

**PHYSICAL AND RHEOLOGICAL PROPERTIES OF  
STARCH-GUM MIXTURES DURING PASTING**



**A THESIS SUBMITTED IN PARTIAL FULFILLMENT  
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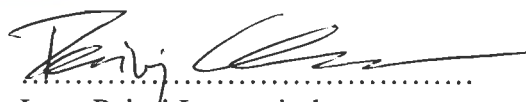
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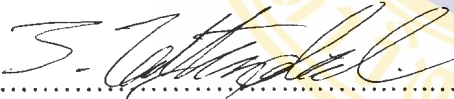
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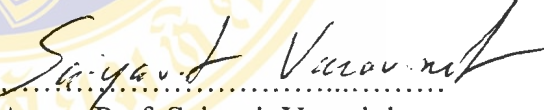
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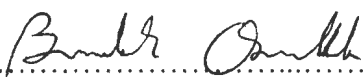
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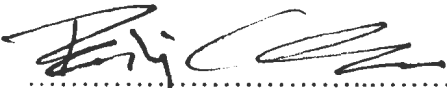
  
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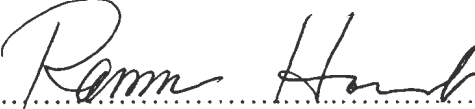
  
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SAIYAVIT VARAVINIT, Dr.Eng., PAIROJ LUANGPITAKSA, D.Agr.,  
BOVORNLAK OONKHANON, Ph.D.****ABSTRACT**

The gelatinization of native and modified tapioca starch embedded in gum matrix was investigated by using a Rapid Visco-Analyzer (RVA), Differential Scanning Calorimeter (DSC), swelling power and solubility index measurements, Scanning Electron Microscope (SEM), and rheometer. Xanthan and guar gums increased RVA peak viscosity of native and modified tapioca starch during pasting synergistically by different phenomena; except for anionic starch-xanthan gum mixture. Guar gum was more effective than xanthan gum in terms of increasing peak viscosity due to the interactions between leached components, amylose and short chain amylopectin, and gums. The increasing viscosity was not affected by swelling power of native and anionic starch suspensions. On the contrary, swelling power of cationic starch was greatly decreased in xanthan gum solution due to aggregation of gum and starch granules. Xanthan gum enwrapped several adjacent granules and induced association between the gelatinized granules only in cationic tapioca starch, enwrapped each granule in native tapioca starch, and did not wrap anionic tapioca starch granules, whereas guar gum partially enwrapped granules and also formed sheet structure for native and modified tapioca starches. DSC studies showed that the presence of gums influenced the gelatinization characteristics of starch significantly by increasing the onset gelatinization temperature and decreasing the gelatinization enthalpy. Dynamic rheological measurement showed a strong interaction occurred in the cationic tapioca starch-xanthan gum mixture and moderate interaction occurred for the rest of mixture (guar gum addition or starch alone) resulting in a decrease in loss tangent. The ionic interaction of gums and starches was found to play an important role on gelatinization characteristics of the mixtures and also rheological properties of the pastes.

**KEYWORDS: CATIONIC TAPIOCA STARCH/ ANIONIC TAPIOCA STARCH/ GUMS/  
STARCH-GUM MIXTURES/ SWELLING POWER/SOLUBILITY/  
GELATINIZATION CHARACTERISTICS/ VISCOELASTICITY**

การศึกษาคุณสมบัติทางกายภาพและรีโอโลยีของของผสมแป้งกับกัมระหว่างการให้ความร้อน  
(PHYSICAL AND RHEOLOGICAL PROPERTIES OF STARCH-GUM  
MIXTURES DURING PASTING)

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บทคัดย่อ

การเกิดเจลลิตินในเซชันของของผสมระหว่างแป้งมันสำปะหลังหรือแป้งคัดแปรกับกัมถูกตรวจวิเคราะห์โดยใช้เครื่อง Rapid Visco-Analyzer (RVA), เครื่อง Differential Scanning Calorimeter (DSC), เครื่อง Scanning Electron Microscope, การวัดกำลังการพองตัวและการละลาย, และเครื่องรีโอมิเตอร์แซนแทนกัมและกัวกัมเพิ่มค่าความหนืดสูงสุดของแป้งมันสำปะหลัง และแป้งคัดแปรแบบทวิคูณ เมื่อเทียบกับแป้งที่ละลายน้ำ ยกเว้นของผสมระหว่างแป้งแอนไอออนิกกับแซนแทนกัมซึ่งไปลดค่าความหนืดสูงสุดระหว่างการให้ความร้อน กัวกัมเพิ่มพิลของความหนืดมากกว่าแซนแทนกัมเนื่องจากความสามารถในการอินเตอร์เร็คชั่นระหว่างอะมิโลส อะมิโลเพกทิน โมเลกุลสั้น กับกัม การเพิ่มความหนืดแบบทวิคูณนี้ไม่ได้เป็นผลมาจากค่ากำลังการพองตัวของแป้งทั้งแป้งมันสำปะหลัง และแป้งแอนไอออนิก ส่วนค่าการพองตัวของแป้งแคทไอออนิกลดลงในแซนแทนกัมเนื่องจากการเกาะกลุ่มของเม็ดแป้ง

แซนแทนกัมหุ้มเม็ดแป้งที่อยู่บริเวณใกล้กัน และเหนี่ยวนำให้เกิดการเกาะกลุ่มกันของเม็ดแป้งพบได้ในแป้งแคทไอออนิก หุ้มแต่ละเม็ดพบได้ในแป้งมันสำปะหลัง และไม่พบการหุ้มในแป้งแอนไอออนิก ส่วนกัวกัมหุ้มเพียงบางส่วนของเม็ดแป้ง และยังมีรูปทรงเป็นแผ่นพบในทั้งแป้งมันสำปะหลัง และแป้งคัดแปร

การศึกษาโดยใช้เครื่อง DSC ได้แสดงว่ากัมมีผลต่อการเกิดเจลลิตินในเซชันอย่างมีนัยสำคัญโดยเพิ่มอุณหภูมิเริ่มเกิดเจลลิตินในเซชัน และลดพลังงานที่ใช้ในการเกิดเจลลิตินในเซชัน

การวัดรีโอโลยีแบบไดนามิกแสดงให้เห็นว่ามีอินเตอร์เร็คชั่นที่แข็งแรงเกิดขึ้นในของผสมแป้งแคทไอออนิกกับแซนแทนกัม และมีอันตรกิริยาขนาดกลางซึ่งพบได้กับของผสมที่เหลือซึ่งมีผลทำให้ลดค่าลอสมเทนเจนต์ เมื่อเปรียบเทียบกับกรณีกัวกัมหรือแป้งอย่างเดียว

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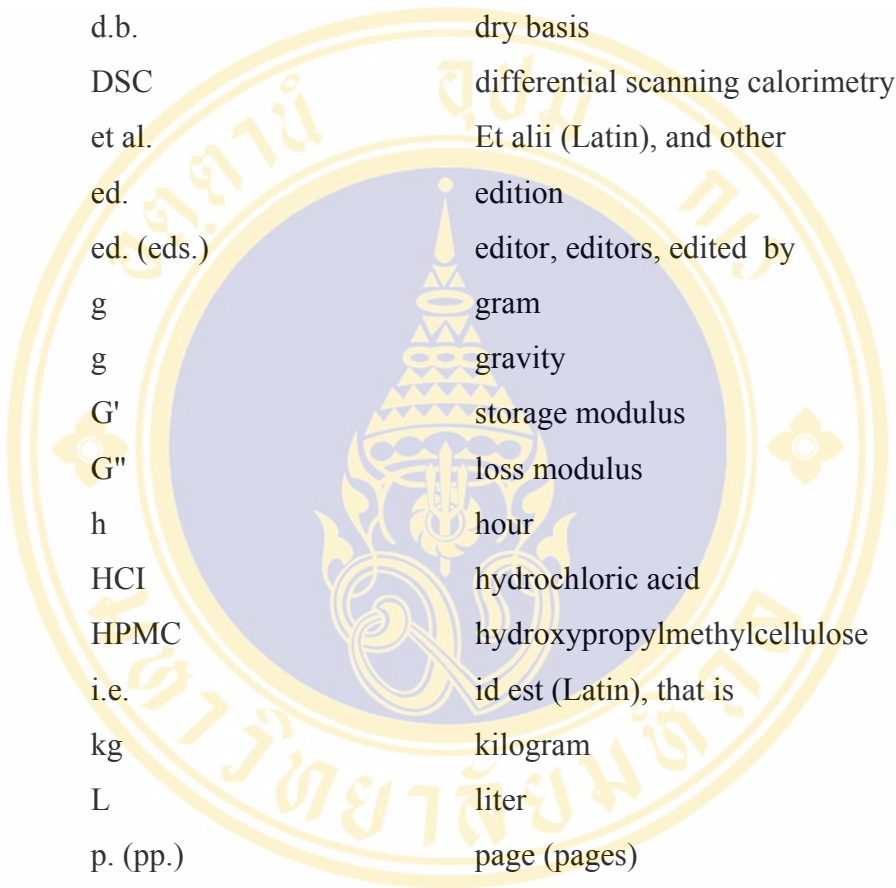
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## LIST OF ABBREVIATIONS



&	and
d.b.	dry basis
DSC	differential scanning calorimetry
et al.	Et alii (Latin), and other
ed.	edition
ed. (eds.)	editor, editors, edited by
g	gram
g	gravity
G'	storage modulus
G''	loss modulus
h	hour
HCl	hydrochloric acid
HPMC	hydroxypropylmethylcellulose
i.e.	id est (Latin), that is
kg	kilogram
L	liter
p. (pp.)	page (pages)
μ	micron
mg	milligram
ml	milliliter
min	minute
M	Molarity
mm	millimeter
nm	nanometer
NaOH	sodium hydroxide
no.	number
rpm	revolution per minute
RVA	Rapid Visco Analyzer

## LIST OF ABBREVIATIONS

(continued)

S	second
SEM	Scanning Electron Microscopy
SHMP	Sodium hexametaphosphate
SOL	Solubility Index
SP	Swelling Power
SPSS	Statistical Package for the Social Sciences
STPP	Sodium tripolyphosphate
$\tan \delta$	G"/G' values
$T_c - T_0$	phase transition temperature range
$T_0, T_p, T_c$	onset, peak, conclusion gelatinization temperature
w/v	weight by volume
w/w	weight by weight
/	per
%	percent
°C	Degree Celsius

## CHAPTER 1

### INTRODUCTION

Tapioca starch is the major energy reserve in plants and serves as the most important carbohydrate source for human and animal. Furthermore, starch polymers are used in large-scale non-food applications such as cationic tapioca starch in the paper industry. Starch for industrial use are often subjected to post harvest chemical or physical modifications such as phosphorylation or hydrolysis in order to decrease gel strength and syneresis. Since these processes are expensive, polluting and frequently result in starch degradation and unwanted by products, adding gums (hydrocolloids) is a desirable alternative (Blennow, Mette Bay-Smidt & Bauer, 2001). Blends of starches and hydrocolloids are widely used in starch containing foods. Hydrocolloids (polysaccharide-gel former such as guar gum, xanthan gum etc.) play an important role in the overall acceptability of foods such as: (i) increasing viscosity of starch dispersion, (ii) improving food texture, (iii) increasing resistance to undesirable physical processes such as crystallization, gravitational sedimentation and mechanical disaggregation, (iv) controlling moisture and water mobility, and (v) reducing costs (Mandala, Palogou & Kostaropoulos, 2002; Wei, Wang & Wu, 2001).

Hydrocolloids have been shown to alter the starch gelatinization. From literatures, it is well known that the addition of hydrocolloids in starch suspension strongly influences the synergistic by increasing viscosity (Alloncle, Lefebvre, Llamas & Doublier, 1989; Liu, Eskin & Cui, 2003). There are few reports about the interactions between starch and gum that clarified the exact mechanism. Christianson, Hodge, Osborne and Detroy (1981) found that guar gum, xanthan gum and carboxymethyl cellulose increased the viscosity of wheat starch due to the function of the media viscosity only in early stage and believed that the increase of paste viscosity was attributed to interactions of gums, leached

component and swollen granules. Shi & BeMiller (2002) found that the interactions between specific gums and specific molecules leached from granules was responsible for increasing of viscosity before starch pasting at low concentrations of starches and gums (no interaction between starch granules and no viscosity increase due to shape and size changes). However, there are few reports on the interaction between gums and modified starch (Abdulmola, Hember, Richardson & Morris, 1996; Krüger, Ferrero & Zaritzky, 2003; Tecante & Doublier, 1999). Lee, Baek, Cha, Park and Lim (2002) reported that xanthan gum reduced paste viscosity significantly, whereas guar gum and alginate increased the viscosity of potato starch and phosphorylated normal maize starch. This result is consistent with those of Shi & BeMiller (2002), who suggest the greatly decreased of peak viscosity between negatively charged gums and potato starch due to the repelling forces between phosphate groups on potato starch and the negative charges on molecules of these gums. There have been researches on the morphology of gelatinization of native starch-gum mixtures using scanning electron microscopy (Jing-ming & Sen-lin, 1990; Mandala, Palogou & Kostaropoulos, 2002).

The present study attempts to provide a more detailed understanding of the mechanisms responsible of gelatinization characteristic of starch-gum mixtures which lead to the production of higher quality starch containing foods. The objectives of this study were to investigate the effects of an ionic interaction of starches and gums on physical and rheological properties of the mixture during and after heating.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Starch

The chemical and microphotography techniques has elucidated that starch is composed of two polymers – amylose and amylopectin. Amylose is a linear molecule consisting of (1-4)-linked  $\alpha$ -D-glucopyranose units; however, the glucose residues are 400 to 4000 units long. Amylopectin is a highly branched glucose polymer containing both  $\alpha$ -1,4-linear and  $\alpha$ -1,6-branched linkages. At one time, it used to say that this branches bushy polymer with branches 20 to 30 glucose residue long, contributes primarily to the viscosity of a prepared food (Ahmad & Williams, 1998). The many different starches range in amylose, on the average, from 16 to 25% and may be as high as 30%. There are some high amylose rice starches which may have as much as 80 to 90% amylose. These starches are unusual and are occasionally used in edible casings. At the other end of the scale, there are the waxy corn starches, waxy rice starches, and waxy sorghum, which contain 100% amylopectin. The amylose contents and average sizes of various starches show in Table 2.1.

The starches obtained from the various sources are used in food systems such as thickeners, stabilizers, gelling agents and emulsifiers. It also modifies texture, improve moisture retention, control water mobility, and maintain overall product quality during storage. Both of the amylose and amylopectin are long chain polymers which can be dissolved or dispersed in water to give the thickening or the viscosity building effect. The starches can also form other composite structures. For example, starch gels are ill-defined composites consisting of swollen granules filling an interpenetrating polymer network. The major polymer in such network is amylose (Liu & Lelievre, 1992).

**Table 2.1** Amylose content and granule size of various starches  
(<http://home3.inet.tele.dk/starch/isi/starch/starch.htm>).

Starch source	amylose (%)	Granule size range ( $\mu\text{m}$ )	Average size ( $\mu\text{m}$ )
Waxy rice	0	2-15	6
High amylose corn	70	4-20	10
Corn	28	2-25	14
Tapioca	17	3-30	14
Waxy sorghum	0	-	-
Wheat	26	3-35	7 and 20
Sweet potato	18	4-40	19
Arrowroot	21	9-40	23
Sago	26	15-50	33
Potato	20	10-100	36

### 2.1.1 Tapioca starch

Basically, tapioca starch (*Manihot esculenta*) is a root starch derived from cassava, or yucca plant. It often used to thicken soups and sweetens the flavor of baked goods, and it makes a pudding. In industry, tapioca starch can take place with less manufacturing and reduced storage costs. These results of tapioca starch give a competitive advantage over the used of potato starch in many application. Modified starches are developed to achieve desirable products. The main types of modified starches are shown in Table 2.2.

**Table 2.2** Modification of starch

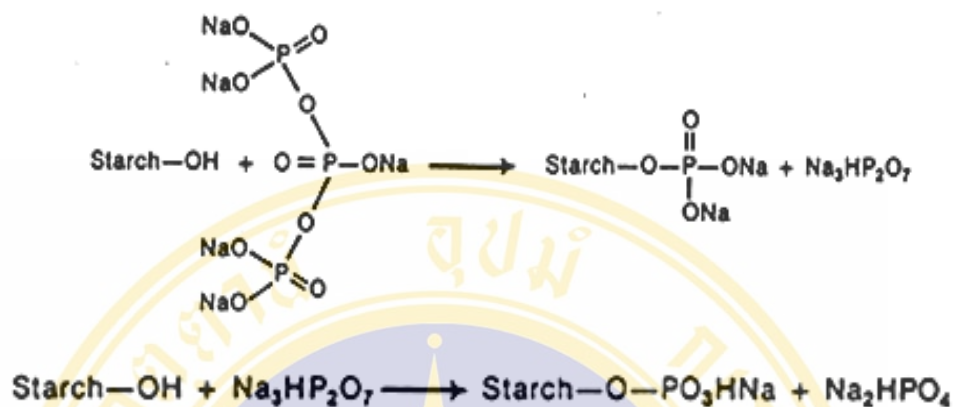
Type of modification	Main objectives	Treatment
Pregelatinized starch	Cold water dispersibility	Drum-drying Extrusion
Low viscosity starches	Lower viscosity	a, b, c, or d
a. Dextrins	Lower viscosity Range of viscosity stability	Dry heat treatment with acid
b. Acid-modified starch	Lower viscosity High gel tendency	Acid hydrolysis (suspension)
c. Oxidized starch	Lower viscosity Improved viscosity stability	Oxidation (in suspension or paste)
d. Enzymatically modified starch	Lower viscosity	Alpha-amylase (paste)
Crosslinked starch	Modification of cooking characteristics	Crosslinking in suspension
Stabilized starch	Improved viscosity stability	Esterification Etherification
Combinations of modifications 1, 2, 3 and/or 4	Combination	Combination
Starch sugars	Sweet saccharides	Acid and/or enzymes

### **2.1.2 Starch phosphates**

Starch phosphates are starch ester derivatives of phosphoric acid such as mono-, di-, and tri-starch phosphate ester. Native starches contain small amounts of phosphorus whereas potato starch contains 0.07 to 0.09 % phosphorus covalently bound to the amylopectin fraction. Normally, 60 to 70 % of the total phosphorus is attached at C-6 while the rest is located on C-3 of the anhydroglucose unit (Solarek, 1986). In the early studies of starch phosphates, the main focus was kept on its physical properties, such as the enhancing effects on starch hydration and starch-paste viscosity. The presence of phosphate groups in starch increases the hydration capacity of paste and, as the result, starch phosphate is correlated to peak viscosity and gel-forming capacity (Blennow, Bay-Smit & Bauar, 2001).

#### **2.1.2.1 Preparation of starch phosphate monoester**

Starch can be phosphorylated by “dry heat” reactions with various inorganic salts, ortho-, pyro-, meta-, or tripolyphosphates. More moderate temperatures (100 to 120°C) can be used in phosphorylating starch with sodium tripolyphosphate (STP). The pH of the STP-starch mixture drops about less than 7.0 to 9.0 during reaction. However, the pyrophosphate can be present from hydrolysis of the STP and then can also react with starch (Solarek, 1986) which is shown in Figure 2.1. Depending on the phosphate concentration, varying amount of phosphate salt are retained in the starch filter cake (Table 2.3)



**Figure 2.1** Reaction of sodium trimetaphosphate in alkaline condition (Solarek, 1986).

**Table 2.3** Slurry impregnation<sup>a</sup> of starch with phosphate salts (Solarek, 1986).

Starch (g)	Salt (type)	Salt in slurry (g)	Slurry water (ml)	Salt retained (g (%))
180	STP <sup>b</sup>	15.5	215	9 (58.1)
180	STP	30.0	400	6 (20.0)
180	STP	15.0	400	3 (20.0)
180	STP	7.5	400	1.5 (20.0)
180	SHMP <sup>c</sup>	12.8	215	7 (57.4)
162	NaH <sub>2</sub> PO <sub>4</sub>	27.6	240	12.1 (43.8)

<sup>a</sup> The phosphate salt was dissolved in the water followed by suspension of the starch, mixing, and filtration.

<sup>b</sup> Sodium tripolyphosphate

<sup>c</sup> Sodium hexametaphosphate

### **2.1.2.2 Utilization of phosphorylated starch**

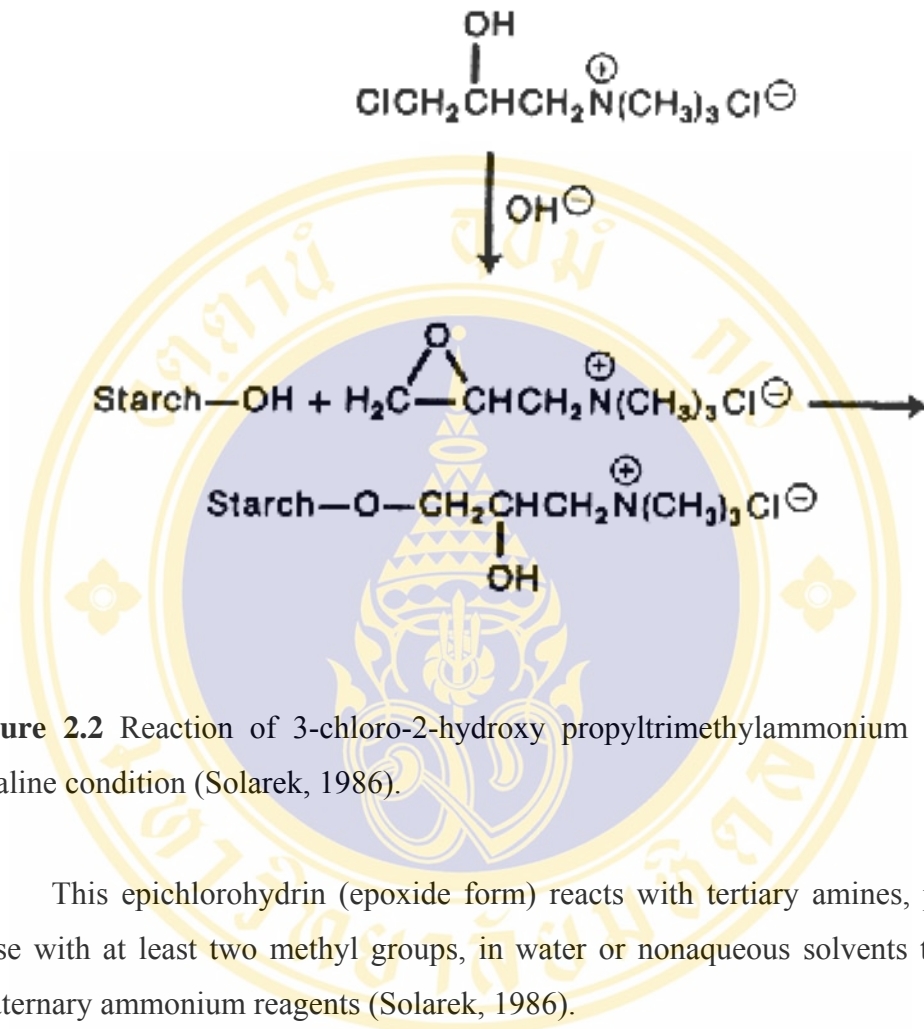
Starch phosphates are useful wet-end additive which can be found in various kinds at applications such as in a paper making industry, the initial adhesive strength for weed pieces, in personal care and pharmaceutical products, a hydrophobic powder (filler). It can be a good stabilizer which can be used as a thickening agent (Solarek, 1986). It also used to substitute with potato starch noodle (Muhammad, Kusnandar, Hashim & Rahman, 1999).

### **2.1.3 Cationic starch**

Cationic starches are starch ester derivative of nitrogen such as amino, imino, ammonium, sulfonium, or phosphonium groups, all of which can carry a positive charge. Such derivatives can be reacted easily with the hydroxyl groups in alkaline medium (Solarek, 1986).

#### **2.1.3.1 Preparation of cationic starch**

Cationic starches can be prepared by the reaction of native starches with various reagents possessing positively charged groups. Among these reagents 2,3-epoxypropyl trimethylammonium chloride and 3-chloro-2-hydroxy propyltrimethylammonium chloride have been used extensively (Auzely-Velty & Rinaudo, 2003). Probably the most popular form of cationic starch is quaternary ammonium groups. The reagent can conveniently be supplied and stored in water in the chlorohydrin form. Treatment of the chlorohydrin with sodium hydroxide readily makes the epoxide which reacts with starch at pH 11.0 to 12.0 as shown in Figure 2.2.



**Figure 2.2** Reaction of 3-chloro-2-hydroxy propyltrimethylammonium chloride in alkaline condition (Solarek, 1986).

This epichlorohydrin (epoxide form) reacts with tertiary amines, particularly these with at least two methyl groups, in water or nonaqueous solvents to form the quaternary ammonium reagents (Solarek, 1986).

### 2.1.3.2 Utilization of cationic starch

Dispersions of cationic starches display improved clarity and stability. Due to their ionic attraction to anionic, cellulosic fibers, cationic starches have become important wet-end additives in paper making. Moreover, cationic starches are excellent flocculants for suspensions of inorganic matter having a negative charge. The cationic starches also used for pharmaceutical compositions (Solarek, 1986).

## 2.2 Hydrocolloids (gums)

Gums are water-soluble polysaccharides or proteins with high molecular weights (up to 1 million) that exhibit a variety of functional properties: thickening, gelling,

film forming, emulsifying, adhesion, etc. Moreover, gums are used in low concentration which can improve achieve cost reductions (Ward & Andon, 2002). The characteristic of various gums show in Table 2.4. They are produced in nature such as cell wall, exudates, storage material, extracellular substances from plants or microorganisms, and exoskeleton of shellfish.

Xanthan gum has a cellulosic backbone which is water soluble by the presence of trisaccharide branches (1,4-linked  $\beta$ -D-glucan: cellulose) attached to every second glucose unit in the main chain. The chemical structure of xanthan gum shows in Figure 2.4. The gum is produced by certain species of *Xanthomonas campestris* and offers unusual texturizing properties (Bahnassey & Breene, 1994). After fermentation, the gum is recovered by precipitation with isopropyl alcohol, then dried and milled. Solutions of xanthan gum are extremely in pseudoplastic and show slight change in viscosity with salt, pH, and temperature variations (Igoe, 1982). The molecular weight of xanthan gum was around  $2 \times 10^6$  g/mole. Unlike other polysaccharide used as food thickeners, including guar gum and locust bean gum, xanthan gum can exists in solution in a rigid, ordered, chain conformation. Formation and melting of the ordered structure occur as sharp, co-operative processes, with no detectable thermal hysteresis, and have been monitored by physical techniques (Sudhakar, Singhal & Kulkarni, 1996).

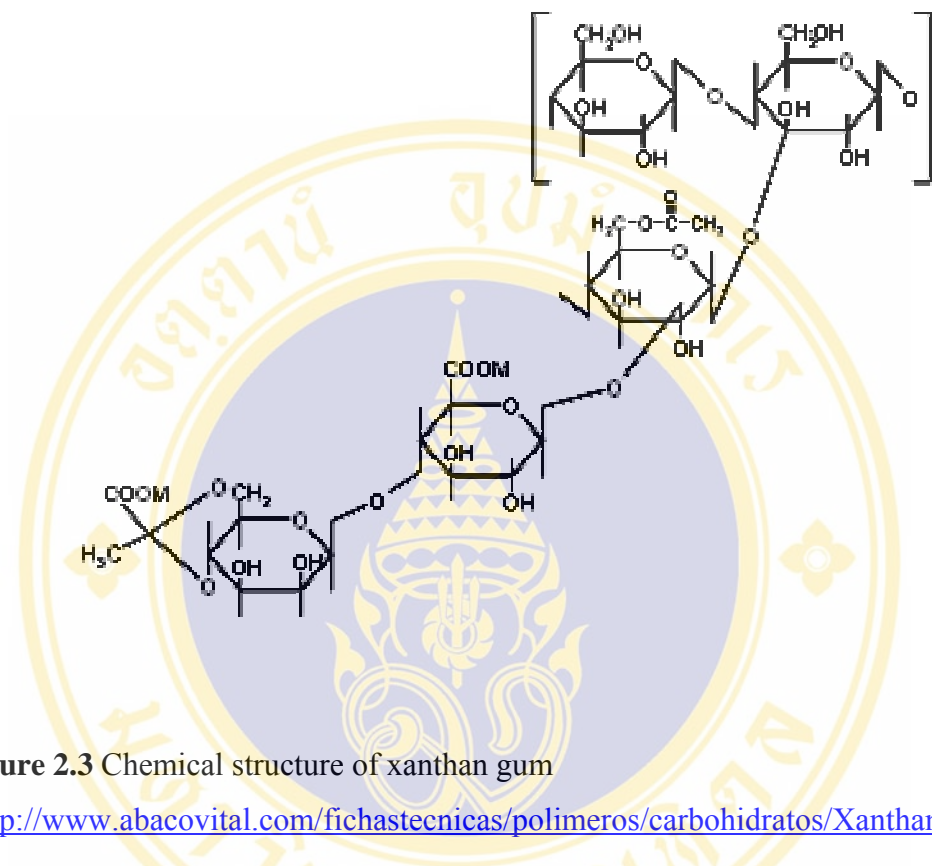
The following is a summary of the many applications for xanthan gum. In wet prepared batters, xanthan gum reduces flour sedimentation; improve gas retention; and provides uniform coating. Use levels of approximately 0.25% of the batter weight are effective in this application. Batters for fish can be stabilized with 0.06% xanthan gum whereas 0.1-0.15% is recommended for thin batters such as those used with shrimps (tempura). Xanthan can also be used in batters for frozen products such as chicken, shrimp or fish. However, moisture control is essential at all stages of cake production and also when formulating a dry cake mix. Xanthan can be adding to the cake batter at 0.05% (total batter weight) without the need for any other formulation change. Dressing is the largest single application of xanthan gum in the food industry. Xanthan gum stabilized to acid and salt, effectiveness at low concentrations. Dressings with xanthan gum have excellent long-term stability and a relatively constant viscosity over a wide temperature range. They pour easily but cling well the salad. Use level is

typically between 0.2-0.4% depending on the oil content. Generally as the oil content of the dressing increases less xanthan gum is required for stabilization.

**Table 2.4** The characteristic of various gums

(<http://www2.unl.ac.uk/~hx14marshar/cho.html>).

Extract or gum	Characteristics	Useful pH range	Uses
Carageenan	Interacts with protein	around 7.0	Dairy products
Guar gum	Cold water soluble, gelling agent, suspensions	approx. 7.5	Ice cream (prevent ice cryst.), gives body, soups, sauces, moisture retention
Xanthan gum	Viscosity stable over wide pH and temperature range, negatively charges side chains	vary	Bakery fillings, sauces, desserts
Locust bean gum	Partial hydrates in cold water fully in hot, good viscosity, reacts with carrageenans	approx. 5.5	Thickener in sauces; ice cream, pie fillings etc. against syneresis
Alginates	Thickener, gelling agent, suspensions	approx. 7.5	Salad dressings, pie fillings, ice cream, pudding



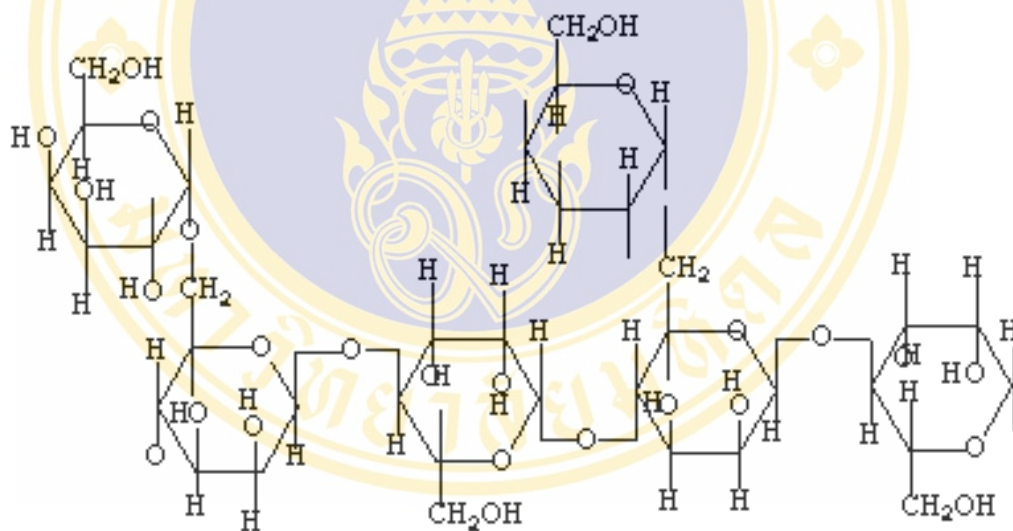
**Figure 2.3** Chemical structure of xanthan gum

(<http://www.abacovital.com/fichastecnicas/polimeros/carbohidratos/Xanthan.htm>).

Guar gum is composed of a straight back bone chain of D-mannopyranose units with side-branching unit of D-galactopyranose on every second unit. The chemical structure of guar gum shows in the Figure 2.4. The source of guar, *Cyamopsis tetragonolobus*, is widely grown in Pakistan and India as cattle feed. In processing, the hull of seed was removed, and the endosperm was separated form the germ. The hull is loosened and cleaned and cleaned by treatment with 55% sulfuric acid and washing by water. The endosperm obtained, containing approximately 80% galactomannan, is ground to a fine particle size. The molecular weight of xanthan gum was around  $2 \times 10^5$  g/mole. Solution of gum are thixotropic, and the viscosity is relatively unaffected by the presence of electrolytes. The rate of hydration and viscosity are increased at higher temperatures and are slightly cloudy due to the presence of insoluble fiber and cellulose. A 1% solution of a byypical commercial guar gum may reach a viscosity of

2700 cps, have a pH of 5.5-6.1, and tend to become more acidic. It will also be relatively stable over the range of pH 4-10.5, and exhibit a slight buffering action.

The following is a summary of the many applications for guar gum. Guar gum has important uses in the food industry as an ice cream stabilizer, where its rate of hydration and water binding property. It is also used to improve the yield of curds in soft cheese and to modify texture, to increase the yield and give greater resiliency to doughs and baked products, and as a binder and lubricant in sausage. It is often used as a thickening or viscosity control agent in beverages, salad dressings, and relishes (Klose & Glicksman, 1968).



**Figure 2.4** Chemical structure of guar gum

(<http://class.fst.ohio-state.edu/FST605/lectures/lect20.html>).

### 2.3 Rheology

Rheology (from the Greek *rheos* meaning ‘stream’) is the study of the flow and deformation of materials the amount of deformation will clearly depend on the area over which the force acts. The rheology is concerned with the two physical quantities: stress and strain (solid) or shear rate (fluid)

$$\text{Shear stress} = \frac{\text{shear (force)}}{\text{area (shear)}} \quad (\text{Pa or N/m}^2)$$

$$\text{Shear rate} = \frac{\text{velocity}}{\text{distance}} \quad (1/\text{s})$$

$$\text{Strain} = \frac{\text{deflection}}{\text{distance}} \quad (-)$$

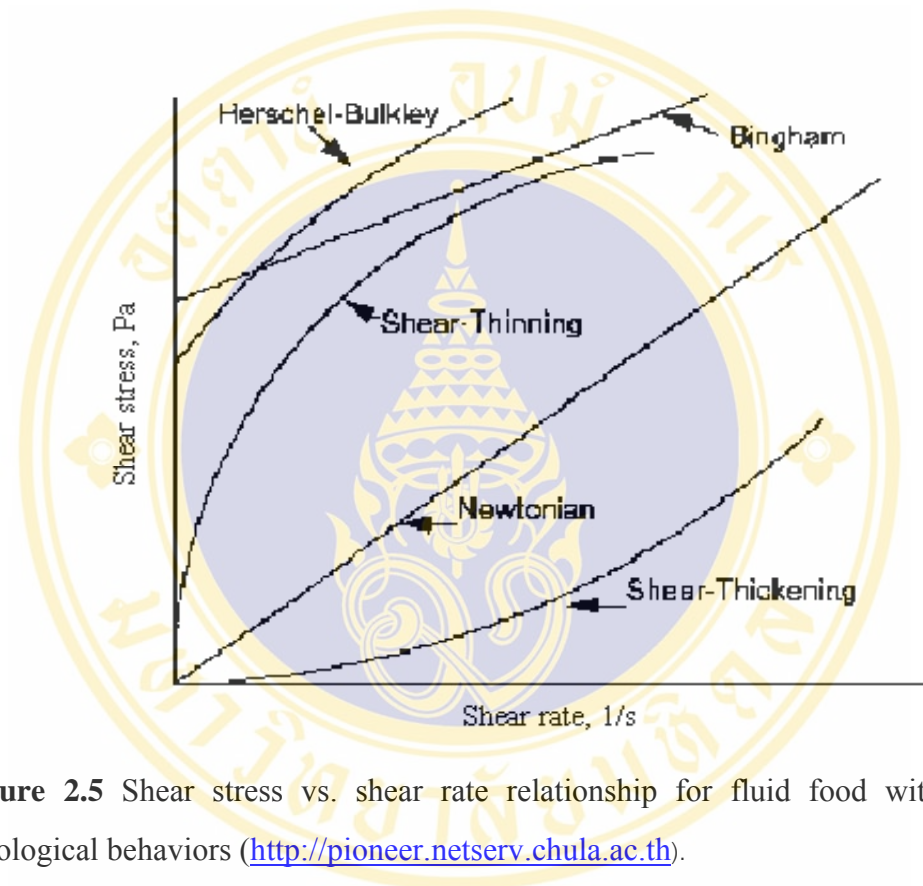
If flow is occurring, the strain is changing with time. In most rheological instruments, the strain is varied (Table 2.5) and the resulting stress within the material is measured.

Various terms are used to describe the rheological properties of materials depending on the mathematical form of the relationship between stress and strain. There are many reasons that the rheology is important: 1. allowed insights into structure, 2. used for quality control during processing, 3. designed processing equipment, 4. reveal food properties.

The only food colloids that are truly Newtonian (if the shear stress is a strictly linear relationship to the rate of shear strain) are soft drinks, which are very dilute dispersions of particles such as milk at temperatures above 35 °C and at shear-rate above 10 1/s. In principle, any interactions between dispersed particles (attractive or repulsive) will lead to non-Newtonian behavior at dispersed phase volume fractions above a few per cent such as milk at lower temperature. The most common type of non-Newtonian flow is shear-thinning (pseudoplasticity) such as starch paste. In many food colloids exhibit shear-thinning due to a breaking down of ‘structure’ under the influence of the shear flow. Another type is shear-thickening (dilatancy) corresponding to an increase in viscosity with increasing shear-rate. This kind of materials tends to occur in densely packed suspensions of non-aggregation.

**Table 2.5** Typical shear rate (<http://www.physica.de>).

Process	Shear rate range (1/s)	Examples of application
Sedimentation of fine particles in a suspension	$10^{-6}$ to $10^{-4}$	Dispersion paints, ceramic suspension, fruit juice
Leveling due to surface tension	$10^{-2}$ to $10^{-1}$	Coatings, printing inks, lacquers, chocolate
Dripping due to gravity	$10^{-2}$ to $10^{-1}$	Dipping varnishes, Dispersion paints
Chewing, swallowing	10 to 100	Cheese, yoghurt, chocolate
Mixing, Stirring	10 to $10^4$	Emulsion, plastisol, polymer blends
Brushing, painting, spraying, blade coating	100 to $10^4$	Brush coating, tooth paste, butter
Rubbing	$10^4$ to $10^5$	Sun milk, skin and other ointments
High-speed coating	$10^5$ to $10^6$	Paper coating



**Figure 2.5** Shear stress vs. shear rate relationship for fluid food with different rheological behaviors (<http://pioneer.netserv.chula.ac.th>).

Ideal elastic and viscous behaviors present two extreme responses of materials to external stresses. In real materials exhibit a response between viscous and elastic. Most foods exhibit some viscous and elastic behavior simultaneously and are called 'viscoelastic'. Dynamic tests were used to characterize property of viscoelastic behavior. These small-amplitude oscillatory tests are commonly performed in order of 1 to 3 or 5%. The frequency dependent functions  $G'(\omega)$  are shear elastic (storage) modulus and shear elastic (loss) modulus, respectively.  $G'$  is a measure of the energy stored and subsequently released per cycle of deformation per unit volume. This storage modulus is the property that relates to the molecular events of elastic nature (Rao, 1999).  $G''$  is a measure of the energy dissipated as heat per cycle deformation per unit volume. This loss modulus is a property related to the molecular events of viscous nature (Rao, 1999). Another commonly used dynamic viscoelastic property is the loss tangent [ $\tan \delta(\omega) = G''/G'$ ] denoted relative effects of viscous and elastic components in a viscoelastic behavior.

The storage modulus,

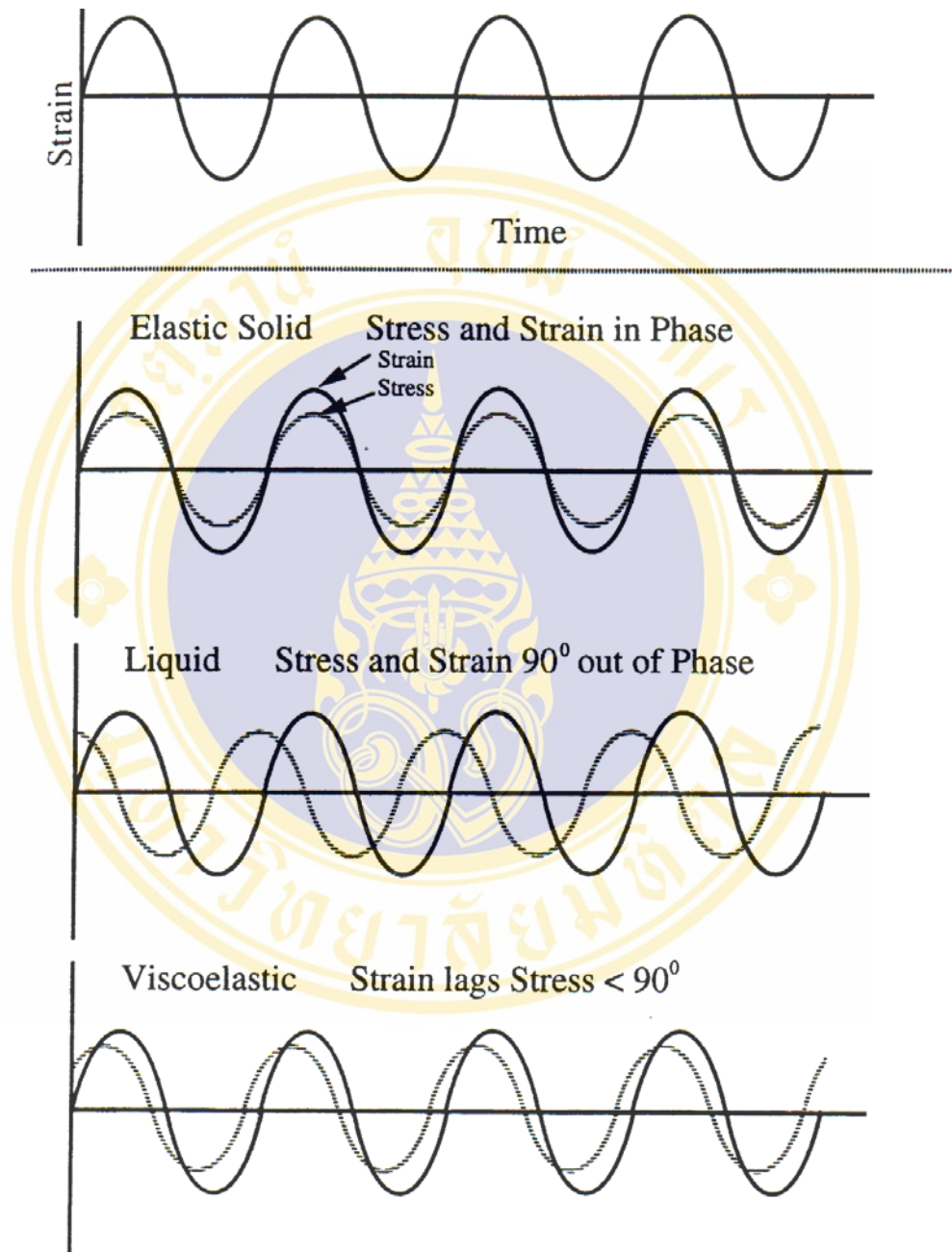
$$G' = \frac{\sigma_0 \cos \delta}{\gamma_0},$$

give the in phase stress amplitude and the loss modulus,

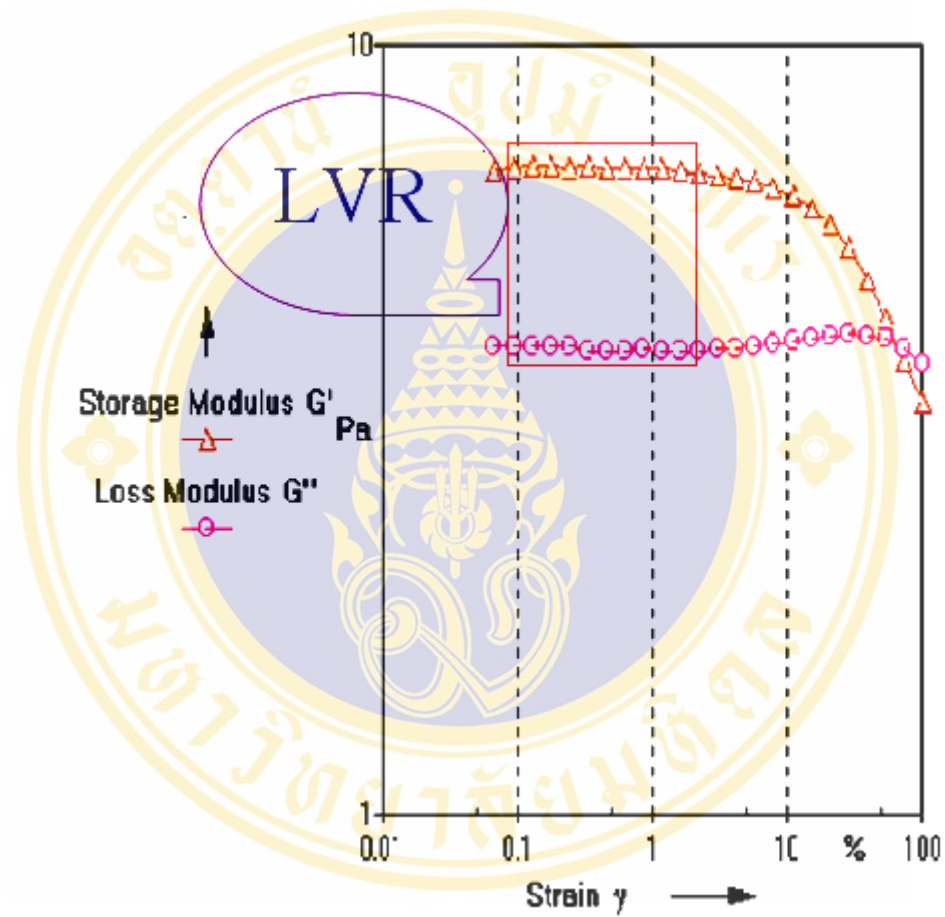
$$G'' = \frac{\sigma_0 \sin \delta}{\gamma_0},$$

give the quadrature stress amplitude (out of phase) as shown in Figure 2.6.

There are often three selected applications such as: (a) deformation sweep at constant frequency ( $G'$  and  $G''$  vs. strain) to determine the maximum deformation attainable by a sample in the linear viscoelastic region (Figure 2.7), (b) frequency sweep ( $G'$  and  $G''$  vs.  $\omega$ ) at constant deformation within the linear viscoelastic range to determine the elastic character of the gel and (c) temperature sweep at constant frequency and deformation within the linear viscoelastic range ( $G'$  and  $G''$  vs. Temperature) to evaluate thermal characteristics. The complex modulus  $G^*$  defined as  $(G'^2 + G''^2)^{1/2}$  represents the global viscoelastic response of the system.



**Figure 2.6** Stress versus strain response of a Newtonian liquid and a perfectly elastic solid in dynamic tests (Rao, 1999).

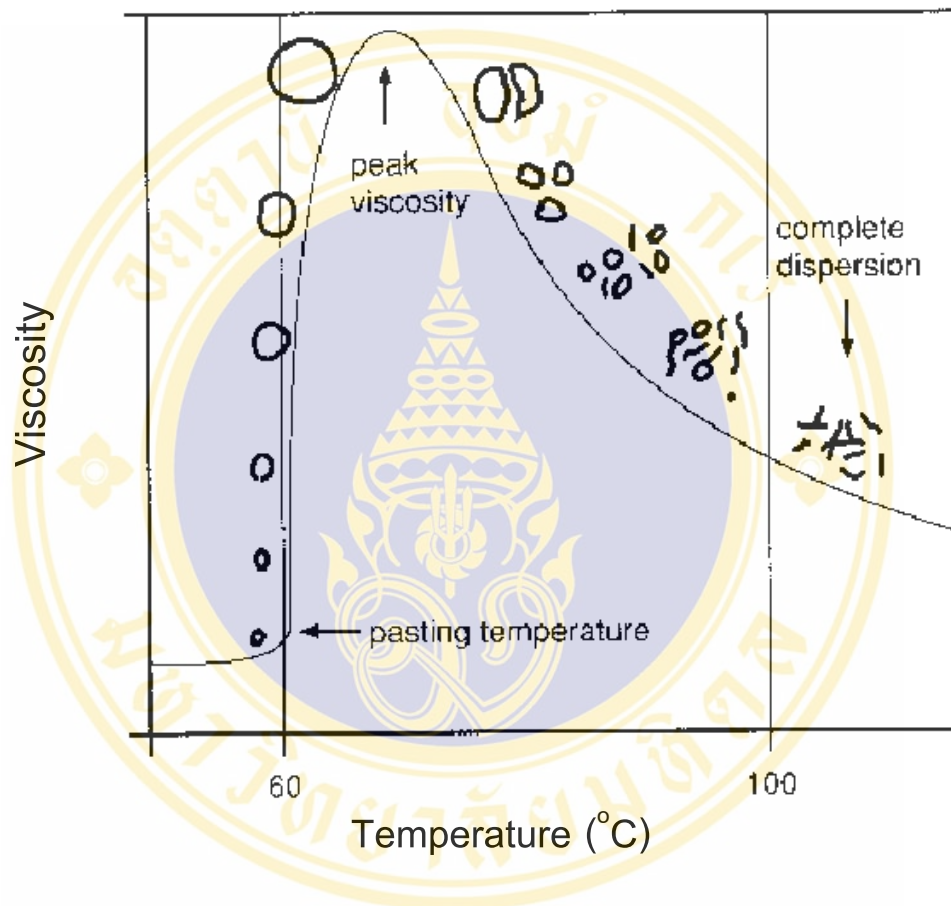


**Figure 2.7** Deformation sweep at constant frequency ( $G'$  and  $G''$  vs. strain) to determine the maximum deformation attainable by a sample in the linear viscoelastic region (LVR).

## 2.4 Starch granule gelatinization

Undamaged starch granules are insoluble in cold water, but can imbibe water reversibly; that is, they can swell slightly, and then return to their original size on drying. When heated in water, starch granules undergo a process called gelatinization. The gelatinization is the disruption of molecular order within granules. Evidence for the loss of order includes irreversible granule swelling, loss of birefringence, and loss of crystallinity (Whistler & BeMiller, 1997). Leaching of amylose occurs during gelatinization, but some leaching of amylose can also occur prior to gelatinization (Shi & BeMiller, 2002). Total gelatinization usually occurs over a temperature range, with larger granules generally gelatinize first.

Continued heating of starch granules in excess water results in further granule swelling, additional leaching of soluble components (primarily amylose), and eventually, total disruption of granules especially with the application of shear forces. This phenomenon results in the formation of a starch paste. Granule swelling and disruption produce a viscous mass consisting of a continuous phase of solubilized amylose or amylopectin and a discontinuous phase of granule remnants (Sasaki, Yasui & Matsuki, 2000). Complete molecular dispersion is not accomplished except, under high temperature conditions, high shear, and excess water, which are seldom occurred in the food products preparation. When 5% starch suspension is gently stirred and heated, granules imbibe water until much of the water is absorbed by them, forcing them to swell, press against each other, and fill the container with a highly viscous starch paste. Such highly swollen granules are easily broken and disintegrated by stirring, resulting in a decrease in viscosity. As starch granules swell, hydrated amylose molecules diffuse through the mass to the external phase, a phenomenon responsible for some aspects of paste behavior. Usually, starch swelling results can be observed using a RVA where the viscoscosity is monitored through out the curves at heating, maintaining, and cooling as shown in Figure 2.8.



**Figure 2.8** Swelling, disruption and dispersion of a starch granule during gelatinization (<http://www.ftns.wau.nl/agridata/starchpackfoam.html>).

Peak viscosity is the maximum viscosity during the heating cycle. It is common to measure pasting temperature and peak time that occur with the peak viscosity. Break down, the second parameter, indicates the disruption of the granules resulted decrease in viscosity (Newport Scientific, 1998).

As the mixture is consequently cooled, re-association between amylose occurs to a greater degree (Figure 2.9). In concentrated mixture, it usually causes the formation of gel and viscosity will increase to a final viscosity. This evidence is commonly referred to the setback viscosity and involves retrogradation. On the other hand, if the concentration is inadequate the precipitation of gel will occur (Figure 2.9). The setback was correlated with texture of several products. High setback viscosity is also associated with syneresis during freeze-thaw cycles.

Final viscosity is the typical parameter used to define quality of products. It indicates the ability of material to form viscous paste or gel after pasting. The final viscosity may or may not plateau depending on the starch and temperature used.

Another method giving quantitative calorimetric results is Differential Scanning Calorimetry (DSC) which reveals the gelatinization temperature. DSC is particularly well suited to investigate the phase transition of starch-water systems because it allows: (1) study of starch gelatinization over a wide range of starch-water ratio; (2) determination of gelatinization temperature above 100 °C; and (3) estimation of gelatinization enthalpies (Biliaderis, Maurice, & Vose, 1969). In this method the sample is submitted to linear heating and the rate of heat-flow in sample, proportional to the instantaneous specific heat, is measured continuously. In other words the temperature of sample is kept at the same value with reference sample and the electrical input necessary for the maintenance of isothermal conditions is measured.

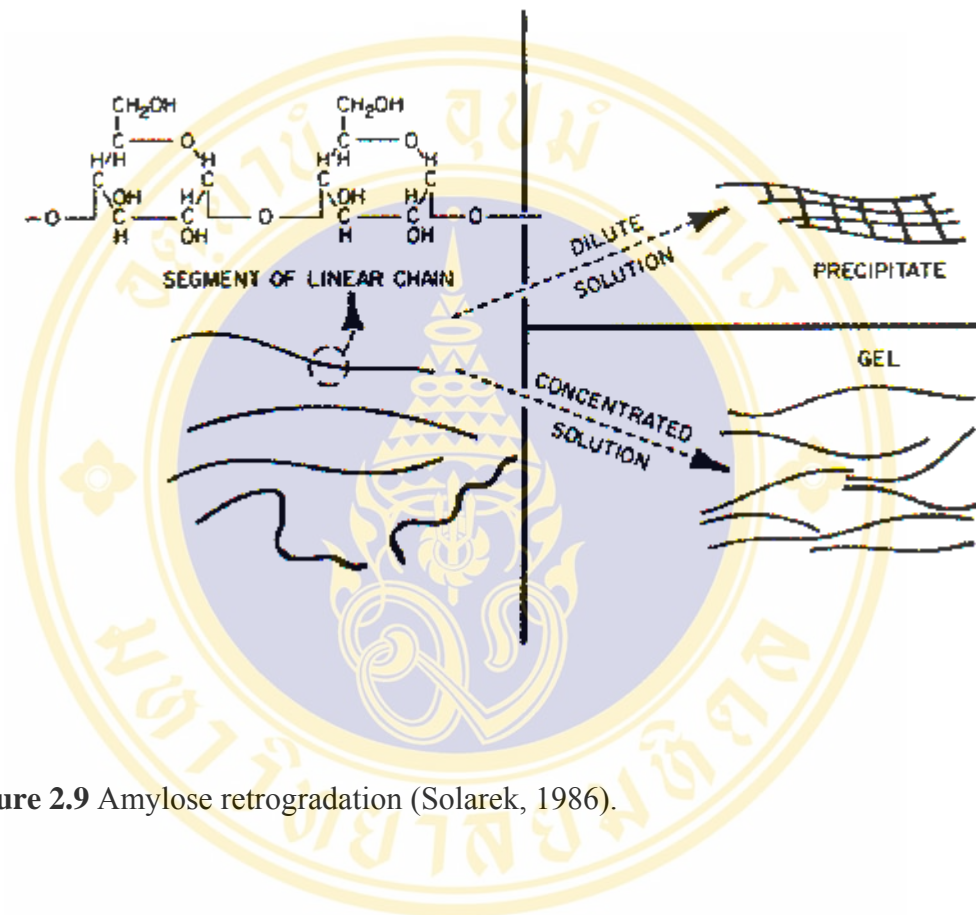


Figure 2.9 Amylose retrogradation (Solarek, 1986).

## 2.5 Gelatinization of starch-gum system

Starch pasting behaviour can be affected by interaction with other materials, either those endogenous in the sample or added in formulations. There are some material that significant interaction such as sugars, lipids, emulsifiers, gums, salts and pH modifiers. The hydrocolloids have been shown to alter the gelatinization of starches. From the scientific literature, it is well known that the addition of hydrocolloids in starch suspension strongly influences the synergistic by increasing viscosity (Alloncle, Lefebvre, Llamas & Doublier, 1989; Liu, Eskin & Cui, 2003). More over, there are few reports about the interactions between starch and gum that focused on clarifies its mechanism.

In preparation starch gum mixture, two procedures were performed: (1) gum was first dispersed in water under magnetic stirring, heated to 80°C for 5 min and cooled to ambient temperature and starch was then slurried in the gum solution; (2) all components were well dry blended prior to slurrying in water. Both procedures resulted in different pasting profiles. The preparateion using technique 1 gave high peak viscosity than technique 2.

Christianson, Hodge, Osborne and Detroy (1981) found that guar gum, xanthan gum and carboxymethyl cellulose increased the viscosity of wheat starch due to function of media viscosity only in early stage and believed that the increase of paste viscosity was attributed to interactions of gums, leached component and swollen granules. Shi and BeMiller (2002) found that interactions between specific gums and specific molecules leached from granules was responsible for the increasing of viscosity before starch pasting at low concentrations of starches and gums (no interaction between starch granules and no any viscosity increase due to shape and size changes). Shi and BeMiller (2002), also reviewed that gum retarded the gelatinization temperature but no one reported that gums decrease either the onset or peak temperatures of gelatinization as determined by DSC. In contrast, Liu et al. (2003) and Rojas et al. (1999) found that gums may interact with the starch to produce an increase or decrease of the gelatinization temperature ranges depending on the type of gums as shown in Table 2.6.

Lee, Baek, Cha, Park and Lim (2002) reported that xanthan gum reduced paste viscosity significantly, whereas guar gum and alginate increased the viscosity of

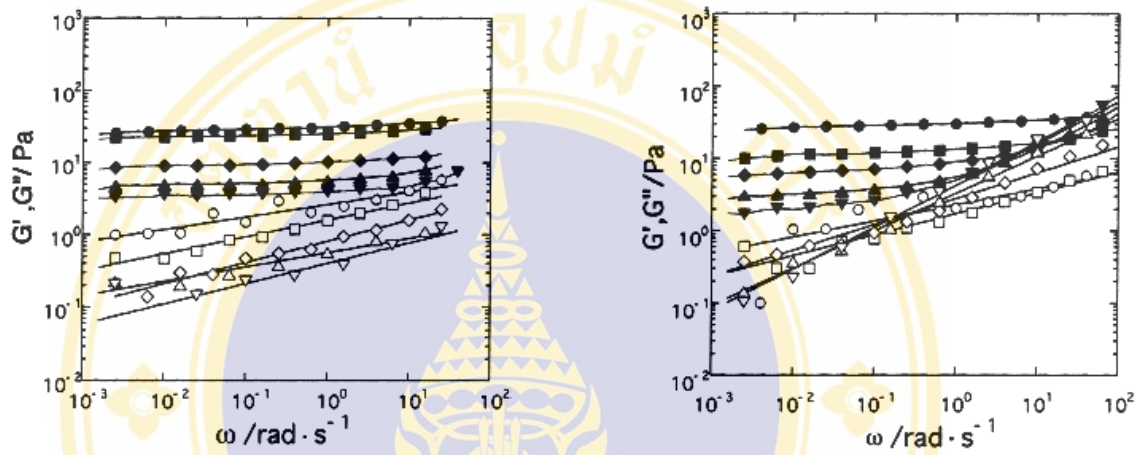
potato starch and phosphorylated normal maize starch. This result is congruent with those of Shi and BeMiller (2002), who suggested that the gums greatly decreased peak viscosity between negatively charged gums and potato starch due to the repelling forces between phosphate groups on potato starch and the negative charges on molecules of these gums. Lii, Tsai, and Tseng (1996) concluded that the major influencing factors on the rheological property of the starch during heating were the granular structure and component, followed by the amount of leached components in the system.

Bahnassey and Breene (1994) reported that the increasing of starch-gum viscosity is due to the releasing of amylose and low molecular weight amylopectin which promotes the formation of polymer complexes and increases the viscosity of the system significantly. In other explanations, Sudhakar, Singhal, and kulkarni (1996) who suggested that gums are located within the continuous phase and the volume of the phase accessible to the gum is reduced, which causes a dramatic increase in concentration in the continuous phase resulted in a very high viscosity.

In other adding system, Yoshimura, Takaya, and Nishinari (1999) indicated that xyloglucan inhibits the formation of three dimensional network structure of corn starch due to incompatibility between unlike polymers, amylose and hydrocolloids as shown in Figure 3.0. Sasaki, Matsuki, and Yasui (2000) suggested that adding nonstarch polysaccharide (wheat grains) to a starch result in a higher storage modulus and faster modulus increase than starch alone due to increased hydrocolloid concentration in the continuous phase.

**Table 2.6** The effect of the hydrocolloid addition on DSC parameters of wheat flour. Hydrocolloid concentration in the mixture was 1% (w/w) flour basis.

Hydrocolloid	T <sub>0</sub>	T <sub>p</sub>	T <sub>c</sub>	Range (°C)	Enthalpy (J/g dry basis)
None	54.7	63.5	74.9	20.2	10.4
Guar gum	55.6	63.4	76.0	20.4	7.9
Pectin	57.4	64.3	73.3	15.9	7.7
Alginate	56.1	62.8	73.2	17.1	7.7
κ-carageenan	56.3	63.4	75.9	19.3	8.2
Xanthan	56.8	63.7	74.5	17.7	9.0
HPMX	57.7	63.9	72.4	14.7	7.7



**Figure 3.0** Incompatibility of corn starch and xyloglucan, frequency dependence of  $G'$  and  $G''$  for dispersion of corn starch (left) and corn starch-xyloglucan mixture (right).

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Starches and gums

Native tapioca starch was kindly supplied by Cho Heng Rice Vermicelli Factory Co. Ltd., Nakornpathom, Thailand. Commercial cationic tapioca starch used (Batch No.121165, General Starch Co., Ltd., Bangkok, Thailand) had 0.35% nitrogen content and 11.64% moisture content. The cationic tapioca starch was quaternary ammonium starch ether. Xanthan gum and guar gum were obtained from Union Chemical 1986 Co., Ltd., Bangkok, Thailand.

#### 3.2 Chemical and reagents

Sodium hydroxide (NaOH), Hydrochloric acid (HCl), and acetic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) were purchased from Merck, Germany. All chemical reagents are analytical grade. Sodium tripolyphosphate was purchased from Monsanto, USA.

#### 3.3 Instruments

The equipment used in this study included Rapid Visco Analyzer (Model RVA 3D+, Newport Scientific, Australia), Differential Scanning Calorimeter (DSC 822<sup>e</sup>, Mettler Toledo, Schwerzenbach, Switzerland), hot air oven (Model SLM 400-800 Memmert, Universal, Germany), sieve size 100 mesh (Laboratory Test Sieve, Endecotts Ltd., England), pH meter (Model HM-12P, TOA electronics Ltd., Japan), moisture analyzer (MA 30-000V2, Sartorius Ao Gottingen, Germany), Rheometer (Physica MCR 300, Anton Paar GmbH, Stuttgart, Germany )

### 3.4 Preparation of anionic tapioca starch

Native tapioca starch was phosphorylated by the procedure of Lim and Seib (1993). Accurately weighted amounts of sodium tripolyphosphate (4.5g) were dissolved in 241 ml of distilled water. The starch (301.5g, db) was mixed into the solution by stirring continuously. The slurry was stirred for 1 h at room temperature and dried in an oven at 40 °C to retain 10-15% moisture. To effect phosphorylation, the dried starch cake was heated for 2 h at 130 °C in a hot air oven. After cooling to room temperature, the starch cake was washed many times by suspending the starch in distilled water and recovering the starch by centrifugation at 2300 rpm for 4 min. Finally, the starch was dried at 40 °C in hot air oven. The phosphate content was determined by Flame Emission Photometry (FEP) using the modified method of AOAC 991.25. Starch was burned in furnace overnight (16h) at 525 °C, and cooled down in a desiccator. Ash was dissolved in 1 ml HNO<sub>3</sub>. After cooling, ash was transferred to 250 ml volumetric flask and dilute to given volume. Determine phosphorus by using the UV-visible detector at 400 nm.

### 3.5 Pasting properties

The pasting properties of starches or starch-gum mixtures suspended in distilled water were determined by a Rapid Visco-Analyzer (Model RVA-4C, Newport Scientific Pty. Ltd., Warriewood, Australia). The slurry concentration of 6% w/v (dry basis) starches (native, anionic, or cationic tapioca starches) was prepared by dispersing 1.5 g (dry basis) of starch in 25 ml distilled water or 0.35% w/v (dry basis) gum solutions. In the case of starch-gum mixtures, gums were first dispersed in distilled water under magnetic stirrings, heated to 80 °C for 5 min and cooled to room temperature. The starch was then slurried in the gum solutions. The dispersions were stirred with a spatula for sufficient duration to avoid formation of lumps, especially in xanthan gum solution. The starch-gum suspensions were poured into aluminum containers and stirred manually using plastic paddle for 20-30 s before insertion into the RVA machine. The heating and cooling cycles were programmed in the following manner. The slurry was held at 50 °C for 1 min, heated to 95 °C within 3 min and then

held at 95 °C for 2 min. It was subsequently cooled to 50 °C within 3 min and then held at 50 °C for 2 min, while maintaining a rotation speed of 160 rpm.

### **3.6 Swelling power and solubility index**

Swelling power (SP) was determined by modifying the method of Mandala and Bayas (2004). The concentration of starch used was less than the close packing concentration (~3.0%) of starch granules (Vandeputte, Derycke, Geeroms & Delcour, 2003). Starch-gum suspensions (1.25% starch and 0.073% gum) were put in centrifugal tubes with closed screw caps and heated in a water bath at 60-90°C for 10 min with minimum shear condition. After heating, the centrifugal tubes were immediately immersed in an ice bath to quickly cool the dispersion to room temperature. After cooling for 5 min, samples were centrifuged at 11,200 ×g at 5 °C for 15 min and supernatant was then removed for the solubilized starch measurement. The supernatant was dried to constant weight in a hot air oven at 105°C. Both precipitated paste and dried supernatant were then weighed. All measurements were done in triplicate. The swelling power (SP) and solubility index (SOL) were calculated based on the assumption that the total amount of gum was remained in the supernatant. The SP is the ratio of the wet weight of precipitated starch gel to its dry weight, whereas the SOL is the percentage of dry mass of solubles in supernatant (after subtraction by dry weight of gum added) to the dry mass of whole starch sample.

### **3.7 Scanning electron microscopy (SEM)**

In this assay, 0.6 g (dry basis) of starch was dispersed in 10 ml distilled water or 0.035% (dry basis) gum solutions. The samples were put in centrifuge tubes and heated in a water bath at temperatures of 64 °C for 5 min with minimum shear condition. After heating, the samples were mixed with 2 % agarose solution of same temperature as fast as possible and were immediately immersed in an ice bath. For the SEM observation, the samples were prepared with the technique of the critical point drying modified from the method of Egelanddal, Langsrud, Nyvold, Sontum, Sorensen, Enersen, Holland, and Ofstad (2001). The samples were chemically fixed in 6% glutaraldehyde in 0.1 M phosphate buffer (pH 7) and were post fixed overnight in 2% osmium tetroxide with 0.1 M imidazole and then dehydrated through a graded

series of ethanol before being critical point dried through CO<sub>2</sub> in a critical point dryer (Hitachi HCP-2). The agars were incisioned with a razor blade and torn before observation by SEM. Finally, the samples were mounted on aluminum nails and coated with platinum/palladium. For the observation of the sample the SEM (SEM S-2500, Hitachi Science Systems, Ibaraki, Japan) was used. The images were captured at magnification 1500× and at an accelerating voltage of 15 keV.

### 3.8 Differential Scanning Calorimetry (DSC)

Gelatinization of starches with and without hydrocolloids was analyzed by using a differential scanning calorimeter (DSC 822<sup>o</sup>, Mottler Toledo, Schwerzenbach, Switzerland) in order to determine gelatinization temperatures and enthalpy values. Starch-gum mixtures (6% starch and 0.35% gum) were prepared by following the method described previously. After hydration for 1 h at room temperature, 10±2 mg of well-stirred starch-gum dispersions were exactly weighed into 40 µl aluminum crucible and hermetically sealed. Scans were performed from 20°C to 90°C at a controlled constant rate of 10°C/min. An empty pan was used as reference and the DSC was calibrated using indium. The transition temperatures reported were the onset (T<sub>o</sub>), peak (T<sub>p</sub>), and conclusion (T<sub>c</sub>) temperatures of the gelatinization endotherm. The gelatinization enthalpy (ΔH) was calculated from the area of the main endothermic peak and expressed in term of J/g of dry starch using the equipment software.

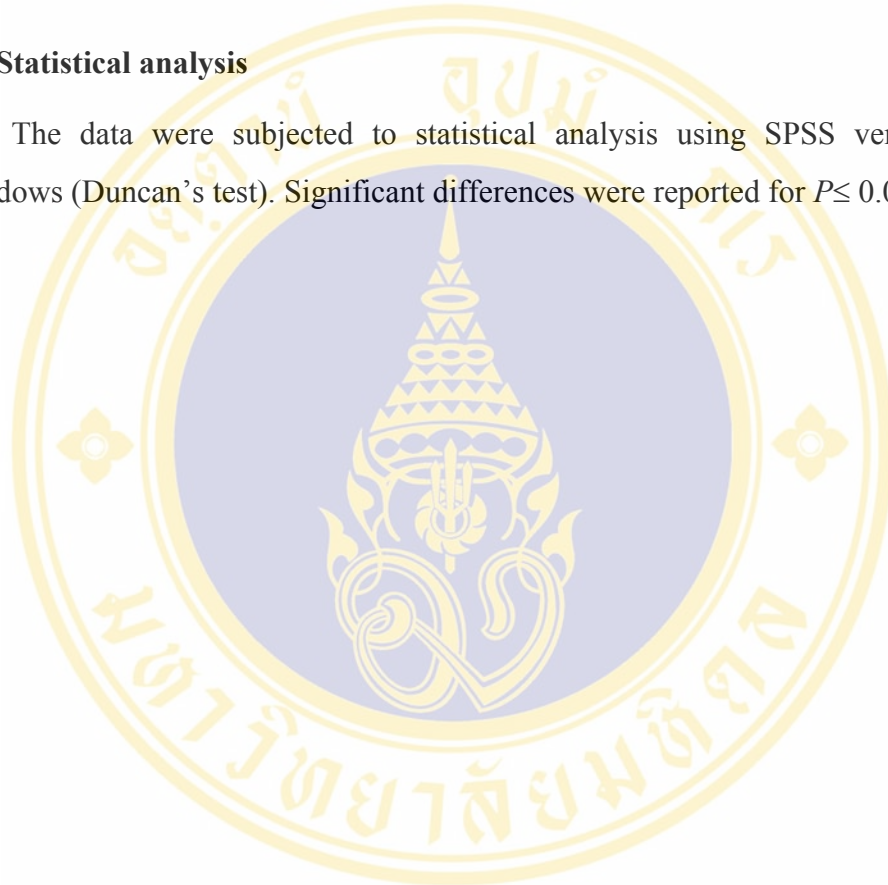
### 3.9 Viscoelastic behaviour

Fresh pastes obtained from the RVA were used for dynamic oscillatory rheological measurement by a rheometer (Physica MCR 300, Anton Paar GmbH, Stuttgart, Germany). Samples were placed into the rheometer measuring system (cone and plate geometry, 50 mm diameter, 1° cone angle, and 0.05 mm gap) which was equilibrated to 25°C. Two steps of rheological measurements were performed: (a) deformation sweeps at constant frequency (10 rad/s) to determine the maximum deformation attainable by a sample in the linear viscoelastic range and (b) frequency sweeps at a constant deformation (0.5% strain) within the linear viscoelastic range.

The mechanical spectra were obtained recording the dynamic moduli  $G'$ ,  $G''$  and  $\tan \delta$  as a function of frequency.  $G'$  is the dynamic elastic or storage modulus, related to the material response as a solid.  $G''$  is the dynamic viscous or loss modulus, related to the material response as a fluid.

#### 4.0 Statistical analysis

The data were subjected to statistical analysis using SPSS version 9.0 for windows (Duncan's test). Significant differences were reported for  $P \leq 0.05$



## CHAPTER 4

### RESULTS

#### 4.1 Pasting profiles

The RVA gelatinization profiles of tapioca starch with and without gums are shown in Figures 4.1-4.3. Pasting properties of native tapioca starch were greatly affected by the addition of gums. From the physico-chemical point of view, it is well known that an addition of gums increase the viscosity of starch pastes. Synergistic effects in viscosity existed in tapioca starch and gums mixture. The rapid increase in viscosity of starch-gum mixtures were detected as the temperature increased from 50 to 95 °C. The viscosity of gums (xanthan and guar gums) suspension was much lower than that of starch suspensions during cooking and cooling cycle.

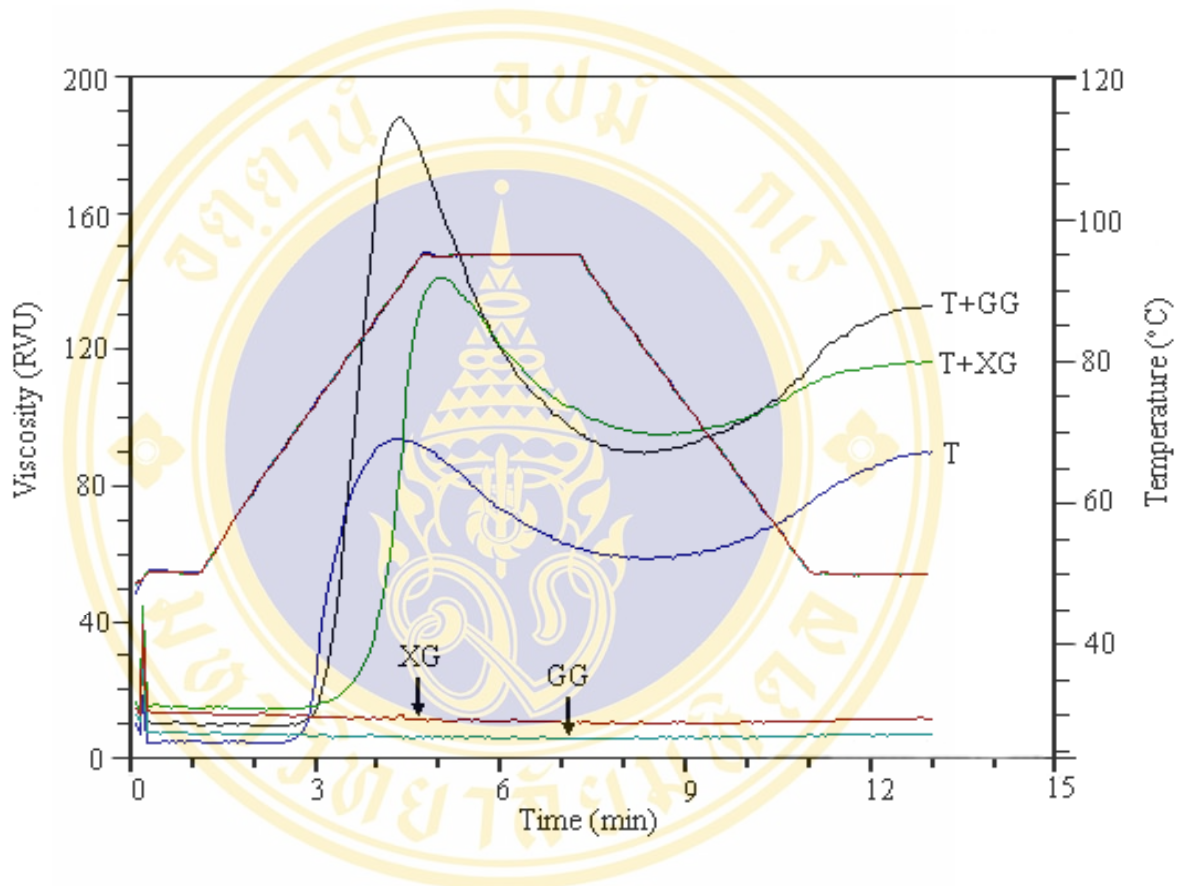
Native tapioca starch-guar gum mixture exhibited significantly ( $P \leq 0.05$ ) higher peak viscosity, breakdown, and final viscosity than starch-xanthan gum mixture and starch alone as shown in Figure 4.1. The setback viscosity of native tapioca starch was significantly ( $P \leq 0.05$ ) decreased by xanthan gum, but increased by guar gum addition. A significant ( $P \leq 0.05$ ) increase in gelatinization temperatures was observed when native tapioca starch was heated in the presence of guar and xanthan gums (Table 4.1).

The phosphorus contents of native and anionic tapioca starches were 2 and 73 mg/100g starch d.b., respectively. Figure 4.2 illustrated that suspensions of anionic tapioca starch in anionic gum solution (xanthan gum) had a significantly ( $P \leq 0.05$ ) lower viscosity during pasting (at 70-95°C) than did a starch in water suspension, whereas guar gum (neutral gum) mixture had a much higher viscosity than of starch alone. The lowest values of breakdown and final viscosity were found in starch-xanthan gum mixture, whereas the opposite trend was observed with guar gum addition. An addition of gums significantly increased the gelatinization temperatures of anionic tapioca starch (Table 4.2).

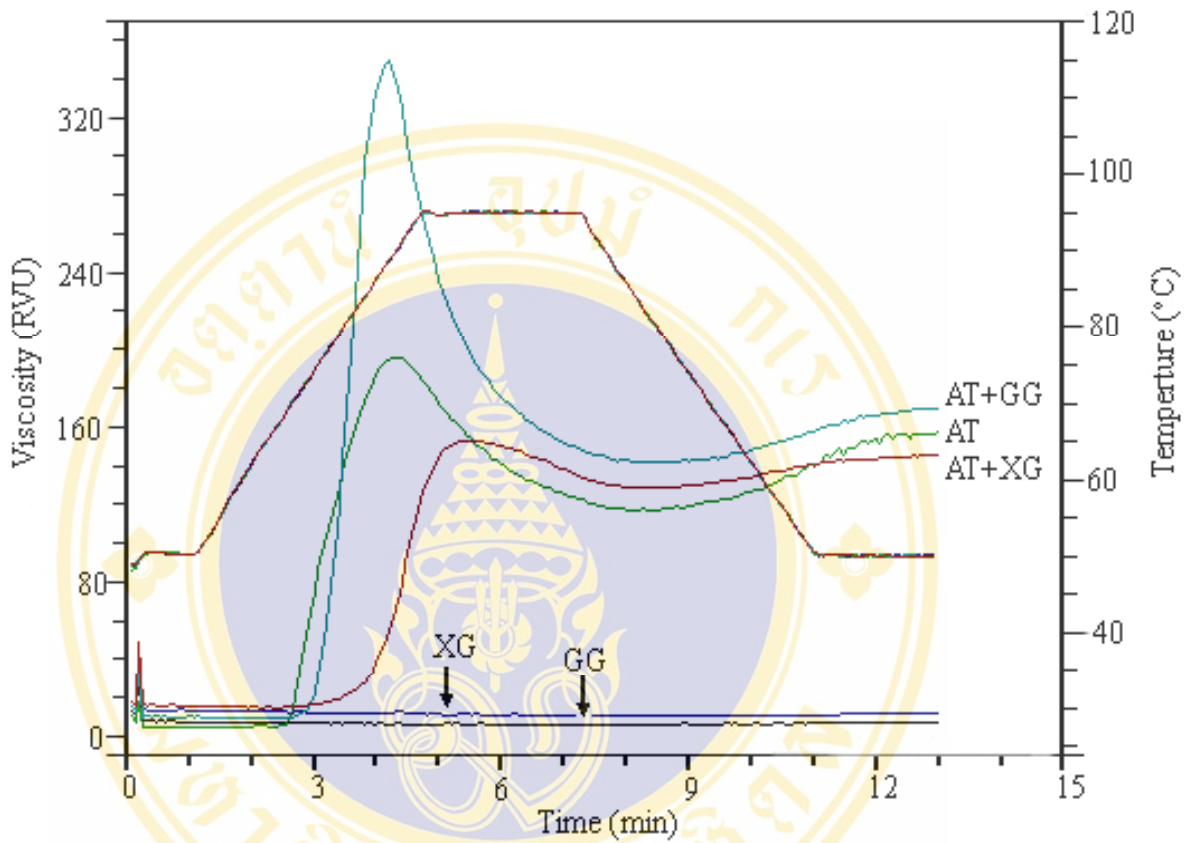
Cationic tapioca starch-guar gum mixture exhibited significantly ( $P \leq 0.05$ ) higher peak viscosity than starch-xanthan gum mixture, whereas the opposite trend was

observed with final viscosities as shown in Figure 4.3. An a addition of xanthan gum resulted in a significantly ( $P \leq 0.05$ ) increased in setback viscosity and pasting temperatures of cationic tapioca starch, whereas guar gum addition showed no effect ( $P > 0.05$ ) on these values (Table 4.3).

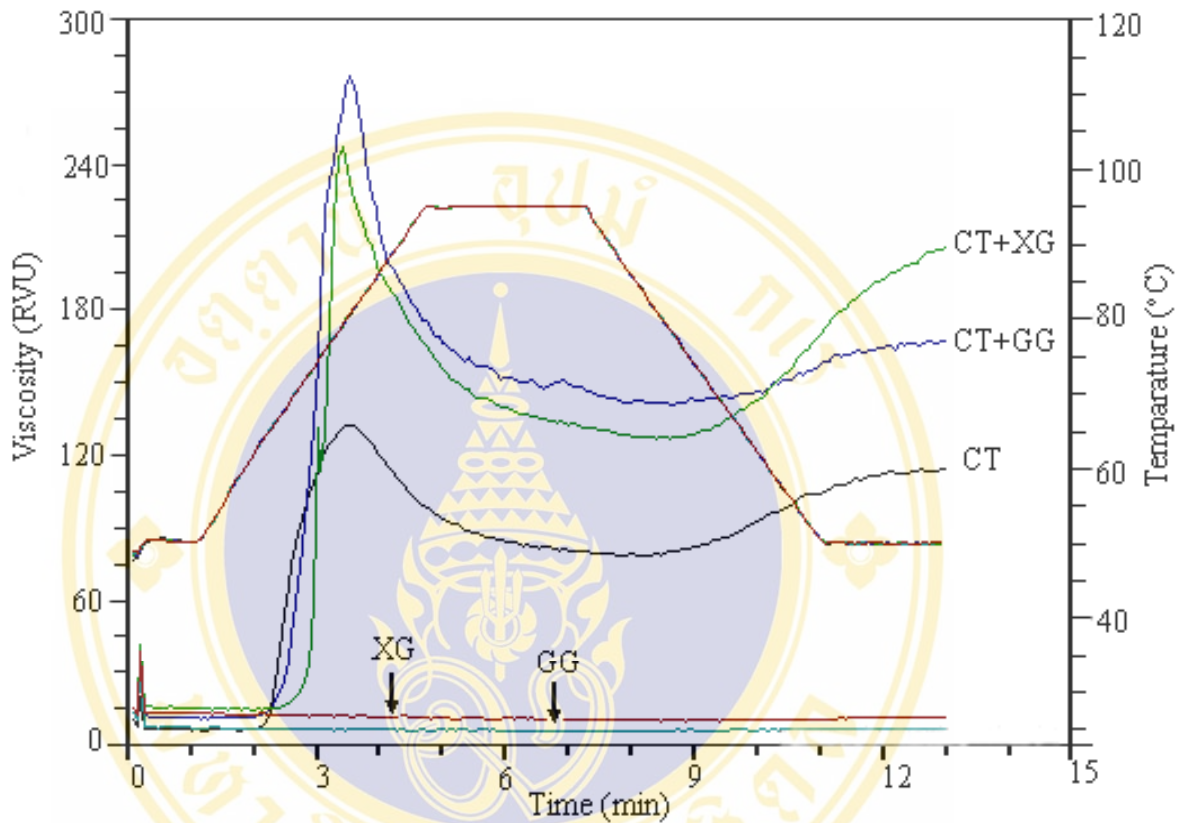




**Figure 4.1** RVA viscosity profiles of 0.35% xanthan gum (XG), 0.35% guar gum (GG), 6% native tapioca starch (T), and native tapioca starch in the presence of guar gum (T+GG) or xanthan gum (T+XG).



**Figure 4.2** RVA viscosity profiles of 0.35% xanthan gum (XG), 0.35% guar gum (GG), 6% anionic tapioca starch (AT), and anionic tapioca starch in the presence of guar gum (AT+GG) or xanthan gum (AT+XG).



**Figure 4.3** RVA viscosity profiles of 0.35% xanthan gum (XG), 0.35% guar gum (GG), 6% cationic tapioca starch (CT), and cationic tapioca starch in the presence of guar gum (CT+GG) or xanthan gum (CT+XG).

**Table 4.1**

Pasting characteristics of 6% native tapioca starch alone (T) and T in the presence of 0.35% guar gum (T+GG) or 0.35% xanthan gum (T+XG) determined by the Rapid Visco-Analyzer (RVA).

Sample	Peak viscosity <sup>a</sup> (RVU)	Breakdown <sup>b</sup> (RVU)	Setback <sup>c</sup> (RVU)	Final viscosity <sup>d</sup> (RVU)	Pasting temperature <sup>e</sup> (°C)
T	96.0±2.8c	33.7±1.1c	34.5±1.2b	96.1±5.5c	68.0±0.4c
T+GG	178.3±8.4a	95.0±3.2a	40.5±2.7a	124.1±7.8a	71.2±0.2b
T+XG	135.6±5.1b	42.4±3.3b	20.0±1.6c	112.0±3.8b	79.9±0.1a

Assays were performed in triplicate.

Mean ± SD, n=3 values followed by the same letter in each column are not significantly different ( $P > 0.05$ )

<sup>a</sup>Maximum viscosity during the heating cycle.

<sup>b</sup>Peak viscosity minus minimum viscosity during the heating cycle.

<sup>c</sup>Final viscosity at 50 °C minus minimum viscosity during the heating cycle.

<sup>d</sup>Final viscosity at 50 °C.

<sup>e</sup>Temperature indicating an initial increase in viscosity.

**Table 4.2**

Pasting characteristics of 6% anionic tapioca starch alone (AT) and AT in the presence of 0.35% guar gum (AT+GG) or 0.35% xanthan gum (AT+XG) determined by the Rapid Visco-Analyzer (RVA).

Sample	Peak viscosity <sup>a</sup> (RVU)	Breakdown <sup>b</sup> (RVU)	Setback <sup>c</sup> (RVU)	Final viscosity <sup>d</sup> (RVU)	Pasting temperature <sup>e</sup> (°C)
AT	196.0±0.3b	79.2±0.6b	45.2±3.9a	161.1±3.8b	64.5±0.8c
AT+GG	347.8±1.1a	204.4±3.3a	27.9±0.1b	171.8±2.3a	69.4±0.0b
AT+XG	148.6±5.3c	22.8±2.4c	17.1±0.8c	143.4±2.5c	81.1±0.4a

Assays were performed in triplicate.

Mean ± SD, n=3 values followed by the same letter in each column are not significantly different ( $P > 0.05$ )

<sup>a</sup>Maximum viscosity during the heating cycle.

<sup>b</sup>Peak viscosity minus minimum viscosity during the heating cycle.

<sup>c</sup>Final viscosity at 50 °C minus minimum viscosity during the heating cycle.

<sup>d</sup>Final viscosity at 50 °C.

<sup>e</sup>Temperature indicating an initial increase in viscosity.

**Table 4.3**

Pasting characteristics of 6% cationic tapioca starch alone (CT) and CT in the presence of 0.35% guar gum (CT+GG) or 0.35% xanthan gum (CT+XG) determined by the Rapid Visco-Analyzer (RVA).

Sample	Peak viscosity <sup>a</sup> (RVU)	Breakdown <sup>b</sup> (RVU)	Setback <sup>c</sup> (RVU)	Final viscosity <sup>d</sup> (RVU)	Pasting temperature <sup>e</sup> (°C)
CT	130.9±1.8c	53.4±1.6c	34.1±1.0b	111.6±1.8c	62.9±1.5b
CT+GG	278.1±8.9a	133.5±4.3a	25.6±0.8b	158.4±6.9b	63.8±0.8b
CT+XG	251.6±14.4b	115.8±11.4b	199.7±7.4a	199.7±7.4a	68.1±1.2a

Assays were performed in triplicate.

Mean ± SD, n=3 values followed by the same letter in each column are not significantly different ( $P > 0.05$ )

<sup>a</sup>Maximum viscosity during the heating cycle.

<sup>b</sup>Peak viscosity minus minimum viscosity during the heating cycle.

<sup>c</sup>Final viscosity at 50 °C minus minimum viscosity during the heating cycle.

<sup>d</sup>Final viscosity at 50 °C.

<sup>e</sup>Temperature indicating an initial increase in viscosity.

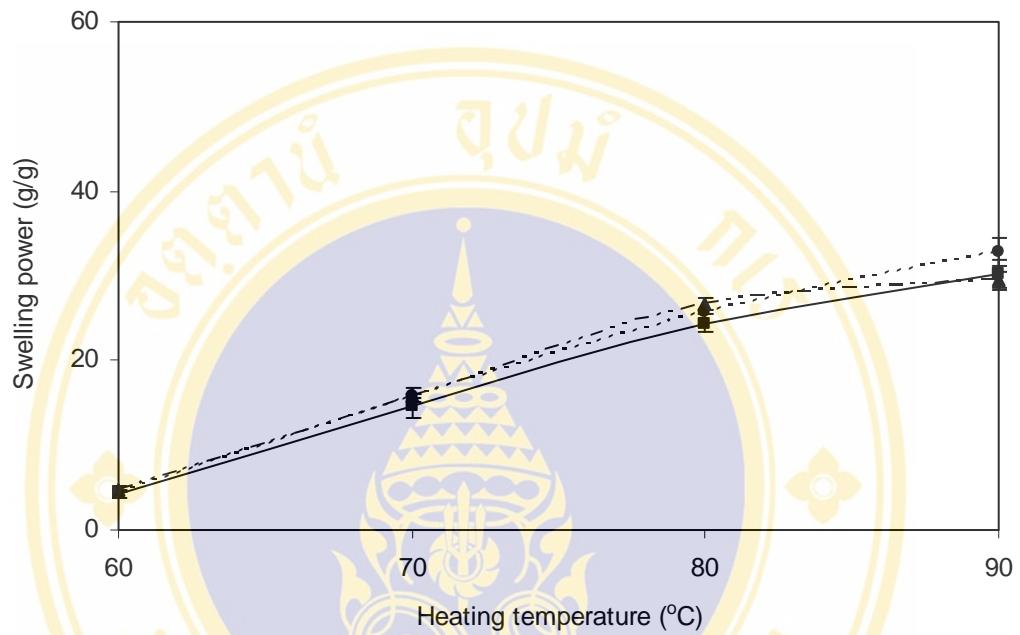
## 4.2 Swelling power and solubility index

The effects of gum addition on the swelling power (SP) and solubility index (SOL) of starch are shown in Figures 4.4-4.9. Statistical analysis was performed comparing SP and SOL values of starch alone and starch-gum mixtures at each temperature from 60 to 90 °C.

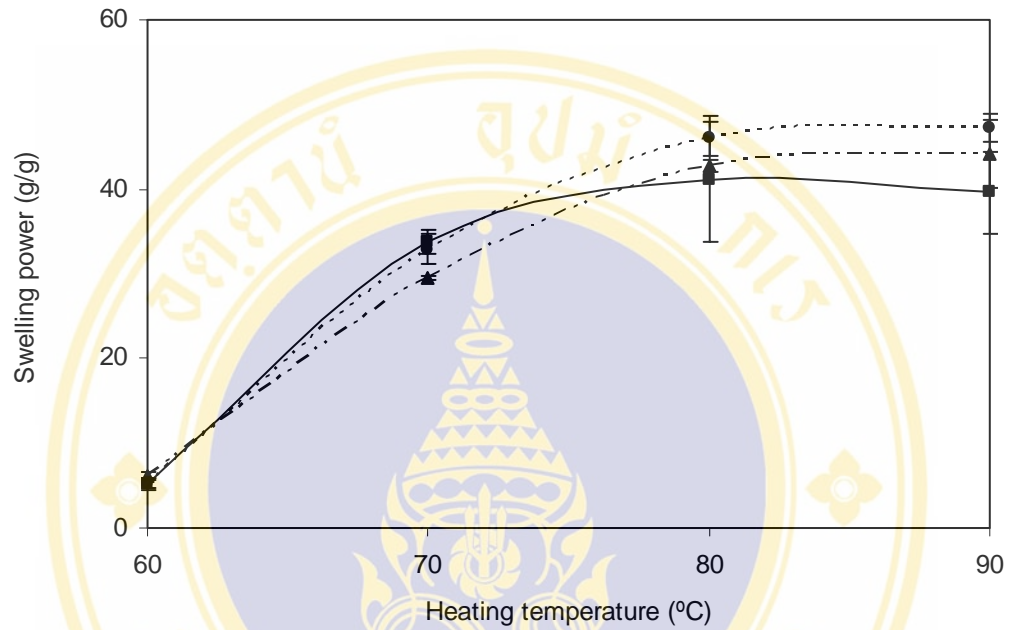
All samples of native tapioca starch with and without gum additions exhibited a sharp increase in SP and SOL with increasing heating temperatures from 60 to 90 °C as shown in Figures 4.4 and 4.7. The SP and SOL profiles of all mixtures were nearly the same as those of starch alone ( $P > 0.05$ ) but sharply increase in SOL for starch-xanthan gum system during 70-90°C.

According to statistical analysis, Figures 4.5 and 4.8 were not significantly ( $P > 0.05$ ) different for average SP and SOL values of all anionic tapioca starch-gum system which were mostly the same as those of starch alone at every heating temperature.

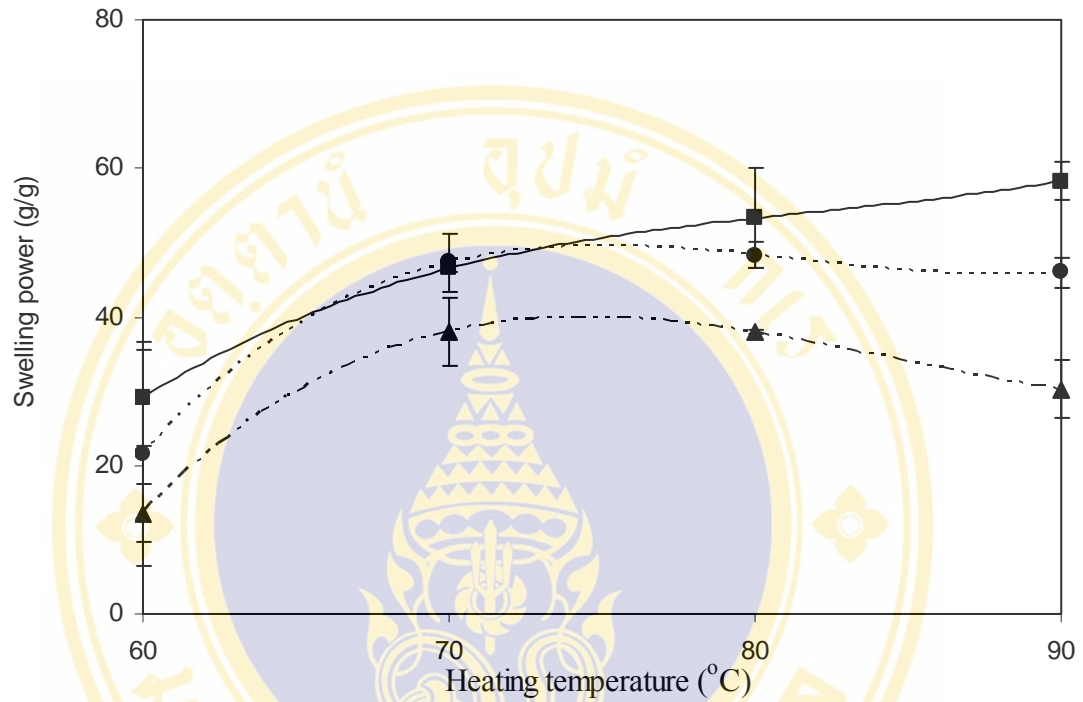
All samples of cationic tapioca starch dispersion exhibited a sharp increase in SP with increasing heating temperatures from 60 to 70 °C followed by a slight increase for cationic tapioca starch and a decrease for starch-gum mixtures from 70 to 90 °C as shown in Figure 4.6. The starch-xanthan gum mixture, however, exhibited a significantly ( $P \leq 0.05$ ) lower SP and SOL values than those of the starch alone in the temperature range tested as shown in Figures 4.6 and 4.9, respectively. The SP and SOL profiles of starch-guar gum mixture were nearly the same as those of starch alone.



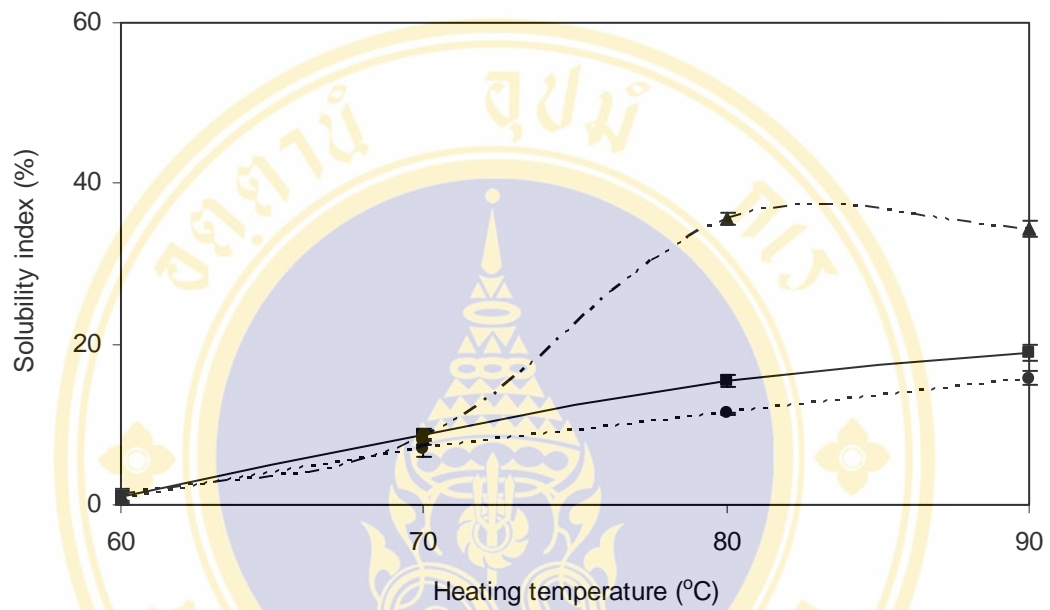
**Figure 4.4** Swelling power (g/g) at different heating temperature of 1.25% native tapioca starch (■), native tapioca starch in the presence of 0.073% guar gum (●) or 0.073% xanthan gum (▲). Error bars represent standard deviations.



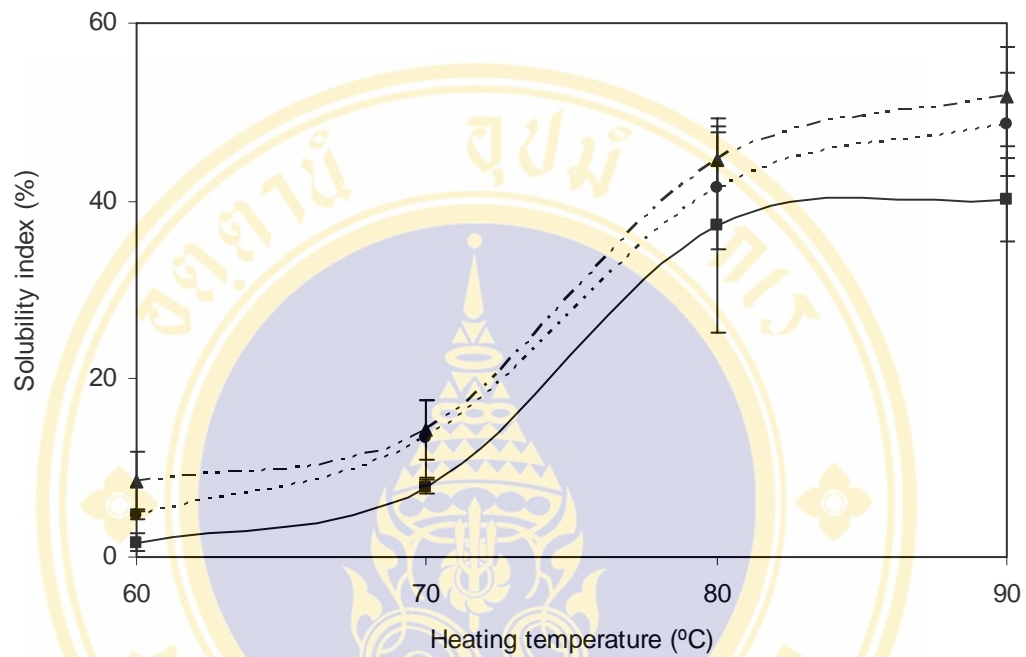
**Figure 4.5** Swelling power (g/g) at different heating temperature of 1.25% anionic tapioca starch (■), anionic tapioca starch in the presence of 0.073% guar gum (●) or 0.073% xanthan gum (▲). Error bars represent standard deviations.



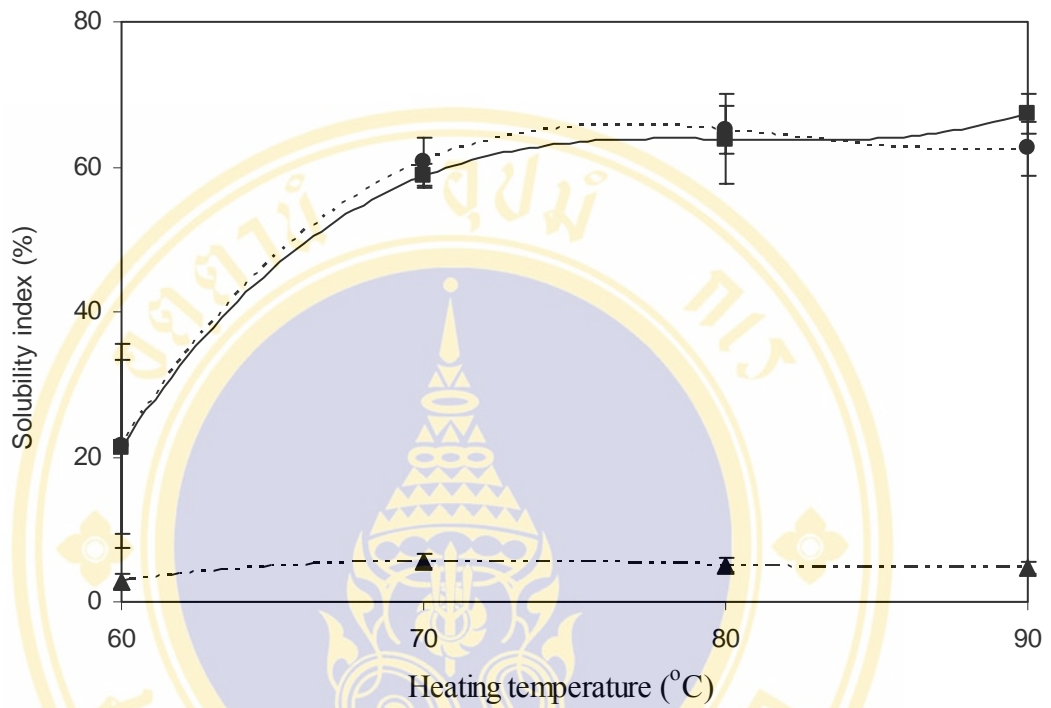
**Figure 4.6** Swelling power (g/g) at different heating temperature of 1.25% cationic tapioca starch (■), cationic tapioca starch in the presence of 0.073% guar gum (●) or 0.073% xanthan gum (▲). Error bars represent standard deviations.



**Figure 4.7** Solubility at different heating temperature of 1.25% native tapioca starch (■), native tapioca starch in the presence of 0.073% guar gum (●) or 0.073% xanthan gum (▲). Error bars represent standard deviations.



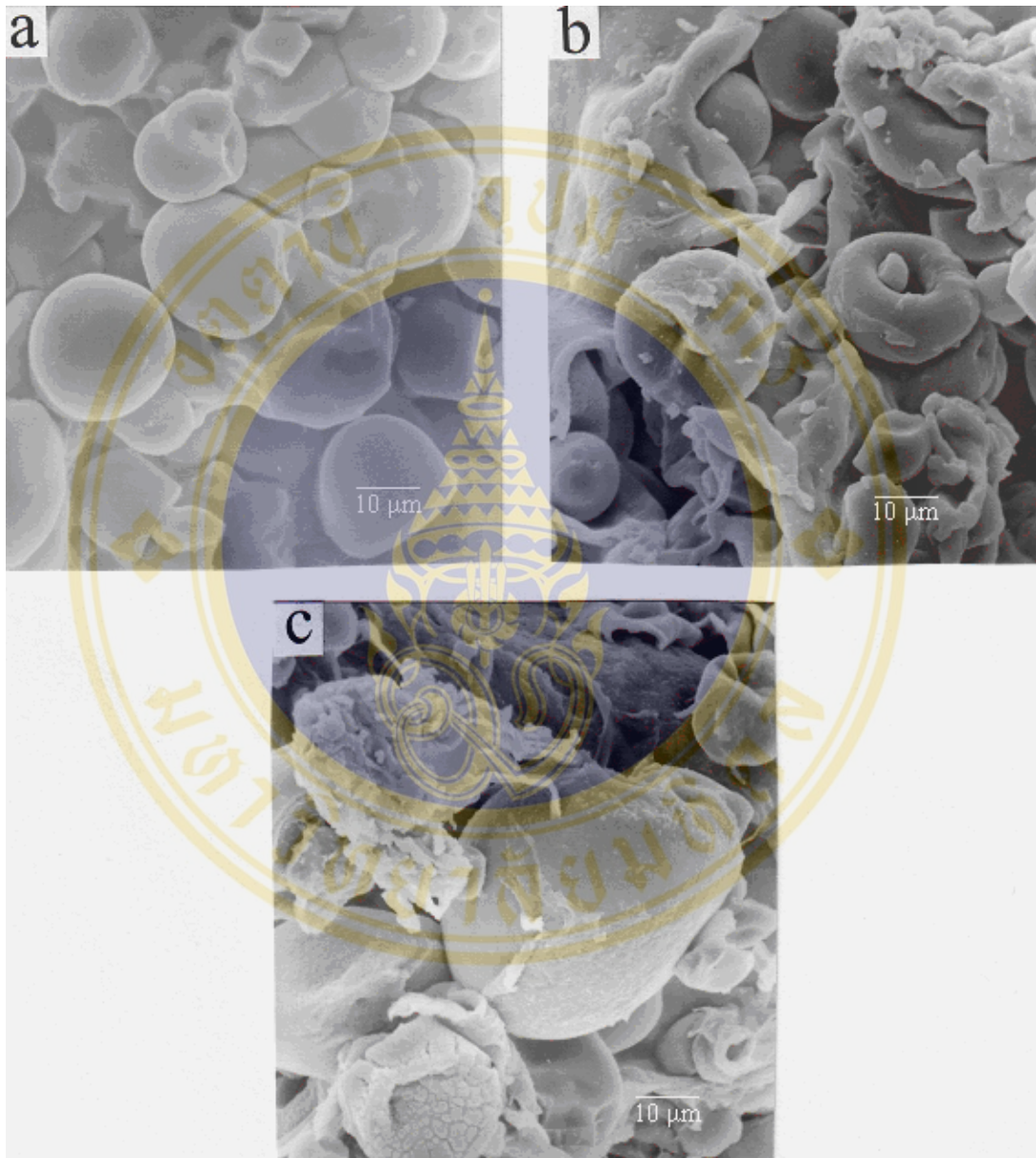
**Figure 4.8** Solubility at different heating temperature of 1.25% anionic tapioca starch (■), anionic tapioca starch in the presence of 0.073% guar gum (●) or 0.073% xanthan gum (▲). Error bars represent standard deviations.



**Figure 4.9** Solubility at different heating temperature of 1.25% cationic tapioca starch (■), cationic tapioca starch in the presence of 0.073% guar gum (●) or 0.073% xanthan gum (▲). Error bars represent standard deviations.

### **4.3 Morphology of native, anionic, cationic tapioca starches with and without gum addition**

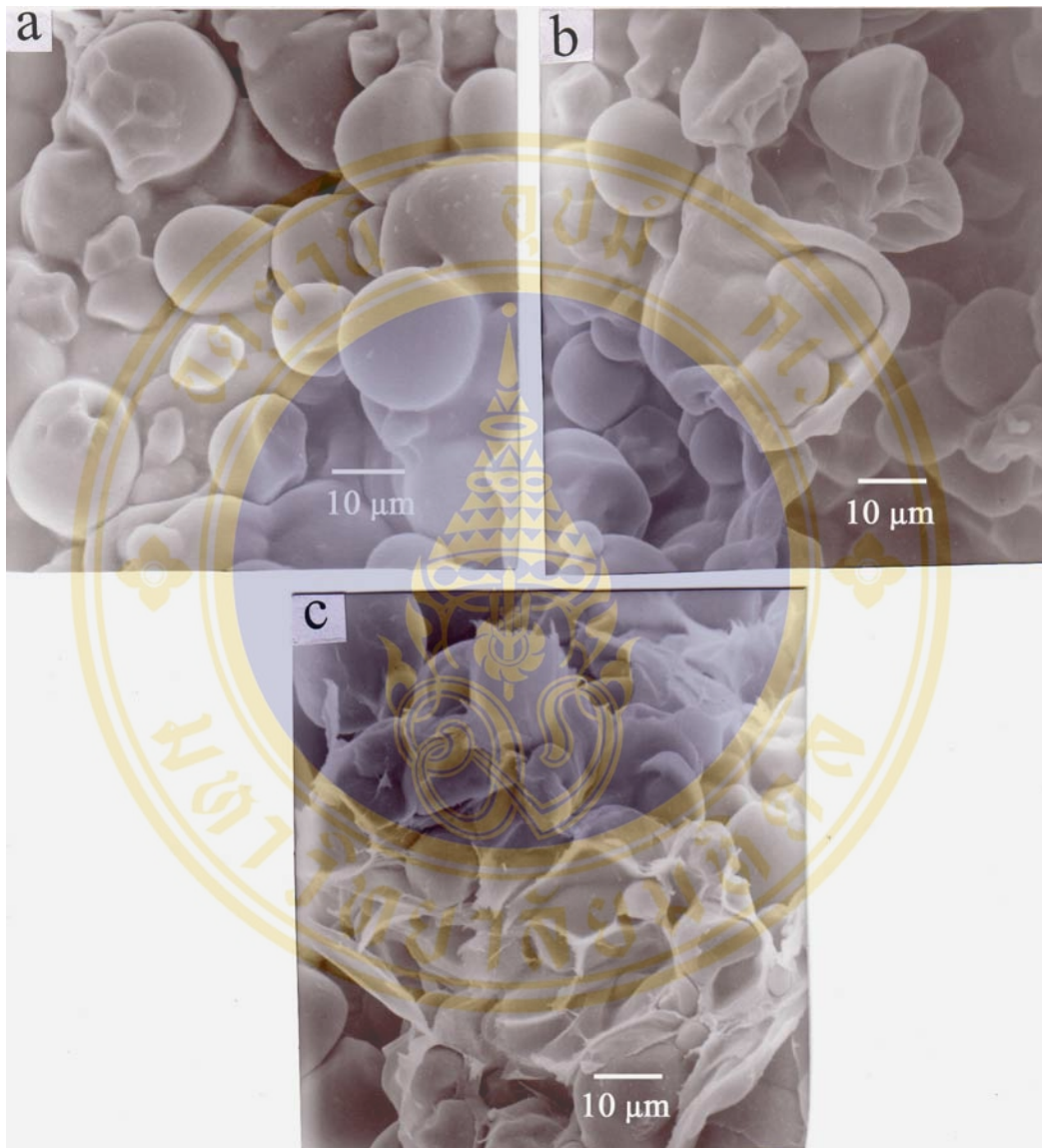
Scanning electron micrographs of starch samples with and without gums are shown in Figures 4.10-4.12. Guar gum formed sheet structure in the gel matrix of heated native tapioca starch granules (Figure 4.10(b)), whereas xanthan gum wrapped the granules totally overwhelmed (Figure 4.10(c)). In case of anionic tapioca starch, guar gum also formed sheet structure (Figure 4.11(b)), whereas xanthan gum did not wrap the granules and folded by itself in the gel matrix (Figure 4.11(c)). In the last combination, the cationic tapioca starch granules dispersed in distilled water appeared large open holes at one end of the granules during gelatinization (Fig. 4.12 (a)). As shown in Figures 4.12(b) and 4.12(c), both guar gum and xanthan gum wrapped the granules but not totally overwhelmed in case of guar gum. It was visualized that xanthan gum wrapped several granules to aggregate them within gel matrix (Fig. 4.12(c)). The granular size of cationic tapioca starch within the gel matrix of xanthan gum was smaller than those within the continuous phase.



**Figure 4.10** Scanning electron micrographs (SEM) of native tapioca starch with and without gums: (a) native tapioca starch, (b) native tapioca starch-guar gum mixture, (c) native tapioca starch-xanthan gum mixture (1500×, Bar = 10 µm).



**Figure 4.11** Scanning electron micrographs (SEM) of anionic tapioca starch with and without gums: (a) anionic tapioca starch, (b) anionic tapioca starch-guar gum mixture, (c) anionic tapioca starch-xanthan gum mixture (1500 $\times$ , Bar = 10  $\mu$ m).



**Figure 4.12** Scanning electron micrographs (SEM) of cationic tapioca starch with and without gums: (a) cationic tapioca starch, (b) cationic tapioca starch-guar gum mixture, (c) cationic tapioca starch-xanthan gum mixture (1500 $\times$ , Bar = 10  $\mu\text{m}$ ).

#### 4.4 Gelatinization temperatures and enthalpy

Onset ( $T_o$ ), peak ( $T_p$ ), conclusion ( $T_c$ ) gelatinization temperatures, and enthalpy ( $\Delta H$ ) determined by the DSC for the starch with and without gum addition are shown in Tables 4.4-4.6. The  $T_c$  values were not significantly ( $P > 0.05$ ) affected by the addition of gums. The  $T_p$  values were slightly increased in case of native and anionic tapioca starches but they were not changed in case of cationic tapioca starch when the gums were added. The  $T_o$  values were significantly ( $P \leq 0.05$ ) increased by the addition of gum, the highest value was observed for the starch-xanthan gum mixture. This result was consistent with the pasting temperature determined by the RVA (Table 4.1-4.3). A significantly ( $P \leq 0.05$ ) decrease in gelatinization enthalpy ( $\Delta H$ ) and phase transition temperature range was observed in the presence of gums as compared to the control.

**Table 4.4**

Thermal properties of 6% native tapioca starch alone (T) and T in the presence of 0.35% guar gum (T+GG) or 0.35% xanthan gum (T+XG) obtained from the DSC thermograms.

Sample	T <sub>0</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)	ΔH (J/g)	T <sub>c</sub> -T <sub>0</sub> (°C)
T	62.2 ± 0.4c	68.9 ± 0.4b	75.6 ± 0.4a	10.1 ± 0.4a	13.4 ± 0.6a
T+GG	63.0 ± 0.1b	69.0 ± 0.2b	75.4 ± 0.2a	9.3 ± 0.2b	12.5 ± 0.1b
T+XG	63.9 ± 0.1a	69.7 ± 0.1a	75.8 ± 0.1a	8.8 ± 0.2b	12.0 ± 0.2b

T<sub>0</sub>, T<sub>p</sub>, T<sub>c</sub> and ΔH are onset, peak, conclusion temperatures, and enthalpy, respectively. Assays were performed in triplicate.

Mean ± SD, n=3 values followed by the same letter in each column are not significantly different (*P* > 0.05)

**Table 4.5**

Thermal properties of 6% anionic tapioca starch alone (AT) and AT in the presence of 0.35% guar gum (AT +GG) or 0.35% xanthan gum (AT +XG) obtained from the DSC thermograms.

Sample	T <sub>0</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)	ΔH (J/g)	T <sub>c</sub> -T <sub>0</sub> (°C)
A	62.2 ± 0.1b	67.8 ± 0.1b	75.2 ± 0.2a	10.7 ± 0.6a	13.0 ± 0.2a
A+GG	63.0 ± 0.2a	69.0 ± 0.5a	75.8 ± 0.8a	9.3 ± 0.4b	12.8 ± 0.7a
A+XG	63.0 ± 0.2a	68.9 ± 0.1a	75.3 ± 0.3a	9.8 ± 0.9b	12.2 ± 0.3a

T<sub>0</sub>, T<sub>p</sub>, T<sub>c</sub> and ΔH are onset, peak, conclusion temperatures, and enthalpy, respectively. Assays were performed in triplicate.

Mean ± SD, n=3 values followed by the same letter in each column are not significantly different (*P* > 0.05)

**Table 4.6**

Thermal properties of 6% cationic tapioca starch alone (CT) and CT in the presence of 0.35% guar gum (CT+GG) or 0.35% xanthan gum (CT+XG) obtained from the DSC thermograms.

Sample	T <sub>0</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)	ΔH (J/g)	T <sub>c</sub> -T <sub>0</sub> (°C)
CT	53.9 ± 0.8c	65.6 ± 0.9a	73.2 ± 0.5a	11.1 ± 0.5a	19.3 ± 1.3a
CT+GG	55.8 ± 0.5b	65.3 ± 0.5a	72.0 ± 0.5a	8.3 ± 0.2b	16.1 ± 0.4b
CT+XG	58.3 ± 1.0a	65.5 ± 0.5a	71.9 ± 0.8a	5.2 ± 1.1c	13.7 ± 0.7c

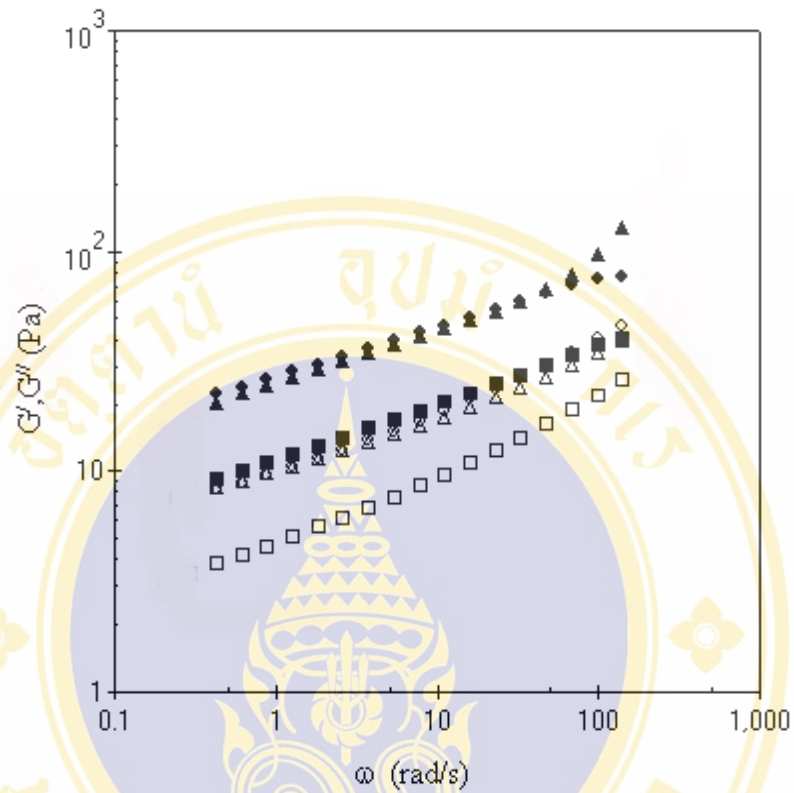
T<sub>0</sub>, T<sub>p</sub>, T<sub>c</sub> and ΔH are onset, peak, conclusion temperatures, and enthalpy, respectively. Assays were performed in triplicate.

Mean ± SD, n=3 values followed by the same letter in each column are not significantly different ( $P > 0.05$ )

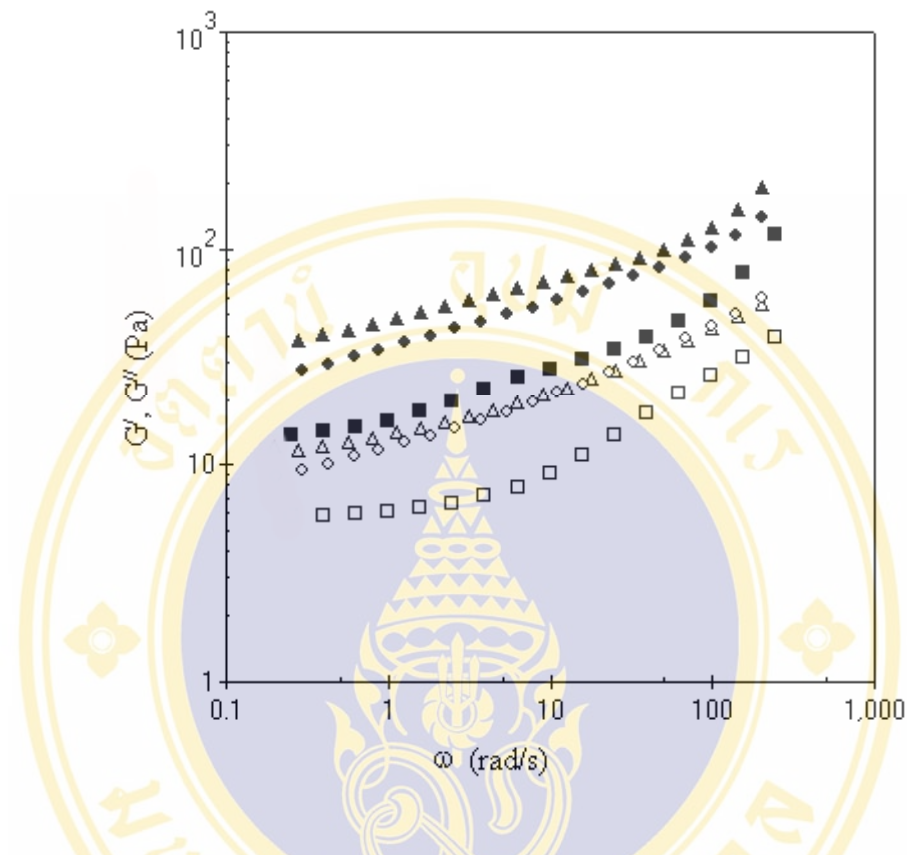
#### 4.5 Viscoelastic behaviour

The mechanical spectra for dispersions of starches with and without gums are shown in Figures 4.13-4.15. Viscoelastic properties can be used to characterize the three-dimensional network structure of starches and starch-gum mixtures. The rheological parameters,  $G'$  and  $G''$  showed significant variation among starch dispersions with and without gum addition when subjected to frequency sweep ranging from 1 to 100 rad/s under deformation of 0.5% strain. Oscillatory rheological assays were not performed in gum systems without starch because of the low magnitude of storage modulus when compared with starch.

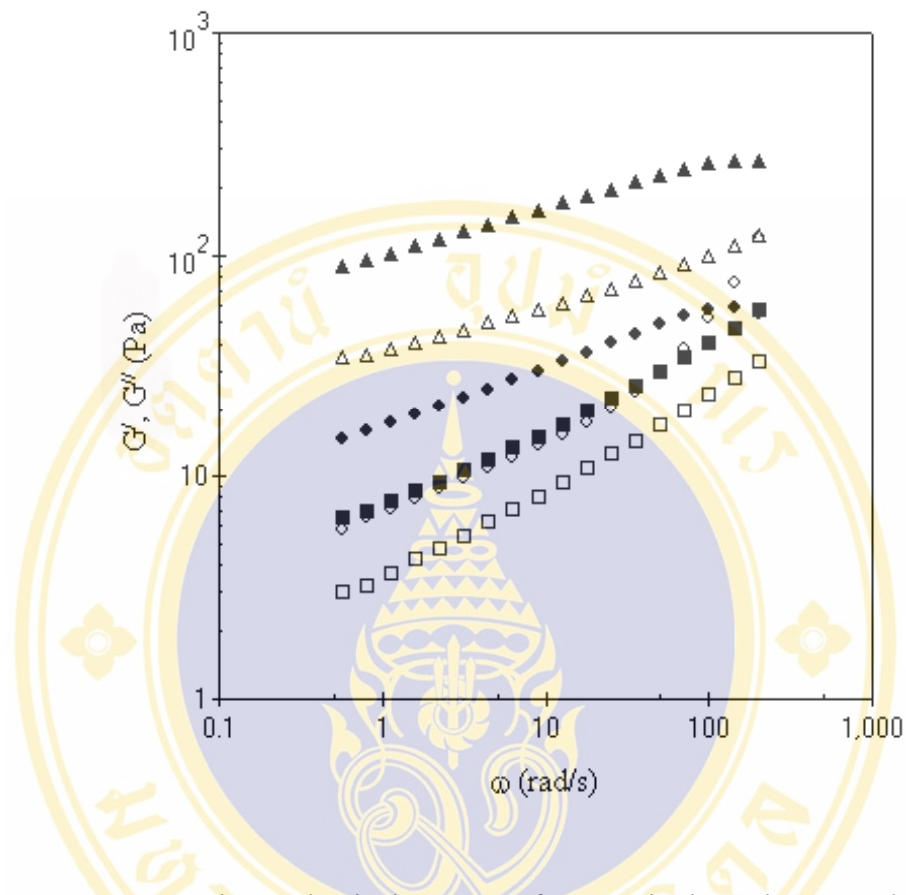
For all samples, the magnitudes of  $G'$  were higher than those of  $G''$  over a range of the oscillatory frequencies studied. The increase in  $G'$  with increasing frequency was accompanied by a corresponding increase in  $G''$ . The  $G'$  and  $G''$  curves of all combinations were almost parallel in the frequency range studied. Addition of xanthan and guar gums increased the  $G'$  values of native and anionic tapioca starch pastes two-fold at 1 rad/s angular frequency, respectively (Figures 4.13-4.14). Surprisingly, addition of xanthan and guar gums increased the  $G'$  values of cationic tapioca starch paste up to fourteen-fold and five-fold at 1 rad/s angular frequency, respectively (Figure 4.15). However, Freitas, Gorin, Neves and Sierakowski (2003) reported that mixing of galactoxyloglucan-corn starch rich in amylose increased the  $G'$  values five-fold at all the chosen frequencies.



**Figure 4.13** Dynamic mechanical spectra of 6% native tapioca starch paste alone ( $T$ : ■, □) and  $T$  in the presence of 0.35% guar gum ( $T+GG$ : ●, ○) or xanthan gum ( $T+XG$ : ▲, △) measured at 0.5% strain and 25 °C. Closed symbols: storage modulus ( $G'$ ), open symbols: loss modulus ( $G''$ ).

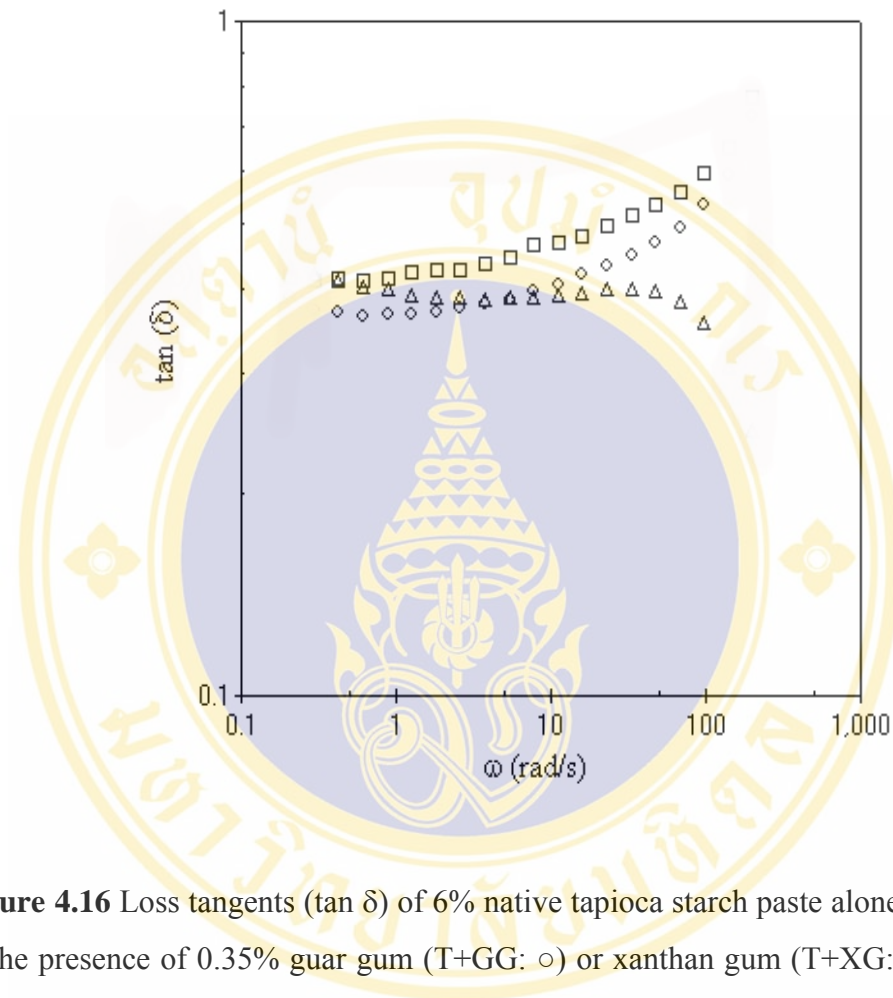


**Figure 4.14** Dynamic mechanical spectra of 6% anionic tapioca starch paste alone (AT: ■,□) and AT in the presence of 0.35% guar gum (AT+GG: ●,○) or xanthan gum (AT+XG: ▲,△) measured at 0.5% strain and 25 °C. Closed symbols: storage modulus ( $G'$ ), open symbols: loss modulus ( $G''$ ).

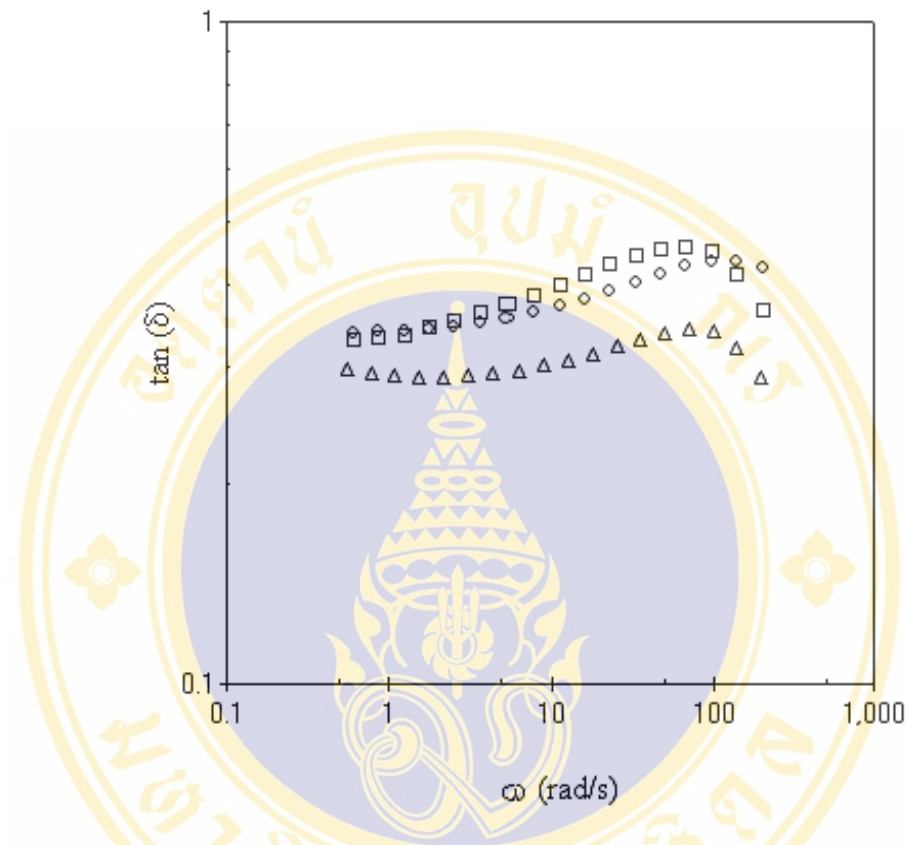


**Figure 4.15** Dynamic mechanical spectra of 6% cationic tapioca starch paste alone (CT:  $\blacksquare, \square$ ) and CT in the presence of 0.35% guar gum (CT+GG:  $\bullet, \circ$ ) or xanthan gum (CT+XG:  $\blacktriangle, \triangle$ ) measured at 0.5% strain and 25 °C. Closed symbols: storage modulus ( $G'$ ), open symbols: loss modulus ( $G''$ ).

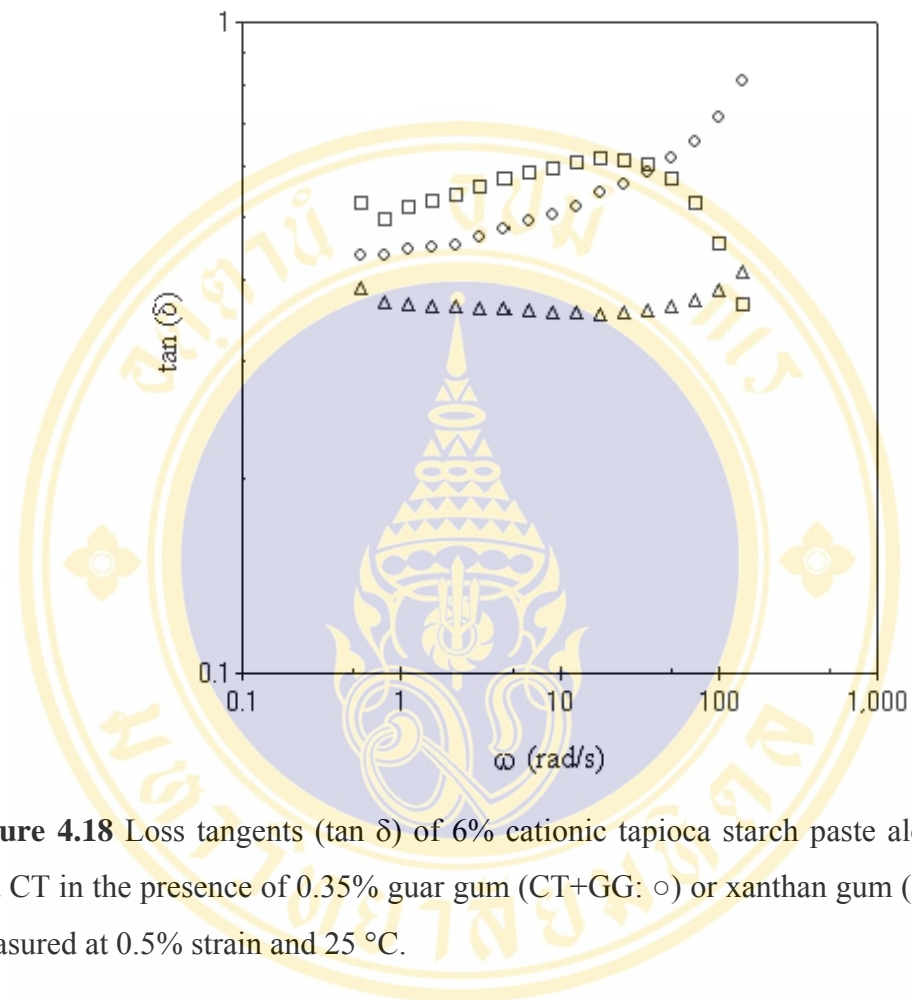
Addition of xanthan gum and guar gum decreased  $\tan \delta$  ( $G''/G'$ ) values of native tapioca starch paste in the range of 0.03-0.05 at 1 rad/s frequency (Figure 4.16). The corresponding  $\tan \delta$  ( $G''/G'$ ) values of the mixtures were much dependent on frequency in guar gum and starch paste systems. Addition of gums also decreased the  $\tan \delta$  values of anionic tapioca starch paste (Figure 4.17) The anionic starch paste with and without gums exhibited a seemingly solid-like behavior mainly at low frequencies. Figure 4.18 shows that addition of xanthan gum resulted in a decrease of the  $\tan \delta$  values of cationic tapioca starch paste from 0.52 to 0.37 at 1 rad/s frequency and remained roughly constant across the range of angular frequencies studied, whereas guar gum exhibited slightly lower  $\tan \delta$  at low frequencies but higher at high frequencies due to the reduction of  $\tan \delta$  of starch at high frequencies. Therefore the starch-xanthan gum mixtures exhibited seemingly more solid like behaviour than the starch-guar gum mixture or starch alone. The overall higher dependence of moduli with frequency suggests a more fluid than rigid system.



**Figure 4.16** Loss tangents ( $\tan \delta$ ) of 6% native tapioca starch paste alone (T: □) and T in the presence of 0.35% guar gum (T+GG: ○) or xanthan gum (T+XG: △) measured at 0.5% strain and 25 °C.



**Figure 4.17** Loss tangents ( $\tan \delta$ ) of 6% anionic tapioca starch paste alone (AT:  $\square$ ) and AT in the presence of 0.35% guar gum (AT+GG:  $\circ$ ) or xanthan gum (AT+XG:  $\triangle$ ) measured at 0.5% strain and 25 °C.



**Figure 4.18** Loss tangents ( $\tan \delta$ ) of 6% cationic tapioca starch paste alone (CT:  $\square$ ) and CT in the presence of 0.35% guar gum (CT+GG:  $\circ$ ) or xanthan gum (CT+XG:  $\triangle$ ) measured at 0.5% strain and 25 °C.

## CHAPTER 5

### DISCUSSION

Gums are known to influence gelatinization and retrogradation of starch. In this work, both guar gum (neutral gum) and xanthan gum (negatively charged gum) affected the pasting peak viscosity of native and modified tapioca starches (Figures 4.1-4.3). The decrease peak viscosity in such combination between negatively charged gum and anionic starch was due to the repelling forces (Shi & BeMiller, 2002). In starch system, Miller, Derby and Trimbo (1972) reported that complex filamentous network of released components of starch in an aqueous dispersion had a high positive correlation with paste viscosity, and believed that it was the principal reason for the large increase in viscosity at high temperature. In case of starch-gum mixture, Christianson, Hodge, Osborne, and Detroy (1981) found that the early onset of initial viscosity was attributed to the first stage of swelling which was dependent on media viscosity only. The later stage increasing of paste viscosity was contributed by the interactions of solubilized starch, gums, and swollen starch granules. In this study, an addition of gums synergistically increased viscosity observed during pasting (Table 4.1-4.3) reflects the contribution of media viscosity in case of neutral and opposite charged starch-gum mixtures. This can also make the shear forces exerted on granules much larger than those encountered in starch-water suspensions (Christianson, Hodge, Osborne & Detroy, 1981). This fact affects significantly the breakdown of granules leading to a significantly ( $P \leq 0.05$ ) higher breakdown viscosity of starch-gum systems as compared with starch alone for all combinations except for anionic starch-xanthan gum mixture as shown in Tables 4.1-4.3.

According to the swelling power measurement by the method of Mandala and Bayas (2004), the assumption that the whole amount of gum is remained in the continuous phase is not completely true due to sedimentation of gum with the starch granules. For the control, the holes of starch granule at one end (Figure 12(a)) are considered as first breaks of granule envelope and to be the passage for amylose removal (Shi & BeMiller 2002) as shown in Figure 12(a). The swelling of starch and

modified starch in water suspension alone was highest due to the fact that granules could swell freely. In case of native and anionic tapioca starches, gums did not affect the swelling power and solubility index of starch dispersion except for solubility of native tapioca starch-xanthan gum mixture at high temperature ( $P > 0.05$ ) as shown in Figures 4.4-4.8. It can imply that synergistic viscosity was due to intermolecular associations more than swelling power (Abdulmola, Hember, Richardson & Morris, 1996). Not only the steric interaction between neutral gum and anionic starch for increasing peak viscosity but also repelling force between anionic starch during heating. The reduction of SP at higher temperatures was likely to be due to the existence of some cloudy solids which were poured out along with clear supernatant. However, the SP profiles obtained from this study were similar to those previously reported by Li and Yeh (2001) for native tapioca starch. Xanthan gum, highly intensity of negatively charged gum, retarded the neutral starch granule sedimentation during centrifugation. From SEM observation, it was found that some granules of native tapioca starch were totally enveloped by xanthan gum and no other form of aggregation was detected (Figure 4.10). This result demonstrated that xanthan gum inhibited starch swelling and prevented amylose leach out, whereas guar gum seemed to have no effect on these properties of starch. Both xanthan and guar gums did not wrap the anionic starch granules as shown in Figure 4.11. It suggested that most of native and anionic tapioca starch granule can swell freely in the gum solutions resulted in no significant difference of swelling power. In case of negatively charge starch-gum mixture, the solubility of this system in the continuous phase of xanthan gum dispersion and aqueous solution can not give the increasing of peak viscosity in the gum solution due to repelling forces between negatively charged starch granules and gum. Macromolecules of xanthan gum were unable to penetrate the granule, and consequently, adsorbed only on the surface and stabilized the granular shape (Gonera & Cornillon, 2002). Mandala, Palogou & Kostaropoulos (2002) found that each granule of potato starch was covered by xanthan gum and no other of aggregation was found. The creation of xanthan gum film around each granule is also referred by Mandala and Bayas (2004), who claimed that this film influenced the behaviour of granules on further swelling and polymer leaching out in wheat starch.

Spectacularly, cationic tapioca starch underwent very slow and restricted swelling at high temperature, indicating strong electrostatic interactions between positive charges on the surface of starch granules and negative charges on the molecules of xanthan gum. It is clear that xanthan gum promoted association of the several granules of cationic tapioca starch to prevent water penetration and inhibit swelling of granules as shown in Figure 4.12. Swelling was demonstrated to be positively related to the amount of soluble solids leached outside the granules during heating (Figures 4.4-4.9). In this study, the significant ( $P \leq 0.05$ ) lower peak viscosity of starch-xanthan gum mixture as compared with starch-guar gum mixture (Table 1) was likely due to their interactions which restricted swelling and limited the increase in viscosity in cationic starch-gum system. We observed that the aggregation process of cationic tapioca starch by xanthan gum was very fast-practically instantaneous-after the starch and the xanthan gum dispersion were blended. This is due to an ion bridging which occurred when xanthan gum simultaneously binds to the surface of adjacent starch granules that have the same charge (McClements, 1999). Moreover, it implied that this strong interaction occurrence also existed between aggregated granules (Lii, Tsai & Tseng, 1996). By far, few reports on the macromolecular characteristics of hydrocolloid and its functions on gelatinization and retrogradation behavior of starch have been found (Funami, Kataoka, Omoto, Goto, Asai & Nishinari, 2005).

Guar gum did not affect the swelling power of the native and modified starch dispersion. Guar gum partially and loosely wrapped the granules and formed sheet structure as shown in Figures 4.10-4.12. For cationic tapioca starch, the higher concentration of starch solubles in the continuous phase of guar gum dispersion gave the higher possibilities for solubles to undergo molecular interaction with gum components (Figure 4.9) which resulted in the higher ( $P \leq 0.05$ ) peak viscosity as compared with cationic tapioca starch-xanthan gum system (Table 1). According to previous investigations, gum molecules interacted with amylose which is dominating in guar gum system (Sudhakar, Singhal & Kulkarni, 1996), however, an opposite phenomenon was observed in xanthan gum system (Mandala & Bayas, 2004).

The evidences observed in this study demonstrated that starch in guar gum dispersion can absorb more water, enhance swelling, and induce a higher concentration of gum and leached amylose in the continuous phase, whereas in

xanthan gum, starch can absorb less water, suppress swelling, and seem to be slightly increase in concentration of gum in the continuous phase, especially aggregation system. The SEM micrographs revealed the association of starch granules in the xanthan gum matrix. These results are congruent with those of Abdulmola, Hember, Richardson, and Morris (1996), who used the small deformation oscillatory measurements to characterize the effect of xanthan gum on the rheological properties of gelatinized waxy maize starch.

Studies by Rao (1999) on corn starch, DSC data were compared with dynamic rheological data. The initial temperature of gelatinization from both methods was about the same. In our case, however, the  $T_p$  from DSC (Table 4.4) was about the same as the pasting temperature from RVA (Table 4.1). It was suggesting that energy was required for reversible swelling of starch granules before the pasting temperatures was reached. A significant shift of  $T_o$  (up to 4.37°C) to higher values was observed due to gum additions. This can be attributed to the different reasons; lower amounts of free water to starch ratio due to immobilization of water molecules by gums (Chungcharoen & Lund, 1987; Biliaderis, Maurice & Vose, 1980), lower heat transfer rates (Krüger Ferrero & Zaritzky, 2003), and mass transfer of water, which could make starch gelatinization more difficult in the presence of gum.

Gum had little or no effect on the gelatinization enthalpy ( $\Delta H$ ) of native and anionic tapioca starches. However, the decreasing of  $\Delta H$  value was described to be positively related to amount of gums. It suggested that such changes in limited amounts of water might contribute to a decrease in endothermic size by reducing the energy difference between the granular starches with and without gums. For cationic tapioca starch, the enthalpy was significantly ( $P \leq 0.05$ ) decreased by addition of gums suggesting a partial gelatinization of crystalline regions in the starch granules due to limited amounts of water (Biliaderis, Maurice & Vose, 1980) and appearance of aggregate. The gums may interact with the starch to produce an increase (Liu, Eskin & Cui, 2003) or decrease (Rojas, Rosell & Benedito de Barber, 1999) of the temperature gelatinization ranges ( $T_c - T_o$ ), depending on the type of gums. The overall effect of gums was a decrease in the gelatinization enthalpy in the range of 0.72-5.89 J/g starch d.b.

Based on dynamic shear data, native and modified tapioca starch pastes with and without gums were rheologically classified as weak gels (Figures 4.13-4.15). The main properties of weak gels are given by Clark and Ross-Murphy (1987) as  $G' > G''$  throughout the accessible frequency range, both  $G'$  and  $G''$  are slightly increased with increasing frequency and the separation of the two moduli ( $\tan \delta = G''/G'$ ) is smaller than 0.1 for typical polysaccharide gels. The increase of  $G'$  values was also related to the rate of amylose and amylose-gum associations occurred during cooling. The increase of  $G'$  can not be attributed to the aggregation of amylopectin because amylopectin retrogradation in long time periods (Biliaderis & Prokopowich, 1994). As suggested by Ferrero, Martino and Zaritzky (1994), gum-amylose associations against amylose-amylose rearrangement, essentially for retrogradation. From the results, it was suggesting that the final viscosity was positively related to the  $G'$  values except for anionic tapioca starch-xanthan gum mixture. From the rheological point of view, the decreasing of  $\tan \delta$  corresponded to more solid like behaviour, that is, a stronger three-dimensional network was constructed by amylose and amylose-gum system (Hsu, Lu & Huang, 2000). The difference between guar gum and xanthan gum can be partly explained by an ionic characteristic and a lower molecular weight of guar gum with respect to xanthan gum. Christianson, Hodge, Osborne, and Detroy (1981) suggested that the strength of amylose-galactomannan interaction depended on the chemical structure of the gums. Oscillatory test showed that dispersions exhibited a predominantly solid-like behaviour which was attenuated on native and modified tapioca starch when guar and xanthan gums were added (Figures 4.16-4.18). In contrary with Yoshimura, Takaya and Nishinari (1999), who suggested that xyloglucan inhibits the formation of three dimensional network structures with corn starch due to incompatibility between unlike polymers, amylose and gums.

The magnitudes of  $\tan \delta$  decreased in the following order, starch alone (control) > guar gum addition > xanthan gum addition as shown in Figures 4.16-4.18. Xanthan gum decreased  $\tan \delta$  of starch paste and seems to be constant over the range studied, possibly due to the strong network formation with starch. Adding of guar gum increased the starch paste rigidity but less than xanthan gum due to their chemical structure. From the results, it was suggesting that final viscosity was not positively related to the viscoelastic properties in case of tapioca starch in gum solutions.

In case of cationic tapioca starch-xanthan gum mixture, it is likely that the ionic interaction of the opposite charges of starch and gum molecules influenced the increase in elastic modulus ( $G'$ ) during cooling. When the starch-gum pastes contain many oppositely charged groups, it is more likely to fold up into a compact structure that maximizes the favorable electrostatic attractions (McClements, 1999). This interaction has been ascribed to electrostatic attraction between the positively-charged quaternary ammonium groups of the cationic tapioca starch and a predominantly negatively-charged region in the side chain of xanthan gum. For the guar gum, galactose branches of non-ionic hydrocolloid inhibit the formation of intra-molecular hydrogen bondings. Either branched or linear molecules of guar gum can interact with amylose molecules via non-covalent hydrogen bonding (Sudhakar, Singhal & Kulkarni, 1996). From the results, the corresponding  $\tan \delta$  values of the starch-guar gum mixtures were more dependent on frequency as compared that of the starch alone, especially at high frequency. This result suggested that guar gum was in an extended conformation in starch-guar gum mixture paste. Moreover, it suggested that starch molecules interacted with guar gum appearing large complex molecular structure which possesses low elastic properties.

## CHAPTER 6

### CONCLUSION

Guar gum and xanthan gum increased viscosity and viscoelasticity of native and modified tapioca starch suspensions during and after heating, respectively; except for anionic starch-xanthan gum mixture in which peak viscosity was decreased during heating. Viscosity of native starch suspension with an addition of gum was synergistically increased due to interaction between leached components of starch and gums but not the swelling of starch granules in case of non-aggregation phenomenon. However, increasing concentrations of gums in the continuous phase resulted in intermolecular associations that play an important role in the viscoelastic behaviour of the composite.

The repelling forces between negatively charged starch and gum demonstrate interactions between gums and solubilized amylose and low-molecular-weight amylopectin molecules. This hypothesis was supported by the results in a decreasing of peak viscosity, no any aggregation of granules, no any wrapped granules by gums, no affect on swelling power but slightly higher in pasting temperature.

The strong electrostatic interactions between cationic starch and anionic xanthan gum resulted in an instantaneous aggregation of granules, whereas non-ionic guar gum formed sheet structure and loosely wrapped the granules. These evidences can be attributed to the lower in swelling power, solubility index, peak viscosity, and loss tangent ( $\tan \delta$ ) but higher in pasting temperature. For all combination, gums increased the rheological parameters  $G'$  and  $G''$  of starch pastes. The ionic interactions between starch and gum molecules play an important role on these properties.

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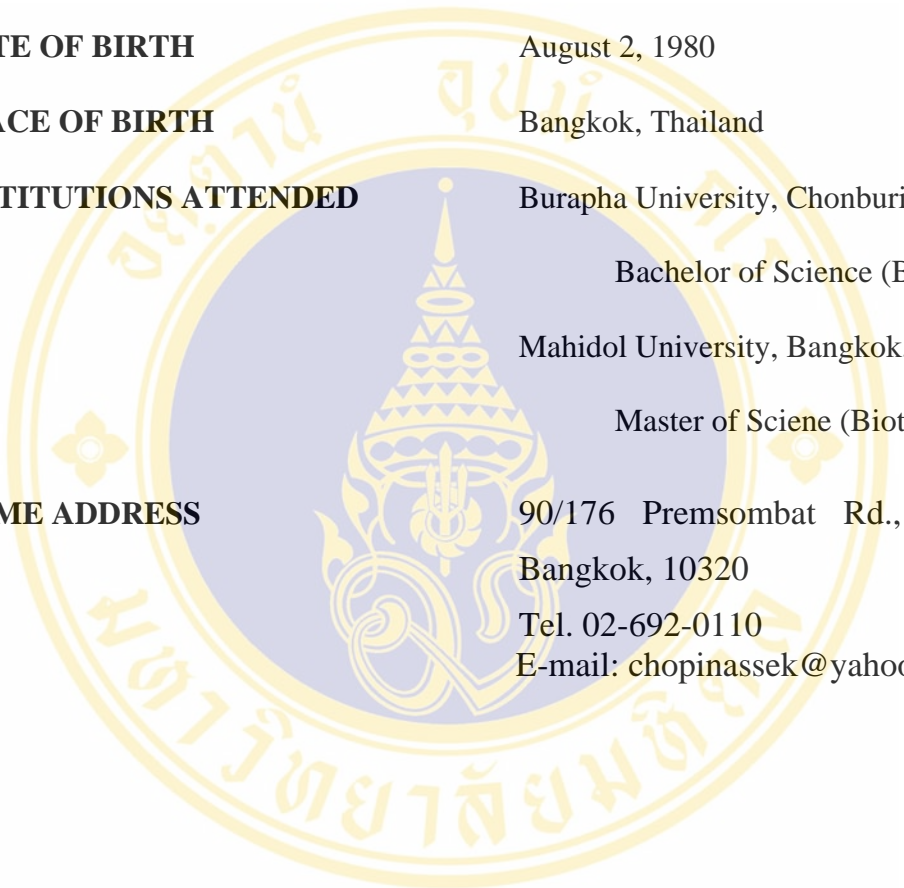
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The image features a large, semi-transparent watermark of the Mahidol University logo in the background. The logo is circular with a blue center containing a golden emblem of a traditional Thai stupa. The outer ring of the logo contains the university's name in Thai script: "มหาวิทยาลัยมหิดล" at the top and "มหาวิทยาลัยราชภัฏวชิราวุธวิทยาลัย" at the bottom.