year.

# 2.5.1 Raw material for rice noodle production

#### Rice flour

Rice flour from different varieties had an effect on rice noodle quality especially stickiness. Rice flour from *Indica* rice is appropriate for noodle production due to its high amylose content, cheap price and high yield of noodle. The broken rice used to produce rice noodle should contain about 27-33% amylose and aged at least for 4 months (Tungtrakul, 1998). Rice flour contains no gluten so quality of rice noodle depends on physicochemical properties of starch because it is structural network of noodle. Amylose is the main component that constructs a gel network and the noodle structure, and resulting in high hardness and high tensile strength because of retrogradation (Mestres, Colonna, and Buleon, 1988; Li and Yeh, 2001). Besides, hard gel of rice flour is preferred for noodle making due to its more stability to overcooking and an ability to retain its form.

# Water

Water quality is important for noodle making. Water should has the pH between 5.5-7.0 and contains not too much magnesium and calcium salt as they affect mainly stickiness of cooked noodle. High magnesium and calcium salt cause the cleavage starch granule and result in lower stickiness of noodle (Hou, 2010).

#### Other ingredients

In the processing of rice noodle, other flour or starch are normally used to improve the process tolerance, reduce cost or to get better noodle quality. For example, modified starch as cross-linking starch is stable to heat treatment and helping starch network forming, so it is benefit for process tolerance (Thomas and Atwell, 1999). Corn starch is added in rice noodle formula because it provides viscosity compensation as reported by Wang *et al.* (2000) who studied the effect of corn starch on the pasting properties of rice flour. Furthermore, corn starch can increase hardness and decrease adhesiveness of rice noodle. Other additives can be salt, sugar etc. (Hou, 2010).

# 2.5.2 Rice noodle production

The production of rice noodle is started from cleaning and separating of impurity from broken rice grain by sifting and washing with water. Then, it is steeped in the cleaned water before milling by a stone mill. Rice noodles are normally made from wet-milled rice flour because wet-milling effectively reduces particle size of rice grain with lower damaged starch (Juliano, 1985) resulting in rice noodles with more desirable softness, smooth surface and firmness (Surojjanamethakul *et al.*, 1998). During broken rice is milled, water is added to decrease the milling temperature. Then, rice flour slurry is filtered through 40-70 mesh sieves to remove coarse flour.

The flour slurry is adjusted to the appropriate concentration of about 38-40% but the dried rice noodle production needs a bit higher flour slurry concentration than 40% (Surojjanamethakul *et al.*, 1998). Flour slurry is carried out to the belt by the roller that is immerging in the slurry. The flat flour slurry coated on the belt passed through the steam tunnel about 1-2 min. to form a sheet of noodle. The cooked noodle sheet is cooled to strengthen the gel, and then it is cut into strand, packed and sold for fresh noodle (Surojjanamethakul *et al.*, 1998). For dried noodle production, the noodle is further dried until moisture content below 12%.

The drying process is applied in rice noodle production to produce dried rice noodle because it extended shelf life and easily to handle. Rice noodle process is observed by researcher. There are two drying steps including pre-drying and the main drying process because rapid drying causes noodle cracking (Hou, 2010). Drying temperature is the important parameter that must be controlled to produce good dried noodle, moreover it may affect on resistant starch content of rice noodle. Casiraghi, Brighenti, and Testolin (1992) found that spaghetti dried at 90°C had lower hydrolyzed starch than spaghetti dried at 50°C, while Rabe and Sievert (1992) reported that there was no enzyme-resistant starch of pasta dried under low temperature conditions. The amount of resistant starch increased with severity of heat treatment in spaghetti (Holm, Koellreutter, and Würsch, 1992). This is in agreement with Yue, Rayas- Duarte and Elias (1999) who studied the effect of drying temperature on properties of starch isolated from pasta and found that drying pasta using ultrahigh temperature (drying temperature at 90 °C) gave the highest resistant starch content as comparing with drying pasta using high temperature (drying temperature at 70 °C) and low temperature (drying temperature at 50 °C), respectively. The higher drying temperature leads to more compact structures formation and crystalline structure reorganization of the resistant starch (Resmini and Pagani, 1983). However, the effect of drying temperature on resistant starch content was studied only in wheat noodle but no research was found in rice noodle.

# CHAPTER III

# MATERIALS AND METHODS

#### 3.1 Materials

Broken rice and cross-linked tapioca starch were obtained from Nor-nit Sukhothai noodle Co. Ltd. (Sukhothai, Thailand). Citric acid (food grade) was purchased from C.T. Chemicals, Co., Ltd. Corn flour (Continental Food Co., Ltd., Thailand) was purchased from local supermarket in Bangkok.

#### 3.2 Native rice flour preparation

Broken rice was ground by wet milling method of Pinthip (2004) with minor modification. Broken rice grain was cleaned with water, and then soaked in water at the ratio 1:1 (w/w) for 3 - 4 hour at room temperature. It was drained and milled with tap water at the ratio of rice grain: water at 1:3. The flour slurry was centrifuged at 1,500 g for 10 min (Owner Foods Machinery, Thailand). The pellet was dried in a tray dryer (Yiew Heng, HA-100S, Thailand) at 40°C for 15 hour. The dried pellet was ground by blender (Kenwood, Major KM620, U.S.A.) and sieved through 70-mesh screen. The rice flour was analyzed for chemical composition i.e. moisture, crude protein, crude fat and ash according to approved methods of AACC 44-15, 46-12, 30-25 and 08-01 (AACC International, 2000). Amylose content was also measured by method of Juliano (1971).

Resistant starch content and physicochemical properties of native rice flour were performed as followed

- Resistant starch content according to AACC International (2000) with Megazyme resistant starch assay kit (K-RSTAR) (Appendix A.1).

- Degree of substitution according to Klaushofer *et al.* (1979) with modification. (Appendix A.2)

- Swelling power and solubility according to Mandala and Bayas (2004) with modification (Appendix A.3).

- Color measurement by a chromameter (Minolta; CR-400, Tokyo, Japan) following the method of Hsu *et al.* (2003). (Appendix A.4).

- X-ray pattern and crystallinity using the X-ray diffractometer (Appendix A.5).

- Pasting properties using the Rapid Visco Analyser (RVA) (Newport Scientific Instruments & Engineering; 4D, Australia) (Appendix A.6).

- Thermal properties using the Differential scanning calorimeter (DSC) (Perkin Elmer, Diamond DSC, USA) (Appendix A.7).

The analyses were carried out in triplicate except resistant starch and thermal properties were done in duplicate. While X-ray pattern and crystallinity measurement were performed in one replicate.

# 3.3 Experimental Procedure

The experimental procedure was divided into 2 parts. The first part was to modify rice flour by citric acid. And the second part was to apply the modified rice flour to produce high fiber dried rice noodle.

#### 3.3.1 Citric acid modification

The study was divided into 2 steps. Firstly, rice flour was treated with citric acid at different reaction temperatures and times. Secondly, the acid-treated rice flour suspension was incubated at different temperature.

#### 3.3.1.1 Effects of reaction temperature and time.

Modified rice flour was prepared following Shin *et* al. (2007) with modification. Two hundred grams of rice flour was dispersed in 300 ml of 0.1 M citric acid (pH of 0.1 M citric acid was 2.32 ± 0.10). The flour slurry (pH of flour slurry was 2.63 ± 0.10) was heated at different temperatures (100, 110 and 120°C) and times (15, 30 and 45 min) in an autoclave. After that, the mixture was cooled in room- temperature water for 30 min before incubating at 45°C for 24 h. The sample was re-dispersed in 800 ml distilled water and neutralized with 1M NaOH to pH 7. The suspension was centrifuged at 3000 rpm for 10 min. (Hettich zentrifugen, Rotanta 460 R, UK). The pellet was washed twice with distilled water before drying at 40 °C until moisture content was below 12%. The dried flour was ground and sieved through 70-mesh screen. The experiment was done in 3x3 factorial design with duplication.

Resistant starch content, amylose content, swelling power and solubility, color, X-ray pattern and crystallinity, pasting properties and thermal properties of acid-treated rice flour were analyzed as in section 3.2. The optimum heating temperature and time was chosen based on the highest amount of resistant starch.

#### 3.3.1.2 Effect of incubation temperature

Rice flour treated with 0.1 M citric acid at the appropriate reaction temperature and time chosen from section 3.3.1.1 was incubated at 5, 30, 45, 60, 75 and 90°C for 24 h. The experiment was done in completely randomized design (CRD) with duplication.

The modified rice flour was analyzed as in section 3.2. The optimum incubation temperature that gave the highest amount of resistant starch was chosen for the next step.

#### 3.3.2 Application of modified rice flour in dried rice noodle

The experiment was divided into 2 steps, the first step is to study the effect of replacing rice flour by the modified rice flour on properties of rice noodle and the second step is to study the effect of drying temperature on dried rice noodle qualities.

#### 3.3.2.1 Effect of modified rice flour substitution.

Rice noodle was prepared according to Figure 3.1 using the factory formulation (flour slurry of 40% (w/v) contained 30% rice flour, 5% corn flour, 5% crosslink tapioca starch and 60% water). The modified rice flour was prepared according to the conditions chosen in section 3.3.1 and substituted at 10, 20 and 30% of rice flour. The sample without substitution was also prepared as control. Rice noodle samples were kept in laminated aluminium foil bag at room temperature before further analyses.

The sample was ground and sieved through 70-mesh screen before resistant starch content analysis as in section 3.2.

Cooking time, cooking loss and rehydration of noodle samples were determined following the AACC International (2000) method 66-50 (Appendix A.8). The cooked noodles were further investigated for texture properties by Texture analyzer (Stable Micro Systems, TA.XT2i, United Kingdom). The compression test using texture profile analysis (TPA) measuring mode and tensile testing were performed following the instructions of the TA.XT2i texture analyzer (Appendix A.9.1 and A.9.2). Cutting test was performed based on AACC International (2000) method 66-50. (Appendix A.9.3). The compression and cutting test were measured in 5 replicates, tensile test was measured in 10 replicates while the experiment was done in 2 replicates.

Flour slurry at the concentration of 40% (w/v)

Leave flour suspension for 15 min to allow flour to absorb water

Pour 65 g of flour suspension into 12x21 cm stainless steel tray, and then steaming for 5 min. Remove noodle sheet from tray and placing it on stainless steel screen

Pre-dry noodle sheet at 70°C for 10 min (moisture content about 45%) Incubate the pre-dried noodle sheet at 5°C for 24 h and then cut into 3 mm-strands

Dry rice noodle at 50°C until moisture content below 12%

Figure 3.1 Diagram of dried-rice noodle preparation

Sensory evaluation using 30 untrained panelists was done for acceptance test. The panelists evaluated the sample using the preference test for color, odor, taste, texture and overall acceptance (5 point Hedonic scale; 1 = dislike extremely; 5 = like extremely). All samples were served separately from soup. The experiment was done in 2 replicates and statistical analysis was performed according to randomized complete block design (RCBD). The optimum substitution level of modified rice flour was chosen based on resistant starch content and the highest sensory score.

#### 3.3.2.2 Effect of drying temperature on rice noodle qualities.

Rice noodle was prepared from the appropriate substitution level of modified rice flour chosen in section 3.3.2.1. The noodle was dried at 50, 60 and 70°C until the final moisture content was around 12%. Dried rice noodles were kept in aluminium foil bag at room temperature before testing.

Rice noodle samples were analyzed for resistant starch content, cooking loss, rehydration, textural properties, and sensory evaluation as in section 3.3.2.1. The experiment was done in 2 replicates. The appropriate drying temperature was chosen based on resistant starch content and the highest sensory score. The final product was analyzed for total dietary fiber following AACC International (2000).

### 3.4 Statistical Analysis

The mean and standard deviations were average from replicate tests. Analysis of variance (ANOVA) was conducted using SPSS version 16.0. The difference between mean values of samples was constructed by LSD multiple range tests at 95% confidence ( $p\leq0.05$ ).

## CHAPTER IV

# **RESULTS AND DISCUSSION**

## 4.1 Citric acid modification

The chemical composition of native rice flour used in this research were 10.06% moisture content, 6.60% protein, 0.42% fat and 0.78% ash. Apparent amylose content of native rice flour was 27.61%, therefore it could be classified as high amylose content flour that was appropriated for producing noodle product (Tungtrakul, 1998).

#### 4.1.1 Effect of reaction temperature and time of citric acid modification

Percent yield of modified rice flour at each heating condition was shown in Appendix C (Table C.1), it was found that increase heating temperature and time resulted in lower yield. This may be because the more severe condition resulted in more soluble short chain saccharides (Shin et al., 2004). Figure 4.1 shows that the native rice flour used in this study contained only 0.65% (dry basis) resistant starch, which was quite low as generally found in all normal rice cultivars (Hu et al., 2004). All modified samples had higher resistant starch content than the native. From ANOVA results (Appendix B.1.1-B.1.2), it was found that resistant starch content and percent degree of substitution (%DS) depended on reaction temperature, time, and interaction between temperature and time. The resistant starch content and %DS of citric acid to starch were found to increase with both increasing treatment temperature and time (Table 4.1). This may be because dehydration of citric acid at high temperature corresponded to the esterification of starch both in the amorphous and crystalline regions resulting in an increase in %DS. Moreover, the bulky esterified groups could hinder starch chain from digestive enzyme resulting in increased resistant starch content of RS4 type (Xie and Liu, 2004; Xie et al., 2006; Shin et al., 2007). The result was similar to previous studies (Xie and Liu, 2004; Xie et al., 2006). However DS in this research was lower comparing to those reported by Xie and Liu (2004) because they used higher citric acid concentration and heating temperature and different treatment method as they used dry condition (5-10% moisture content). Comparing to Shin et al. (2007), the DS found was 0.027 which was also higher than DS found in this research eventhough the modified method used was the same. This may be because they treated starch at higher temperature. So resistant starch content in this research might be from retrograded starch which was classified as RS3 type because retrogradation rice flour may occurred during incubation of heated with 0.1 M citric acid in excess water at temperature above gelatinization temperature (Englyst et al., 1992). Moreover, high temperature induced acid hydrolysis of amylose and amylopectin resulting in an increase in linear short chain starch which supported chain mobility for rearrangement and crystalline forming, so resistant starch was increased (Thompson, 2000). Furthermore, the amylose-lipid complex could also be formed during long heating and incubating period causing the increase in this complexation and increase in resistant starch content (Kaur and Singh, 2000; Evangelica et al., 2011). Besides, it was also found that the polymorph of modified rice flour was changed as shown in Figure 4.2. From the X-ray diffraction pattern (Figure 4.2), the native rice flour used in this study was A-type starch that was common in rice starches (Themeier *et al.*, 2005). Its peaks show at  $2\theta = 15.3^{\circ}$  and  $23.4^{\circ}$ , and double peak at 17° and 18° (Hizukuri et al., 2006). While the diffraction pattern of all modified rice flour was B- and V-type patterns. The crystalline peak of the modified rice flour at mild condition (heated at 100°C for all times) became smaller than the native but an increase in heating temperature and time caused the higher peak. The peaks of rice flour treated at higher temperature and time (especially treated at 120°C/45 min) were obviously found at  $2\theta = 17^{\circ}$  and  $23^{\circ}$  indicating the B-type X-ray pattern and at  $2\theta = 7$ -8°, 13° and 20° indicating the V-type X-ray pattern (Hizukuri et al., 2006). The B-type pattern resulted from amylose retrogradation, and the V-type pattern was from the complexation of amylose and lipid (Shamai *et al.*, 2003; Shin *et al.*, 2009). This may be because the peak of native rice flour disappeared after acid treatment as the crystalline of native rice flour was melted during heating period and the new crystalline was formed (Singh *et al.*, 2003). Comparing to the gelatinized rice starch without citric acid, Shin *et al.* (2009) found that X-ray pattern of the gelatinized rice starch without citric acid was also B- and V-type, however the peaks indicating B-type were very small. The diffraction peaks of the modified rice flour were obviously higher due to citric acid treatment.

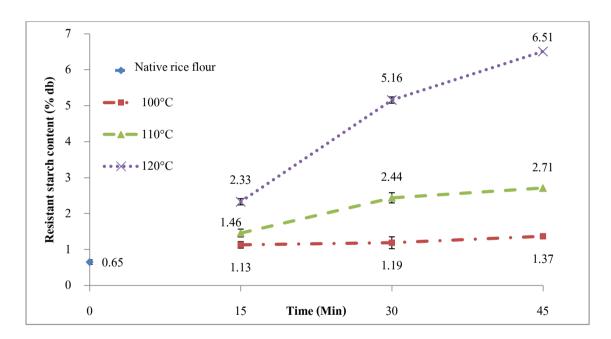


Figure 4.1 Effect of reaction temperature and time on resistant starch content of native and modified rice flour.

The relative crystallinity of the modified rice flours (Table 4.1) was lower than the native rice flour because the crystalline of untreated rice flour was melted during heating. Besides, the relative crystallinity of the modified rice flours treated at higher temperature and longer time were found to be higher. This could be explained by the more severe heating conditions caused the degradation of starch chain and recrystallisation and also promoted the formation of amylose-lipid complex during heating (Kaur and Singh, 2000).

Table 4.1 Effect of reaction temperature and time on percent degree of substitution(%DS) and relative crystallinity of native and modified rice flour

Temperature(°C)	Time (min)	%DS	Relative crystallinity (%)
Native ri	ce flour	-	25.35
100	15	$0.57 \pm 0.01^{a}$	10.37
	30	$0.62 \pm 0.02^{b}$	9.27
	45	$0.74 \pm 0.02^{cd}$	9.26
110	15	$0.73 \pm 0.00^{\circ}$	9.45
	30	$0.74 \pm 0.01^{cd}$	9.61
	45	$0.75 \pm 0.01^{d}$	10.81
120	15	$0.75 \pm 0.01^{d}$	13.37
	30	$0.79 \pm 0.01^{e}$	19.28
	45	$0.81 \pm 0.01^{f}$	21.04

a, b, c,... Means with different letter in each column are significantly different ( $p \leq 0.05$ )

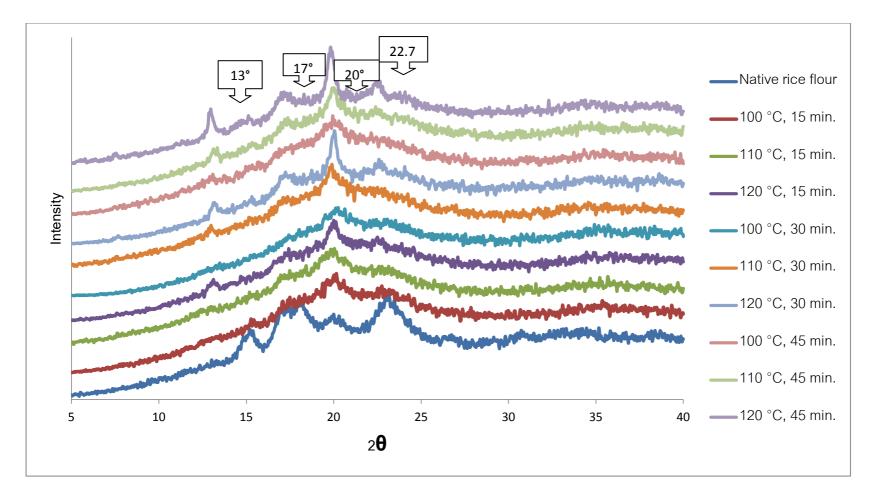


Figure 4.2 Effect of temperature on X-ray diffraction patterns of native and acid treated rice flour.

Table 4.2 illustrates thermal properties of native rice flour and the effect of reaction temperature and time on thermal properties of modified rice flour. Figure 4.3 illustrates DSC thermogram of modified rice flour of native and modified rice flour at different heating temperature for 45 min. It was found that the first peak of endotherm expressed the melting of amylopectin crystalline. The melting temperatures and enthalpy of melting found in native rice flour were significantly higher than those of modified rice flour ( $p \leq$ 0.05) because the native amylopectin crystalline was melted during heating with citric acid solution and the retrograded amylopectin was formed, but the new crystalline was not as strong as the native one (Vandeputte et al., 2003b). The native rice flour was found to have amylose-lipid complex (3<sup>rd</sup> peak endotherm) which was melted at about 90-108°C, while the modified rice flour expressed various results depending on the treatment conditions. The modified samples at 100°C with various time exhibited endothermic transition at 76 - 109°C (2<sup>nd</sup> peak endotherm) which might refer to the low molecular weight amylose re-association (Ziegler, Nordmark, and Woodling, 2003). These were related to X-ray diffraction pattern as the acid-treated samples at 100°C showed small peaks at  $2\theta = 17^{\circ}$  and  $23^{\circ}$ . These were corresponded to the increase in RS3. The 2<sup>nd</sup> peak endotherm might also be referred to the amorphous or type I amylose-lipid complex which was melted at temperature below 100°C. Moreover, the severe conditions expressed endothermic transition at 110 - 125°C (3<sup>rd</sup> peak endotherm) which was the character of more ordered amylose-lipid complex and it was melted at high temperature than the native (Yoon and Lee, 1998) and the higher condition resulted in the higher melting temperature. This result implied that the new crystalline was stronger than the native. The higher treatment conditions resulted in the increase in enthalpy suggesting the more crystalline formation. This may be because heating flour slurry at high temperature followed by incubating at 45°C for 24 h promoted the

Temperature	Time		The 1 <sup>st</sup> melting peak			The 2 <sup>nd</sup> me	lting peak	The 3 <sup>rd</sup> me	lting peak
(°C)	(min)	To (°C)	Tp (°C)	Tc (°C)	∐H (J/g)	Tr (°C)	∐H (J/g)	Tr (°C)	∐H (J/g)
Native rice	flour	61.40±0.44 <sup>b</sup>	71.10±0.16 <sup>d</sup>	85.37±0.82 <sup>c</sup>	11.04±1.35°	-	-	91.68-107.50	1.80
100	15	54.74±4.10 <sup>ª</sup>	62.57±0.61 <sup>°</sup>	67.01±0.43 <sup>ª</sup>	0.55±0.72 <sup>ab</sup>	76.39-86.75	1.24	-	-
	30	55.48±0.88 <sup>ª</sup>	62.49±0.16 <sup>bc</sup>	67.85±0.69 <sup>ab</sup>	0.35±0.03 <sup>ª</sup>	90.82-108.98	2.52	-	-
	45	53.52±0.75 <sup>ª</sup>	62.43±0.33 <sup>bc</sup>	68.28±0.41 <sup>ab</sup>	0.53±0.05 <sup>ab</sup>	89.85-108.20	2.79	-	-
110	15	54.36±2.41 <sup>ª</sup>	$62.01 \pm 0.70^{abc}$	69.19±2.60 <sup>b</sup>	0.47±0.10 <sup>ab</sup>	89.97-107.97	2.31	-	-
	30	53.38±1.71 <sup>ª</sup>	$62.16 \pm 0.22^{abc}$	68.20±0.81 <sup>ab</sup>	0.58±0.06 <sup>ab</sup>	92.10-112.08	2.21	111.30-120.15	0.22
45		53.81±1.96 <sup>ª</sup>	62.19±0.42 <sup>abc</sup>	68.53±0.50 <sup>ab</sup>	0.78±0.15 <sup>ab</sup>	97.54-106.89	1.74	111.04-121.25	0.90
120	15	54.76±2.48 <sup>ª</sup>	$62.08 \pm 0.61^{abc}$	68.05±0.65 <sup>ab</sup>	$0.50 \pm 0.09^{ab}$	93.88-108.89	1.61	111.30-121.92	1.68
	30	54.74±0.49 <sup>ª</sup>	61.82±0.45 <sup>ab</sup>	68.53±0.47 <sup>ab</sup>	$0.96\pm0.12^{b}$	-	-	109.31-123.44	2.49
	45	54.24±0.52 <sup>ª</sup>	61.60±0.60 <sup>ª</sup>	68.51±0.85 <sup>ab</sup>	1.02±0.19 <sup>b</sup>	-	-	113.37-125.03	3.73

Table 4.2 Effect of reaction temperature and time on thermal properties of native and modified rice flour

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ )

To, Tp, Tc, Tr and A mean onset temperature, peak temperature, conclusion temperature, melting temperature range and enthalpy, respectively.

formation of amylose-lipid complex with the higher temperature giving the more order crystalline (Gelders *et al.*, 2004).

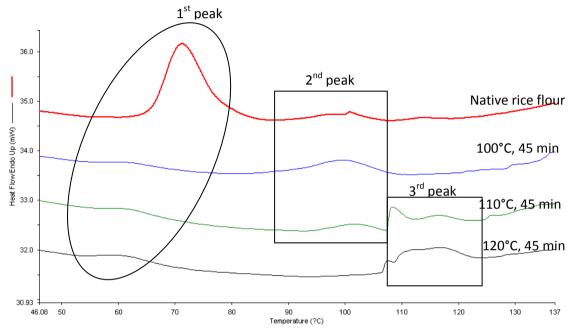


Figure 4.3 DSC thermogram of native and modified rice flour at 45 min heating time

The effects of heating temperature and time on amylose content, swelling power and solubility at 75 °C of modified rice flour were shown in Table 4.3. From ANOVA (Appendix B.1.7-B.1.9), it was found that amylose content, swelling power and solubility at 75°C depended on temperature, time, and interaction between temperature and time. Amylose content increased from 27.61% (native rice flour) to 33.84% (modified at 120°C, 45 min) and was found to increase with both increasing temperature and time. This may be due to the fact that the modified rice flour contained more short linear chains derived from the acid hydrolysis of amylopectin and amylose that could bind with iodine (Shin *et al.*, 2004). Native rice flour had obviously lower solubility at 75 °C than those modified samples. The more severe condition caused the greater change because of higher degradation efficiency. The short linear chains could bind with water and dissolved easily after heating (Shin *et al.*, 2009). Similar result was reported by Shin

*et al.* (2004) who studied the partial acid hydrolysis on formation of resistant tuber starch. Swelling power at 75 °C of modified rice flour was also found to be higher than the native flour except the samples treated at 120°C for 30 and 45 min. Swelling power increased at mild condition (at 100°C), but decreased at more severe condition. This may be because the starch granule was damaged during gelatinization causing the release of amylopectin and amylose, and the disruption of hydrogen bonding between starch chains by acid that allowed starch chain to bind with water. But at high temperature (120°C), the substitution of citric acid was promoted and the hydroxyl groups of starch were esterified resulting in restricted swelling of starch (Xie and Liu, 2004; Olayide, 2004; Musiliu and Oludele, 2010). Moreover, the formation of amylose-lipid complex at high temperature could reduce starch swelling (Tester and Morrison, 1990).

Table 4.3 Effect of temperature and time on amylose content, solubility and swellingpower at 75°C of native and modified rice flour

Temperature(°C)	Time(min)	Amylose content (%)	Solubility(g/g)	Swelling power (%)
Native rice	e flour	27.61 ± 0.60 <sup>a</sup>	$2.40 \pm 0.10^{a}$	$8.75 \pm 0.10^{\circ}$
	15	$28.18 \pm 0.64^{ab}$	5.17 ± 0.57 <sup>b</sup>	$10.29 \pm 0.59^{f}$
100	30	$28.69 \pm 0.53^{bc}$	$5.14 \pm 0.46^{b}$	10.11 ± 0.58 <sup>ef</sup>
	45	$29.49 \pm 1.25^{cde}$	$6.08 \pm 0.92$ <sup>c</sup>	$10.22 \pm 0.18^{ef}$
	15	$28.69 \pm 0.91^{bc}$	$5.80 \pm 0.51^{bc}$	10.11 ± 0.19 <sup>ef</sup>
110	30	$29.93 \pm 0.62^{de}$	$9.42 \pm 0.74^{d}$	$9.79 \pm 0.19^{de}$
	45	$30.10 \pm 0.48^{de}$	$14.28 \pm 0.63^{f}$	$9.50 \pm 0.31^{d}$
	15	$29.39 \pm 0.69^{cd}$	13.10 ± 1.32 <sup>e</sup>	$9.62 \pm 0.35^{d}$
120	30	$30.25 \pm 0.66^{\circ}$	$13.95 \pm 0.91^{f}$	$7.96 \pm 0.34^{b}$
	45	$33.84 \pm 0.47^{f}$	16.22 ± 0.48 <sup>g</sup>	$7.21 \pm 0.19^{a}$

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ )

From the color measurement (Table 4.4), the modified rice flour had lower lightness value (L value) but higher yellow color (b value). The overall color change expressed as whiteness (WI) of all modified samples were found to be lower than native sample This is because citric acid reaction caused discoloration of starch (Reddy and Yang, 2010). Increasing temperature significantly caused the greater change. This may be because under prolonged heating time with citric acid at higher temperature, protein and carbohydrate in flour were hydrolyzed to amino acid and reducing sugar causing Maillard reaction to occur eventhough the pH of the flour suspension was 3.0.

Table 4.4 Effect of reaction temperature and time on color of native and modified rice

Temperature(°C)	Time(min	) L	а	b	WI
Native rice	flour	72.24 ± 0.12 <sup>d</sup>	$-0.97 \pm 0.02^{a}$	1.48 ± 0.03 <sup>ª</sup>	72.18 ± 0.12 <sup>d</sup>
	15	$66.09 \pm 0.69$ bc	-0.81 ± 0.06 <sup>b</sup>	$4.06 \pm 0.06$ <sup>b</sup>	65.84± 0.68 <sup>bc</sup>
100	30	$66.50 \pm 0.49^{\circ}$	$-0.80 \pm 0.04$ <sup>b</sup>	$4.19 \pm 0.07$ <sup>c</sup>	$66.23 \pm 0.48$ <sup>c</sup>
	45	$65.92 \pm 0.43^{\rm bc}$	$-0.77 \pm 0.04$ bc	$4.30 \pm 0.09^{de}$	65.64± 0.42 <sup>bc</sup>
	15	$65.54 \pm 0.66^{ab}$	$-0.77 \pm 0.02^{bc}$	4.22± 0.12 <sup>cd</sup>	65.27± 0.64 <sup>ab</sup>
110	30	$65.67 \pm 0.56^{ab}$	$-0.75 \pm 0.39^{cd}$	$4.46 \pm 0.08^{f}$	65.38± 0.55 <sup>ab</sup>
	45	$65.91 \pm 0.49^{bc}$	$-0.79 \pm 0.02^{bc}$	4.43± 0.03 <sup>f</sup>	65.61 ± 0.49 <sup>b</sup>
	15	$65.78 \pm 0.26^{abc}$	$-0.72 \pm 0.02^{d}$	4.39± 0.10 <sup>ef</sup>	65.49± 0.26 <sup>ab</sup>
120	30	$65.61 \pm 0.82^{ab}$	-0.69 ± 0.03 <sup>e</sup>	$4.68 \pm 0.07^{g}$	65.28± 0.81 <sup>ab</sup>
	45	$65.21 \pm 0.53^{a}$	$-0.71 \pm 0.06^{de}$	$4.80 \pm 0.12^{h}$	$64.88 \pm 0.53^{a}$

flour

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ )

Pasting temperature of modified rice flour was found to be increase with increasing time when heated at 100°C but the higher heating condition, RVA did not detected pasting temperature. This is because pasting properties of modified rice flour was reduced due to higher heating condition. The pasting properties of treated rice flour

were significantly lower than the native flour (Table 4.5 and Figure 4.4). Citric acid treatment obviously reduced peak viscosity, trough viscosity and final viscosity as the starch chain length was reduced and low-molecular-weight starch chains occurred by acid hydrolysis (Orozco-Martinez and Betancur-Ancona, 2004). Setback of all modified rice flours was lower than native sample suggesting that modified rice flour exhibited less tendency to retrograde. This might be because the modified rice flour had more short chain amylose which was less prone to re-association within short period during RVA measurement (Shin *et al.*, 2009). Besides, the hydroxyl groups of modified rice flour were esterified so the formation of hydrogen bonding was limited (Olayide, 2004). From Figure 4.3, it was found that under the most severe condition, there was no peak in RVA curve. Similar result was found for rice starch treated with 0.1 M citric acid at 128°C for 14 h (Shin *et al.*, 2007).

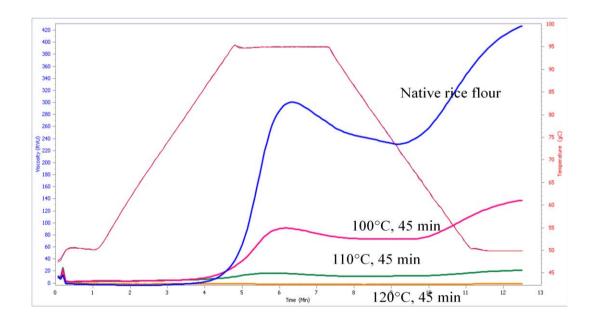


Figure 4.4 Effect of temperature on RVA pasting profile of native and modified rice flour at 45 min heating time

Temperatur	Time	Pasting	Peak viscosity	Trough viscosity	Breakdown	Final viscosity	Setback
(°C)	(min)	Temperature (°C)	(RVU)	(RVU)	(RVU)	(RVU)	(RVU)
Native ri	ce flour	87.72±0.31	$301.83 \pm 2.60^{h}$	227.17± 6.50 <sup>g</sup>	74.67±5.40 <sup>f</sup>	437.61 ±14.14 <sup>h</sup>	210.45 <sup>f</sup> ±20.51
100	15	91.10±0.52	160.07±12.91 <sup>g</sup>	122.93± 16.19 <sup>f</sup>	37.14±4.28 <sup>e</sup>	211.96 ±15.23 <sup>g</sup>	89.03 ± 7.23 <sup>e</sup>
	30	91.40±1.23	$129.70 \pm 5.70^{f}$	$99.34 \pm 6.85^{\circ}$	30.36±3.48 <sup>d</sup>	183.22 ±8.57 <sup>f</sup>	$83.89 \pm 7.40^{\circ}$
	45	92.68±0.49	99.56 ± 8.18 <sup>e</sup>	$79.17 \pm 6.10^{d}$	20.39±2.70 <sup>°</sup>	144.36 ±9.31 <sup>°</sup>	$65.19 \pm 5.01^{d}$
110	15	90.23±0.89	96.85± 22.88 <sup>e</sup>	80.60 ± 16.61 <sup>d</sup>	16.25± 6.77 <sup>b</sup>	142.29 ± 31.22 <sup>e</sup>	61.70 ±15.72 <sup>d</sup>
	30	-	$31.35 \pm 0.85^{d}$	25.84 ± 1.43 <sup>°</sup>	5.52 ±1.01 <sup>ª</sup>	47.84 ± 1.03 <sup>d</sup>	$22.00 \pm 2.19^{\circ}$
	45	-	14.14 ± 1.71 <sup>bc</sup>	$9.20 \pm 1.37^{ab}$	$4.95 \pm 0.59^{a}$	$17.39 \pm 2.48^{bc}$	$8.20 \pm 1.32^{ab}$
120	15	-	$20.78 \pm 3.64^{cd}$	15.95 ± 3.49 <sup>bc</sup>	$4.84 \pm 0.29^{a}$	$30.49 \pm 5.03^{\circ}$	14.54 ±1.58 <sup>bc</sup>
	30	-	$3.18 \pm 0.66^{ab}$	$1.51 \pm 0.74^{a}$	$1.67 \pm 0.29^{a}$	$3.67 \pm 0.53^{ab}$	$2.15 \pm 0.73^{a}$
	45	-	$1.0 \pm 2.54^{a}$	$-0.97 \pm 1.82^{a}$	$1.97 \pm 0.73^{a}$	$0.54 \pm 2.44^{a}$	$1.52 \pm 0.63^{a}$

Table 4.5 Effect of reaction temperature and time on RVA pasting properties of native and modified rice flour

a, b, c,... Means with different letter in each column are significantly different ( $p \leq 0.05$ )

### 4.1.2 Effect of incubation temperature on citric acid modification

Percent yield of modified rice flour at different incubation temperature was shown in Appendix C (Table C.2), it showed that increase incubation temperature resulted in lower yield. The analysis of variance showed that incubation temperature significantly affected the resistant starch content and DS of modified rice flour ( $p \leq$ 0.05) (Appendix B.2.1-B.2.2). Resistant starch content of the modified rice flour was slightly increased when the incubation temperature increased from 5 °C to 75°C and was dramatically increased when incubation temperature was 90°C (Figure 4.5). This result was corresponded to the DS shown in Table 4.6 which was not significantly different when incubation temperature increased from 30-75°C but significantly increased at 90°C incubation temperature. As DS related to esterification so the higher DS inferred the more esterified starch formed which resulted in increased resistant starch (Xie and Liu, 2004). Moreover, during incubation amylose rearrangement and recrystallisation were performed which also resulted in increased resistant starch content. This result was similar to Onyango et al. (2006) who studied the formation of RS3 from acid-hydrolysed cassava starch. Besides, from the complex formation measured by X-ray diffractrometer (Figure 4.6 and Table 4.6), the peak of all modified rice flour was obviously found at  $2\theta$  = 13° and 20° which indicated the V type X-ray pattern resulted from the complexation of amylose and lipid. And it was also found the peaks located at  $2\theta$  = 17° and 23° which indicated the B-type pattern of amylose retrogradation. Thus the modified samples had the combination of V- and B- type pattern. Furthermore, crystallinity was also increased with increasing incubation temperature which might be because more recrystallisation, amylose retrogradation and amylose-lipid complex formation were occurred. However, the extent of recrystallisation was found to be depended on the incubation temperature. The less ordered form of complex formation occurred rapidly at temperature below 70-80°C, while the more ordered and stable complex was favored at higher temperature (Biliaderis, 1992; Kaur and Singh, 2000). Moreover, the formation of new crystalline is three-stage process as nucleation (formation of nuclei), propagation (crystal growth of the nuclei) and maturation (crystal growth and perfection). The nucleation and propagation step determine the overall recrystallisation (Eerlingen et al., 1993). Propagation step proceeds rapidly when the incubation temperature approaches the melting temperature (Eerlingen et al., 1993). So the relative crystallinity of modified rice starch when incubated at 90°C was higher than those from all other conditions because this incubation temperature is closed to the melting temperature of starch (113-125 °C) as show in the 3<sup>rd</sup> peak of Table 4.2.

The effect of incubation temperature on thermal properties of modified flour was also found. From DSC thermogram (not shown), the modified rice flour exhibited the third peak representing the amylose-lipid complex. The melting enthalpy of the complex increased with increasing incubation temperature especially at 90°C incubation temperature (Table 4.7) indicating the more amylose-lipid complex was formed at high temperature (Biliaderis, 1992). This was in agreement with the increase in relative crystallinity (Table 4.6) and similar to the results reported by Shin *et al.* (2009) that crystallinity of the citric acid-treated rice starch increased due to more ordered amylose–lipid complex, repolymerisation of starch and removal of the amorphous region by citric acid.

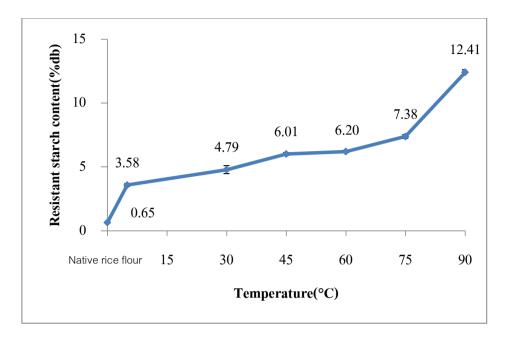


Figure 4.5 Effect of incubation temperature on resistant starch content of native and modified rice flour.

 Table 4.6 Effect of incubation temperature on %DS and relative crystallinity of modified

 rice flour

-	Incubation temperature	%DS	Relative crystallinity (%)
	5°C	$0.63 \pm 0.01^{a}$	20.63
	30°C	$0.73 \pm 0.04$ <sup>b</sup>	20.28
	45°C	$0.76 \pm 0.02$ <sup>b</sup>	21.04
	60°C	$0.75 \pm 0.06$ <sup>b</sup>	20.96
	75°C	$0.72 \pm 0.02$ <sup>b</sup>	23.32
	90°C	$0.82 \pm 0.02$ °	29.97

a, b, c,... Means with different letter in each column are significantly different ( $p \leq 0.05$ )

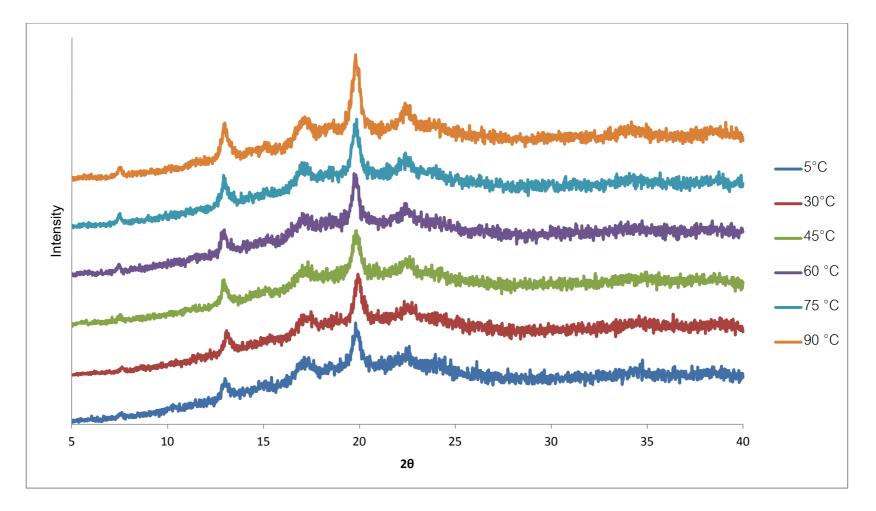


Figure 4.6 Effect of incubation temperature on X-ray diffraction patterns of modified rice flour.

Incubation temperature	Melting temperature (°C)	Enthalpy (J/g)
5°C	108.27-124.13	1.92
30°C	111.69-122.22	1.76
45°C	113.37-125.03	3.73
60°C	112.16-121.97	3.01
75°C	99.06-122.55	4.62
90°C	107.16-129.93	17.17

Table 4.7 Effect of incubation temperature on thermal properties of modified rice flour

Amylose content and solubility of modified sample also increased, while WI decreased with incubation temperature (Table 4.8). Increasing incubation temperature resulted in the greater change during incubation. As the heated acidified rice flour slurry was incubated, the starch hydrolysis was still in action causing an increase in short chain amylose. The higher incubation temperature might induce more starch hydrolysis (Onyango *et al.*, 2006). Solubility was also increased due to the increase in short chain amylose. Similar results were reported by others (Shin *et al.*, 2004; Shin *et al.*, 2007). Swelling power of modified rice flour slightly increased when incubation temperature increased from 5 to 75°C but decreased at 90°C. This may be because the esterification of starch chain (as shown by DS) reduced the hydroxyl group of starch to bind with water resulting in decreased swelling power. Moreover, the formation of amylose lipid complex during incubation could also reduce starch hydration and swelling. (Xie and Liu, 2004; Olayide, 2004). However, %DS was not significantly different when incubated at 30 to 75°C ( $p \leq 0.05$ ) but it was significantly higher at 90°C ( $p \leq 0.05$ ).

Incubation	Amylose content	Solubility	Swelling	WI
 temperature	(%)	(g/g db.)	power (%)	
5°C	$32.19 \pm 0.60$ <sup>a</sup>	12.41 ± 1.28 <sup>a</sup>	$6.48 \pm 0.24^{a}$	$66.59 \pm 1.29^{cd}$
30°C	30.97 ± 1.18 <sup>ª</sup>	13.07 ± 0.51 <sup>ª</sup>	$6.74 \pm 0.33^{ab}$	$66.87 \pm 0.71^{d}$
45°C	$33.84 \pm 0.47$ <sup>b</sup>	$16.22 \pm 0.48^{b}$	$7.20 \pm 0.19^{abc}$	65.41 ± 0.35 <sup>b</sup>
60°C	34.24 ± 1.00 <sup>b</sup>	$16.32 \pm 0.33^{b}$	$7.41 \pm 0.20^{bc}$	$66.06 \pm 0.26^{bc}$
75°C	37.28 ± 0.91 <sup>°</sup>	$16.93 \pm 0.49^{b}$	7.58 ± 1.65 <sup>°</sup>	$65.99 \pm 0.39^{bc}$
90°C	45.59 ± 1.16 <sup>d</sup>	18.9 2± 1.33 <sup>°</sup>	$6.74 \pm 0.09^{ab}$	$63.20 \pm 0.73^{a}$

 Table 4.8 Effect of incubation temperature on amylose content, solubility and swelling power at 75°C and whiteness index (WI) of modified rice flour

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ )

Incubation temperature did not affect pasting properties of modified rice flour (Figure 4.7). All modified rice flour at different incubation temperature showed no RVA peak due to the same reason as described in section 4.1.1.

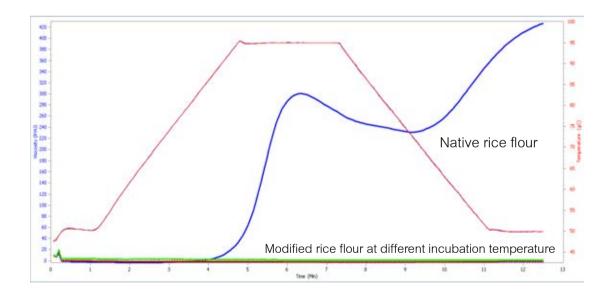


Figure 4.7 Effect of incubation temperature on RVA pasting profile of native and modified rice flour (heat at 120°C for 45 min) at different incubation temperature.

4.2 Effect of modified rice flour substitution on resistant starch content and quality of rice noodle.

Resistant starch content of control sample (0% substitution) and 2 commercial samples was between 1.1-1.7% (Table 4.9) as some starch was retrograded during noodle processing and retrograded starch was classified as RS3. Increasing % modified rice flour substitution resulted in significantly higher resistant starch content of rice noodle ( $p \leq 0.05$ ) (Table 4.10). This was because modified rice flour had higher resistant starch content than the native one. Commercial noodles had lower cooking loss and higher rehydration comparing to the prepared samples without or with modified rice flour, however the cooking loss of noodle was still in the range between 1.3-10.25 (g/100g) of those reported by others (Sandhu, Kaur, and Mukesh, 2010; Cham and Suwannaporn, 2010; Yadav, Yadav, and Kumar, 2011). Increasing % substitution was found to increase %cooking loss of rice noodle (Table 4.10). This may be because modified rice flour had higher solubility due to more short linear chain, which could easily bind with water and dissolve in cooking water (Bhattacharya, Zee, and Corke, 1999; Sandhu et al., 2010). However, the effect of substitution on rehydration did not show until the substitution was 30%. This may be because of the uncertainties intermolecular association of starch system such as starch-starch and starch-protein interactions in the noodle making. Also, the differences in swelling and solubility properties of various starch and flour can generate the unique physical properties of their blend that cannot interpret by the mixing ratio (Marti, Pagani, and Seetharaman, 2011; Yadav et al., 2011).

Noodle sample	Resistant starch	Cooking loss	Rehydration
	content (%db)	(g/100 g dry noodle)	(g/100 g dry noodle)
0% substitution noodle	$1.30 \pm 0.03^{b}$	$4.50 \pm 0.27^{b}$	$294.60 \pm 7.67^{a}$
Commercial sample 1	$1.66 \pm 0.06^{\circ}$	$3.83 \pm 0.22^{a}$	335.94 ± 9.54 <sup>b</sup>
Commercial sample 2	1.16 ± 0.03 <sup>ª</sup>	$3.53 \pm 0.29^{a}$	$319.56 \pm 6.64^{b}$

Table 4.9 Resistant starch content, cooking loss and rehydration of 0% substitution and

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ )

Table 4.10 Effect of modified rice flour substitution on resistant starch content, cooking

 % Substitution on	Resistant starch	Cooking loss	Rehydration
 noodle	content (%db)	(g/100 g dry noodle)	(g/100 g dry noodle)
0%	$1.30 \pm 0.03^{a}$	$4.50 \pm 0.27^{a}$	$294.60 \pm 7.67^{ab}$
10%	$2.08 \pm 0.08$ <sup>b</sup>	$4.57 \pm 0.31^{ab}$	286.89 ± 9.56 <sup>ª</sup>
20%	$3.01 \pm 0.04$ <sup>c</sup>	$5.14 \pm 0.26^{bc}$	290.41 ± 8.52 <sup>ª</sup>
30%	$3.55 \pm 0.08$ <sup>d</sup>	$5.46 \pm 0.47$ °	311.22 ±14.87 <sup>b</sup>

loss and rehydration of noodle

commercial noodle

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ )

According to texture measurement and sensory evaluation of various noodle, the samples were cooked in boiling water at each optimum time. All prepared noodle and commercial sample 1 were cooked for 4 min while commercial sample 2 was cooked for 3 min before texture and sensory test. The result shows that commercial noodles had lower springiness, tensile strength, and cutting force, but similar hardness and cohesiveness to the control (Table 4.11). This may be because of the difference of ingredient and process. Increasing percent substitution from 10% to 30% resulted in noodle having lower hardness, cohesiveness, tensile strength, and cutting force but higher in springiness (Table 4.12). Moreover, higher rehydration of the sample resulted

in softer texture of the noodles (Kasemsuwan, Bailey, and Jane, 1998; Bhattacharya *et al.*, 1999). Besides, more water rehydration could reduce firmness and elasticity of noodles (Sandhu *et al.*, 2010). Therefore, tensile strength and cutting force were reduced because they related to elasticity and breaking strength of noodle. While cohesiveness determined disruption of noodle structure during first compression, the cohesiveness of noodle with 30% substitution level was significantly lower than other substitution levels indicating that it was easily separated (Yadav *et al.*, 2011). Therefore, it can be concluded that noodle with higher level of modified rice flour substitution would break easier, had lower strength, less gummy and cohesiveness.

The sensory liking scores of noodle showed that percent substitution affected the sensory attributes except odor and taste (Table 4.13). The color score was found to decrease with increasing percent substitution while odor and taste were not significantly different ( $p \ge 0.05$ ). Decreasing in color acceptance might result from the lower whiteness of the modified rice flour due to acid treatment. Texture and overall acceptance score of noodle with 0% substitution were the highest and were not significantly different from noodles with 10 and 20% substitution, however these scores were significantly higher than those of 30% substitution. This result was corresponded with the textural properties measured by the texture analyzer (Table 4.12). So, it could be concluded that the textural properties of noodle with 20% substitution were closed to the control noodle.

Noodle sample	Hardness <sup>ns</sup> (kg)	Springiness <sup>ns</sup>	Cohesiveness <sup>ns</sup>	Tensile strength (g)	Cutting force (g)
Control	21.80±1.48	0.77±0.04	0.88±0.01	25.46±2.92 <sup>°</sup>	593.76±25.03 <sup>°</sup>
Commercial sample 1	21.77±2.18	0.74±0.04	0.88±0.02	23.21±3.74 <sup>b</sup>	502.82±49.68 <sup>b</sup>
Commercial sample 2	21.81±1.16	0.74±0.05	0.88±0.01	17.24±1.11 <sup>ª</sup>	378.67±19.58 <sup>ª</sup>

Table 4.11 Textural properties of control and commercial noodle

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ )

ns in columns are not significantly different ( $p \ge 0.05$ )

Table 4.12 Effect of modified rice flour substitution on textural properties of noodle.

% Substitution on	Hardness (kg)	Springiness	Cohesiveness	Tensile strength (g)	Cutting force (g)
noodle					
Control	21.80 ±1.48 <sup>ab</sup>	0.77±0.04 <sup>ª</sup>	0.88±0.01 <sup>b</sup>	25.46±2.92°	593.76±25.03 <sup>°</sup>
10	24.10 $\pm$ 1.56 $^{\circ}$	0.77±0.04 <sup>ª</sup>	0.89±0.01 <sup>b</sup>	27.03±2.40 <sup>°</sup>	675.19±56.38 <sup>d</sup>
20	22.59±1.04 <sup>b</sup>	0.81±0.04 <sup>b</sup>	0.88±0.02 <sup>b</sup>	22.99±6.73 <sup>b</sup>	532.29±57.55 <sup>b</sup>
30	21.03 ±1.24 <sup>a</sup>	0.81±0.02 <sup>b</sup>	0.86±0.01 <sup>ª</sup>	16.18±2.75 <sup>ª</sup>	400.83±20.67 <sup>a</sup>

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ )

% Substitution	Color	Odor <sup>ns</sup>	Taste <sup>ns</sup>	Texture	Overall acceptance
Control	$4.0 \pm 0.9^{\circ}$	3.2 ± 1.0	3.5 ± 0.9	3.6 ± 0.9 <sup>b</sup>	$3.6 \pm 0.9^{b}$
10	$3.7 \pm 0.7^{bc}$	3.3 ± 0.9	3.2 ± 1.0	3.0 ± 1.2 <sup>ª</sup>	$3.3 \pm 0.9^{ab}$
20	$3.6 \pm 0.8^{b}$	3.4 ± 0.9	3.4 ± 0.8	3.3 ± 1.0 <sup>b</sup>	$3.5 \pm 0.8^{b}$
30	2.8 ± 1.0 <sup>ª</sup>	3.1 ± 1.1	3.4 ± 0.9	3.1 ± 1.0 <sup>ª</sup>	$3.1 \pm 0.9^{a}$

Table 4.13 Effect of modified rice flour substitution on sensory liking score of noodle.

\* 5 point line scale (1 = dislike very much; 5 = like very much)

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ ) ns in each column are not significantly different ( $p \ge 0.05$ )

# 4.3 Effect of drying temperature on resistant starch and quality of rice noodle.

Rice noodles with 20% substitution of modified rice flour were dried at 50, 60 and 70°C until its moisture content was about 12% and drying curves of each drying temperature were shown in Appendix C (Figure C.1-C.3). The drying time was found to be 3.5, 1 and 0.75 h, respectively. Resistant starch content, cooking loss and rehydration of rice noodle with varying drying temperature were shown Table 4.14. Resistant starch and cooking loss of noodle were not significantly different ( $p \ge 0.05$ ) among different drying temperature, although, previous studies reported that increase drying temperature resulted in higher resistant starch content (Holm *et al.*, 1992; Yue, Rayas-Duarte, and Elias, 1999). This may be because rice noodle was flat so drying time was very short (0.75-3.5 hr.) compared to 6.5-18 h used for drying pasta (Yue *et al.*, 1999). So, the time for reorganization to form compact structure of starch might be limited due to the short drying time. However, percent rehydration of noodle drying at 60 and 70°C was slightly increased. This may be because the shorter drying times at 60 and 70°C (1 and 0.75 h) might result in weaker structure which could absorb more water.

Table 4.14 Effect of drying noodle at 50, 60 and 70°C on resistant starch content,cooking loss and rehydration.

Drying	Resistant starch <sup>ns</sup>	Cooking loss <sup>ns</sup>	Rehydration
temperature	(%db)	(g/100 g dry noodle)	(g/100 g dry noodle)
50°C	$3.00 \pm 0.04$	4.89 ± 0.95	292.98 ± 10.05 <sup>b</sup>
60°C	3.01 ± 0.16	$4.82 \pm 0.58$	310.45 ± 12.26 <sup>ª</sup>
70°C	$2.98 \pm 0.07$	$4.83 \pm 0.48$	$309.14 \pm 9.94^{ab}$

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ ) ns in columns are not significantly different ( $p \ge 0.05$ )

Dried rice noodles were cooked for 4 min in boiling water before texture measurement and sensory evaluation. From texture measurement it was found that cooked rice noodle with 20% substitution and dried at 60 and 70°C were significantly lower in hardness, springiness, tensile strength and cutting firmness than that dried at 50°C, while cohesiveness was not significantly different ( $p \ge 0.05$ ) (Table 4.15). This was because rice noodle dried at 60 and 70°C had higher percent rehydration, the more rehydrated water caused the softer texture (Kasemsuwan *et al.*, 1998; Bhattacharya *et al.*, 1999). Moreover, the sensory liking score of cooked rice noodle dried at 50°C showed significantly higher in taste, texture and overall acceptance than those of the samples dried at 60 and 70°C (Table 4.16). While color and odor liking score of cooked rice noodle with different drying temperature were not significantly different ( $p \ge 0.05$ ). The highest texture score of rice noodle dried at 50°C was supported by textural properties because of its highest hardness, springiness, tensile strength and cutting force. Besides, the overall acceptance score of noodle was also higher than others, so drying at 50°C was the most suitable for the high-fiber noodle production as it gave the

highest acceptance noodle. The dried rice noodle with 20% modified rice flour substitution and dried at 50°C contained 2.89% total dietary fiber.

Drying temperature	Hardness (kg)	Springiness	Cohesiveness <sup>ns</sup>	Tensile strength (g)	Cutting force (g)
50°C	20.58 ± 0.53 <sup>b</sup>	$0.82 \pm 0.02^{b}$	$0.86 \pm 0.01$	21.71 ± 2.73 <sup>b</sup>	571.95 ± 94.71 <sup>b</sup>
60°C	19.18 ± 1.31 <sup>ª</sup>	$0.80 \pm 0.02^{ab}$	$0.86 \pm 0.02$	$14.59 \pm 3.64^{a}$	$440.63 \pm 60.38^{a}$
70°C	18.96 ± 0.72 <sup>ª</sup>	$0.79 \pm 0.02^{a}$	$0.87 \pm 0.01$	15.20 ± 3.36 <sup>ª</sup>	467.10 ± 29.80 <sup>ª</sup>

Table 4.15 Effect of drying temperature on textural properties of noodle

a, b, c,... Means with different letter in each column are significantly different ( $p \le 0.05$ )

ns in columns are not significantly different ( $p \ge 0.05$ )

Drying temperature	Color <sup>ns</sup>	Odor <sup>ns</sup>	Taste	Texture	Overall acceptance
50°C	3.80 ± 0.56	3.67 ± 0.73	3.88 ± 0.76 <sup>b</sup>	$4.03 \pm 0.45$ <sup>b</sup>	$3.88 \pm 0.49^{b}$
60°C	$3.98 \pm 0.89$	$3.47 \pm 0.83$	$3.47 \pm 0.87^{a}$	$3.50 \pm 0.87^{a}$	$3.53 \pm 0.91^{a}$
70°C	3.75 ± 0.89	$3.68 \pm 0.57$	$3.42 \pm 0.53^{a}$	$3.32 \pm 0.50^{a}$	$3.53 \pm 0.57^{a}$

\* 5 point line scale (1 = dislike very much; 5 = like very much)

a, b, c,... Means with different letter in each column are significantly different ( $p \leq 0.05$ )

ns in columns are not significantly different ( $p \ge 0.05$ )

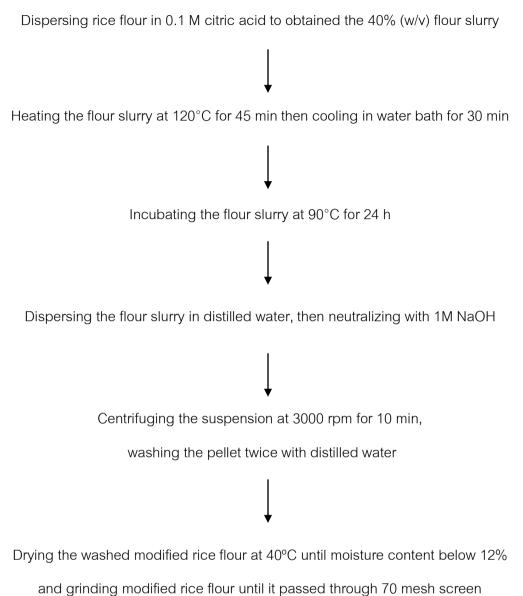
# CHAPTER V

# CONCLUSION

## 5.1 CONCLUSIONS

Rice flour was treated with 0.1 M citric acid to produce rice flour containing higher resistant starch. The modification process was shown in Figure 5.1. The highest resistant starch content was 12.41%. Amylose content, solubility and relative crystallinity of modified rice flour increased from 27.61%, 2.40% and 25.35% to 45.59%, 18.92% and 29.97%, respectively, while swelling power and whiteness index reduced from 8.75 and 72.18 to 6.74 and 63.20. X-ray pattern of modified rice flour was changed from A-type to combination of B- and V-type patterns. The pasting properties of modified rice flour showed that the more ordered amylose-lipid complex was formed.

For dried high fiber rice noodle development, the optimum substitution level of modified rice flour was 20% giving higher resistant starch content of 3.0% compared to 1.30% (0% substitution) of control noodle and the highest sensory acceptance. Cooking loss of 20% substitution rice noodle cooked in boiling water for 4 min increased from 4.50% to 5.14% while rehydration and hardness were not significant different comparing with control noodle. Tensile strength and cutting force of 20% substitution rice noodle were lower than the control. The optimum drying temperature was 50°C giving the noodle with the highest sensory acceptance, hardness, tensile strength and cutting force. The developed high-fiber rice noodle contained 2.89% total dietary fiber.



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Figure 5.1 Diagram of modified rice flour preparation.

#### REFERENCES

AACC International. 2000. <u>Approved Methods of the American Association of Cereal</u> <u>Chemists</u>. 10th ed. St. Paul, MN, USA.

AACC Report. 2001. The definition of dietary fiber. Cereal Foods World. 46: 112–126.

- Asp, N.G., and Bjorck, I. 1992. Resistant Starch. <u>Trends Food Science and Technology</u>. 3(5): 111–114.
- BeMiller, J.N. 1997. Starch modification: Challenges and prospects. <u>Starch/Starke</u>. 49(4): 127–131.
- Berry, C.S. 1986. Resistant starch formation and measurement of starch that survives exhaustive digestion with amylolytic enzymes during the determination of dietary fiber. <u>Journal of Cereal Science</u>. 4: 301–314.
- Bhattacharya, M., Zee, S. Y., and Corke, H. 1999. Physicochemical properties related to quality of rice noodles. <u>Cereal Chemistry</u>. 76: 861-867.
- Biliaderis, C.G. 1992. Structures and phase transitions of starch in food system. <u>Food</u> <u>Technology</u>. 46: 98-109.
- Björck, L., Gunnarsson, A., and Stergard, K. 1989. A study of native and chemically modified potato starch. Part II. Digestibility in the rat intestinal tract. <u>Starch/Starke</u>.
  41: 128–134.
- Bourne, M. C. 1978. Texture profile analysis. Food Technology. 32: 62.66.
- Casiraghi, M.C., Brighenti, F., and Testolin, G. 1992. Lack of effect of high temperature drying on digestibility of starch in spaghetti. <u>Journal of Cereal Science</u>. 15:165-174.
- Cham, S., and Suwannaporn, P. 2010. Effect of hydrothermal treatment of rice flour on various rice noodles quality. <u>Journal of Cereal Science</u>. 51: 284–291.
- Charalampopoulos, D., Wang, R., Pandiella, S.S., and Webb, C. 2002. Application of cereals and cereal components in functional foods: A review. <u>International Journal</u> <u>of Food Microbiology</u>. 79: 131–141.
- Chung, H.J., Liu, Q., and Hoover, R. 2009. Impact of annealing and heat-moisture treatment on rapidly digestible, slowly digestible and resistant starch levels in

native and gelatinized corn, pea and lentil starches. <u>Carbohydrate Polymers</u>. 75: 436–447.

- Collado, L.S., and Corke, H. 2003. Starch properties and functionalities. <u>Characterization</u> <u>of Cereals and Flours: Properties, analysis and application</u>, pp. 473-500. New York: Marcel Dekker, INC.
- Cooke, D., and Gidley, M.J. 1992. Loss of crystalline and molecular order during starch gelatinization: Origin of the enthalpic transition. <u>Carbohydrate Research</u>. 227: 103-112.
- Eerlingen, R.C., and Delcour, J.A. 1995. Formation, analysis, structure and properties of type III enzyme resistant starch. <u>Journal of Cereal Science</u>. 22: 129-138.
- Eerlingen, R.C., Deceuninck, M., and Delcour, J.A. 1993. Enzyme-resistant starch. II.
  Influence of amylose chain length on resistant starch formation. <u>Cereal Chemistry</u>.
  70 (3): 345-350.
- Eliasson, A.C. and Gudmundsson, M. 1996. Physicochemical and functional aspects. Eliasson ed., <u>Carbohydrate in Food</u>, pp. 431–503. New York: Marcel Dekker, INC.
- Elleuch, M., Bedigian, D., Roiseux, O., Besbes, S., Blecker, C., and Attia, H. 2011.
   Dietary fibre and fibre-rich by-products of food processing: Characterisation, technological functionality and commercial applications: A review. <u>Food</u> <u>Chemistry</u>. 124: 411-421.
- Englyst, H.N., Kingman, S.M., and Cummings, J.H. 1992. Classification and measurement of nutritionally important starch fractions. <u>European Journal of Clinical Nutrition</u>. 46: 33-50.
- EURESTA. 1992. European FLAIR concerted action on resistant starch. EURESTA Newsletter III, 7.
- Evangelica F.Z., Elena S.Z., Esther, S., Estrella S., Casilda, N., Juana F.L., and Jose, A. P. 2011. Resistant starch as prebiotic: A review. <u>Starch/Starke</u>. 00: 1–10.
- Ever, A.D., and Steven, D.J. 1985. Starch Damaged. <u>Advances in Cereal Science and</u> <u>Technology</u>, 3rd, pp. 321-349. St. Paul, USA: Pomeranz.

Fennema, O.R. 1996. Food Chemistry, 3rd ed., pp.191-192. New York: Marcel Dekker.

- Gelders, G.G., Vanderstukken, T.C., Goesaert, H., and Delcour, J.A. 2004. Amylose– lipid complexation: A new fractionation method. <u>Carbohydrate Polymers</u>. 56: 447– 458.
- Gonzalez, S.R.A., Mora, E.R., Hernandez, S.H., Sanchez, R.M., and Bello, P.L.A. 2007.The influence of time and storage temoerature on resistant starch formation from autoclaved debranched banana starch. <u>Food Research International</u>. 40: 304-310.
- Haralampu, S.G. 2000. Resistant starch—a review of the physical properties and biological impact of RS3. <u>Carbohydrate Polymers</u>. 41: 285–292.
- Higgins, J.A., Dana, H.R., Donahoo, W.T., Brown, I.L., Bell, M.L., and Bessesen, D.H.
  2004. Resistant starch consumption promotes lipid oxidation. <u>Nutrition</u>
  <u>Metabolism</u>. 1: 1–8.
- Hizukuri, S., Abe, J., and Hanashiro, I. 2006. Starch: analytical aspects. In A.-C. Eliasson (Ed.), <u>Carbohydrates in food</u> (2nd ed.). pp. 347–429. Boca Raton, FL: CRC Press.
- Holm, J., Koellreutter, B., and Würsch, P. 1992. Influence of sterilization, drying and oat bran enrichment of pasta on glucose and insulin responses in healthy subjects and on the rate and extent of in vitro starch digestion. <u>European Journal of Clinical</u> <u>Nutrition</u>. 46: 629-640.
- Hou, G. G. 2010. <u>Asian Noodles: Science, Technology, and Processing</u>. Hoboken, NJ: John Wiley and Sons.
- Hsu, C.L., Chen, W. Weng, Y.M., and Tseng, C.Y. 2003. Chemical composition, physical properties, and antioxidant activities of yam flours as affected by different drying methods. <u>Food Chemistry</u>. 83: 85-92.
- Hu, P., Zhao, H., Duan, Z., Linlin, Z., and Wu, D. 2004. Starch digestibility and the estimated glycemic score of different types of rice differing in amylose contents. <u>Journal of Cereal Science</u>. 40: 231-237.
- Jacobs, H., Eerlingen, R.C., Spaepen, H., Grobert, P.J., and Delcour, J.A. 1998. Impact of annealing on the susceptibility of wheat, potato and pea starch hydrolysis with pancreatin. <u>Carbohydrate Research</u>. 305: 193–207.

- Jane, J., Chen, Y.Y., Lee, L.F., Mcpherson, A., and Wong K.S., Radosavljevic, M. and Kasemsuwan, T. 1999. Effect of amylopectin branch chain length and amylose content on the gelatinization and pasting properties of starch. <u>Cereal Chemistry</u>. 76: 629-637.
- Juliano, B. O. 1971. A simplified assay for mill-rice amylose. <u>Cereal Science Today</u>. 16(10): 334-340, 360.
- Juliano, B.O. 1985. Rice: Chemistry and Technology. <u>The American Association of</u> <u>Cereal Chemistry</u>. pp. 443- 524. Minnesota, USA.
- Juliano, B. O. 1992. Structure, chemistry, and function of the rice grain and its fractions. <u>Cereal Foods World</u>. 37: 772–774.
- Kasemsuwan, T., Bailey, T., and Jane, J. 1998. Preparation of clear noodles with mixtures of tapioca and high-amylose starches. <u>Carbohydrate Polymers</u>. 32: 301– 312.
- Kaur, K. and Singh, N. 2000. Amylose-lipid complex formation during cooking of rice flour. <u>Food Chemistry</u>. 71: 51.
- Kennedy, G., and Burlingame, B. 2003. Analysis of food composition data on rice from a plant genetic resources perspective. <u>Food Chemistry</u>. 80: 589–596.
- Kim, W.K., Chung, M.K., Kang, N.E., Kim, M.H., and Park, O.J. 2003. Effect of resistant starch from corn or rice on glucose control, colonic events, and blood lipid concentrations in streptozotocin-induced diabetic rats. <u>Journal of Nutritional</u> <u>Biochemistry</u>. 14: 166–172.
- Klaushofer, V.H., Berghofer, E., and Pieber, R. 1979. Quantitative Bestimmung von Citronensaure in Citratstarken. <u>Starch/Starke</u>. 31: 259–261. Cited Shin, S. I., Lee, C. J., Kim, D.I., Lee, H. A., Cheong, J.J., and Chung, K. M. 2007. Formation, characterization, and glucose response in mice to rice starch with low digestibility produced by citric acid treatment. <u>Journal of Cereal Science</u>. 45: 24–33.

- Klaushofer, V.H., Berghofer, E., and Steyrer, W. 1978. Starkecitrate-Produktion und anwendungstechnische Eigenschaften. <u>Starch/Starke</u>. 30: 47–51. Cited Xie, X., and Liu, Q. 2004. Development and physicochemical characterization of new resistant citrate starch from different corn starches. <u>Starch/Starke</u>. 56: 364–370.
  Knight, J.W. 1969. The starch industry. Oxford: Pergamon Press.
- Lai, H.M. 2001. Effect of hydrothermal treatment on the physicochemical properties of pre gelatinization rice flour. <u>Food Chemistry</u>. 72: 455-463.
- Lamberts, L Brijs, K., Mohamed, R., Verhelst, N., and Delcour, J. A. 2006. Impact of browning reactions and bran pigments on color of parboiled rice: <u>Journal of Agricultural and Food Chemistry</u>. 54: 9924-9929.
- Light, J. M. 1990. Modified food starches: Why, what, where, and how. <u>Cereal Foods</u> <u>World</u>. 35: 1081.
- Li, J. Y., and Yeh, A. I. 2001. Relationships between thermal, rheological characteristics and swelling power for various starches. <u>Journal of Food Engineering</u>. 50: 141-148.
- Lii, C.Y., Shao, Y.Y. and Tseng, K.H. 1995. Gelation mechanism and rheological properties of rice starch. <u>Cereal Chemistry</u>. 72: 393-400.
- Lu, Z.H., Sasaki, T., Li, Y.Y., Yoshihashi, T., Li, L.T., and Kohyama, K. 2009. Effect of amylose content and rice type on dynamic viscoelasticity of a composite rice starch gel. <u>Food Hydrocolloids</u>. 23: 1712-1719.
- Lunn, J., and Buttriss, J.L. 2007. Carbohydrates and dietary fiber: A review. <u>Nutrition</u> <u>Bulletin</u>. 32: 21-64.
- Mandala, I.G., and Bayas, E. 2004. Xanthan effect on swelling, solubility and viscosity of wheat starch dispersions. <u>Food Hydrocolloids</u>. 18: 191–201.
- Marti, A., Pagani, M. A., and Seetharaman, K. 2011. Understanding starch organization in gluten-free pasta from rice flour. <u>Carbohydrate Polymers</u>. 84: 1069-1074.
- Martin, M., and Fitzgerald, M.A. 2002. Proteins in rice grains influence cooking properties. Journal of Cereal Science. 36: 285-294.

- Mestres, C., Colonna, P., and Buleon, A. 1988. Characteristics of starch networks within rice flour noodles and mungbean starch vermicelli. <u>Journal of Food Science</u>. 6: 1809-1812.
- Milasinovic, M. S., Radosavljevic, M. M., and Dokic, L.P. 2010. Effects of autoclaving and pullulanase debranching on the resistant starch yield of normal maize starch. <u>Journal of Serbian Chemical Society</u>. 75(4): 449–458.
- Miles, M.J., Morris, V.J., Orford, P.D., and Ring, S.G. 1985. The roles of amylose and amylopectin in the gelation and retrogradation of starch. <u>Carbohydrate Research</u>. 135: 271–281.
- Morais, M.B., Feste, A., Miller, R.G., and Lifichitz, C.H. 1996. Effect of resistant starch and digestible starch on intestinal absorption of calcium, iron and zinc in infant pigs. <u>Paediatration Research</u>. 39(5):872–876.
- Musiliu, O.A. and Oludele, A.I. 2010. Material properties and compaction characteristics of natural and pregelatinized forms of four starches. <u>Carbohydrate Polymers</u>. 79(4): 818–824.
- Noda, T., Nishiba, Y., Sato, T., and Suda, I. 2003. Properties of starches from several low-amylose rice cultivars. <u>Cereal Chemistry</u>. 80: 193-197.
- Noda, T., Takahata, Y., Sato, T., Ikoma, H., and Mochida, H. 1996. Physicochemical properties of starches from purple and orange freshed sweet potato roots and two levels of fertilize. <u>Starch/Starke</u>. 48: 395-399.
- Olayide, S.L. 2004. Composition, physicochemical properties and retrogradation characteristics of native, oxidised, acetylated and acid-thinned new cocoyam (*Xanthosoma sagittifolium*) starch. <u>Food Chemistry</u>. 87: 205–218.
- Ong, M.H., and Blanshard, J.M.V. 1995. Texture determinants in cooked, parboiled rice
  I: Rice starch amylose and the fine structure of amylopectin. <u>Journal of Cereal</u> <u>Science</u>. 21: 251-260.
- Onyango, C., Bley, T., Jacob, A., Henle, T., and Rohm, H. 2006. Influence of incubation temperature and time on resistant starch type III formation from autoclaved and acid-hydrolysed cassava starch. <u>Carbohydrate Polymers</u>. 66: 494–499.

- Orozco-Martinez, T., and Betancur-Ancona, D. 2004. Indigestible starch of *P. lunatus* obtained by pyroconversion: changes in physicochemical properties. <u>Starch/Starke</u>. 56: 241–247.
- Prajongwate Satmalee. 2006. <u>Acceleration of aging rice stick noodle by using low</u> <u>temperature</u>. Master's Thesis, Department of Food Science and Technology, Faculty of Agro -Industry, Kasetsart University.
- Pinthip Rumpagaporn. 2004. <u>Modification of rice flour by heat moisture treatment</u>. Master's Thesis, Department of Food Science and Technology, Faculty of Agro -Industry, Kasetsart University.
- Qi, X., Tester, R.F., Snape, C.E., and Ansell, R. 2003. Molecular basis of the gelatinization and swelling characteristics of waxy rice starches grown in the same location during the same season. <u>Journal of Cereal Science</u>. 25: 363-376.
- Rabe, E., and Sievert, D. 1992. Effects of baking, pasta production, and extrusion cooking on formation of resistant starch. <u>European Journal of Clinical Nutrition</u>. 46: 105-107.
- Raben, A., Tagliabue, A., Christensen, N.J., Madsn, J., Holst, J.J., and Astrup, A. 1994.
   Resistant starch: the effect on postprandial glycemia, hormonal response and satiety. <u>American Journal of Clinical Nutrition</u>. 60: 544–551.
- Reddy, N., and Yang, Y. 2010. Citric acid cross-linking of starch films. <u>Food Chemistry</u>. 118: 702-711.
- Resmini, P., and Pagani, M. A. 1983. Ultrastructure studies of pasta: A review. <u>Food</u> <u>Microstructure</u>. 2:1-12, 98.
- Sandhu, K.S., Kaur, M., and Mukesh. 2010. Studies on noodle quality of potato and rice starches and their blends in relation to their physicochemical, pasting and gel textural properties. <u>LWT - Food Science and Technology</u>. 43: 1289-1293.
- Shamai, K., Bianco-Peled, H., and Shimoni, E. 2003. Polymorphism of resistant starch type III. <u>Carbohydrate Polymers</u>. 54: 363–369.

- Shin, S., Byun, K., Park, H., and Moon, T.W. 2004. Effect of partial acid hydrolysis and heat-moisture treatment on formation of resistant tuber starch. <u>Cereal Chemistry</u>. 81(2): 194–198.
- Shin, S. I., Lee, C. J., Kim, D.I., Lee, H. A., Cheong, J.J., and Chung, K. M. 2007. Formation, characterization, and glucose response in mice to rice starch with low digestibility produced by citric acid treatment. <u>Journal of Cereal Science</u>. 45: 24– 33.
- Shin, S. I., Lee, C. J., Kim, M. J., Choi, S. J., Choi, H. J., Kim, Y., and Moon, T. W. 2009. Structural characteristics of low-glycemic response rice starch produced by citric acid treatment. <u>Carbohydrate Polymers</u>. 78: 588–595.
- Singh, N., Singh, J., Kaur, L., Sodhi, S. N., and Gill, S. B. 2003. Morphological, thermal and rheological properties of starches from different botanical sources. <u>Food</u> <u>Chemistry</u>. 81: 219-231.
- Sodhi, N.S., and Singh, N. 2003. Morphological, thermal and rheological properties of starches separated from rice cultivars grown in India. <u>Food Chemistry</u>. 80: 99–108.
- Surojjanamethakul, V., Tungtrakul, P., Varanyanond, W., and Supansri, R. 1998. Effects of partial replacement of rice flour with various starches on the physicochemical and sensory properties of "Sen Lek" noodle. <u>Kasetsart Journal</u>. 36: 55-62.
- Tako, M., and Hizukuri, S. 2000. Retrogradation mechanism of rice starch. <u>Cereal</u> <u>Chemistry</u>. 77: 473–477.
- Teo, C.H., Karim, A.A., Cheah, P.B., Norziah, M.H., and Seow, C.C. 2000. On the role of protein and starch in the ageing non-waxy rice flour. <u>Food Chemistry</u>. 69: 229– 236.
- Tester, R.F., and Morrison, W.R. 1990. Swelling and gelatinization of cereal starches. I. Effects of amylopectin, amylose, and lipids. <u>Cereal Chemistry</u>. 67(6): 551-557.
- Thai Industrial Standards Institute. 1990. <u>Thai Community Standard Product: Rice</u> <u>Noodle</u> [Online]. Available from: <u>http://www.tisi.go.th</u>[2010, February 25]

- Tharanathan, R. 2005. Starch-value addition by modification. <u>Critical Reviews in Food</u> <u>Science and Nutrition</u>. 45: 371–384.
- Themeier, H., Hollmann, J., Neese, U., and Lindhauer, M.G. 2005. Structural and morphological factors influencing the quantification of resistant starch II in starches of different botanical origin. <u>Carbohydrate Polymers</u>. 61: 72–79
- Thomas, D.I., and Atwell, W.A. 1999. <u>Starches: Practical Guide for the Food Industry</u>. pp. 1-30. Minesot, USA: Eagon Press.
- Thompson, D. B. 2000. Strategies for the manufacture of resistant starch. <u>Trends in Food</u> <u>Science and Technology</u>. 11: 245–253.
- Tsai, M.L., Li, C.F., and Lii, C.Y. 1997. Effects of granular structures on the pasting behaviors of starches. <u>Cereal Chemistry</u>. 74(6): 750-757.
- Tungtrakul, P. 1998. Quality and physicochemical properties of rice related to rice noodle. <u>Report of National Food Research Institute</u>, 62: 19.
- Vandeputte, G.E., Derycke, V., Geeroms, J., and Delcour, J.A. 2003a. Rice starch II: Structural aspects provide insight into swelling and pasting properties. <u>Journal of</u> <u>Cereal Science</u>. 38: 53-59.
- Vandeputte, G.E., Vermeylen, R., Geeroms, J., and Delcour, J.A. 2003b. Rice starch I: Structural aspects provide insight into crystallinity characteristics and gelatinization behavior of granular starch. <u>Journal of Cereal Science</u>. 38: 43-52.
- Vandeputte, G.E., Vermeylen, R., Geeroms, J., and Delcour, J.A. 2003c. Rice starch III: Structural aspects provide insight in amylopectin retrogradation properties and gel texture. <u>Journal of Cereal Science</u>. 38: 1-8.
- Voravinit, S., Shobsngob, S., Varanyanond, W., Chinachoti, P., and Naivikul, O. 2003. Effect of amylose content on gelatinization, retrogradation and pasting properties of flours from different cultivars Thai rice. <u>Starch/Starke</u>. 55: 410-415.
- Wang, H.H., Sun, D.W., Zeng, Q., and Lu, Y. 2000. Effect of pH, corn starch and phosphates on the pasting properties of rice flour. <u>Journal of Food Engineering</u>.
  46: 133–138.

- Whistler, R.L., and BeMiller, J.N. 1997. <u>Carbohydrate: Chemistry for Food Scientists</u>. Minnesota: Eagan Press.
- Wong, K.S., Kubo, A., Jane, J., Harada, K., Satoh, H., and Nakamura, Y. 2003. Structures and properties of amylopectin and phytoglycogen in the endosperm of sugary-1 mutants of rice. <u>Journal of Cereal Science</u>. 37: 139-149.
- Xie, X., and Liu, Q. 2004. Development and physicochemical characterization of new resistant citrate starch from different corn starches. <u>Starch/Starke</u>. 56: 364–370.
- Xie, X., Liu, Q., and Cui, S. W. 2006. Studies on the granular structure of resistant starches (type 4) from normal, high amylose and waxy corn starch citrates. <u>Food</u> <u>Research International</u>. 39: 332–341.
- Yadav, B. S., Yadav, R. B., and Kumar, M. 2011. Suitability of pigeon pea and rice starches and their blends for noodle making. <u>LWT - Food Science and</u> <u>Technology</u>. 44: 1415-1421.
- Yoon, J. Y., and Lee, Y. E. 1998. Influence of amylose content on formation and characteristics of enzyme-resistant starch. <u>Journal of Food Sciences and Nutrition</u>. 3(4): 303–308.
- Yue, P., Rayas-Duarte P., and Elias, E. 1999. Effect of drying temperature on physicochemical properties of starch isolated from pasta. <u>Cereal Chemistry</u>. 76(4): 541–547.
- Zhao, X-H., and Lin, Y. 2009. Resistant starch prepared from high-amylose maize starch with citric acid hydrolysis and its simulated fermentation *in vitro*. <u>European Food</u> <u>Research Technology</u>. 228: 1015–1026.
- Zhou, Z.K., Robards, K., Helliwell, S., and Blanchard, C. 2002. Composition and functional properties of rice. International <u>Journal of Food Sciences and</u> <u>Technology</u>. 37: 849–868.
- Ziegler, G. R., Nordmark, T. S., and Woodling, S. E. 2003. Spherulitic crystallization of starch: Influence of botanical origin and extent of thermal treatment. <u>Food</u> <u>Hydrocolloids</u>. 17: 487–494.

APPENDICES

## APPENDIX A

## ANALYTICAL METHODS

#### A.1 Resistant starch determination

Resistant starch content was determined according to AACC Method 32-40 (AACC, 2000).

#### Instruments

- 1. Shaking water bath
- 2. Water bath
- 3. Centrifuge (EBA 21; Hettich zentrifugen)
- 4. Centrifuge (ROTANTA 460R; Hettich zentrifugen)
- 5. Spectophotometer (Genesys 10 uv; Spectronic)

#### Enzymatic and chemical reagents

The enzymatic reagents, glucose standard solution and resistant starch control

from 1. -6. were supplied from resistant assay kit (Megazyme, Ireland)

- 1. Pancreatic α-amylase (Pancreatin, 3 Ceralpha Units/mg)
- 2. Amyloglucosidase (12 mL, 3300 Units/ml on soluble starch)
- 3. Glucose Oxidase/Peroxidase(GOPOD) Reagent Buffer
- 4. GOPOD Reagent Enzyme
- 5. Glucose Standard Solution
- 6. Resistant Starch Control
- 7. 2 M Potassium Hydroxide (KOH)
- 8. 0.1 M Sodium maleate buffer, pH 6.0 plus 5 mM calcium chloride dehydrate

9. 1.2 M Sodium acetate buffer, pH 3.8

10. 100 mM Sodium acetate buffer, pH 4.5

11. Absolute ethanol

12. 50% v/v Ethanol

13. Stock Amyloglucosidase (AMG) solution (300 Units/ml on soluble starch). This enzymatic reagent was prepared by dilute 2 ml of enzyme (2.) to 22 ml of buffer (8.)

14. Pancreatic  $\alpha$ -amylase (10 mg/ml) plus AMG (3 U/ml). This solution was prepared by suspend 1 g. of enzyme (1.) in 100 ml of buffer (8.), and added 1 ml of enzyme solution (14.)

15. GOPOD reagent. The solution was prepared by dilute GOPOD reagent buffer(3.) to 1 L with distilled water. Using this buffer dissolved GOPOD reagent enzyme (4.)

#### Procedure

Measurement of resistant starch content was divided into 2 steps. First, nonresistant starch was hydrolyzed and removed following by analysis of resistant starch.

#### (a) Non-resistant starch hydrolysis and solubilisation

A sample of 100 ± 5 mg was accurately weight into screw cap tube, and then 4.0 ml of pancreatic  $\alpha$ -amylase (10 mg/ml) containing AMG (3 U/ml) was added to each tube. The tube was covered with paraffin film, tightly caped and mixed on a vortex and then placed horizontally in a shaking water bath. The solution was incubated at 37°C for exactly 16 hour with continuous shaking at 100 rpm. After incubation, the solution was treated with 4.0 ml of absolute ethanol with vigorous shaking. The tube was centrifuged at 3,000 rpm for 10 min., the supernatant was drained while the pellet was washed twice with 8 ml of 50% ethanol, and centrifuged at 3,000 rpm for 10 min. The washed pellet was used for resistant starch measurement.

#### (b) Resistant starch analysis

The pellet from (a) was re-suspended in 2 ml of 2 M KOH with stirring by a magnetic stirrer for 20 minute in an ice/water bath, then the 1.2 M sodium acetate buffer (pH 3.8) 8 ml was added to each tube with stirring by magnetic stirrer. AMG (3300 U/ml) 0.1 ml was added to the tube immediately, after that the solution was incubated at 50°C for 30 min with intermittent mixing on a vortex mixer.

For sample containing > 10% RS content, the sample was dilute with water before centrifuged while sample containing < 10% RS content, the sample was directly centrifuged at 3,000 rpm for 10 minute.

The 0.1 ml of diluted or undiluted supernatants was transfer in duplicate in to the glass test tubes and then the aliquots were treated with 3.0 ml of GOPOD reagent following by incubated at 50°C for 20 min. Each solution were measured the absorbance at 510 nm against the reagent blank. Blank contained 0.1 ml of 0.1 M sodium acetate buffer (pH 4.5) and 3.0 ml of GOPOD reagent. Glucose standards were the mixture of 0.1 ml of glucose (1 mg/ml) and 3.0 ml of GOPOD reagent. The percent of resistant starch was calculated as follows

Samples containing > 10% Resistant starch

Resistant starch =  $\Delta E \times F \times 100/0.1 \times 1/1000 \times 100/W \times 162/180$ =  $\Delta E \times F/W \times 90$ 

Samples containing < 10% Resistant starch

Resistant starch =  $\Delta E \times F \times 10.3/0.1 \times 1/1000 \times 100/W \times 162/180$ =  $\Delta E \times F/W \times 9.27$ 

#### Where:

- $\Delta E$  = Absorbance (reaction) read against the reagent blank
- F = Conversion from absorbance to micrograms of glucose
- W = The initial weight of the dried sample (g)

#### A.2 Degree of substitution determination

Resistant starch content was determined according to AACC Method 32-40 (AACC, 2000).

#### Instruments

1. Water bath

#### Chemical reagents

- 1.1 M KOH
- 2.5 M acetic acid
- 3. Sodium borate buffer (pH 8.5)
- 4. Indicator (0.3 g; Murexide: sodium sulfate 1:500, w/w)
- 5. 0.05 M copper sulfate solution

#### Procedure

Modified rice flour was 3.50 g, and dispersed in 2ml distilled water. And then the sample was dissolved in 50 ml of 1 M KOH. The suspension was heated in a boiling water bath for 10 min before cooled to room temperature. After that the pH of sample was adjusted to 8.5 using 5M acetic acid, and mixed with 25 ml sodium borate buffer following by 0.3 g indicator. Distilled water was added until the solution was 300 ml. The

sample was titrated with 0.05 M copper sulfate solution until the indicator color changed from red–violet to pink-orange. DS was calculated using the following equation

$$DS = \frac{162 \text{ W}}{100 \text{M} - (\text{M}-1) \text{ W}}$$

Where:

W = Percent by weight of substituent

= [bound citrate (g)/sample (g)-bound citrate (g)]x100

 M = Weight addition of one glucose ring unit which was substituted by the citric acid

#### A.3 Swelling power and solubility

Swelling power and solubility were analyzed according to Mandala and Bayas (2004) with modification.

#### Instruments

- 1. Shaking water bath
- 2. Centrifuge (EBA 21; Hettich zentrifugen)
- 3. Hot air oven

#### Procedure

Flour dispersion of 0.1 g (db) and water 5 g was heated in a continuous shaking water bath at temperatures 75 °C for 30 min. The mixture was cooled to room temperature in ice-water bath for 1 min. then the suspension was centrifuged at 3000 rpm for 15 min. Precipitated paste was separated from supernatant and weighed while

supernatant was dried at 105 °C until constant weight. Swelling power and solubility were calculated as shown in the following equation

Swelling power	=	Weight of sediment paste (g)
		Initial weight of the dried solid (g)
Solubility	=	Weight of the dried supernatant (g) x 100
		Initial weight of the dried solid (g)

#### A.4 Color measurement

The color of rice flour sample was measured following the method of Hsu *et al.* (2003).

#### Instruments

1. Spectrophotometer (Minolta, CR-400, Japan)

#### Procedure

Flour sample was added into sample holder using for color measurment. The spectrophotometer measured in Hunter system which expressed in L, a and b. The whiteness index (WI) was calculated using the following equation

$$WI = 100 - ((100-L)^{2} + a^{2} + b^{2})^{1/2}$$

#### A.5 X-ray pattern and relative crystallinity

X-ray pattern analysis was performed using X-ray diffractometer and relative crystallinity was calculated using EVA Diffract software (Bruker GmbH, Germany).

#### Instruments

X-ray diffractometer (Bruker GmbH, Bruker D5005, Germany)

#### Procedure

Powder sample was packed in a cell and then exposed to the X-ray beam with X-ray generator. The scanning regions of Bragg's angle (2 $\alpha$ ) were 5 - 40°. The relative crystallinity of sample was quantitatively estimated using EVA Diffract software. The area over diffractogram was integrated. The relative crystallinity was expressed as a percentage of the ratio of diffraction peak area to the total area.

#### A.6 Pasting properties

Pasting properties of native and modified rice flour were measured using a Rapid Visco Analyser (RVA). Analysis was done using AACC Method 61-02 (AACC International, 2000) with modification.

#### Instruments

Rapid Visco Analyser (RVA) (Newport Scientific Instruments & Engineering, model 4D, Australia).

#### Procedure

Rice flour was 3.50 g, and mixed with 25.0 ml water (12% moisture basis). Then it was put into the equipment. The flour slurry was equilibrated at 50°C for 1 min. with rotation speed of 960 rpm for the first 10 sec, following by 160 rpm for the remainder. The slurry was heated from 50°C to 95°C at a rate of 12°C/min. and maintained at 95°C for 2.5 min. Subsequently, the sample was cooled to 50°C at the same rate, and held at

50°C for 1.4 min. Peak viscosity, trough viscosity, final viscosity, breakdown and set back were recorded in RVU.

#### A.7 Thermal properties

Thermal properties of sample were performed using Differential Scanning Calorimetry (DSC).

#### Instruments

The Pyris Diamond DSC (Perkin Elmer, Diamond DSC, U.S.A.) equipped with an intercooler unit (Perkin Elmer, Model 2P, U.S.A.) and using nitrogen gas purge.

#### Procedure

The 7 mg of sample was approximately weighed into stainless steel pan and 21 ml of distilled water was added to obtain the suspension of 1:3 (w/w). The pan was hermetically sealed and left overnight at room temperature. The pan was heated from 30°C to 140°C at a heating rate of 10°C/ min in DSC. The reference was an empty stainless steel pan. The thermal transitions of sample were calculated automatically by Pyris Diamond software (Perkin Elmer, Connecticut, USA). They were defined as onset temperature, *T*o (°C), peak temperature, *T*p (°C), conclusion temperature, *T*c (°C) and the enthalpy of melting,  $\Delta$ H (J/g). The gelatinization temperature range was calculated as (*T*c - *T*o) and the melting transition enthalpy,  $\Delta$ H was calculated based on an initial dried weight of sample.

#### A.8 Cooking time, cooking loss and rehydration

The solids loss to cooking water was expressed as cooking loss which was performed following the AACC (2000) method 66-50.

#### Instruments

Hot air oven

#### Procedure

#### Cooking time

The 300 ml of water was boiled on hot plate, and then 25 g of about 5 cm long noodle sample was added in boiling water, the cooking time was counting immediately. Water temperature and volume were maintained consistent during the test. A piece of noodle was removed every 30 sec and put between two pieces of clear glass. Cooking time was recorded when center core of noodle just white.

#### Cooking loss and rehydration

The 300 ml of water was boiled on hot plate, and then 25 g of noodle sample was cooked in boiling water for each cooking time. The volume was constantly maintained during test by makeup boiling water. After cooking time is reached, the sample was rapidly drained. The cooked noodle was rinsed with 50 ml of water for 30 s and held at room temperature for 10 min. before weighing. The cooking and rinsed water were collected into preweighed beaker. It was evaporated at 105°C until constant weight, cooled in desiccator and reweighed to get the dried solid loss weight. Cooking loss and rehydration were calculated from

(%) Cooking loss =	The weight of dried solid loss x 100
	The weight of initial dried noodle
(%) Rehydration =	The weight of cooked noodle x 100
	The weight of initial dried noodle

75

#### A.9 Textural properties

Textural properties of noodle were carried out by Texture analyzer model TA.XT2i (Stable Micro Systems, United Kingdom). The texture profile analysis (TPA), tensile and cutting test was determined.

#### A.9.1 Texture profile analysis (TPA) test

The TPA testing was measured using a cylindrical aluminium probe (100mm diameter; P/100). The measurement was carried out following the instructions with the TA.XT2i texture analyzer. The 10 noodle strands arranging in horizontal (1 layer) were placed on the base and the probe was placed in the center. The cylinder probe with a 1 mm/sec pre-test speed, 5 mm/sec test speed and 5 mm/sec post-test speed was compressed 2 times onto the noodle strands for 75% of their thickness. The textural parameters obtained were hardness, springiness, cohesiveness. The profile curve with the definition of texture parameter were shown in Figure A.1.

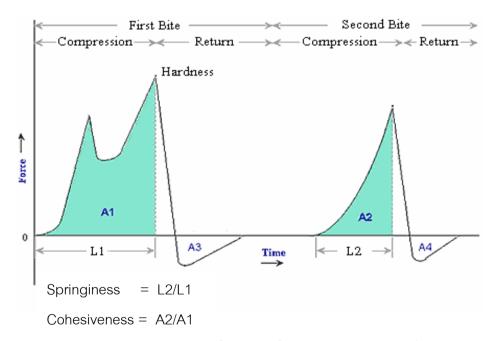


Figure A.1 resture prome curve and definitions of standard TPA terms (Bourne, 1978).

#### A.9.2 Tensile Test

The measurement was carried out following the instructions with the TA.XT2i texture analyzer. A noodle (longer than 10 cm) was placed through the slots in the parallel A/SPR probes. The roller probes were extended the noodle using tension mode with a 1 mm/sec pre-test speed, 3 mm/sec test speed and 10 mm/sec post-test speed and 50 mm distance. The force was plotted against the distance (extension) to get a force-extension curve (Figure A.2). The maximum force (g) that used to pull the noodle strand until tearing was determined.

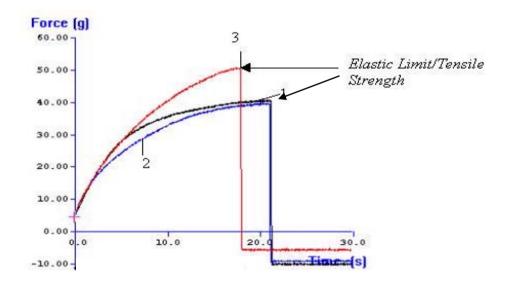


Figure A.2 Texture profile curve (Tensile strength) and definitions of standard terms (Application study for TA.XT2)

#### A.9.3 Cutting Test

The measurement was evaluated according to standard method 16-50 (AACC, 2000) of pasta and noodle firmness. The cutting test was carried out using HDP/BS blade set. The 10 noodles strands were placed on the base of the texture analyzer and cut crosswise by the blade. Testing condition mode was a 1 mm/sec pre-

test speed, 2 mm/sec test speed and 10 mm/sec post-test speed. The force-distance curves were obtained (Figure A.3) and the maximum cutting stress (g) was determined.

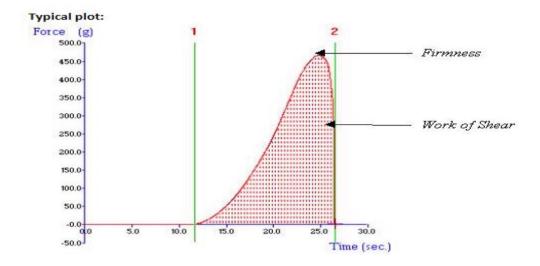


Figure A.3 Texture profile curve (cutting force) and definitions of standard terms (Application study for TA.XT2)

## APPENDIX B

## STATISTICAL ANALYSIS DATA

Table B.1 ANOVA: overall effect of reaction temperature (100, 110 and 120°C) and time(15, 30 and 45 min) on response variables of modified rice flour

Table B.1.1 Dependent Variable: Resistant starch

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	75.357	2	37.679	1.700E3	.000
time	22.304	2	11.152	503.265	.000
Temperature * time	17.654	4	4.414	199.178	.000
Error	.598	27	.022		
Total	378.132	36			

Table B.1.2 Dependent Variable: Degree of substitution

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	1.273E-5	2	6.364E-6	597.533	.000
time	4.106E-6	2	2.053E-6	192.771	.000
Temperature * time	2.437E-6	4	6.092E-7	57.199	.000
Error	2.875E-7	27	1.065E-8		
Total	.002	36			

Table B.1.3 [	Dependent Variable: To
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Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	3.542	2	1.771	.424	.659
time	9.360	2	4.680	1.120	.341
Temperature * time	10.020	4	2.505	.600	.666
Error	112.788	27	4.177		
Total	106747.755	36			

Table B.1.4 Dependent Variable: Tp

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	2.203	2	1.102	4.676	.018
time	.009	2	.004	.018	.982
Temperature * time	.803	4	.201	.852	.505
Error	6.362	27	.236		
Total	139020.286	36			

Table B.1.5 Dependent Variable: Tc

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	7.270	2	3.635	2.401	.110
time	.849	2	.424	.280	.758
Temperature * time	7.644	4	1.911	1.262	.309
Error	40.875	27	1.514		
Total	168007.704	36			

Table B.1.6 Depend	ent Variable: Enthalpy
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Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	.804	2	.402	5.861	.008
time	.459	2	.230	3.346	.050
Temperature * time	.388	4	.097	1.413	.256
Error	1.852	27	.069		
Total	18.379	36			

Table B.1.7 Dependent Variable: Amylose

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	52.653	2	26.326	49.110	.000
time	52.811	2	26.405	49.257	.000
Temperature * time	26.478	4	6.619	12.348	.000
Error	24.123	45	.536		
Total	48238.510	54			

Table B.1.8 Dependent Variable: Swelling

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	37.928	2	18.964	147.357	.000
time	10.085	2	5.043	39.184	.000
Temperature * time	9.393	4	2.348	18.248	.000
Error	5.791	45	.129		
Total	4856.094	54			

Table B.1.9 Dependent Varia	able: Solubility
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Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	723.032	2	361.516	604.886	.000
time	161.170	2	80.585	134.834	.000
Temperature * time	91.099	4	22.775	38.107	.000
Error	26.895	45	.598		
Total	6302.064	54			

Table B.1.10 Dependent Variable: Whiteness index

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	4.514	2	2.257	7.190	.002
time	.594	2	.297	.946	.396
Temperature * time	2.023	4	.506	1.611	.188
Error	14.126	45	.314		
Total	231794.328	54			

Table B.1.11 Dependent Variable: Peak viscosity

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	138359.152	2	69179.576	765.539	.000
time	27930.972	2	13965.486	154.542	.000
Temperature * time	7319.442	4	1829.861	20.249	.000
Error	4066.523	45	90.367		
Total	384216.744	54			

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	83698.967	2	41849.484	586.484	.000
time	18401.733	2	9200.866	128.942	.000
Temperature * time	5106.555	4	1276.639	17.891	.000
Error	3211.048	45	71.357		
Total	235726.777	54			

Table B.1.12 Dependent Variable: Trough viscosity

Table B.1.13 Dependent Variable: Breakdown

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	6921.812	2	3460.906	363.703	.000
time	992.286	2	496.143	52.139	.000
Temperature * time	382.972	4	95.743	10.062	.000
Error	428.209	45	9.516		
Total	18823.857	54			

Table B.1.14 Dependent Variable: Final viscosity

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	263317.572	2	131658.786	843.010	.000
time	51486.911	2	25743.455	164.835	.000
Temperature * time	16474.727	4	4118.682	26.372	.000
Error	7027.964	45	156.177		
Total	745727.477	54			

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	50112.959	2	25056.480	578.336	.000
time	8358.975	2	4179.487	96.468	.000
Temperature * time	3433.712	4	858.428	19.814	.000
Error	1949.630	45	43.325		
Total	144688.745	54			

Table B.2 ANOVA: overall effect of incubation temperature (5, 30, 45, 60, 75 and 90°C)on response variables of modified rice flour

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	188.697	5	37.739	1.196E3	.000
Error	.568	18	.032		
Total	1275.797	24			

Table B.2.2 Dependent Variable: Degree of substitution

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	7.836E-6	5	1.567E-6	13.878	.000
Error	2.033E-6	18	1.129E-7		
Total	.001	24			

## Table B.2.3 Dependent Variable: Amylose

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	568.269	5	113.654	143.307	.000
Error	15.862	20	.793		
Total	33428.395	26			

Table B.2.4 Dependent Variable: Swelling

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	5.651	5	1.130	2.269	.073
Error	14.941	30	.498		
Total	1796.765	36			

## Table B.2.5 Dependent Variable: Solubility

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	181.720	5	36.344	51.643	.000
Error	21.113	30	.704		
Total	9014.097	36			

Table B.2.6 Dependent Variable: Whiteness index

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	52.209	5	10.442	20.591	.000
Error	15.213	30	.507		
Total	155412.448	36			

 Table B.3 ANOVA: overall effect of modified rice flour substitution on response variables

of rice noodle

Table B.3.1	Dependent Variabl	e: Resistant starch
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Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	11.901	3	3.967	1.183E3	.000
Error	.040	12	.003		
Total	110.914	16			

Table B.3.2 Dependent Variable: Cooking loss

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	3.538	3	1.179	10.200	.000
Error	2.312	20	.116		
Total	581.678	24			

Table B.3.3 Dependent Variable: Rehydration

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	2085.709	3	695.236	6.269	.004
Error	2218.105	20	110.905		
Total	2103960.736	24			

Table B.3.4 Dependent Variable: Hardness

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	5.144E7	3	1.715E7	9.464	.000
Error	6.522E7	36	1811736.471		
Total	2.016E10	40			

## Table B.3.5 Dependent Variable: Springiness

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	.021	3	.007	5.302	.004
Error	.047	36	.001		
Total	25.053	40			

## Table B.3.6 Dependent Variable: Cohesiveness

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	.003	3	.001	4.771	.007
Error	.007	36	.000		
Total	30.823	40			

## Table B.3.7 Dependent Variable: Tensile

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	1376.238	3	458.746	53.203	.000
Error	655.313	76	8.623		
Total	43950.374	80			

## Table B.3.8 Dependent Variable: Cutting

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	401519.701	3	133839.900	70.962	.000
Error	67898.835	36	1886.079		
Total	1.259E7	40			

Table B.3.9	Dependent	Variable:	Color
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Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	52.933	3	17.644	24.070	.000
Error	173.000	236	.733		
Total	3194.000	240			

Table B.3.10 Dependent Variable: Smell

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	2.283	3	.761	.811	.489
Error	221.567	236	.939		
Total	2720.000	240			

Table B.3.11 Dependent Variable: Taste

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	3.112	3	1.037	1.294	.277
Error	189.183	236	.802		
Total	2879.000	240			

Table B.3.12 Dependent Variable: Texture

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	11.646	3	3.882	3.772	.011
Error	242.850	236	1.029		
Total	2783.000	240			

Table B.3.13 Dependent Variable: Overall acceptance

Source	Sum of Squares	df	Mean Square	F	Sig.
Substitution	9.312	3	3.104	4.010	.008
Error	182.683	236	.774		
Total	2919.000	240			

Table B.4 ANOVA: overall effect of drying temperature (50, 60 and 70°C) on responsevariables of modified rice flour

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	.002	2	.001	.076	.927
Error	.090	9	.010		
Total	107.852	12			

 Table B.4.2 Dependent Variable: Cooking loss

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	.018	2	.009	.018	.982
Error	7.366	15	.491		
Total	430.169	18			

### Table B.4.3 Dependent Variable: Rehydration

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	1135.768	2	567.884	4.867	.023
Error	1750.110	15	116.674		
Total	1668422.738	18			

Table B.4.4 Dependent Variable: Hardness

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	15.553	2	7.777	9.225	.001
Error	22.760	27	.843		
Total	11529.221	30			

Table B.4.5 Dependent Variable: Springiness

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	.004	2	.002	4.800	.016
Error	.011	27	.000		
Total	19.456	30			

Table B.4.6 Dependent Variable: Cohesiveness

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	.001	2	.000	1.271	.297
Error	.005	27	.000		
Total	22.285	30			

Table B.4.7 Dependent Variable: Tensile

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	623.850	2	311.925	29.251	.000
Error	607.834	57	10.664		
Total	18916.475	60			

## Table B.4.8 Dependent Variable: Color

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	1.811	2	.906	1.163	.315
Error	137.833	177	.779		
Total	2800.000	180			

## Table B.4.9 Dependent Variable: Smell

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	1.744	2	.872	1.692	.187
Error	91.250	177	.516		
Total	2433.000	180			

## Table B.4.10 Dependent Variable: Taste

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	7.878	2	3.939	7.285	.001
Error	95.700	177	.541		
Total	2422.000	180			

## Table B.4.11 Dependent Variable: Texture

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	16.633	2	8.317	20.469	.000
Error	71.917	177	.406		
Total	2443.000	180			

Source	Sum of Squares	df	Mean Square	F	Sig.
Temperature	4.900	2	2.450	5.285	.006
Error	82.050	177	.464		
Total	2485.000	180			

Table B.4.12 Dependent Variable: Overall acceptance

## APPENDIX C

# PERCENT YIELD OF MODIFIED RICE FLOUR AND DRYING CURVE OF RICE NOODLE

Table C.1 Percent yield (%db) of modified rice flour at different heating temperature and

time

Temperature Time	100	110	120
15	84.79 ± 4.88	73.53 ± 0.02	78.72 ± 1.91
30	76.30 ± 1.00	76.47 ± 3.02	75.03 ± 0.62
45	78.44 ± 2.93	74.65 ± 1.28	70.77 ± 0.27

Table C.2 Percent yield (%db) of modified rice flour at different incubation temperature

Temperature	%Yield
5	83.42 ± 2.36
30	74.07 ± 2.13
45	70.76 ± 0.27
60	64.88 ± 0.55
75	57.38 ± 0.58
90	35.06 ± 4.36

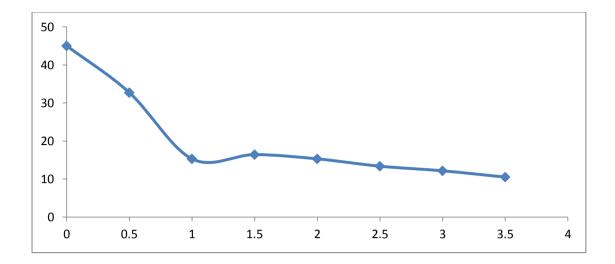


Figure C.1 Drying curve of 20% substitution rice noodle drying at 50°C

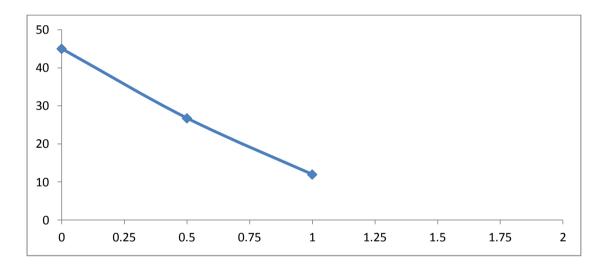


Figure C.2 Drying curve of 20% substitution rice noodle drying at 60°C

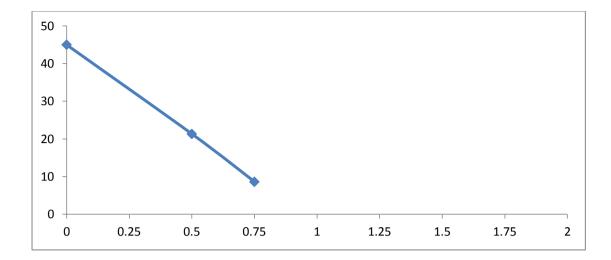


Figure C.3 Drying curve of 20% substitution rice noodle drying at 70°C

## APPENDIX D PICTURE OF MODIFIED RICE FLOUR AND RICE NOODLE PROCESSING









Figure D.1 Rice flour slurry after heating and incubating at 45°C, a) Heated rice flour in beaker with cover, b) Surface of Heated rice flour after incubating at 45°C



Figure D.2 Modified rice flour after drying at  $40^{\circ}$ C



Figure D.3 Noodle sheets after aging at 5°C for 24 h



Figure D.4 Cutting noodle sheets using machine (Jianyongyamianji, China)



Figure D.5 Noodle before drying

#### VITAE

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Proceedings of the fourth international conference on science and technology for sustainable development of the greater mekhong sub-region (oral presentation), 23-24 January, 2012. Khon Kaen University, Khon Kaen, Thailand.