รายงานวิจัยฉบับสมบูรณ์

โครงการ

“การวิเคราะห์สมบัติทางกายภาพของสารผสมระหว่างแป้งมันสำปะหลังและไฮโดรคอลลอยด์ที่มีส่วนประกอบอาหารอื่นเพื่อการพัฒนาผลิตภัณฑ์”

โดย

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สัญญาเลขที่ RMU5380042

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ชื่อนักวิจัย: รศ. ดร. รุ่งนภา พงศ์สวัสดิ์มานิต
ภาควิชาพัฒนาผลิตภัณฑ์ คณะอุตสาหกรรมเกษตร มหาวิทยาลัยเกษตรศาสตร์

ส่วนประกอบหลายชนิดมีการใช้ในสูตรอาหารเพื่อกำหนดสมบัติทางหน้าที่ของผลิตภัณฑ์ แป้งมันสำปะหลังมักใช้เป็นสารให้ความหนืด อันตรกิริยาระหว่างแป้งมันสำปะหลัง (TS) และไฮโดรคอลลอยด์ที่เลือก (แซนแทนกัม) ที่เกี่ยวข้องกับเจลาติไนเซชันและรีโทรกราเดชันระหว่างการให้ความร้อนและทำให้เย็นตามลำดับ มีบทบาทสำคัญต่อการกำหนดคุณภาพสุดท้ายของผลิตภัณฑ์ที่มีแป้งเป็นส่วนประกอบโดยเฉพาะในสูตรอาหารที่มีน้ำตาล เกลือ หรือกรด จากการศึกษาผลของแซนแทนกัม (Xan) ต่อพฤติกรรมเพสติงและเจลาติไนเซชันของ 5%TS พบว่าการเตรียมตัวอย่างและสภาวะของการวัดค่ามีผลต่อสมบัติทางรีโอโลจีของของผสม TS/Xan ซึ่งมีความสำคัญต่อกระบวนการแปรรูปในอุตสาหกรรม เมื่อวิเคราะห์การเปลี่ยนแปลงสมบัติความร้อนและรีโอโลจีของเจล TS และ TS/Xan เก็บที่อุณหภูมิต่ำ (5°C) ซึ่งมีความเข้มข้นพอลิแซ็กคาไรด์รวม = 25%w/w พบว่า ค่า storage Young's moduli ของเจล TS และ TS/Xan เพิ่มขึ้นเมื่อเก็บนานขึ้นและการเปลี่ยนแปลงอุณหภูมิมีผลต่อค่านี้มากในเจล TS เมื่อเก็บนานขึ้น เนื่องจากการเชื่อมโยงข้ามที่เปราะบางของอะไมโลเพกทิน แต่ผลของอุณหภูมิลดน้อยลงในเจล TS/Xan ดังนั้น Xan สามารถยับยั้งการเกิดรีโทรกราเดชันของเจล TS ที่เก็บที่ 5°C เป็นเวลานานขึ้น การให้ความร้อนเป็นขั้นตอนสำคัญสำหรับการเตรียมผลิตภัณฑ์ที่มีแป้งเป็นส่วนประกอบและมีผลต่อคุณภาพผลิตภัณฑ์เนื่องจากการแตกสลายของโมเลกุลแป้ง การแทนที่แป้งมันสำปะหลังบางส่วนด้วยแซนแทนกัมช่วยปรับปรุงสมบัติเพสติงและความคงตัวทางด้านการแช่แข็งและละลายของระบบ TS ที่ผ่านการให้ความร้อน การเติมซูโครส (10-30%) ในเพสต์ของ TS/Xan เพิ่มอัตรา viscosity breakdown ระหว่างการให้ความร้อนที่อัตราการเฉือนและอุณหภูมิคงที่หนึ่งๆ ส่วนการเติมเกลือ (NaCl) มีผลทำให้อุณหภูมิเพสติง setback และความหนืดสุดท้ายของของผสม TS และ TS/Xan เพิ่มขึ้นแต่ค่า breakdown ของ TS ลดลง นอกจากนี้ ยังพบว่า Xan สามารถเพิ่มความหนืดและความคงตัวทางด้านการแช่แข็งและละลายของเพสต์ TS ในอาหารที่มีความเป็นกรด สุดท้ายในโมเดลอาหาร พบว่า TS สามารถใช้ในการเตรียมสปองจ์เค้กเพื่อดัดแปลงเนื้อสัมผัสในอุตสาหกรรมขนมอบและ Xan สามารถใช้ในน้ำเชื่อมผลไม้เพื่อเพิ่มคุณภาพและความคงตัวในด้านความหนืดระหว่างการให้ความร้อนและการเก็บ

คำหลัก: เจลาติไนเซชัน รีโทรกราเดชัน สมบัติเพสติง สมบัติความร้อน ความคงตัวในการเก็บ

Abstract

Project Code: RMU5380042

Project Title: Analysis of physical properties of tapioca starch – hydrocolloid mixtures containing other food ingredients for product development

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Many ingredients are added into foods to determine the functional properties of products. Tapioca starch (TS) is used as a favorable thickener. The ingredient interactions between TS and selected hydrocolloids (xanthan gum) related to gelatinization and retrogradation on heating and cooling, respectively, play an important role to determine final qualities of starch-based products especially in the food formulation containing sugar, salt or acidulant. The effect of xanthan gum (Xan) on pasting and gelatinization behavior of 5% w/w TS was investigated. The results revealed that sample preparation and measuring conditions influence the rheological properties of TS/Xan mixtures, which should be taken into account in food production. Changes in the thermal and rheological properties of TS gels with and without Xan (total polysaccharide concentration = 25% w/w) were investigated under storage at 5°C. The storage Young's moduli values of stored TS and TS/Xan gels increased with increasing storage time and became more temperature dependent with storage time due to the weak cross-linkage of amylopectin molecules in the TS gels but became less dependent in the system containing Xan. Then, Xan could retard the retrogradation of TS gels stored at 5°C for longer storage times. Heating is an important step for preparing starch-based products and affecting product quality due to starch degradation. Substitution of Xan for TS improved pasting properties and freeze-thaw stability of TS-based system undergone heating. Addition of sucrose (10 to 30%) in TS/Xan pastes increased the rate of viscosity breakdown during RVA heating under constant shear and temperature. The sodium chloride (NaCl) addition enhanced pasting temperature, setback and final viscosity of TS and TS/Xan dispersions but decreased RVA breakdown values of only TS system. Xan could be used to enhance the viscosity and freeze-thaw stability of TS pastes under acidic condition of food product. Finally, in food model, TS could be used in sponge cake preparation for modifying textures in the baking industry and Xan can be applied to fruit syrup for enhancing quality and stability in terms of viscosity during heating and storage.

Keywords: Gelatinization, retrogradation, pasting properties, thermal properties, storage stability

Executive summary

In food industry, the quality of a food product depends on the quality of its constituent ingredients and the nature of their interactions. Some ingredients are added for determining the functional properties of products. Starch is one of the most important polysaccharides used in food systems for controlling rheological properties of foods under gelatinization and retrogradation of starch granules during processing. To enhance the quality and shelf life of the products, non-starch polysaccharides have been widely used to improve stability, modify texture, change both gelatinization and rheological properties and maintain overall qualities during storage and distribution in food chain by controlling rheological and textural properties of products.

Since many ingredients such as sugar, salt or acidulant are widely added in the food formulation, ingredient interactions affecting food product quality can occur within or among these constituent components. The contributions of different interactions to the qualities of a product depend on many factors (such as the degree of processing, the condition of distribution and storage). A through understanding of these interactions concerning with quantifying important physicochemical mechanisms in food seems to be very necessary for food scientists to develop new products with multi-component systems that are tasty, satisfying, healthful and convenient to meet the consumer expectation.

Thailand is a major cassava producer and the largest exporter in the world. Tapioca starch (TS), produced from cassava roots, is a favorable thickener used in food industries due to its high viscosity, clear appearance, and low production cost, compared to other starches. However, starch pastes often suffer from low stability against shear or other mechanical stimuli. Viscosity of a starch paste decreases when mechanically disturbed. TS has traditionally been used as a thickener. The ingredient interactions between TS and non-starch carbohydrates related to gelatinization and retrogradation during heating and cooling play an important role to determine the final qualities of starch-based product. These rheological and thermal properties of starch/hydrocolloid mixtures not only play an important role of texture modification, but also affect the overall qualities of starch-based products during storage in food chain. Xanthan gum (Xan), anionic microbial heteropolysaccharide, is produced by *Xanthomonas campestris*. Xan dispersions are known to show a weak gel behavior at low shear rates where they show a high viscosity and the weak gel structure is disrupted on application of shear. Because of these unique and useful properties Xan is widely used in food industry. It is soluble in hot or cold water and solutions exhibit high viscosities even at low concentrations with high pseudoplastic behaviour. At low concentrations, Xan produces a high viscosity permitting suspension of particulates, and inhibition of emulsion droplet association. Upon shaking, stirring or pouring (shearing) the viscosity decreases markedly (shear-thinning) but recovers completely upon removal of shear. The viscosity is retained over the wide range of pH, temperature and ionic strength. These characteristics satisfy requirements for a thickening and suspending agent.

Therefore, the influence of selected hydrocolloid (Xan) on rheological properties and thermal stability of TS was investigated. The influence of temperature, sucrose, salt and acidulant on the rheological properties, thermal properties and freeze-thaw stability of TS mixtures with and without the hydrocolloid was also determined for discussion of storage stability and shelf life extension.

The effect of Xan on pasting and gelatinization behavior of TS was investigated. Rheological measurements of TS/Xan mixtures with 5% w/w total polysaccharide concentration at different mixing ratios (10/0, 9.5/0.5, 9/1 and 8.5/1.5) were performed to understand the pasting and gelatinization behavior of TS with and without Xan on heating – cooling cycle using a rapid visco-analyser (RVA) and conventional rheometers. Pasting temperatures, peak viscosity, final viscosity and breakdown values of TS increased with increasing Xan content but the opposite result was observed in setback value. Xan increased storage modulus (G') and loss modulus (G'') of TS dispersions during gelatinization process. Temperature dependence of steady shear viscosity became less pronounced with increasing Xan content on both cooling and reheating indicating that Xan made the mixture more thermally stable. Pastes of TS/Xan tended more solid-like, i.e., G' larger than G'', with increasing Xan. The storage modulus of TS/Xan paste increased when kept at 10ºC indicating the network formation. All the results suggest that the sample preparation and measuring conditions influence the rheological properties of TS/Xan mixtures, which should be taken into account in food production.

Changes in the thermal and rheological properties of TS with and without Xan (total polysaccharide concentration = 25% w/w) were investigated using a Differential Scanning Calorimeter, Rheolograph Gel and Texture Analyser. The gelatinization temperatures of TS shifted to higher values with the Xan concentration. Xan enhanced the retrogradation of TS during the initial stage of storage but retarded the process for a further storage time at 5°C. The onset temperature of all reheated TS/Xan gels decreased with increasing storage time indicating thermally unstable structure formation after a longer storage time. Storage Young's moduli *(E')* of the TS and TS/Xan gels stored at 5°C increased with increasing storage time. The E' values became more temperature dependent with storage time due to the weak cross-linkage of amylopectin molecules in the gels but became less dependent in the system containing Xan. TS/Xan gels kept for 14 days showed lower Young's moduli than TS gels from the compression test confirming retardation of the retrogradation process by Xan. The results suggested that Xan could retard the retrogradation of TS gels for longer storage times.

Heating is an important step for preparing starch-based products. The heating affects the quality of the products due to gelatinization and degradation of starch. In this study, effect of thermal treatment on pasting properties of TS with and without Xan under constant shear was investigated using a rapid visco-analyzer (RVA). Freeze-thaw stability of TS and TS/Xan pastes was also determined. The mixtures of 5% (w/w) TS and TS/Xan (mixing ratio = 9/1) at pH 7 were prepared for the measurements. Final viscosities decreased with heating time at 95ºC. Higher heating time increased the breakdown of gelatinized TS and TS/Xan mixtures ($p<0.05$). Substitution of Xan for TS depressed the setback of the TS pastes ($p<0.05$). Changes in viscosity values of both TS and TS/Xan mixtures during heating at 95˚C with a constant shear rate of RVA profile exhibited pseudo-first-order reaction with respect to heating time. From the repeated freeze-thaw treatment, TS pastes containing Xan exhibited the lower water separation compared with those of TS pastes alone at the same heating time. The results may have important implications for industrial applications with improved pasting properties and freeze-thaw stability of TS-based products

Sugars and hydrocolloids are used in starch-based product formulations during processing for improving the final quality of foods. Effect of sucrose (0 to 30%) on thermal and pasting properties of 5% w/w TS and Xan mixtures was investigated using differential scanning calorimeter (DSC), rapid visco-analyzer (RVA) and rheometer. Sucrose increased gelatinization temperatures and enthalpies of TS and TS/Xan dispersions. RVA pasting temperatures, peak viscosity, final viscosity, breakdown and setback values of TS/Xan mixtures increased with increasing sucrose concentration (p<0.05). Addition of sucrose in all TS/Xan pastes increased the rate of viscosity breakdown during RVA heating under constant shear and temperature. Setback values of TS/Xan pastes increased with sucrose addition but decreased significantly with increasing Xan content. Xan enhanced thermal stability of steady shear viscosities to TS pastes with and without sucrose. Linear regression from pasting profile revealed a good relationship for predicting final viscosity. These results could facilitate the development of TS-based products with improved thermal and pasting properties.

Salt is one of food ingredients used in formulation. Addition of salt into products containing starch or starch-hydrocolloid may change the gelatinization leading to the difference in viscosity or gel texture. Therefore, sodium chloride (NaCl) was selected to investigate the effect of salt on pasting properties and texture profile analysis (TPA) of TS and Xan mixtures. The mixtures of TS and Xan (5% w/w) at mixing ratios of 10/0, 9.5/0.5 and 9/1 were prepared to study the effect of salt addition (400 mM NaCl) on pasting properties using a rapid visco analyzer (RVA). For higher concentration of 25% (w/w) TS and Xan, the mixtures with mixing ratios of 10/0, 9.875/0.125 and 9.75/0.25 and NaCl (0, 400 mM) were prepared in a plastic tube with 22 mm diameter and then kept at 5ºC for 24 h before TPA measurement using texture analyzer. The values of pasting temperature, setback and final viscosity of TS and TS/Xan dispersions were significantly increased with NaCl addition. The NaCl decreased breakdown values of TS but increased those of TS/Xan mixtures. The hardness of TS gels decreased with Xan and NaCl addition. The cohesiveness of gels without NaCl increased with Xan concentration whereas the values of both TS and TS/Xan gels exhibited no significant difference in the presence of NaCl (p>0.05).

The acidity of the TS/Xan mixtures decreased with increasing acid concentration. Citric acid provided the highest acidity in TS/Xan mixtures among the selected acidulants. The TS containing higher Xan content revealed a higher pH value (decreasingthe acidity of the system). The peak and final viscosities, setback of TS decreased with increasing acid concentration but Xan addition retarded the degree of reduction of those parameters and significant lower water separation compared with those of TS alone. Xan could be used to enhance the viscosity and freeze-thaw stability of TS pastes under acidic condition of food product.

During heating process and storage, the viscosity reduction of fruit syrup stabilized by starch is a problem in food industry due to the starch degradation especially at low pH system. The influence of Xan on the rheological properties of syrups with different heating time and during storage was investigated. Blueberry syrups were prepared using 4% total concentration of polysaccharides with different mixing ratios of modified tapioca starch (MTS) and Xan (MTS/Xan = 4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3). The syrups were heated to 90°C and further heating for 20, 40, 60 and 80 min. All formulations with different heating times exhibited the lower viscosity with shear rate. Viscosities of the syrups containing Xan were higher than

those without Xan. The syrup containing 0.2%Xan (MTS/Xan = 3.8/0.2) obtained from heating at 90ºC for 40 min was selected to evaluate the quality change during storage according to the highest sensory scores of thickness and overall liking. The syrup with 0.2% Xan substitution for MTS exhibited the higher viscosity and lower rate of viscosity reduction than that without Xan. Zero-order equations were used for shelf life evaluation of the syrups. Overall liking scores of the syrup with 0.2% Xan before and after storage for 16 weeks were not significantly different ($p>0.05$) and exhibited higher scores than those without Xan. The results suggest that Xan can be applied to the fruit syrup for enhancing the quality and stability in terms of viscosity during heating and storage.

The type of flour used in a sponge cake plays an important role in improving product quality. The possibility of cake preparation using TS as partial substitution for wheat flour (WF) for further application in the food industry was investigated. Sponge cake batter formulations containing flour blends of WF (10–20 %) and TS (0–10 %) at three mixing ratios (100:0, 75:25 and 50:50) were studied. Apparent viscosity of batters was determined from steady shear measurement and decreased with increasing TS substitution for WF. The batter density decreased with increasing TS content, indicating a higher amount of air incorporated into the cake batter during mixing. The specific volume of cakes after baking at 175 ºC for 20 min increased with increasing TS substitution. The TPA hardness values of baked cakes containing 50 % TS substitution were significantly ($p<0.05$) lower than those prepared from only WF. Tenderness and overall liking scores of cakes prepared from WF and TS (mixing ratio = 50:50) were significantly ($p<0.05$) higher than those prepared from only WF. The results suggest that partial replacement of WF by TS up to 50 % decreased batter viscosity and density leading to higher specific volume and lower hardness in sponge cakes after baking. Therefore, TS could be used in sponge cake preparation for modifying textures in the baking industry.

The research findings from this project enhance the understandings of how Xan changes the physical properties of TS with and without other food ingredients (sucrose, sodium chloride, food acidulants) during process and storage. In addition, based on the basic research gained from the project, the application in food products was carried out and revealed that product quality and shelf life can be enhanced. Much better in prediction and control of quality of the food product containing TS and Xan during processing and storage can be performed. The gained knowledge can be further applied to process and product development of high quality starch-based products in food industry and finally reduce the cost of the competitiveness of the food industry by reducing expenditures both time and money. Finally, the high quality of young PhD researchers from this project was also obtained.

Project title: Analysis of physical properties of tapioca starch – hydrocolloid mixtures containing other food ingredients for product development

Introduction

The qualities of food product related to appearance, flavor, texture and stability are dependent on the food ingredients incorporated in the food system. Starch is a biopolymer and defines as a homopolymer consisting only one monomer, D-glucose (Friedman, 1995; BeMiller & Whistler, 1996) and composed of amylose and amylopectin. Starch is one of the most important functional food biopolymers and widely used in food formulations as a functional ingredient to many products, such as sauces, puddings, confectionery and a variety of low-fat products. Starch has been widely used not only as a main ingredient in many products such as noodles and bakery products but also as a thickener, stabilizer, or gelling ingredient in food products.

Starch used for food gel preparation plays an important role in product development especially for modifying the texture or shape setting. At high concentrations of starch, three-dimensional networks are obtained after starch dispersions are heated and cooled. Heating starch dispersions above a certain temperature leading to swelling and disintegration of starch granules is known as gelatinization. Then, upon cooling, starch gels are formed if the concentration of the starch paste is high enough (normally > 6%) (Clark and Ross-Murphy, 1987; Miles et al., 1985) as a consequence of the aggregation of amylose chains forming ordered junction zones. The starch gelation process is also described as occurring after a hot paste containing amylose is cooled and becomes more elastic with solid-like characteristics (BeMiller, 2011). The starch gel, a thermodynamically unstable system, is generally regarded as composed of composite networks in which swollen starch granules are embedded in a continuous three-dimensional network of aggregated amylose chains with junction zone formation (Ring, 1985) or entanglements called the initial phase of retrogradation. Further reorganization proceeds in starch gels during storage resulting in an increase in the rigidity of the gel by amylopectin (Biliaderis, 1991; Miles et al., 1985; Temsiripong et al., 2005; Yoshimura et al., 1996) depending on many factors such as the type of starch, the starch paste concentration, the heating and cooling conditions, the pH, and the presence of solutes such as salts and sugars (Swinkels, 1985). When gelatinized, TS forms a clear paste with a bland taste and high viscosity and is used in many food applications (Pongsawatmanit et al., 2006; Muadklay and Charoenrein, 2008). However, starch based formulations are subjected to different processing conditions leading to changes in structural and rheological properties during heating and cooling.

In general, native starches are packed in granules. The characteristics of starch granular swelling, gelatinization and pasting are the important functionalities as an ingredient in food systems for controlling rheological properties of foods (Nishinari, Zhang & Ikeda, 2000; Nishinari et al., 2000). In food processing, gelatinization and pasting of starch granules occur during heating process along with shear leading to changes in starch granules and viscosity. On cooling, retrogradation occurs due to the reassociation of starch molecules, leading to forming a gel or an increase in viscosity (Whistler & BeMiller, 1999). Native starch pastes often suffer from low stability against shear or other mechanical moduli. It is usually the case that the viscosity of a

starch paste decreases when mechanically disturbed (Temsiripong, Pongsawatmanit, Ikeda & Nishinari, 2005). During distribution and storage, starch pastes may proceed the transformation of starch biopolymer molecules: namely, chain aggregation and recrystallization. In frozen food, it is difficult to maintain product in a constant and optimum frozen state undergoing the repeated freeze-thaw cycles during storage and transportation leading to the changes in syneresis and related rheological properties (Lee, Baek, Cha, Park & Lim, 2002). Starch-based products can be formulated to have different pH values. The changes in viscosity or gelling properties of starch-based products with low pH during storage may occur and lower food stability. These factors are the driving force for food industry to develop a high quality product which can be maintained throughout the processing, distribution and storage. Since starch is a major polysaccharide composed of amylose and amylopectin molecules, on heating, the decrease in the molecular weight due to shorter polymer chains affects many properties of starch-based products, such as cold paste viscosity, water solubility and absorption, the degree of retrogradation and gelling properties (Mua and Jackson, 1997; Pongsawatmanit and Srijunthongsiri, 2008).

Another important ingredient used in food industry is hydrocolloid. Most hydrocolloids used in food industry perform a number of functions including thickening and gelling properties, stabilizing emulsions and foams, inhibiting ice and sugar crystal formation and retrogradation, preventing organoleptic properties etc (Williams & Phillips, 2000). These properties are important for consumer acceptance. Therefore, non-starch polysaccharides or hydrocolloids (also called gums, biopolymers) have been widely used in the food industry to improve stability and maintain overall qualities during storage and distribution in food chain by controlling rheological and textural properties of foods (Pongsawatmanit & Srijunthongsiri, 2008). Hydrocolloids are widely used in starch-based product formulations for improving the final quality of foods, induced by the differences in the gelatinization and viscoelastic properties of starch (BeMiller, 2011; Funami, 2009). Incorporation of a proper amount of hydrocolloids may improve or maintain desirable textural properties and stability of most starch-based products during a long storage period (Temsiripong, Pongsawatmanit, Ikeda & Nishinari, 2005; Tester & Sommerville, 2003; Lee, Baek, Cha, Park & Lim, 2002; Christianson et al., 1981; Funami et al., 2005; Mandala *et al.*, 2002).

Therefore, starch and hydrocolloids are often mixed and used in food systems to control moisture and water mobility, provide a proper texture, improve overall product quality and stability, facilitate processing and reduce cost of production (Yoshimura et al., 1996; Mandala et al. 2004). Many researchers investigated the effects of blending of starch and hydrocolloids to modify and control the pasting properties, rheological properties, thermal properties and freeze-thaw stability of starch such as corn starch/xyloglucan mixtures (Yoshimura el al., 1999), corn starch/konjac-glucomanan mixtures (Yoshimura et al., 1996), TS/xyloglucan mixtures (Pongsawatmanit et al., 2006; Temsiripong et al., 2005), cassava, corn, oat and potato starch/Xan mixtures (Sikora et al., 2008), wheat starch/Xan, guar gum and cellulose gum mixtures (Christianson et al., 1981), rice starch/gellan, carrageenan and glucomanan mixtures (Huang et al., 2007), cereal starch/galactomanan mixtures (Alloncle et al., 1989), corn starch/guar gum mixtures (Sudhakar et al., 1995), rice starch/xanthan gum mixtures (Viturawong et al., 2008). The viscoelastic properties are important in the processing of starch foods, and the processing conditions such as stirring and extrusion sometimes play a key role on the final texture of starch products (Tsutsui et al. 2006). There are other investigations reporting about properties of

starch/hydrocolloid mixtures. Pasting properties of potato starch were affected using carboxymethyl cellulose (CMC), carrageenans, alginate and xanthan gum (Shi and BeMiller, 2002). RVA peak and final viscosities of TS increased with increasing xyloglucan content (Temsiripong *et al.*, 2005; Pongsawatmanit *et al.*, 2006). Peak viscosity of 13% wheat starch system during gelatinization increased with the addition of 0.5-1.0% hydrocolloids (guar gum, tara gum, locust bean gum and konjac glucomannan) (Funami *et al.*, 2005). Pongsawatmanit and Srijunthongsiri (2008) have reported the rheological properties and freeze–thaw stability in the systems of the partial substitution of starch with Xan at a fixed total polysaccharide for improving the quality of TS-based products. The effect of heating on starch breakdown and the quality of starch-based products such as waxy corn starch-water system under heating-shearing condition was also reported (van den Einde *et al.*, 2004). In addition, starch/hydrocolloid mixture is used as a texture modifier, understanding of its rheological and thermal properties is important for enhancing the quality and shelf life of the products. Thus, various studies on rheological and thermal properties of mixtures between starches and hydrocolloids have been reported (Christianson, Hodge, Osborne & Detroy, 1981; Funamai et al., 2008; Sudhakar, Singhal & Kulkarni, 1995; Temsiripong, Pongsawatmanit, Ikeda & Nishinari, 2005; Yoshimura, Takaya & Nishinari, 1999). The extent of crystalline parts in starch granule swelling or melting during gelatinization is influenced by the presence of hydrocolloids and synergistic interactions between hydrocolloids and starch (Shi & BeMiller, 2002). In general, the viscosity of the mixed system is greatly higher than the starch alone since most biopolymers are strongly hydrophilic and compete with the starch for water (Christianson, Hodge, Osborne & Detroy, 1981; Funami, Kataoka, Omoto, Goto, Asai & Nishinari, 2005).

In terms of storage, syneresis of the starch can be lower during cold storage by mixing with hydrocolloids such as the systems of corn starch and konjac-glucomannan or corn starch and xyloglucan (Yoshimura, Takaya & Nishinari, 1998; Yoshimura, Takaya & Nishinari, 1999). Retrogradation of the starch can be altered depending on the type and concentration of individual components in the mixed systems during storage. For example, the freeze-thaw stability of sago starch containing galactomannan was improved by preventing the aggregation of amylose and amylopectin (Ahmad & Williams, 2001) while xyloglucan molecules prevent the gelatinized corn starch structure reordering after 7 days of storage by decreasing the retrogradation and syneresis of the corn starch pastes (Yoshimura, Takaya & Nishinari, 1999). Xyloglucan addition in TS pastes was also lower the water separation compared with that of TS paste only from freeze-thaw cycle experiments (Pongsawatmanit, Temsiripong, Ikeda, & Nishinari**,** 2006). In addition, even storage of starch-based gels with high moisture content at low temperature is one method to increase shelf life, this could enhance retrogradation in the products leading to changes in quality, especially in the texture of the stored product. Hydrocolloids have been widely used in food formulation to improve or to maintain the overall quality during distribution and storage by modifying the rheological and textural properties of foods. Many studies have reported the effect of hydrocolloids on starch paste and/or gel properties (Chen et al., 2009; Christianson et al., 1981; Kim and Yoo, 2006; Mandala and Bayas, 2004; Shi and BeMiller, 2002; Yoshimura et al., 1998).

Thailand is a major cassava producer and the largest exporter in the world. The export value of cassava and products in 2007 was 48,671 million Baht and increased by 11.9% compared with those in 2006, respectively (Office of Agricultural Economics, 2008). The export value of cassava products in 2008 was 47,721 million

Baht (Office of Agricultural Economics, 2009). According to the Customs Department complied by Thai Tapioca Starch Association, quantity and value of exported TS in 2008 were 1.2 million ton and about 15,000 million Baht, respectively (Thai Tapioca Starch Association, 2009).

Tapioca starch (TS), produced from cassava roots, is one of the most favorable thickener used in the food industry (Sriroth, Santisopasri, Petchalanuwat, Kurotjanawong, Piyachomkwan & Oates, 1999) especially in Southeast Asia (Biliaderis, 2009; Rapaille and Vanhemelrijck, 1997; Temsiripong et al., 2005). Due to its high viscosity, clear appearance, and low production cost, compared to other starches. TS is differentiated from other starches because it contains about 17-20% amylose with very low protein and lipid contents (Breuninger et al., 2009). For application of TS at low concentration in foods, TS is used for preparing pudding, pastry fillings, soup and baby food products (Moore, Tuschhoff, Hastings & Schanefelt, 1984). In contrast, high concentration of TS is used as a major ingredient to form a gel such as tapioca pearl and various types of desserts. TS pastes often suffer from low stability against shear or other mechanical stimuli and TS gels are subjected to the deterioration induced or caused by retrogradation (Pongsawatmanit, Temsiripong & Suwonsichon, 2007).

Xanthan gum (Xan), anionic microbial heteropolysaccharide, is produced by *Xanthomonas campestris*. The main chain consists of β-D-(1,4)-linked glucose, which is the same as in cellulose. A trisaccharide side chain, consisting of α-D-manose, β-D-glucuronic acid, and β-D-mannose is attached to every second glucose residue of the main chain. The gum is used in the food industry for improving the stability of many food products. It is a unique hydrocolloid providing an excellent stability in thermal and acid systems (Morris, 1995). There are many foods using starch and Xan mixture for improving the quality of product (Chantaro, and Pongsawatmanit, 2010). For example, structure of the strawberry sauces thickened with potato starch and xanthan gum provided stable sensory and textural properties of the dessert sauces for 3-month storage (Sikora *et al.*, 2001). There have been many studies on the conformation of Xan (Morris, 2006), and it is well established that the double helical conformation changes into coil conformation on heating, and the disordered coil returns into helices on cooling but this renaturation process is still a matter of debate (Matsuda, Biyajima, & Sato, 2009). The midpoint transition temperature is reported to be 40-50°C depending on the ionic strength. Xan dispersions are known to show a weak gel behavior at low shear rates where they show a high viscosity and the weak gel structure is disrupted on application of shear (Ross-Murphy, Morris & Morris, 1983; Morris, 2006). Because of these unique and useful properties Xan is widely used in food industry. It is soluble in hot or cold water and solutions exhibit high viscosities even at low concentrations with high pseudoplastic behaviour. At low concentrations, Xan produces a high viscosity permitting suspension of particulates, and inhibition of emulsion droplet association. Upon shaking, stirring or pouring (shearing) the viscosity decreases markedly (shear-thinning) but recovers completely upon removal of shear. The viscosity is retained over the wide range of pH, temperature and ionic strength (Morris, 2006; Sworn, 2009). These characteristics satisfy requirements for a thickening and suspending agent. The thermal and rheological properties of the TS/Xan were investigated in a system with the total polysaccharide concentration at about 6% or lower (Chaisawang and Suphantharika, 2006; Chantaro and Pongsawatmanit, 2010a; 2010b; Pongsawatmanit and Srijunthongsiri, 2008; Pongsawatmanit, Yakard and Suwonsichon, 2011; Sikora et al., 2008). Sae-kang and Suphantharika, (2006) investigated the thermal properties of a 24.0% TS/Xan mixture

using differential scanning calorimetry (DSC) but the hardness and rupture strength were determined at 6.0% TS/Xan after repeated freeze-thaw cycles. For application in the food industry, both the thermal and rheological properties should be investigated at the same high total polysaccharide concentration to gain knowledge for further application in TS-based products such as pudding, jelly, and steamed layer dessert during manufacturing and storage.

Other food ingredients such as sweetness, sourness and saltiness added into food formulation are important parameters for determining the functional properties of food systems and the product acceptance from consumers. Therefore, the effects of these seasonings are important to study for gaining the understanding how to control the rheological and textural properties and stability of food products with other ingredients.

Sugars considered as low molecular weight components compared with polysaccharides are used in food formulation for taste and stability modification in food. Sugars can alter thermal and physical properties of TS containing xyloglucan (Pongsawatmanit, Temsiripong & Suwonsichon, 2007). The effect of sugar on gelatinization and retrogradation of starches such as increasing gelatinization temperatures of starches or decreasing the swelling of starch granules has been studied (Baek, Yoo, & Lim, 2004; Chungcharoen & Lund, 1987; Ikeda, Yabuzoe, Takaya & Nishinari, 2001; Kruger, Ferrero & Zaritzky, 2003; Pongsawatmanit, Thanasukarn & Ikeda, 2002). Most of sugars exhibit anti-plasticising effect leading to the lower amount of amylose leaching and higher gelatinization temperatures and enthalpy (Ahmad & Williams, 1999; Kohyama & Nishinari, 1991). Effect of sucrose on the freeze–thaw stability of rice starch gels using microstructure and freezable water was determined by Arunyanart and Charoenrein (2008).

Salt is another important food ingredient since rheological properties of hydrocolloids in food systems depend on many factors such as previous thermal and mechanical treatment, presence or absence of electrolytes and non-electrolytes (Marcotte, Taherian, Trigui & Ramaswamy, 2001). Salt (an ionic species) was added to hydrocolloid suspensions to improve the efficiency of thermal process such as ohmic heating (Yongsawatdigul, Park & Kolbe, 1995). Usually, 0.5 to 1.0% salt concentration is used in sauce (Kim et al., 1996). Marcotte, Taherian, Trigui and Ramaswamy (2001) reported that for hydrocolloid or starch suspensions containing 1% salt, power law model was fitted to shear stress vs. shear rate data to obtain the consistency coefficient (m) and the flow behavior index (n) for starch and pectin whereas the Herschel–Bulkley model was used for carrageenan and Xan.

When the acidulants are used in food formulation, the pH of the food is modified. Starch stability at different pH values is another parameter to be considered for food preparation. Hirashima, Takahashi and Nishinari (2005) investigated the influences of various acid additions before and after gelatinization on the viscoelasticity of corn starch pastes by adjusting pH to be 3 to 6. The viscosity of the pastes exhibited different values compared with that of the control (pH 6.3) depending on the pH due to hydrolysis of amylose and amylopectin chains occurred from adding acids leading to the decrease in viscosity at lower pH. Effect of pH and Xan on freeze-thaw stability of TS was also investigated by Sae-kang and Suphantharika (2006) and Srijunthongsiri and Pongsawatmanit (2006).

Fruit syrup, an example of food product, is one of the important ingredients that can be created to have different flavor, taste, color and texture properties using different sugars, acids, fruit flavors, fruit puree, colorants including polysaccharides. In food industry, many types of polysaccharides are used in syrup as a thickening

agent to modify the rheological properties of the products (Bedi *et al.*, 2005) and hence increase the stability. Starch is one of the polysaccharides widely used for enhancing the viscosity. However, starch-based syrup is subjected to both shear stress and thermal treatment during processing resulting in the breakdown of starch molecules. Since the viscosity of the syrup is one of the important quality parameters to be considered in food application and is observed to decrease after the heat and shear treatments leading to instability of viscosity during storage (Temsiripong *et al.*, 2005; Biliaderis, 2009).

Since the quality of the ingredients and the nature of their interactions influence the quality of a final food product, cake is one type of air-leavened product in the bakery industry. The quality of cakes depends on many factors such as the ingredients used for batter preparation, aeration of batters and process conditions. There are many reports investigating the quality of cake batter determining the final quality of cake products (Sakiyan *et al.,* 2004; Yang and Foegeding, 2010). Batters are obtained by aerating the liquid mixture via mechanical mixing to form a foam structure in order to obtain cakes as the final product; therefore, these batters are complex emulsion systems whose density and rheological properties play an essential role in determining the characteristics of the resulting cakes. High quality cakes can be characterized as having various attributes, including high volume, uniform crumb structure, tenderness and a long shelf life with tolerance to staling (Gelinas *et al.*, 1999). The expansion of cake products comes from the volume of air bubbles entrapped in the cake batter and the liquid part in the system. The cake expansion increases with increasing temperature of the batter according to the gas laws and with increasing water vapor pressure from the liquid in the mixture (Matz, 1992). As the ingredients play an important functional role in the structure and eating quality of the product (Conforti, 2006), cake batters prepared from whole eggs containing egg yolk lipids exhibit very fine bubbles in the crumb (internal structure) of baked products leading to a silky and tender texture. In addition, a formula based on egg yolks containing added shortening further changed the structural qualities of both the batter and the baked cake (Matz, 1992). Baking powder is also used in sponge cake and has been suggested to be added at the final stage of ingredient mixing (Matz, 1992).

Not only wheat flour but also other flour types have been investigated for developing cakes of lower cost and better quality in terms of consumer acceptance (Turabi *et al.,* 2008). The cakes studied were prepared from various types of flour such as wheat–chickpea flour blends (Gomez *et al.,* 2008), rice flour (Turabi *et al.,* 2008) and flour obtained from wheat, rye, and barley (Gomez *et al.,* 2010). However, the effect of partial substitution of wheat flour (WF) with TS on the quality of the batter and the sponge cake has rarely been investigated. Therefore, the objective of the present study was to establish the influence of partial substitution of WF with different levels of TS in the cake formulation on the rheological properties, density and microscopic analysis of cake batters. In addition, the influence of the partial substitution of WF with TS on cake volume, texture and the sensory properties of baked cake was also determined. The results of the present study could be used to design cake emulsions with improved properties needed for further applications in product and process development

Therefore the objectives of this research project were:

1. To understand the influence of studied hydrocolloids on the modification of physical properties (such as rheological properties, gelatinization, retrogradation) of tapioca starch-based system.
2. To know the effect of hydrocolloid on thermal stability and/or freeze-thaw stability for application in TS– hydrocolloid systems containing acid, sugar or salt.
3. To gain the information for the potential application of hydrocolloids to starch-based products for predicting and controlling the stability in terms of rheological and physico-chemical properties during distribution and storage from viewpoints of texture and stability modification with at least one patent or mini-patent to be registered.
4. To publish the research findings gained in peer-reviewed international journals and to obtain high quality of young researchers (PhD and master students) from this projects

2. Materials and methods

2.1 Effect of heating-cooling on rheological properties of tapioca starch paste with and without xanthan gum

2.1.1 Materials:

Tapioca starch (TS) (Siam Modified Starch, Pathumthani, Thailand) and xanthan gum (Xan) (CP Kelco, San Diego) were used without any further purification. The moisture content of the TS and Xan was 11.1 and 8.6%, respectively determined by the hot air oven method at 105°C (AOAC, 2000). Both polysaccharides were mixed on a dry basis and used without any further purification. Silicone oil or mineral oil was used to prevent water loss during measurement for a Haake Rheostress-600 and a Physica MCR 301, respectively.

2.1.2 Pasting property measurement using rapid visco ∕ ubstitu (RVA)

Pasting properties of 5% w/w TS and Xan mixtures at different mixing ratios (TS/Xan = 10/0, 9.5/0.5, 9/1 and 8.5/1.5) were observed using a rapid visco ubstitu (RVA) (RVA-4, Newport Scientific, Narrabeen, Australia). For each mixture of TS/Xan, precalculated amounts of Xan were added to preweighed distilled water in RVA canisters and allowed to disperse throughout the sol for at least 6 h. TS was added to achieve a total weight of 28 g for preparing 5% w/w TS/Xan pastes. The dispersions were kept at room temperature for a further 30 min to hydrate the starch. Each suspension was stirred manually to disperse the sample uniformly before measurement. The pasting profile of the sample and agitation speeds of the paddle were monitored during thermal treatment according to the method of Pongsawatmanit et al. (2006) as follows: equilibrating the starch slurry at 50°C for 1 min, increasing the temperature to 95°C at a heating rate of 6 °C/min, holding the temperature at 95°C for 5 min, decreasing the temperature to 50ºC at 6°C/min, and holding at 50°C for the remainder of the run. The total run time was 23 min. Agitation of paddle was started at 960 rpm for the first 10 s and kept constant at 160 rpm until the end of the experiment. Pasting profiles were evaluated in triplicate and the average values of pasting parameters were reported.

2.1.3 Dynamic viscoelastic measurement of TS/Xan mixtures during gelatinization

A Haake Rheostress-600 (Thermo Electron, Germany) equipped with a C60/2Ti cone and plate geometry (60 mm diameter, 2° cone angle and 0.105 mm gap) was used to investigate storage (G') and loss moduli (G'') of 5% w/w TS/Xan mixtures at different mixing ratios (9.5/0.5, 9/1 and 8.5/1.5) under heating for gelatinization. A dispersion of TS alone (10/0) was not prepared for the small deformation oscillatory measurement due to the sedimentation of starch granules. Precalculated amounts of Xan were added to preweighed distilled water and allowed to disperse throughout the sol for at least 6 h at room temperature using a magnetic stirrer to ensure the complete hydration of the polysaccharide. Then, TS was added into the dispersions with stirring for a further 30 min. Each TS/Xan suspension was loaded on the plate of the rheometer and covered with a thin layer of silicone oil (viscosity about 0.65×10^6 to 1×10^6 mPa.s) to minimize evaporation loss. The angular frequency was fixed at 1.0 rad/s and 5% strain was set to obtain the data within the linear viscoelastic strain region. The TS/Xan samples were heated from 10 to 95°C at a heating rate of 1°C/min.

2.1.4 Temperature dependence of steady shear viscosity of TS/Xan mixtures

Temperature dependence of steady shear viscosity measurement for 5% w/w TS/Xan mixtures at different mixing ratios (TS/Xan = 9.95/0.05, 9.5/0.5, 9/1 and 8.5/1.5) were determined using a rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany) with cone and plate geometry (50 mm diameter, 1° cone angle and 0.05 mm gap) at a shear rate of 10 s^{-1}. Sedimentation of native starch granules during the measurement is sufficiently retarded by adding a small amount of Xan (0.025%) for TS substitution. TS/Xan dispersions were prepared using the same method stated in 2.3, then placed on the plate and covered with mineral oil to prevent water loss during heating – cooling cycle. The TS/Xan dispersions were heated from 10 to 95°C, subsequently cooling from 95 to 10°C, then reheating from 10 to 95°C. The same scan rate (1°C/min) was used for heating and cooling.

2.1.5 Steady shear viscosity measurement of TS/Xan pastes

Gelatinized TS/Xan mixtures (10/0, 9.5/0.5, 9/1 and 8.5/1.5) obtained from the RVA experiment were used for steady shear viscosity measurement. The pastes in RVA canisters (at temperature about 50°C) were removed, kept in controlled temperature chamber at 50°C and measured within 1 h. Cone and plate fixture (50 mm diameter, 1°cone angle and 0.05 mm gap) was used in a rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany). Each TS/Xan paste was placed onto the measuring plate preset at 25 and 50°C for at least 2 min and immediately covered with a small amount of mineral oil to prevent water loss during measurement. The shear rate was stepwisely increased from 0.01 to 100 s^{-1} (15 min of running time). Shear stress and viscosity values were obtained as a function of shear rate.

Flow behaviors of the TS/Xan pastes were analysed using a power law model as shown in equation (1):

$$\tau = K(d\gamma/dt)^n , \qquad (1)$$

where τ = shear stress (Pa), $d\gamma/dt$ = shear rate (s^{-1}), K = consistency coefficient ($Pa.s^n$), and n = flow behavior index. Shear stress and shear rate data were fitted to power law model and the consistency coefficient and flow behavior index were calculated (Ketjarut et al., 2010).

2.1.6 Effect of cooling and reheating on storage and loss moduli of TS/Xan pastes

The changes in dynamic rheological properties of gelatinized TS/Xan pastes were studied during cooling and reheating cycle using a C60/2Ti cone and plate geometry (60 mm diameter, 2° cone angle and 0.105 mm gap). The 5% w/w TS/Xan suspensions (10/0, 9.5/0.5, 9/1 and 8.5/1.5) were heated at 92°C for 30 min in a water bath and stirred at constant rate during heating with a magnetic stirrer. Immediately after cooking, TS/Xan pastes were poured on the plate of the rheometer which had been pre-heated at 90°C and covered with silicone oil immediately. The measurements were carried out by cooling from 90 to 10°C and subsequently heating from 10 to 90°C at the rate of 1°C/min with angular frequency at 1 rad/s and 5% strain. The effect of short term storage at low temperature on the storage and loss moduli was evaluated by holding at 10°C for 10 h after cooling the fresh gelatinized TS/Xan pastes to 10°C, and then reheating again to 90°C at the rate of 1°C/min.

2.1.7 Statistical analysis

Each measurement was carried out using at least two freshly independently prepared samples. The results were reported as mean and standard deviation. Statistical analysis was performed using SPSS V.12 statistical software (SPSS (Thailand) Co., Ltd.).

2.2 Thermal and rheological properties of tapioca starch gels with and without xanthan gum under cold storage

2.2.1 Materials

Tapioca starch (TS) (Siam Modified Starch, Pathum Thani, Thailand) and xanthan gum (Xan) (Keltrol F, CP Kelco, San Diego, CA, USA) were used in the experiments. The moisture content of the TS and Xan was 11.1 and 8.6%, respectively, determined by a hot air oven method at 105°C (AOAC, 2000). The amylose content of TS was 18.0% determined according to the method of Juliano (1971). The concentrations of both polysaccharides were calculated based on a dry basis and used without any further purification. Silicone oil with a viscosity of about 0.65-1×10^6 mPa.s was used as the heating medium to control the temperature and prevent water loss during measurement of the dynamic viscoelasticity.

2.2.2 Preparation of gels

Gel preparation and measurement procedures were performed according to Yoshimura et al. (1996) with a slight modification. Powders of TS or of the TS and Xan mixture were calculated and weighed for gel preparation of 25% w/w TS and TS/Xan (mixing ratio of 9.5/0.5 = 23.75% TS and 1.25% Xan, respectively). TS was dispersed in preweighed distilled water in a separable flask to achieve a total weight of 200 g using a motorized stirrer with a mixing blade (propeller shape with 40 mm diameter) at 340 rpm for 30 min at room temperature. In the case of the TS/Xan mixture, a precalculated amount of Xan was added to the preweighed distilled water and stirred for at least 6 h with a magnetic stirrer to ensure complete hydration of the polysaccharide before TS addition in a separable flask. The dispersion (TS or TS/Xan) was heated in an oil bath to 95°C and heated further by holding at 95-98°C for 30 min with continuous stirring at 340 rpm. Boiled hot distilled water was added into the hot mixtures for adjusting the total polysaccharide concentration to 25% w/w TS or TS/Xan dispersions and then mixed immediately. Hot mixtures were poured into cylindrical Teflon molds with 20 mm diameter (20 mm or 30 mm height for the compression test and dynamic measurement, respectively), placed under a glass cover and packed in plastic bags before cooling in an ice-bath for 20 min. To prevent water evaporation, the gels were kept within the Teflon mold and covered with plastic film and finally packed in plastic bags before placing in a refrigerator at 5°C. Samples were taken after 4, 7, 10, and 14 days for dynamic viscoelasticity measurement and a uniaxial compression test.

2.2.3 Determination of gelatinization and retrogradation of TS and TS/Xan mixtures using differential scanning calorimetry

The thermal properties of 25% w/w TS and TS/Xan mixtures with mixing ratios of 10/0, 9.875/0.125, 9.75/0.25 and 9.5/0.5 were measured using a differential scanning calorimeter (DSC822^e, Mettler-Toledo GmbH, Greifensee, Switzerland). Precalculated amounts of Xan were added to preweighed distilled water and allowed to disperse throughout the sol for at least 6 h at room temperature using a magnetic stirrer to ensure full hydration of the polysaccharide. TS was added into the dispersions with continued stirring for a further 30 min. About 15 mg of the dispersions were weighed directly into a 40-µL aluminum DSC pan and the pan was hermetically sealed. Gelatinization behaviors of TS/Xan mixtures were investigated by heating the pans from 25°C to 110°C at a heating rate of 5°C/min. Another empty DSC pan was used as a reference. The onset temperature (T_o), peak temperature (T_p)

and conclusion temperature (T_c) were determined based on DSC thermograms. The sharpness of the transition peak was measured as the width at the half-peak height (the "half width", $\Delta T_{1/2}$). Gelatinization enthalpy (ΔH_1) expressed as J/g dry starch was evaluated based on the area of the main endothermic peak. After the first-run heating, the gelatinized TS and TS/Xan pastes were cooled down to 25°C with a cooling rate of 10°C/min and kept at 5°C for 1, 4, 7, 14, 21, and 28 days. The stored samples were then reheated again to study the effect of Xan on the retrogradation of TS using the parameter of the retrogradation ratio determined by dividing the enthalpy of disintegration of the ordered structure (ΔH_2) in the second-run heating by the gelatinization enthalpy in the first-run heating (ΔH_1). Each sample pan was weighed before and after measurement to ensure that no weight was lost during the measurement. Four independent sets of samples were prepared and the average value was reported.

2.2.4 Dynamic viscoelasticity measurement of cylindrical TS/Xan gels kept under cold storage

The dynamic viscoelasticity of 25% w/w TS and TS/Xan (mixing ratio = 9.5/0.5) gels (cylindrical shape with 20 mm diameter and 30 mm height) were measured using a Rheolograph Gel (Toyo Seiki Seisakusho Ltd., Tokyo, Japan). The storage (E') and loss (E'') Young's moduli of TS and TS/Xan gels were determined as a function of the storage time according to Nishinari et al. (1980) and Yoshimura et al. (1996) with a slight modification. The temperature dependence of the E' and E'' values for 25% w/w TS and TS/Xan gels stored at 5°C for 4, 7, and 14 days were also measured by increasing the temperature of the gels from 20 to 55°C (step ①), then decreasing from 55 to 20°C (step ②), and finally increasing again from 20 to 55°C (step ③). The E' and E'' values were determined at 5°C intervals. The measurement conditions were set within a linear viscoelastic regime as follows: longitudinal vibrations with frequency at 3 Hz, amplitude at 100 μm and applied strain with a value of 0.0033. The measurement temperature was controlled in a silicon oil bath. Gels were held at each measured temperature for 15 min before starting the measurement process at each set temperature.

2.2.5 Compression test of TS/Xan cylindrical gels stored in cold storage

Prepared cylindrical gels (20 mm diameter and 20 mm height) of 25% w/w TS and TS/Xan (mixing ratio = 9.5/0.5) were evaluated after storing at 5°C for 4, 7, 10, and 14 days for a compression test using a Texture Analyser (TA.XT plus, Stable Micro Systems, London, UK.) with a 50-kg loading cell. The gels were held at room temperature (25±2°C) for about 2 h before measurement. A program of compression tests was used to compress the TS or TS/Xan gels by a distance of 18 mm (90% compression of the original sample height according to a preliminary test) at a speed of 30 mm/min using a 50-mm diameter probe. The breaking stress (σ_B) and breaking strain (ε_B) of the gels were determined from a force-deformation curve according to the method of Yoshimura et al. (1996). The value of σ_B defined as F_B/A_o, was estimated by the force at which a gel was broken (F_B) divided by the initial cross sectional area (A_o). The value of ε_B defined as $\Delta h_B/h_o$ was estimated by the deformation at which a gel was broken (Δh_B) divided by the initial height (h_o) of the sample. Then, Young's modulus (E) was estimated from an initial slope of the stress-strain plot ($E = \sigma/\varepsilon$ at small ε). At least 15 cylindrical gels were tested to obtain an average value and standard deviation of measurement.

2.2.6 Statistical analysis

Each measurement was carried out using at least two fresh, independently prepared samples. The results were reported as the mean value and standard deviation. The data were subjected to analysis of variance (ANOVA) using the SPSS V.12 statistical software package (SPSS (Thailand) Co., Ltd., Bangkok, Thailand). Duncan's multiple range test was also applied to determine the difference of means from the ANOVA, using a significance test level at 5% (p <0.05).

2.3 Effect of heating time on the quality of tapioca starch and xanthan gum mixture

2.3.3 Materials

Tapioca starch (TS) (Siam Modified Starch, Pathumthani, Thailand) and Xanthan gum (Xan) (CP Kelco, San Diego) were used without any further purification. The moisture contents of TS and Xan were 11.1% and 8.6%, respectively determined by the hot air oven method at 105˚C (AOAC, 2000). NaOH was analytical grade for adjusting the pH of TS and TS/Xan mixtures.

2.3.2 Preparation of TS/Xan mixture: TS/Xan dispersions with and without Xan were prepared at two mixing ratios (TS/Xan = 10/0 and 9/1) of 5% total polysaccharide concentration. Precalculated TS was added into RVA canisters containing deionized distilled water to achieve a total weight of 28 g for RVA measurement. In the case of 5% TS/Xan mixture, Xan were dispersed in the deionized distilled water in RVA canisters and allowed to disperse for at least 6 h before adding TS. All dispersions were further kept at room temperature for 30 min to hydrate the starch. Then 0.1 N NaOH was used to adjust the mixture pH to be 7 and mixed for 2 min to disperse the sample uniformly before RVA measurement. The pH values of the dispersions before and after RVA measurements were 7.02 – 7.08. To prevent microbial spoilage sodium azide (0.04%) was also added into all TS/Xan mixtures.

2.3.3 Rapid visco-analyser (RVA) measurement with different heating time at 95 ℃

Pasting properties of 5% w/w TS was determined using a rapid visco-analyser (RVA) (RVA-4, Newport Scientific, Narrabeen, Australia). The TS/Xan dispersions were stirred manually to disperse the sample uniformly before measurement. The RVA pasting profile were monitored during a thermal treatment according to the method of Pongsawatmanit *et al.* (2006) with the modification of holding time at 95°C as follows: equilibrating the starch slurry at 50°C for 1 min, increasing the temperature to 95°C at a heating rate of 6°C/min, holding the temperature at 95°C for 5, 10 and 15 min, decreasing the temperature to 50°C at 6°C/min, and holding at 50°C for the remainder of the run. Then total run times were 23, 28 and 33 min for 5, 10 and 15 min heating time, respectively. Agitation speed of paddle was started at 960 rpm for the first 10 s and kept constant at 160 rpm until the end of the experiment. Pasting profiles were evaluated in triplicate and the average values of evaluated pasting parameters were reported.

2.3.4 Freeze-thaw stability measurement

Gelatinized TS and TS/Xan pastes with pH 7 obtained from different holding time (5, 10 and 15 min) at 95˚C from RVA measurements were used for freeze-thaw stability evaluation. Each mixture was poured into 10 mL plastic tubes, centrifuged to

remove entrapped air bubbles and cooled at 5˚C for overnight before keeping in the freezer. All pastes were stored in the freezer (-25°C) for 22 h, and then thawed at 40°C for 2 h repeatedly up to seven cycles. For water separation from thawed TS and TS/Xan pastes, 5-ml plastic syringes without the tip and plunger were used by placing a single piece of filter paper on the bottom of the syringes, topping up with 0.02–0.03 g cotton, and then adding deionized distilled water to moisten the cotton (Pongsawatmanit *et al.*, 2006). The cotton layer was finally pressed with a glass rod to ensure a complete seal at the bottom of the syringe. The syringes were centrifuged at 2100 g for 10 min to remove excess water from the cotton and then weight. Thawed paste samples (W_s) (about 2.5 g ±0.1 mg) of TS and TS/Xan pastes at selected freeze–thaw cycles were added into each syringe and centrifuged at 2100 g for 10 min. The weight before (W_b) and after (W_a) centrifugation were recorded. The percentage of water separation was calculated based on the weight of thawed TS or TS/Xan pastes as shown in the following equation (2.3.3):

$$\text{Water separation (\%)} = (W_b - W_a) \times 100 / W_s. \qquad (2.3.3)$$

At least three measurements were carried out to ensure the reproducibility of the data.

2.3.5 Statistical analysis

Each measurement was carried out using at least three freshly prepared samples. The results were reported as the mean and standard deviation. Statistical analysis was performed using SPSS V.12 statistical software (SPSS (Thailand) Co., Ltd.).

2.4 Influence of sucrose on thermal and pasting properties of tapioca starch and xanthan gum mixtures

2.4.1. Materials

Tapioca starch (TS) was supplied by Chorchaiwat Industry Co., Ltd. (Cholburi, Thailand). The moisture and amylose contents of the starch were 11.52% and 19.4% determined by the hot air oven method at 105°C (AOAC, 1995) and high performance size exclusion chromatography (HPSEC) (modified method of Govindasamy et al., 1992), respectively. Xanthan gum (Xan) (CP Kelco, San Diego) containing 12.73% w/w moisture content was also determined using hot air oven at 105°C (AOAC, 1995). Both polysaccharides were mixed on a dry basis and used without any further purification. Sucrose (Merck, Germany) was used as provided.

2.4.2 Differential scanning calorimetry measurement

Thermal properties of TS and Xan mixtures with and without sucrose were performed using a differential scanning calorimeter (DSC822e, Mettler-Toledo GmbH, Switzerland). The total polysaccharide content of 5% w/w TS/Xan mixtures with mixing ratios of 10/0, 9.5/0.5 and 9/1 was selected to study the effect of sucrose (0 to 30% w/w). Precalculated amounts of Xan were added to preweighed deionized distilled water and allowed to disperse throughout the sol for at least 6 h at room temperature (25 °C) using a magnetic stirrer to ensure fully hydration of the polysaccharide. TS or TS mixed with sucrose were added into the dispersions with continued stirring for a further 30 min. About 15 mg of the dispersions were weighed directly into a 40-µl aluminum DSC pan and the pans were hermetically sealed. The gelatinization behaviors of TS and Xan mixtures containing sucrose were investigated by heating the pans from 25°C to 110°C at the rate of 5°C/min. A sealed empty pan was used as a reference. Onset temperature (T_o) peak temperature (T_p) and conclusion

temperature (T_c) were determined based on heating DSC thermograms. Gelatinized enthalpy expressed as J/g dry starch was evaluated based on the area of the main endothermic peak. The sample pan was weighed before and after measurements to ensure that no weight was lost during the measurement. Three freshly prepared samples were measured and each average value was reported.

2.4.3 Rapid Visco Analyser (RVA) measurement

Pasting properties of 5% w/w TS and Xan mixtures at different mixing ratios (TS/Xan = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) containing sucrose (0 to 30%) were determined using a rapid visco ubstitu (RVA) (RVA-4, Newport Scientific, Narrabeen, Australia). For each mixture of TS/Xan/sucrose, precalculated amounts of Xan were added to preweighed deionized distilled water in RVA canisters and allowed to disperse throughout the sol for at least 6 h. TS with and without sucrose was then added to achieve a total weight of 28 g for preparing 5% w/w TS/Xan pastes containing 0 to 30% sucrose. The dispersions were kept at room temperature for a further 30 min to hydrate the starch. Each suspension was stirred manually to disperse the sample uniformly before measurement. The pasting profile of the sample and agitation speeds of the paddle were monitored during a thermal treatment according to the method of Pongsawatmanit et al. (2006) as follows: equilibrating the starch slurry at 50°C for 1 min, increasing the temperature to 95°C at a heating rate of 6°C/min, holding the temperature at 95°C for 5 min, decreasing the temperature to 50°C at 6°C/min, and holding at 50°C for the remainder of the run. The total run time was 23 min. Agitation speed of paddle was started at 960 rpm for the first 10 s and kept constant at 160 rpm until the end of the experiment. Pasting profiles were evaluated in triplicate and the average values of evaluated pasting parameters were reported.

2.4.4 Steady shear viscosity measurement

Selected gelatinized TS/Xan/Sucrose mixtures obtained from the RVA experiments were used for steady shear viscosity measurement using a rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany). All pastes were centrifuged at 190 g for 2 min to remove air bubbles and then a portion of each paste was placed onto the measuring plate using cone and plate geometry (50 mm diameter, 1°cone angle and 0.05 mm gap) which was equilibrated to the measured temperatures (25 and 50°C) beforehand. Sample temperature was kept constant at 25°C or 50°C for at least 2 min before starting the measurement. Apparent viscosity was recorded by increasing the shear rate from 0.01 to 100 s^{-1}.

2.4.5 Data and statistical analysis

Each of the measurements was carried out using at least three freshly prepared samples. The results were reported as the mean and standard deviation. Statistical analysis was performed by SPSS V.12 statistical software (SPSS (Thailand) Co., Ltd.). Linear regression was conducted to relate the RVA final viscosity with the xanthan and sucrose contents to predict a set of response/dependent variables.

2.5 Effect of sodium chloride on physical properties of TS containing Xan

2.5.1 Materials:

Tapioca starch (TS) (Siam Modified Starch, Pathumthani, Thailand) and Xanthan gum (Xan) (CP Kelco, San Diego) were used without any further purification. The moisture contents of TS and Xan were 11.1% and 8.6%, respectively determined by the hot air oven method at 105˚C (AOAC, 2000). Sodium chloride (NaClX (Merck, Germany) were analytical grade and used as provided.

2.5.2 Rapid visco-analyser (RVA) measurement

TS/Xan dispersions with and without Xan were prepared at three mixing ratios (TS/Xan = 10/0, 9.5/0.5 and 9/1) of 5% total polysaccharide concentration. Precalculated TS was added into RVA canisters containing deionized distilled water or 400 mM salt solution to achieve a total weight of 28 g for RVA measurement. In the case of 5% TS/Xan mixture, precalcutated amounts of Xan were dispersed in the deionized distilled water or 400 mM salt solution in RVA canisters and allowed to disperse for at least 6 h before adding TS. All dispersions were further kept at room temperature for 30 min to hydrate the starch. Pasting properties of 5% w/w TS with and without 400 mM NaCl were determined using a rapid visco-analyser (RVA) (RVA-4, Newport Scientific, Narrabeen, Australia). The TS/Xan dispersions were stirred manually to disperse the sample uniformly before measurement. The RVA pasting profile were monitored during a thermal treatment according to method of Pongsawatmanit *et al.* (2006). Pasting profiles were evaluated in triplicate and the average values of evaluated pasting parameters were reported.

2.5.3 Texture profile analysis (TPA) measurement

In texture measurements of 25% (w/w) TS/Xan gels (mixing ratios of TS/Xan = 10/0, 9.875/0.125 and 9.75/0.25) with and without NaCl (400 mM). Precalculated TS was added into deionized distilled water or 400 mM salt solution to achieve a total weight of 150 g. In the case of 25% TS/Xan mixture, precalcutated amounts of Xan were dispersed in the deionized distilled water or 400 mM salt solution and allowed to disperse for at least 6 h before adding TS at room temperature. Then the mixtures were stirred for 30min and then degassed under vacuum for 15–30 min before heating to about 65ºC in a controlled temperature water bath (95ºC) for partial gelatinization. According to our preliminary test, holding the TS or TS/Xan mixtures (150 g) at 95ºC for about 90 s with continuous stirring could avoid the sedimentation of starch granules before subsequent full gelatinization. The hot dispersions were immediately transferred into a plastic tube (250×22mm diameter), sealed with rubber bands at both ends and heated in a boiling-water bath for completing starch gelatinization by maintaining the sample temperature at 95–98ºC for 30min. The gelatinized mixtures were cooled in an iced-water bath for 10 min and stored at 5ºC for 24 h. Then, all TS/Xan gels with and without NaCl were cut into cylinders with 20±0.5 mm length and 22±0.3mm diameter before the compression test at 25ºC using the Texture Analyzer (TA-500, Lloyd Instruments Ltd., UK) equipped with a texture NEXYGEN™ software program (Ametek, Inc., UK). A standard double-cycle program was used to compress the gels for a distance of 10 mm (50% compression of the original sample height) at a speed of 50 mm/min using a 50-mm diameter probe with a flat end in both upward and downward direction without time allowed to elapse between the two compression cycles. At least 10 cylinder gels were measured to get an average of all texture parameters for each mixture. The texture parameters reported in this study were hardness, springiness, cohesiveness and chewiness.

2.5.4 Statistical analysis

Each measurement was carried out using at least three freshly prepared samples. The results were reported as the mean and standard deviation. Statistical analysis was performed using SPSS V.12 statistical software (SPSS (Thailand) Co., Ltd.).

2.6 Effect of acidulents on pasting properties and freeze-thaw stability of tapioca starch with and without xanthan gum

2.6.1. Materials

Tapioca starch (TS) (Siam Modified Starch, Pathumthani, Thailand) and xanthan gum (Xan) (CP Kelco, San Diego) were used without any further purification. The moisture content of the TS and Xan was 11.1 and 8.6%, respectively determined by the hot air oven method at 105°C (AOAC, 2000). Analytical grade acetic acid (RCI Labscan, Thailand), citric acid (Univar, Australia) and lactic acid (Univar, Australia) were used without further purification.

2.6.2. Rapid visco-analyser (RVA) measurement

The pasting properties of 5% w/w TS and Xan mixtures (TS/Xan = 10/0, 9.5/0.5 and 9/1) with acetic acid or citric acid or lactic acid (concentration = 0, 1, 5 and 10 mM) were determined using a rapid visco-analyser (RVA) (RVA 4500, Perten Instruments, Hägersten, Sweden). TS/Xan dispersions with and without Xan (5% total polysaccharide concentration) were prepared at three mixing ratios (TS/Xan = 10/0, 9.5/0.5 and 9/1). Precalculated TS was added into RVA canisters containing deionized distilled water to achieve a total weight of 28 g for RVA measurement. In the case of the 5% TS/Xan mixture, Xan was dispersed in the deionized distilled water in the RVA canisters and allowed to disperse for at least 6 h before adding the TS to ensure fully hydration of the biopolymer. All dispersions were kept at room temperature for a further 30 min to hydrate the starch. Then, acetic acid or citric acid or lactic acid were added into the mixtures with 0, 1, 5 and 10 mM of acid concentration, which was followed by mixing for 2 min.

Then TS/Xan dispersions were stirred manually to mix the sample uniformly before measurement. The RVA pasting profile was monitored during thermal treatment, according to the method of Pongsawatmanit et al. (2006): equilibrating the starch slurry at 50°C for 1 min; increasing the temperature to 95°C at a heating rate of 6°C /min; holding the temperature at 95°C for 5 min; decreasing the temperature to 50°C at 6°C/min; and holding at 50°C for the remainder of the run. The total run time was 23 min. The agitation speed of the paddle commenced at 960 rpm for the first 10 s and was kept constant at 160 rpm until the end of the experiment. The TS/Xan pastes from RVA measurement were further analyzed for freeze-thaw stability. The pH values of all dispersions were determined before and after RVA measurements. Sodium azide (0.02%) was also added into the TS/Xan mixtures to prevent microbial spoilage.

2.6.3. Freeze-thaw stability measurement

The freeze-thaw stability of gelatinized TS and TS/Xan (9/1) pastes containing different acid concentration (0, 1, 5 and 10 mM) obtained from RVA measurement was investigated. Each paste mixture was poured into 10 mL plastic tubes, centrifuged at 2100×g for 2 min to remove entrapped air bubbles and kept at 5°C overnight,

before being kept in a freezer (-25°C) for 22 h. All pastes were thawed at 40°C for 2 h repeatedly up to nine cycles. The water separation was determined from repeated freeze-thaw cycles of 1, 3, 6 and 9.

Five mL plastic syringes without the tip and plunger were used for water separation in the thawed TS and TS/Xan pastes with and without acidulants, by placing a single piece of filter paper on the bottom of each syringe, topping up with 0.02–0.03 g cotton, and then adding deionized distilled water into moisten the cotton (Pongsawatmanit et al., 2006, Chantaro and Pongsawatmanit, 2011). The cotton layer was pressed with a glass rod to ensure a complete seal at the bottom of the syringe. The syringes were centrifuged at 2100×g for 10 min to remove excess water from the cotton and then weighed. Thawed paste samples (W_s) (about 2.5 g ±0.1 mg) of the TS and TS/Xan pastes from the selected freeze-thaw cycles were added into each syringe and centrifuged at 2100×g for 10 min. The weights before (W_b) and after (W_a) centrifugation were recorded. The percentage of water separation was calculated based on the weight of the thawed TS or TS/Xan pastes with and without acidulants using Equation (2.6.1):

$$\text{Water separation (\%)} = (W_b - W_a) \times 100 / W_s \qquad (2.6.1)$$

At least three measurements were carried out to ensure the reproducibility of the data.

2.6.4. Statistical analysis

Each of the mentioned measurements was carried out using at least three freshly prepared samples. The results were reported as the mean and standard deviation. Statistical analysis was performed by SPSS V.12 statistical software (SPSS (Thailand) Co., Ltd.).

2.7 **Effect of xanthan gum on the quality of syrup thickened by modified starch during heating and storage**

2.7.1 Materials:

Modified tapioca starch (MTS) (Siam Modified Starch, Thailand) as hydroxypropy distarch phosphate (HDP) (E1442) and commercial xanthan gum (Xan) (Dessen Biochemical, China) were used in this study. Commercial sucrose, 42% DE glucose syrup, citric acid monohydrated, blueberry flavor and food colorants were purchased from local suppliers. Frozen blueberry puree (TSS = 10.6ºBrix, pH = 3.46) prepared from IQF process was used. Oriented polyamide (OPA) film (360±5 mm length, 240±5 mm wide, 100 ±10 μm thickness) was used for packing the syrup during the storage test.

2.7.2 Blueberry syrup preparation for various heating time

Blueberry syrup containing 4% total concentration of polysaccharides were prepared with the different mixing ratios of MTS and Xan (MTS/Xan = 4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3). Each formulation consists of other ingredients with the fixed percentages: 54% of sugars (glucose syrup and sucrose), 10% blueberry puree, 31.2% water and 0.8% of citric acid, sorbic acid, color and flavor.

A batch of blueberry syrup (2 kg) was prepared for each formulation. MTS was added into water for preparing MTS dispersion. In the case of MTS/Xan mixture, Xan was mixed with a part of sucrose from the formulation, dispersed in the water,

and stirred for 1 h throughout the sol before adding MTS. Then fruit puree, sugar, glucose syrup, color were added and mixed using stirrer for further 1 h at room temperature to hydrate the starch and hydrocolloid.

Each mixture was heated using water bath and stirred until the temperature of syrup reaching 90°C. The citric acid and sorbic acid were added when the syrup temperature being about 70°C. The flavor was added finally at 90°C. Each syrup formulation was further heated for 80 min and sampled out for viscosity measurement at 20, 40, 60 and 80 min of heating time.

2.7.3 Quality measurement of blueberry syrup

Apparent viscosity of prepared blueberry syrup (16 ml) from each heating time at 90°C was measured as a function of shear rate ranged from 2.5 to 62.5 s^{-1} at 25±0.1°C using rotational viscometer (DV-III, Brookfield-RVT) with small sample adapter's coaxial cylinder geometry and SC4-29 spindle. Sample temperatures were kept constant at least 5 min before starting measurement. Flow characteristics of the syrups were evaluated.

Blueberry syrups with and without Xan with selected heating time at 90°C were analyzed for total soluble solids using a refractometer (Atago, Japan), pH with pH meter and water activity using a dew point hygrometer, Aqualab Series 3B (Decagon Devices, Pullman, Washington, USA) at 25°C. The sensory evaluation of the products with and without Xan was performed using 30 untrained panelists for preference test. Each sample syrup (20 g) with and without Xan was served in a cup with pieces of bread. The panel was asked to rate the liking of quality attributes according to appearance, color, odor, thickness and overall liking using 9 point hedonic scale with 1 = dislike extremely; 9 = like extremely.

2.7.4 Quality change of blueberry syrup during storage

Blueberry syrup formulation containing Xan exhibiting a good quality in terms of viscosity and sensory evaluation from 2.2 was selected for quality change during storage. Twenty kilograms of syrups with and without Xan (as control) were prepared by heating the syrups for 40 min at 90°C, hot filling into OPA bag (500 g), hermetically sealing, cooling and keeping at ambient temperature (average 30±3ºC) for 4 months. The syrups were sampled out for quality measurement at some certain periods of time. The viscosity, total soluble solid and pH values were determined as mentioned methods above.

Sensory evaluation of the product with and without Xan before and after 4 months storage was performed using 30 untrained panelists for preference test as mentioned method above.

2.7.5 Statistical analysis

All measurements were performed at least in two replication. Mean values were reported with standard deviation. An analysis of variance (ANOVA) was done to determine the significant difference of the treatment parameters of the quality properties. Duncan's multiple range test was also applied to determine the difference of mean ($p<0.05$) from ANOVA.

2.8 Quality of batter and sponge cake prepared from wheat-tapioca flour blends

2.8.1 Materials:

Tapioca starch (TS) was purchased from Siam Modified Starch Co., Ltd. (Pathum Thani, Thailand) with 11.1 % moisture, 1.0 % protein and 0.2 % ash contents on a wet basis and was determined using a hot air oven at 105 °C, by the Kjeldahl method, and by dry ashing in a furnace at 550 °C, respectively, according to the methods of AOAC (2000). Wheat flour (WF) for cake preparation containing 11.6 % moisture, 7.9 % protein and 0.4 % ash contents on a wet basis (AOAC, 2000) was used in the study. Fresh whole eggs, whole milk powder, baking powder with double-action, emulsifier (SP®), sugar and butter containing 1.5 % salt (Orchid®) were purchased from a supermarket and used without any further purification.

2.8.2 Cake preparation

The experiments used sponge cake batter formulations containing WF (10–20 %) and TS (0–10 %) to obtain flour blends at three mixing ratios (WF:TS = 100:0, 75:25 and 50:50), 28.0 % liquid whole eggs, 2.0 % whole milk powder, 0.4 % baking powder, 1.6 % emulsifier, 24.0 % sugar, 16.0 % butter and 8.0 % water. In the cake batter preparation (500 g), the liquid whole eggs, water, sugar and emulsifier were mixed in a Kitchen-Aid mixer (5K5SS, St. Joseph, MI, US with machine speeds from 1 to 10) at speed 3 for 1 min and further mixed at speed 6 for 9 min. Then, dry ingredients (the flour blend of WF and TS, whole milk powder and baking powder) were added simultaneously to the mixture at speed 1 for 1 min and further mixed at speed 3 for 2 min. The melted butter was added finally and mixed at speed 1 for 20 s. Each batter formulation (125 g) was placed in an aluminum pan (8.5 × 16 × 5 cm) and baked in an electric oven (Teba™, TFL10-31) at 175 ºC for 20 min. After baking, the cakes were removed from the pans, cooled upside down on a wire rack for 30 min at room temperature and kept in plastic bags to prevent drying before being measured for physical properties and sensory evaluation within 12 h.

2.8.3 Batter quality measurement

Apparent viscosity: The shear stress and apparent viscosity of the prepared batters were recorded as a function of a shear rate range between 2.5 and 62.5 s^{-1} controlled at 25 °C using a rotational viscometer (DV-III, Brookfield-RVT) with the coaxial cylinder geometry of the small sample adapter and the SC4- 29 spindle according to the method of Ketjarut *et al.* (2010). Sample temperatures were kept constant for at least 5 min before starting measurements. The flow behavior of each batter formulation was evaluated using a power law model as shown in Equation (2.8.1) by plotting *ln* (shear stress) and *ln* (shear rate) to obtain the consistency coefficient (*K*) and flow behavior index (n):

$$\tau = K\dot{\gamma}^{n} \qquad (2.8.1)$$

where: τ = shear stress (Pa)

$\dot{\gamma}$ = shear rate (s^{-1})

K = consistency coefficient ($Pa.s^{n}$)

n = flow behavior index.

The coefficient of determination (R^2) was also calculated. All measurements were carried out at a controlled temperature (25 ± 2 ºC). At least three replications were completed.

Batter density: The batter was filled into an aluminum cup immediately after removal from the mixer, leveled off using a rubber spatula and weighed. The batter

density was calculated as the ratio of the batter weight (W_1) to the distilled water weight (W_2) filled in the same cup (modified from Gomez *et al.*, 2007). The density of the water was 1 g/cm^3.

Microscopic analysis: For each cake batter sample with and without TS substitution, a thin layer of freshly prepared samples was prepared immediately by placing a drop of the batter on a microscope slide and covering with a cover slip. The samples were observed under an optical microscope (Model CH30RF200, Olympus®, Tokyo, Japan) with a 10× magnification. A digital camera was mounted on the microscope for taking photographs.

2.8.4 Cake quality determination

Specific volume: The final cake volume was obtained using the rapeseed displacement method. The cake was cut into 25 × 25 × 25 mm cubes. Then, one piece of cake was weighed (W_o), placed in a container and the rest of the container volume was filled with rapeseed (V_2). The volume of the empty container (V_1) was calculated by filling with rapeseed. Both V_1 and V_2 were later determined by a graduated cylinder and the difference between V_1 and V_2 was defined as the cake volume (V_o). The specific volume was then calculated as the ratio of the volume to weight (V_o/W_o).

Crumb texture: Texture profile analysis (TPA) was performed to evaluate the texture of the cakes using a Texture Analyzer (TA-500, Lloyd Instruments Ltd., UK) equipped with the texture NEXYGEN™ software program (Ametek, Inc., UK). The cake samples were cut into 25 × 25 × 25 mm cubes before TPA measurement. A standard double-cycle program was used to compress the samples at a speed of 50 mm/min with 50 % deformation using a 50 mm diameter probe (modified from Pongsawatmanit *et al.*, 2007) without the waiting time before starting the second compression. Hardness (N), cohesiveness (no unit), springiness (mm) chewiness (Nm) and gumminess (N) were calculated by the software program. At least 5 samples were measured to obtain an average value of all texture parameters for each formulation.

Sensory evaluation: An affective test for sensory evaluation of sponge cake containing different TS levels was performed using 30 untrained panelists (the students and staff of the Department of Product Development, Kasetsart University). Each panelist was presented with individual cake samples (about 3 × 3 × 1.5 cm) with and without TS that had been baked within the previous 12 h and were placed on a tray in a plastic bag coded with a three-digit random number and served in a randomized order. During the panel session, water was provided to panelists to minimize any residual effect before testing a new sample. Each panelist was asked to rate the liking of quality attributes according to appearance, color, odor, tenderness and overall liking of each sample using a 9-point hedonic scale (1 = dislike extremely, 5 = neither dislike nor like, and 9 = like extremely).

2.8.5 Statistical analysis

All measurements were performed using three replications. The results were reported as the mean value with standard deviation. The data were subjected to analysis of variance (ANOVA) using the SPSS V.12 statistical software package (SPSS (Thailand) Co., Ltd.). Duncan's multiple range test (DMRT) was also applied to determine significant differences at the 5 % level of significance ($P<0.05$) between the treatment parameters associated with the properties of the batter and baked cake.

3. Results and Discussion

3.1 Effect of heating-cooling on rheological properties of tapioca starch paste with and without xanthan gum

3.1.1 RVA pasting properties

Typical RVA pasting behaviour of 5% w/w TS/Xan mixtures (mixing ratios = 10/0, 9.5/0.5, 9/1 and 8.5/1.5) observed by RVA is shown in Fig. 3.1.1. The viscosity of Xan dispersion (0.75%) observed by RVA showed a normal temperature dependence in the range from 50 to 95 °C; it decreased gradually with increasing temperature and then showed a constant value at 95 °C, then increased gradually with decreasing temperature. In this temperature range, Xan is believed to be in disordered conformation and does not show order-disorder conformational change. However, addition of Xan resulted in a significant alteration on RVA pasting properties of TS (Fig. 3.1.1).

At temperature below 50°C, the native starch granules are insoluble in water leading to very low viscosities in starch suspensions at the beginning of pasting measurement. The viscosity of TS/Xan suspensions increased with increasing Xan content due to the thickening function of Xan except that of TS/Xan suspension at mixing ratio = 9.5/0.5 due to the sensitivity of instrument. When starch granules are further heated in excess water, they absorb a large amount of water. Pasting temperature, a temperature at which viscosity shows a steep increase, of TS increased significantly from 68.9 to 73.2°C with an increase Xan concentration from 0 to 0.5% (Table 3.1.1) which are in good agreement with a previous report (Pongsawatmanit and Srijunthongsiri, 2008) even the pasting temperatures from this experiment were lower than previously observed data due to the harvesting time leading to the difference in physicochemical properties of TS (Sriroth et al., 1999). The pasting temperature of TS decreased when Xan concentration in the mixture was higher than 0.75% (Table 3.1.1). Decrease in the pasting temperature results from the increase in the effective concentration of starch in the continuous phase (Alloncle et al., 1989; Yoshimura et al., 1998).

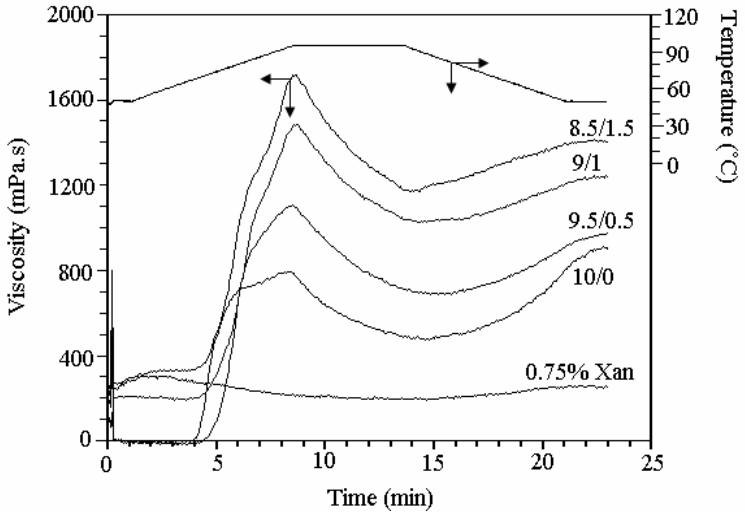


Fig. 3.1.1 Typical RVA pasting profiles of 5% w/w TS/Xan mixtures (mixing ratio = 10/0, 9.5/0.5, 9/1, and 8.5/1.5). Heating and cooling rate: 6 ºC/min. Rotation speed of the paddle: 960rpm for 10 s and then kept at 160rpm throughout the experiment time.

Table 3.1.1 RVA pasting properties of 5% w/w TS/Xan mixtures at various mixing ratios of 10/0, 9.5/0.5, 9/1 and 8.5/1.5.

TS/Xan	Pasting temperature (˚C)	Peak viscosity (mPa.s)	Breakdown (mPa.s)	Final viscosity (mPa.s)	Setback (mPa.s)
10/0	68.9±0.5c	793±5d	329±7c	882±14d	419±10a
9.5/0.5	72.8±0.2a	1053±24c	361±17c	972±13c	280±2b
9/1	73.2±0.4a	1498±13b	473±13b	1250±11b	226±17c
8.5/1.5	71.2±0.2b	1677±14a	529±11a	1367±12a	219±7c

Mean ± standard deviation values followed by a different lower-case letter within the same column are significantly different ($p<0.05$) by Duncan's multiple range test.

Above a gelatinization temperature range, the starch granules undergo an irreversible process known as gelatinization, which is marked by the crystalline melting, loss of birefringence and solubilization. At these temperatures, the starch granules began to swell and disintegrated, then amylose chains released out from the granules leading to an increase in the viscosity. As the temperature increased further, the viscosity increased to peak viscosity, which is defined as the equilibrium point between swelling and polymer leaching which cause an increase in viscosity. Peak viscosity also indicates the water-binding capacity of the starch or mixture. The addition of Xan in the range from 0 to 0.75 % enhanced the peak viscosity of the TS pastes from 793 mPa.s to 1677 mPa.s. This result can be interpreted by assuming that the system is a dispersed system consisting of starch granules dispersed in hydrocolloids which are dissolved in the continuous phase (Temsiripong et al., 2005). The effective concentration of hydrocolloids would then increase as the volume of the phase accessible to the hydrocolloids was reduced due to swelling of the starch granules during pasting. This resulted in a pronounced increase in the viscosity of the continuous phase (Alloncle et al., 1989). The increase in the viscosity of this suspension may be also explained as the increase of the volume fraction of the dispersed phase (starch granules) due to swelling. However, the contribution of the increase in volume fraction before the rupture of starch granules may be much smaller than the contribution from the increase in the viscosity of the continuous phase. Another important contribution to the increase in viscosity may be the direct synergistic interaction among amylose molecules leached out on heating with xanthan molecules leading to network structure. Peak viscosity often correlated with final product quality, and also provides an indication of the viscous load for a mixing cooker.

When the starch granules are held at high temperature (usually 95°C) and mechanical shear stress, swollen granules break up and amylose molecules leach out into solution and undergo alignment resulting in a decrease in viscosity. The difference of the peak viscosity and minimum viscosity of RVA profile is defined as breakdown. Breakdown of TS/Xan pastes increased from 329 mPa.s to 529 mPa.s with increasing Xan content from 0 to 0.75%. The rate of viscosity reduction depends on the temperature and degree of mixing or shear stress applied to the mixture and the nature of material itself.

When the starches are subsequently cooled, re-association between macromolecules constituting starch especially amylose molecules occurs and viscosity increase to a final viscosity which is a parameter to indicating the ability of the material to form a viscous paste or gel on cooling. The addition of Xan increased

significantly the final viscosity of the TS paste (882 mPa.s to 1367 mPa.s) as well as an increase in peak viscosity. The difference between the final viscosity and the minimum viscosity after peak viscosity is called as setback which can be correlated with texture of products. Therefore, Xan enhanced pasting temperature, peak and final viscosities, and breakdown. However, Xan could reduce setback significantly (419 mPa.s to 219 mPa.s) slowing down the short-term retrogradation. This is different from the effect of xyloglucan which enhanced the short term retrogradation but retarded a long term retrogradation of corn starch and TS (Yoshimura et al, 1999; Temsiripong et al, 2005).

3.1.2 Temperature dependence of storage and loss moduli on heating for TS/Xan mixtures

The thermal scanning rheological measurements of 5% w/w dispersions of TS and Xan mixtures were performed by a Haake Rheostress-600. The samples were subjected to small oscillatory strains in the linear viscoelastic region and G' and G'' of the mixtures as a function of temperature are shown in Fig. 3.1.2. Changes in G' and G'' values of Xan alone (0.25, 0.5 and 0.75%) were almost negligible compared with those of TS/Xan mixtures (Fig. 3.1.2). The G' and G'' of 0.75% Xan dispersions exhibited the same trend as those of RVA at temperatures below 60°C (Fig. 3.1.1). At a low concentration (0.25% Xan), G' was almost constant from 10°C to 35°C, then G' start to decrease until 65°C with the lowest value, and then G' increased with heating to higher temperatures. In the case of higher Xan concentration (0.5 and 0.75%), G' of 0.5 and 0.75% Xan increased slightly with increasing temperature until 55 and 60°C, respectively, and then slightly decreased. In a 0.25% Xan dispersion, Xan molecule existing as a helical structure converts to a coil conformation with a lower viscosity under elevated temperature conditions and low ionic strength. The midpoint transition temperature of the Xan was reported to be about 55 °C depending on ionic strength (Craig et al., 1997). In 0.5 and 0.75% Xan, an initial increase in G' and G'' occurred due to an initial entanglement of the coil formation during the transition process in the temperature range of 35 to 80 °C (Craig et al., 1997) or the helix-coil transformation (Westra, 1989) whereas G' and G'' decreased with increasing temperature due to the breaking down of the helix to the random coil conformation completely.

The G' and G'' of TS/Xan dispersions were higher than those of Xan alone due to the hydrated water of starch granule. Increase in the G' and G'' is mainly caused by the gelatinization of starch because Xan did not show a steeper increase in the moduli above 60°C. The increase in both G' and G'' of TS/Xan suspensions was promoted by increasing Xan concentration (Fig. 3.1.2). However, the patterns for thermal and rheological behaviors of TS/Xan dispersions before starch gelatinization depend on those of Xan dispersions. During heating, the starch granules swell followed by leaching of small amylose molecules leading to an increase in G' and G'' to maximum values and then the moduli decreased indicating destruction of starch granule. This process is called gelatinization. G' of all TS/Xan mixtures was larger than G'' and both moduli increased with increasing content of Xan (Fig. 3.1.2). The maximum G' increased with increasing Xan content but the maximum of $G''$was not so dependent on Xan content. The results also showed that the difference between G' and G'' tended to be larger with increasing Xan concentration. When tan δ (= G''/G') values were plotted against the temperature (data not shown), tan δ of TS/Xan dispersions revealed almost constant values in the temperature range of 10 °C to 35°C, then started to increase due to the swelling and gelatinization of starch until the temperature reached

to 60°C, followed by decreasing value. At the end of the heating treatment at 95°C, solid-like characteristics ($G' > G''$) were obtained.

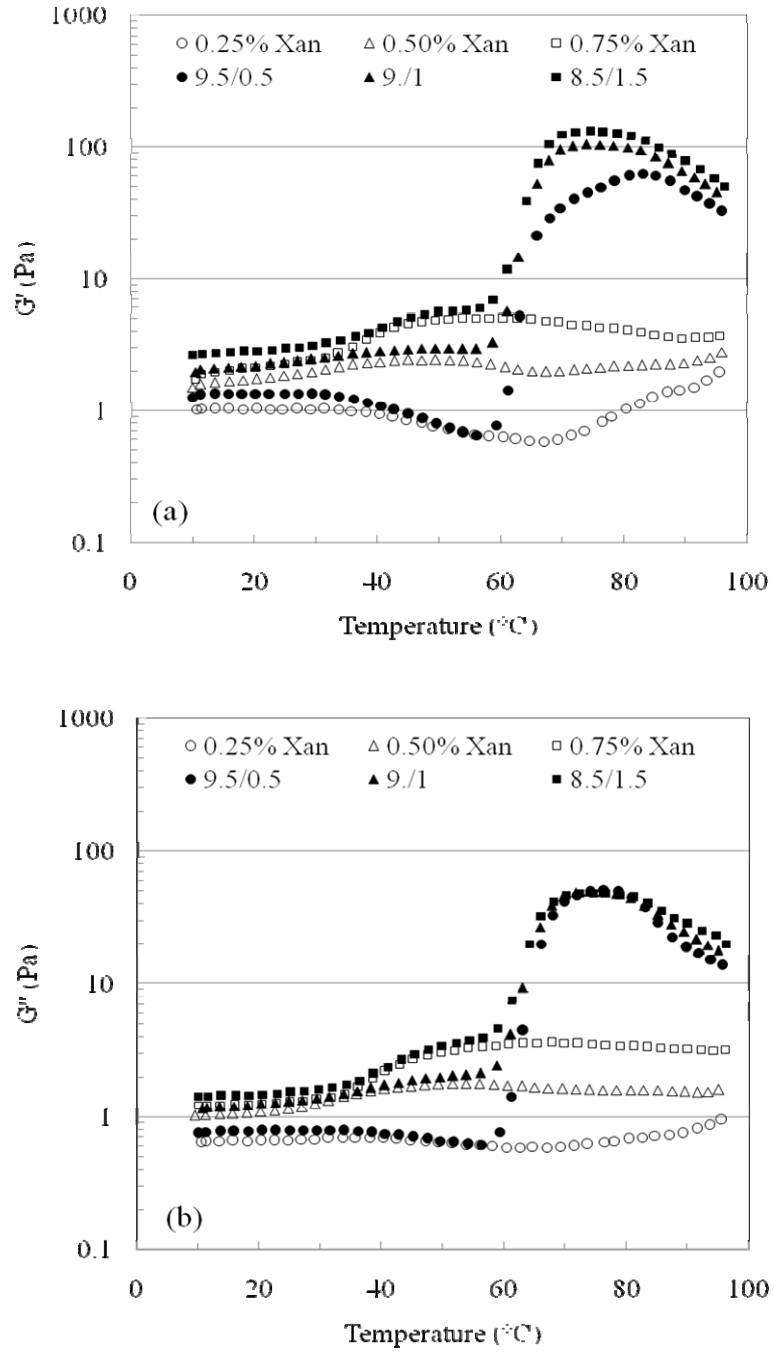


Fig. 3.1.2 Temperature dependence of the storage (a) and loss (b) moduli on heating of 5% w/w TS/Xan dispersions (9.5/0.5, 9/1 and 8.5/1.5) (solid) and Xan dispersions (0.25, 0.5 and 0.75%) (open) during heating from 10 to 95°C (angular frequency: 1 rad/s, scan rate 1 °C/min, 5% strain).

3.1.3 Temperature dependence of steady shear viscosity for TS/Xan mixtures

The thermal scanning measurement of steady shear viscosity of 5% w/w TS/Xan dispersion (9.95/0.05, 9.5/0.5, 9/1 and 8.5/1.5) on heating from 10 to 95°C, cooling from 95 to 10°C, and reheating from 10 to 95°C were performed using the Physica rheometer with a shear rate of 10 s^{-1} and heating rate of 1°C/min. The presence of 0.025% Xan in the TS/Xan (= 9.95/0.05) mixture effectively retarded the sedimentation of TS granules during experiments. Fig. 3.1.3 shows the temperature dependence of steady shear viscosity at four mixing ratios (9.95/0.05, 9.5/0.5, 9/1 and 8.5/1.5). The steady shear viscosity of dispersions of Xan alone (0.5% and 0.75%) was also measured at the same measurement condition of TS/Xan mixtures. Before the gelatinization process (temperature < 60°C), the viscosity of TS/Xan dispersions increased with increasing Xan content from 0.025 to 0.75% due to the thickening ability of Xan. Viscosity values of TS/Xan at the mixing ratios = 9.95/0.05 and 9.5/0.5 were constant in the temperature range from 10 to 60°C (Fig. 3.1.3a and 3.1.3b) whereas the viscosity at mixing ratios = 9/1 and 8.5/1.5 started to slightly increase at the temperature approximately 35°C (Figs. 3.1.3c and 3.1.3d). An increase in viscosity at this temperature was expected due to an initial entanglement of the coil formation during the transition process (Craig et al., 1997) or the helix-coil transformation (Westra, 1989) as was discussed in the previous section. The viscosity of Xan dispersions (0.5 and 0.75%) was similar with dispersions of TS/Xan before gelatinization took place. Christainson et al. (1981) reported that the initial viscosity of dispersion was recognized to the first swelling stage depending on media viscosity only, the later increasing of paste viscosity due to the interaction of solubilized starch, gums, and swollen starch granules.

The viscosity of TS/Xan dispersions was dramatically increased by the gelatinization of TS after heating the dispersion to 62 to 63°C (Fig. 3.1.3a-d). Irreversible swelling of granules occurs when the dispersion is heated above the gelatinization temperature. Gelatinization results in a loss of molecular orientation and breakdown of the crystal structure (Morris, 2006). Swelling of the granules leads to solubilization of amylose molecules with increasing viscosity of dispersion to the maximum value. The viscosity then decreased under shearing and heating due to the further disruption of starch granules and amylose leaching. The leached-out polymer molecules were more or less aligned in the direction of flow leading to gradual decrease in viscosity at a constant temperature (95°C) (Pongsawatmanit et al., 2007). Peak viscosity of TS/Xan mixtures increased with increasing Xan content which is in a good agreement with a previous RVA results. In addition, the temperature at which the viscosity showed the maximum shifted to higher temperatures with increasing Xan concentration.

After the TS/Xan mixtures were gelatinized and heated to 95°C, obtained TS/Xan pastes were cooled down from 95 to 10°C, immediately. The viscosity of TS/Xan increased with decreasing temperature according to the re-association of amylose molecules. Then the cooled pastes were reheated again from 10 to 95°C, the viscosity of TS/Xan paste decreased with increasing temperature, as expected. The viscosity of TS/Xan on cooling from 95 to 10°C and reheating from 10 to 95°C did not coincide, and the values during cooling were higher than those during reheating (Fig. 3.1.3a-3d).

Steady shear viscosity of TS/Xan pastes at a shear rate of 10 s^{-1} on cooling (from 95 to 10°C) and reheating (from 10 to 95°C) became less temperature dependent with increasing Xan concentration (Fig. 3.1.3) due to the thermal stability of the viscosity of Xan. From RVA results (Fig. 3.1.1 and Table 3.1.1), Xan reduces

the short term retrogradation due to the lower setback of the pastes containing Xan on cooling (section 3.1.3.1). The changes in steady shear viscosity of TS/Xan pastes at low temperatures in Fig. 3.1.3 decreased with increasing Xan content, which means that Xan reduces the short term retrogradation. The consistency in the results between the RVA (Fig. 3.1.1) and steady shear viscosity (Fig. 3.1.3) was expected because both were observed at large deformations at a shear rate.

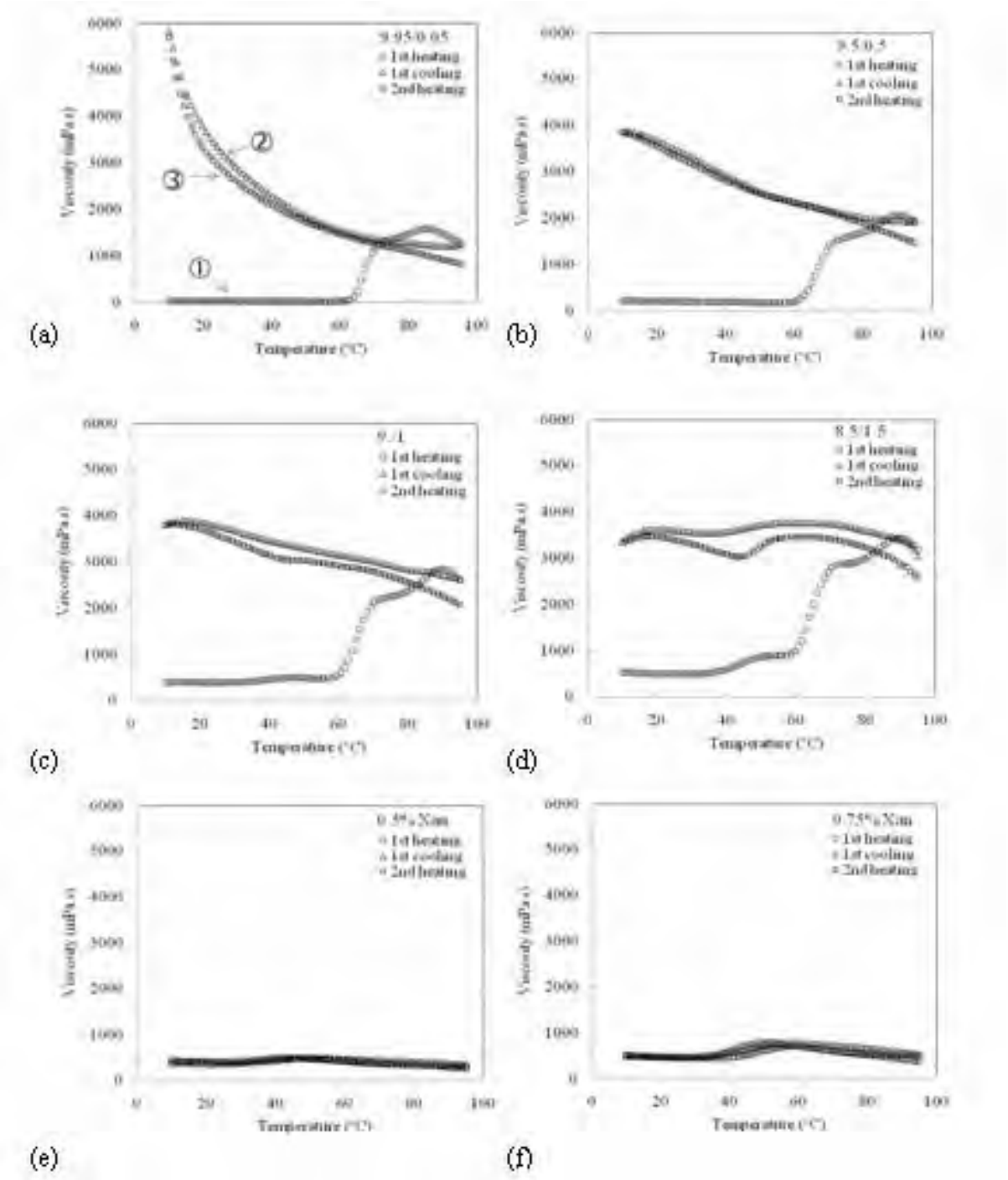


Fig. 3.1.3 Temperature dependence of steady shear viscosity of 5% w/w TS/Xan mixtures: 9.95/0.05 (a), 9.5/0.5 (b), 9/1 (c) and 8.5/1.5 (d), and 0.5%Xan (e) 0.75%Xan (f). Shear rate: 10 s^{-1}. Heating –cooling condition: ① heating from 10 to 95°C ② cooling from 95 to 10°C, ③ and finally reheating from 10 to 95°C at the rate of 1 °C/min.

3.1.4 Steady shear viscosity measurement of TS/Xan pastes

To confirm shear thinning behavior of TS/Xan pastes at selected temperatures, steady shear viscosity of 5% w/w TS/Xan (0/0, 9.5/0.5, 9/1 and 8.5/1.5) from RVA experiment was determined as a function of shear rate at 25 and 50°C. All gelatinized TS pastes with and without Xan exhibited shear thinning behavior (Fig. 3.1.4). As expected, viscosity of all TS/Xan pastes at lower temperature (25°C) was higher than that at higher temperature (50°C). At 25°C, TS/Xan pastes exhibited lower viscosity than those of TS paste at shear rate > 0.5 s^{-1} (Fig. 3.1.4a). However, when temperature of experiment was performed at 50°C, the viscosities of only TS pastes were lower than those of pastes containing Xan in the studied shear rate range (Fig. 3.1.4c) indicating the contribution of thermal stability of Xan to TS pastes. Moreover, the increase in the viscosity at lower shear rates was observed with increasing xanthan content. This phenomenon could be explained by the highly ordered network of entangled, stiff molecules of Xan with amylose molecules and starch granules, but the details should be studied further.

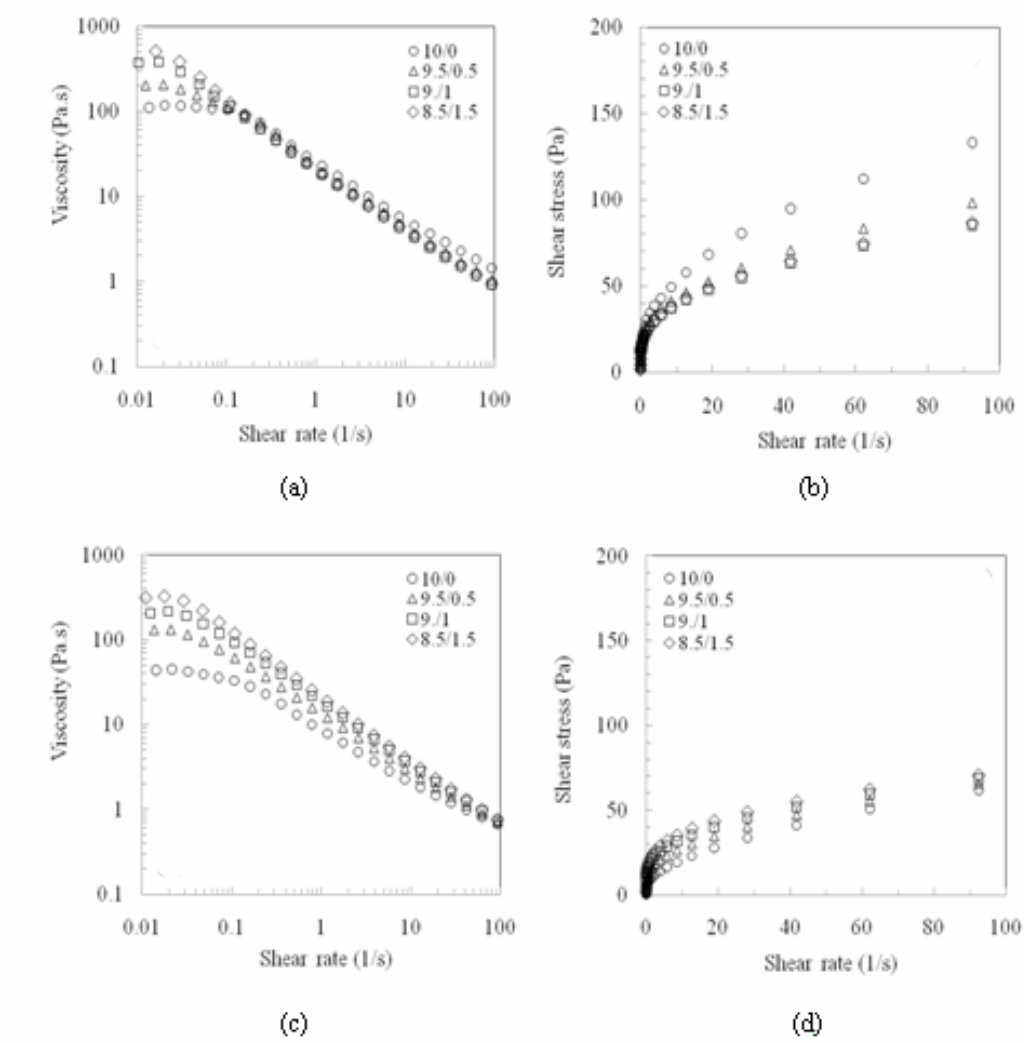


Fig. 3.1.4 Shear rate dependence of the steady shear viscosity (25ºC (a), 50ºC(c)) and of shear stress (25ºC (b), 50ºC(d)) for 5% w/w gelatinized TS/Xan pastes (mixing ratios = 10/0, 9.5/0.5, 9/1 and 8.5/1.5). The pastes (50°C) from RVA measurement kept in controlled temperature chamber at 50°C and measurement within 1 h.

Flow curves of TS/Xan pastes are plotted at 25 and 50°C as shown in Fig. 3.1.4b and 3.1.4d. All pastes exhibited pseudoplastic behavior. The power law (Equation 1) was found to model all TS/Xan pastes with different mixing ratios with r^2 = 0.95-0.99 for both 25 and 50°C. The consistency coefficient (*K*) of all TS pastes increased with increasing Xan substitution (0 to 0.75%) especially at 50°C from 6.2 to 18.4 Pa.s^n, respectively. We observed that addition of 0.75% Xan in TS pastes decreased the flow behavior index of the pastes from 0.44 to 0.31 and 0.48 to 0.30 for 25 and 50°C, respectively. The results suggest that substitution of Xan in TS pastes enhanced the shear thinning behavior showing the deviation of *n* from the Newtonian value (one) (Table 3.1.2).

Table 3.1.**2** Power law parameters (*K* = consistency coefficient, n = flow behavior index) of 5% w/w TS/Xan pastes with different mixing ratios (10/0, 9.5/0.5, 9/1 and 8.5/1.5) determined from the shear rate range 0.01-100 s^{-1} at 25 and 50 °C.

Temperature (°C)	TS/Xan	*K* (Pa.s^n)	*n* (-)	r^2
25	10/0	16.4±2.6cd	0.437±0.008b	0.941
	9.5/0.5	19.5±1.7abc	0.367±0.016c	0.969
	9/1	20.8±2.2ab	0.319±0.010d	0.970
	8.5/1.5	21.9±0.2a	0.308±0.001de	0.963
50	10/0	6.2±1.4f	0.478±0.016a	0.987
	9.5/0.5	12.3±0.7e	0.380±0.011c	0.982
	9/1	15.6±2.4d	0.324±0.007d	0.972
	8.5/1.5	18.4±2.0bcd	0.295±0.012e	0.947

Mean ± standard deviation values followed by different letters are significantly different ($p<0.05$) by Duncan's multiple range test within the same column.

3.1.5 Effect of cooling and reheating on viscoelastic properties of TS/Xan pastes

Influence of cooling (from 90 to 10ºC) and immediately reheating (from 10 to 90ºC) on *G′* and *G″* of 5% w/w TS/Xan pastes (mixing ratio = 10/0, 9.5/0.5, 9/1 and 8.5/1.5) was examined using a Rheostress 600. All TS/Xan pastes were prepared by heating at 92°C for 30 min for ensuring fully gelatinization of starch. The *G′* and *G″* of all TS/Xan pastes increased with decreasing temperature from 90 to 10°C (Fig. 5a-5d). The pastes of TS alone (Fig. 3.1.5a) showed *G″* slightly larger than *G′* but the opposite results were found for TS pastes containing Xan. At the same temperature, both *G′* and *G″* of TS pastes increased with increasing Xan content. However, the *G′* values were much higher than G″ especially in TS/Xan with mixing ratios of 9/1 and 8.5/1.5. The storage modulus *G′* of the pastes at 10°C increased with increasing Xan content (Fig. 3.1.5a-5d) with the values about 1, 5, 16 and 26 Pa for mixing ratios of TS/Xan = 10/0, 9.5/0.5, 9/1 and 8.5/1.5, respectively. The increase in G′ of TS/Xan on cooling was induced by the formation of a solid-like network structure. In addition, the *G′ ′* at 10ºC for Xan/TS samples is much larger than that for Xan alone and that for TS alone, indicating some synergistic interaction between TS and Xan at quiescent condition.

After lowering the temperature to 10°C, it was immediately raised from 10 to 90°C. Then, *G′* and *G″* of the pastes decreased on reheating. Once the network structure was formed on cooling, the structure was maintained at low temperatures. The *G′* values during reheating were higher than those during cooling, indicating freshly gelatinized paste forming initial inter-connected amylose network between the swollen granules and Xan after heating exhibiting less pronounced solid-like

properties than the structure network of retrograded amylopectin, amylose and Xan formed after a certain period of time. It is obvious that Xan plays an important role in creating the solid-like properties (Fig. 3.1.5) and enhances the viscosity of TS/Xan pastes (Fig. 3.1.3), suggesting that the rheological behaviors of 5% w/w TS on cooling and reheating could be modified with Xan.

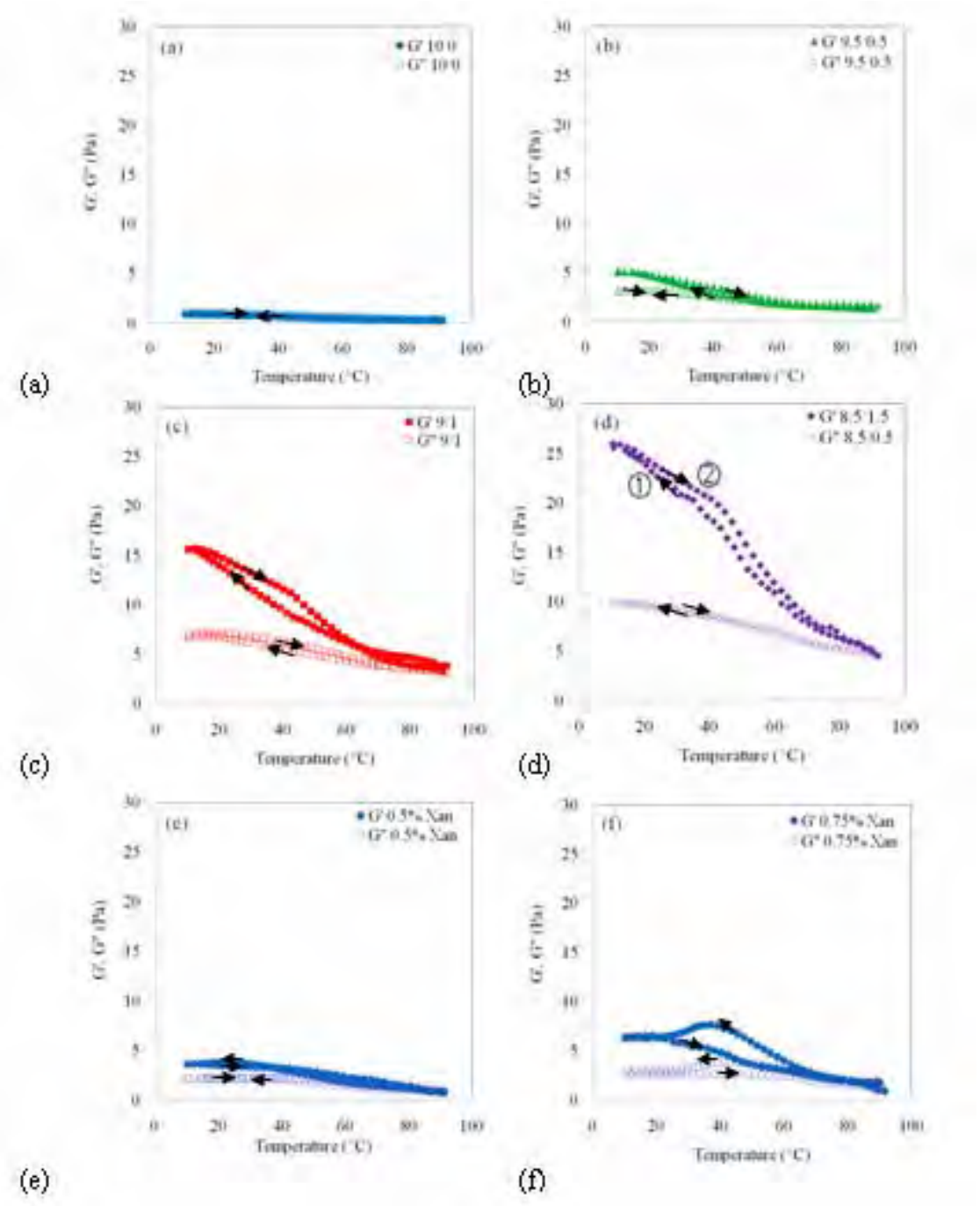


Fig. 3.1.5 Changes in *G′* and *G″* of 5% w/w TS/Xan pastes at different mixing ratios; 10/0 (a), 9.5/0.5 (b), 9/1 (c) and 8.5/1.5 (d) on ① cooling from 90 to 10ºC and ② subsequently heating from 10 to 90ºC. 0.5% Xan (e) and 0.75% Xan (f) were also measured. (frequency: 1 rad/s, scan rate at 1 ºC/min, 5% strain).

Xan dispersions (0.5% and 0.75%) were also prepared by heating at 92°C for 30 min for determining the changes of G' and G'' (Fig. 3.1.5e-5f) under the same cooling and heating condition as those of TS/Xan pastes. The G' and G'' of 0.5% and 0.75% Xan dispersions increased with decreasing temperatures from 90 to 10°C and showed the highest G' and G'' on cooling in the temperature range about 25 and 35-40°C, respectively. After lowering the temperature to 10°C, it was immediately raised from 10 to 90°C. The G' and G'' decreased when reheating from 10 to 90ºC. Both Xan dispersions (0.5 and 0.75%) exhibited solid like property (so-called weak gel bahaviour) more than liquid like property when dissolved in water due to $G' > G''$ on cooling and reheating (Morris, 2006). We observed the opposite phenomena from those of TS/Xan that both moduli of 0.75% Xan on cooling from 90 to 10°C were higher than those on reheating from 10 to 90°C. The change in Xan conformation on heating above transition temperatures results in melting of the ordered structure and the structure returns to its original state upon cooling is believed to the difference in solid like properties and depending on Xan concentration (Norton et al., 1984).

In food preparation, many starch based sauces or soups are kept for a certain time after heating (including gelatinization) and cooling before reheating. Then, in this section, storage time on storage and loss moduli at low temperature (10°C) before reheating was investigated for further application in food product. The prepared TS/Xan pastes at 90ºC were cooled from 90 to 10ºC, then held for 10 h at 10ºC, and reheated to 90ºC. The changes in G' upon cooling and reheating process of 5% w/w TS/Xan pastes at various ratios (10/0, 9.5/0.5, 9/1 and 8.5/1.5) were recorded and plotted by comparing the values with and without holding at 10ºC for 10 h (Fig. 6). The G' values of Xan alone (0.5 and 0.75%) were also investigated for comparison. For the case of holding all pastes at 10ºC for 10 h, the G' values of a paste of 5% w/w TS alone (Fig. 3.1.6a and 3.1.6b) did not change during holding period indicating that the network structure formation from leached amylose molecules was almost negligible. On the other hand, G' of TS/Xan pastes (9.5/0.5, 9/1, 8.5/1.5) increased conspicuously indicating that Xan enhanced the structural formation of TS pastes during holding at 10°C for 10 h (Fig. 3.1.6b). To observe the rate of network formation in TS/Xan pastes, changes in G' and G'' of all TS/Xan pastes and 0.5% and 0.75% Xan during holding at 10ºC as a function of time (10 h) are presented in Fig. 3.1.7. For individual polysaccharide, the G' and G'' of TS alone (10/0) was not changed and only slightly increased in the 0.5% and 0.75% Xan (Fig. 7). However, during holding the pastes of TS/Xan (9.5/0.5, 9/1 and 8.5/1.5) at 10ºC for 10 h, G' and G'' increased obviously and this increase was promoted with increasing Xan content (Fig. 3.1.7) suggesting amylose and amylose-Xan associations occurring during the holding time at 10ºC. Then, Xan contributes to network formation of TS pastes leading to enhance the solid-like properties or network structure formation obtained from amylose-Xan associations. However, types of starch and hydrocolloid influence on the structure formation of starch. Yoshimura et al. (1999) reported that xyloglucan inhibits the formation of three dimensional network structure of corn starch and the phase arrangement of the two components in the system is not bi-continuous arrangement leading to a composite gel formed by only one component (corn starch) without the contribution from xyloglucan to the network formation. These were in agreement with the previous report for the mixtures of Xan and locust bean gum (Craig et al., 1997).

After holding at 10ºC, the TS/Xan pastes were reheated to 90ºC at 1ºC/min heating rate. The larger hysteresis loops between cooling and reheating curves of TS/Xan pastes (9.5/0.5, 9/1, 8.5/1.5) were observed (Fig. 3.1.6a and 3.1.6b) compared with those observed without holding at 10ºC for 10 h. In addition, the loop areas of TS/Xan pastes increased with increasing Xan concentration confirming the enhancement of network structure formation obtained from amylose-Xan associations during aging.

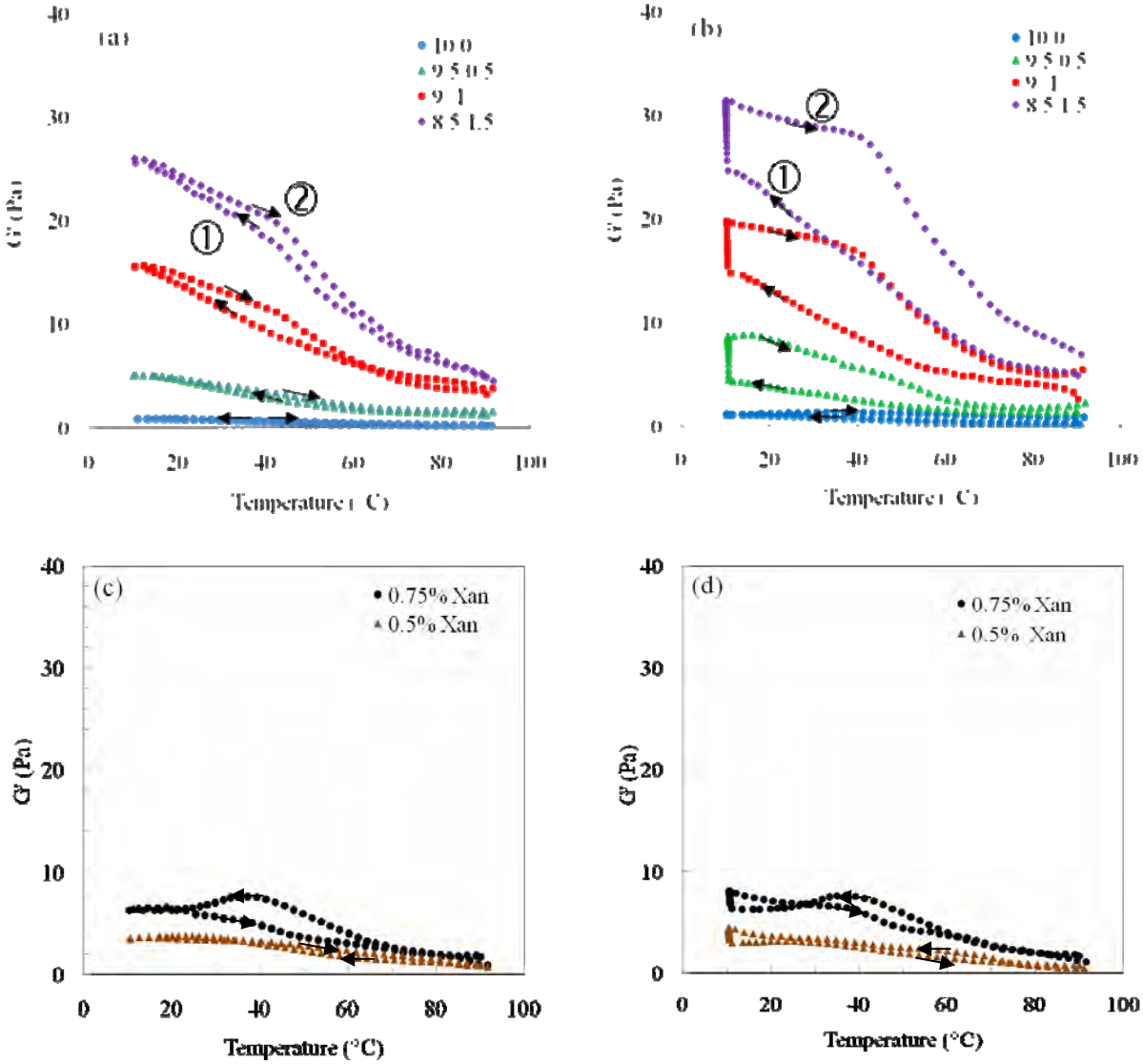


Fig. 3.1.6 Changes in *G′* on cooling and reheating process of 5% w/w TS/Xan pastes (10/0, 9.5/0.5, 9/1 and 8.5/1.5) (a, b) and 0.5% and 0.75% Xan (c, d). The cooling-heating cycle: (a, c) ① cooling from 90 to 10ºC and subsequently ② heating from 10 to 90ºC; and (b, d) ①cooling from 90 to 10ºC, holding at 10ºC for 10 h and ② reheating from 10 to 90ºC (frequency: 1 rad/s, scan rate at 1 ºC/min, 5% strain).

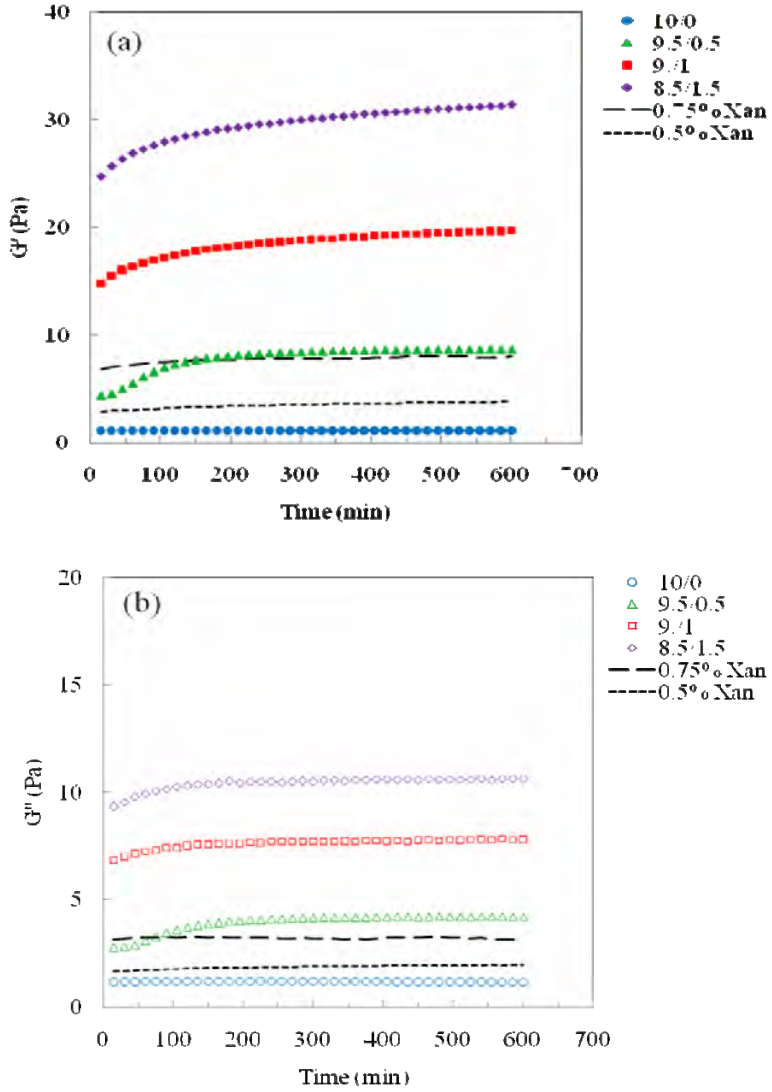


Fig. 3.1.7 Changes in G' (a) and G'' (b) of 5% w/w TS/Xan pastes (mixing ratios = 10/0, 9.5/0.5, 9/1 and 8.5/1.5) at 10ºC for 10 h after cooling to 10ºC from 90ºC. The pastes were heated at 92 ºC for 30 min followed by cooling to 10ºC at 1ºC/min and holding for 10 h (frequency: 1 rad/s, scan rate at 1 ºC/min, 5% strain).

In conclusion, the influence of Xan on pasting and rheological properties of TS was observed by increasing gelatinization temperature, peak and final viscosity, and breakdown but decreasing setback values. G' and G'' iors of TS dispersions and pastes depended on Xan concentration. Thermal stability of TS paste in terms of steady shear viscosity was obtained by adding Xan. Freshly prepared TS pastes containing Xan showed larger G' compared with TS pastes and G' increased with increasing Xan for both on cooling and heating. Holding TS/Xan pastes for 10 h after cooling to 10ºC enhanced the structure formation between leached amylose and amylose-Xan reassociation leading to much larger G' on reheating from 10 to 90ºC than those without holding time. Partial substitution of TS with Xan could improve pasting and rheological properties of TS dispersion and paste.

3.2 Thermal and rheological properties of tapioca starch gels with and without xanthan gum under cold storage

3.2.1 Gelatinization and retrogradation of TS and TS/Xan gels using differential scanning calorimetry

Differential scanning calorimetry (DSC) was used as a thermal analysis technique to determine the effect of Xan on the gelatinization and retrogradation of TS in this study. DSC thermograms of 25% w/w TS/Xan mixtures at different mixing ratios (10/0, 9.875/0.125, 9.75/0.25 and 9.5/0.5) showed single large endothermic DSC peaks (Fig. 3.2.1) on the first-run heating from 25°C to 110°C indicating the disintegration of the native starch structure (Zobel & Stephen, 1995). Dispersions of individual Xan (0.625% and 1.25%) alone with a concentration equivalent to those in the TS/Xan mixtures (= 9.75/0.25 and 9.5/0.5) and with a high concentration of 10% Xan did not show any exothermic or endothermic peak using the DSC equipment with a heating rate at 5ºC/min. The gelatinization temperatures of TS with and without Xan under the endothermic DSC peaks were about 56 to 76°C implying the temperatures required to disrupt the cluster of amylopectin chains (Taggart and Mitchell, 2009). The onset temperatures (T_o), peak temperatures (T_p), and conclusion temperatures (T_c) of all examined TS/Xan mixtures ranged from 56.4±0.4 to 57.1±0.4 °C, 65.9±0.1 to 66.8±0.1 °C and 74.7±0.2 to 75.8±0.1 °C, respectively, with increasing Xan content in the system from 0 to 1.25%. The gelatinization temperature slightly shifted to higher temperatures with an increasing Xan content ($p<0.05$) indicating that Xan alters the gelatinization temperatures of TS. Three possible mechanisms were expected. The first mechanism involved the interaction of the starch with Xan leading to a more stable structure (Yoshimura et al., 1996). The second mechanism involved an increase in the effective concentration of TS since the water required for gelatinization is taken by Xan substitution. The estimation of an increase in effective concentration of TS is not easy because it is difficult to estimate the amount of water taken by Xan. In addition, the gelatinization temperature was reported to be independent of the starch concentration below 35% (Biliaderis, et al., 1986; Yoshimura et al., 1996). Finally, the third mechanism involved lower heat transfer rates (Krüger et al., 2003) due to the higher viscosity contributed from the hydrocolloid. Since a high concentration of Xan (1.25%) in the TS/Xan mixture (mixing ratios = 9.5/0.5) was used, available water for gelatinization was reduced due to an increase in the hydration of Xan assumed to be located in the continuous phase leading to the higher pasting temperatures (Hirashima et al., 2005; Pongsawatmanit & Srijunthongsiri, 2008). The results showed a good agreement with those reported in previous studies of the system of TS and xyloglucan mixtures (Temsiripong et al., 2005), corn starch-konjac-glucomannan mixtures (Yoshimura et al., 1996), or corn starch-xyloglucan mixtures (Yoshimura et al., 1999). The difference in the gelatinization temperatures of TS alone from the present report and those of Temsiripong et al. (2005) was anticipated from the difference in the cassava cultivar used for the TS preparation and the time of conditions at harvest leading to the differences in the physicochemical properties of TS (Sriroth et al., 1999).

The gelatinization enthalpy of all TS and TS/Xan dispersions, indicating the energy required to gelatinize starch granules, was evaluated from the area under the single, large endothermic DSC curve observed during the first-run heating and defined as ΔH_1. The ΔH_1 values of all TS/Xan mixtures were similar to those of TS dispersion being about 13.3-13.5 J/g dry starch ($p>0.05$), suggesting that Xan did not associate synergistically with the TS molecules. Similar results were observed in the

case of corn starch mixed with xyloglucan (Yoshimura et al., 1999). The temperatures at half width ($\Delta T_{1/2}$) indicating the sharpness of the transition DSC thermogram and the ($T_p - T_o$) values of TS/Xan mixtures were similar to those of TS with the values ranging about 8.6-8.7°C and 9.4-9.7°C, respectively ($p>0.05$), suggesting that Xan (<1.25% w/w) exhibited no influence on the gelatinization process of TS for a total polysaccharide concentration of 25% w/w.

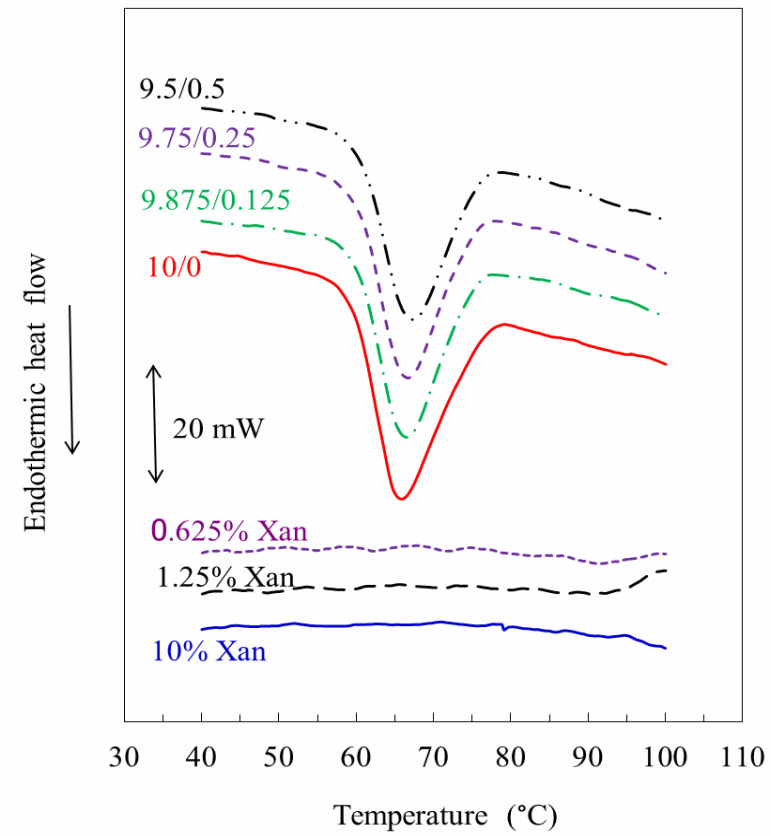


Fig. 3.2.1 Typical DSC thermograms of 25% w/w TS and TS/Xan mixtures at various mixing ratios (10/0, 9.875/0.125, 9.75/0.25 and 9.5/0.5). Thermograms of Xan dispersions (0.625, 1.25 and 10%) are also shown. Heating rate = 5ºC/min.

Starch granules consist of crystalline and amorphous regions. Gelatinization is a process in which the crystalline region in the starch granules is changed into an amorphous region. To investigate the extent of retrogradation in this study, the reheating DSC endothermic peak was used to estimate the disintegration of the ordered structures during retrogradation (Kohyama & Nishinari, 1991) by again reheating to 110°C the TS and TS/Xan pastes that had been kept at 5°C. Fig. 3.2.2 shows the typical reheating DSC curves of stored gelatinized TS and TS/Xan (= 9.5/0.5) gels with different storage times. The reheating DSC curves revealed smaller endothermic peaks compared with those of the first-run heating. The area under the peak increased with increasing storage time indicating a higher association extent of the amylose/amylopectin molecules under cold storage due to retrogradation.

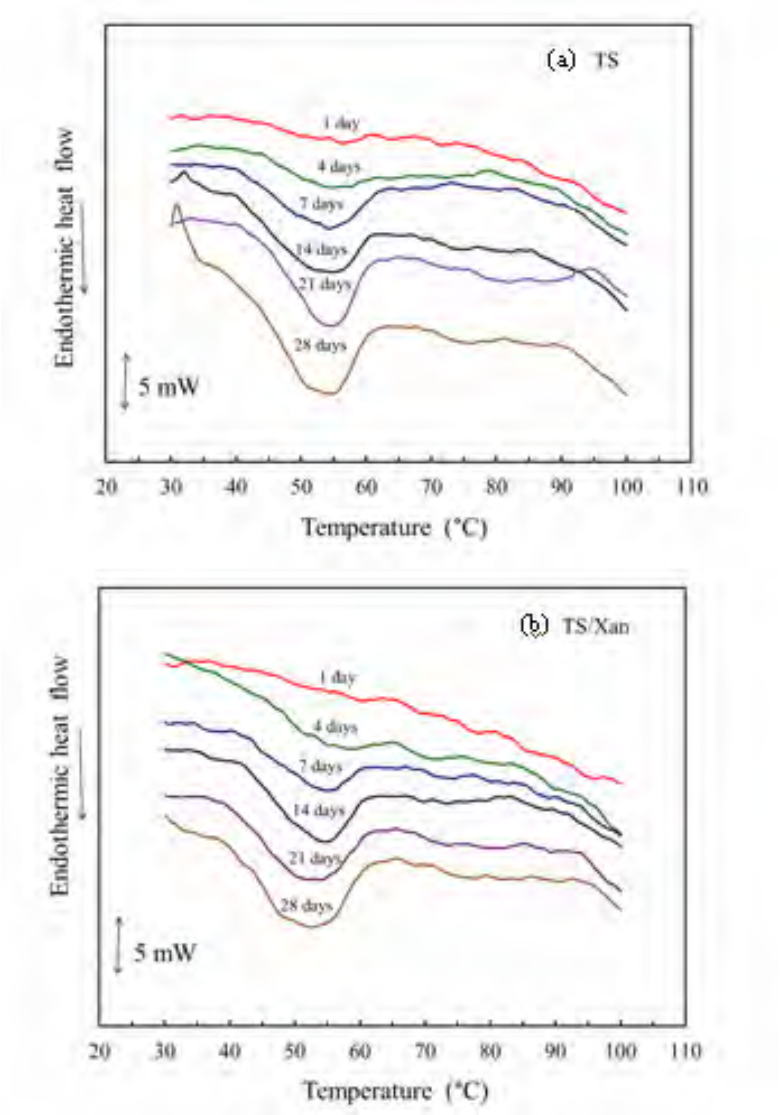


Fig. 3.2.**2** Typical reheating DSC thermograms of 25% w/w TS (a) and TS/Xan (mixing ratio = 9.5/0.5 with 23.75% TS and 1.25% Xan) (b) after storing at 5°C for 1, 4, 7, 14, 21, and 28 days and reheating to 110°C. Heating rate = 5°C/min.

In the present work, the term "retrogradation ratio" [= (ΔH_2)/(ΔH_1)] is used to express the extent of retrogradation in the sample (Kohyama & Nishinari, 1991). The gelatinization enthalpy (ΔH_1) was obtained from the first-run heating. The reheating enthalpy (ΔH_2) determined from the area under the peak of the second-run heating can be considered as the heat required for disintegration of the reassociated starch structure after retrogradation. At the same storage time after 7 days, the retrogradation ratio decreased with increasing Xan content in the TS system (Fig. 3.2.3a). The TS/Xan gels exhibited a lower rate of retrogradation than those of TS indicating Xan retarded the reassociation of amylose and amylopectin at low temperatures. The results revealed a good agreement with those previous reports on retrogradation in starch containing hydrocolloids. Substitution of a small portion of starch with either konjac glucomannan or xyloglucan increased the retrogradation ratios in the initial stage of storage but both hydrocolloids retarded an increase in the retrogradation ratio of the starch over longer storage (Temsiripong et al., 2005; Yoshimura et al., 1996;

Yoshimura et al., 1999). Xanthan is a branched, ionic polysaccharide, and the primary backbone consists of a repeating unit of 1,4-linked β-D-glucose as in cellulose. A trisaccharide side chain, α-D-mannose, β-D-glucuronic acid, and β-D-mannose is attached to every second glucose residue of the main chain. The side chain may play an important role in retarding the TS gel development during longer storage. The results suggest that Xan could retard the retrogradation of TS which is useful for application in chilling TS-based products. The first order reaction was applied in the present study to explain how fast the retrogradation process proceeds as a function of storage time as shown in Equation (3.2.1):

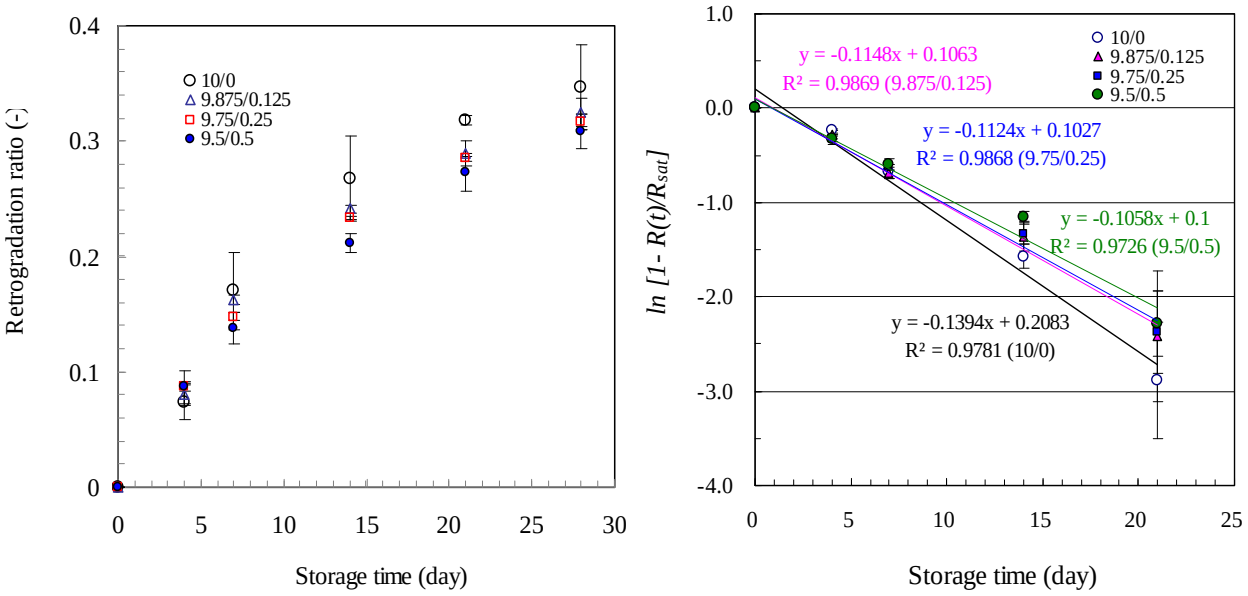
$$R(t) = R_{sat}(1 - e^{-k(t-t_0)}) \qquad (3.2.1)$$

When t_o = initial storage time = 0, Eq. (3.2.2) was derived from Eq. (3.2.1):

$$ln\,[1- R(t)/R_{sat}] = -k\,t \qquad (3.2.2)$$

Where $R(t)$ = the retrogradation ratio at storage time t, R_{sat} = the retrogradation ratio at the saturation value, k = the kinetic rate constant for the first order reaction (n = 1). Fig. 3.2.3b presents the first order reaction of retrogradation using Eq. (3.2.2) with R^2 >0.973 and the kinetic rate constants (k) of the retrogradation process obtained from the slopes of the plots. The retrogradation ratio value after 28 storage days was obtained from the regression equation using a polynomial equation (n = 2, R^2 >0.99, data not shown) and used as R_{sat} for each mixing ratio. When the rate constant (k) of each TS/Xan mixing ratio was plotted as a function of the Xan concentration (Fig. 3.2.3c), the results revealed that adding Xan retarded the retrogradation process of TS gel.

However, the onset temperature (T_o) values of the disintegration of reassociated starch structure after retrogradation of stored TS and TS/Xan pastes (Table 3.2.1) were about 36-48°C and lower than those of the first-run heating (56.4-57.1°C). The observed T_o values for both TS and TS/Xan gels from the second-run heating decreased with increasing storage time (Table 3.2.1, $p<0.05$) but the TS/Xan gels (especially with mixing ratio = 9.5/0.5) revealed higher T_o values for the same storage time. The results implied that the structure formed after a longer storage time was thermally unstable and could be disintegrated at lower temperatures in the second-run heating. In addition, the peak temperatures (T_p) of the second-run heating of TS with and without Xan were almost constant (52-56°C) and lower than those of the first-run heating (65.9-66.8°C). The conclusion temperatures (T_c) of the second-run heating (60-63°C) were also lower than those obtained from the first-run gelatinization (74.7-75.8°C). The ΔH_2 values for all TS and TS/Xan mixtures from the DSC second-run heating increased with increasing storage time confirming that reassociation of amylose/amylopectin molecules in the retrogradation process was enhanced during longer storage but was thermally unstable with lower values of T_o, T_p, and T_c. The ΔH_2 values of TS containing Xan were lower than those of TS alone indicating that Xan retarded the reassociation of amylose and amylopectin during storage.



(b)

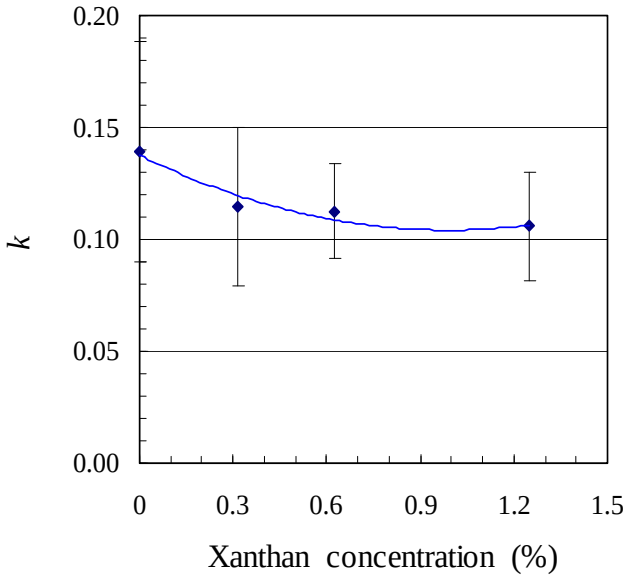


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Fig. 3.2.**3** Retrogradation ratio ($\Delta H_2/\Delta H_1$) of 25% w/w TS/Xan mixtures (mixing ratios = 10/0, 9.875/0.125, 9.75/0.25 and 9.5/0.5) as a function of storage time at 5°C (a) with DSC reheating rate at 5°C/min. The kinetic rate constants of the first order reaction were determined from the slope of plots (b) and are presented as a function of Xan concentration in the TS/Xan mixtures (c).

Table 3.2.1 DSC onset temperatures (To) (based on deviation from base line) and enthalpy of disintegration of ordered structure from the second-run heating of 25% w/w TS/Xan pastes (mixing ratios = 10/0, 9.875/0.125, 9.75/0.25, and 9.5/0.5) after storing for 1 to 28 days at 5°C and reheating to 110°C with heating rate 5°C/min

Storage time (day)	T_o (°C) of TS/Xan gels at mixing ratio				ΔH_2 (J/g dry starch) of TS/Xan gels			
	10/0	9.875/0.125	9.75/0.25	9.5/0.5	10/0	9.875/0.125	9.75/0.25	9.5/0.5
1	43.5 ± 0.6^{aB}	47.0 ± 0.7^{aA}	47.5 ± 1.0^{aA}	47.8 ± 0.6^{aA}	0.02 ± 0.01^{eA}	0.02 ± 0.00^{fAB}	0.02 ± 0.00^{dAB}	0.01 ± 0.00^{fB}
4	41.9 ± 1.1^{bC}	42.7 ± 0.7^{bC}	45.5 ± 0.6^{bAB}	47.4 ± 1.2^{aA}	0.99 ± 0.04^{dA}	1.06 ± 0.11^{eA}	1.15 ± 0.03^{eA}	1.16 ± 0.19^{eA}
7	40.0 ± 0.2^{cB}	41.3 ± 0.6^{cA}	41.4 ± 1.0^{cA}	41.5 ± 0.5^{bA}	2.28 ± 0.21^{cA}	2.13 ± 0.08^{dA}	1.99 ± 0.05^{dBC}	1.84 ± 0.16^{dC}
14	39.5 ± 0.8^{cB}	40.4 ± 0.8^{cdAB}	41.1 ± 0.9^{cA}	40.9 ± 1.0^{bA}	3.72 ± 0.44^{bA}	3.33 ± 0.26^{cAB}	3.21 ± 0.23^{cB}	2.98 ± 0.25^{cB}
21	39.0 ± 0.8^{cA}	39.6 ± 0.8^{dA}	39.2 ± 0.4^{dA}	39.5 ± 0.5^{cA}	4.40 ± 0.26^{aA}	3.98 ± 0.29^{bB}	3.86 ± 0.14^{bB}	3.79 ± 0.24^{bB}
28	36.3 ± 0.8^{dC}	38.0 ± 0.9^{eB}	38.2 ± 0.4^{dAB}	39.3 ± 0.5^{cA}	4.55 ± 0.44^{aA}	4.50 ± 0.14^{aA}	4.34 ± 0.09^{aA}	4.22 ± 0.20^{aA}

Mean ± standard deviation values of T_o and ΔH_2 (n = 4) within the same column followed by different lower case superscript letters ($^{a\text{-}f}$) for different storage time and within the same row by different upper case superscript letters ($^{A\text{-}B}$) for different TS/Xan mixing ratios are significantly different ($p < 0.05$) by Duncan's multiple range test

3.2.2 Dynamic viscoelasticity of cylindrical TS gels with and without Xan under cold storage

The TS/Xan mixture revealed a significant difference in gelatinization temperatures without any changes in the TS gelatinization enthalpy and transition peak indicating no interaction of TS and Xan during the disintegration of the native starch structure (Section 3.2.1). Therefore, the TS/Xan mixture (mixing ratio = 9.5/0.5 consisting of 23.75% TS and 1.25% Xan) was selected for evaluating changes in the rheological properties of TS gels with and without Xan during storage at 5°C.

The changes in the E' and E'' values of 25% w/w TS and TS/Xan cylindrical gels (20 mm diameter and 30 mm height) after storage at 5°C for 4, 7, and 14 days as a function of temperature are shown in Fig. 3.2.4. Cylindrical gels could not form and be taken out of the Teflon mold before storage. The temperature increased up to 55°C because the cylindrical shape of the TS/Xan gels was deformed when the temperature was raised to higher temperatures above 55°C.

Before starting the temperature cycling, the E' and E'' values of all TS gels with and without Xan substitution were recorded at 20°C. The E' values, indicating the solid-like properties, increased with increasing storage time (Fig. 3.2.5a) at 5°C. E'' values of TS gel also increased from 1350 to 5550 Pa for storage of 4 and 14 days, respectively, whereas those of TS/Xan (9.5/0.5) increased from 2250 to 4950 Pa. The E' values of the TS/Xan gels were lower than those of TS after 7 and 14 days of storage (Fig. 3.2.5a). The results suggested that partial substitution of TS with Xan could retard the retrogradation process of the TS gel. It was observed that the E' value of the TS/Xan gel was higher than that of the TS gel alone after storage for 4 days. The result was in good agreement with the DSC retrogadation result. The structure of Xan plays a dominant role in the structure contributing to solid-like properties in the TS gel in the initial stage of storage. For a longer storage time, the reassociation of amylose/amylopectin molecules on retrogradation contributed to the higher solid-like properties indicated by the higher E' (Fig. 3.2.5a) and ΔH_2 (Table 3.2.1) values.

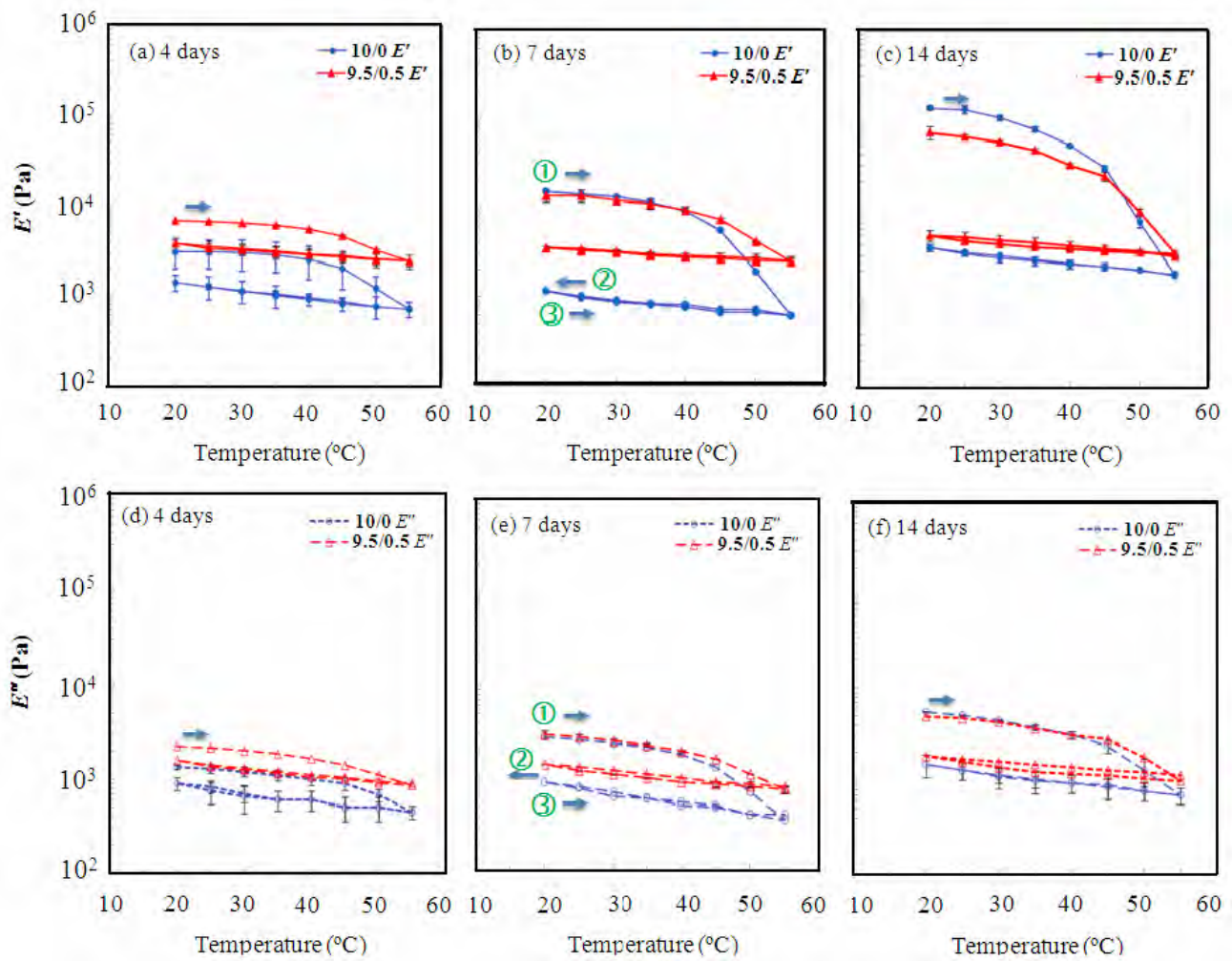


Fig. 3.2.4 Temperature dependence of storage (E') and loss (E'') Young's moduli of 25% w/w TS/Xan gels (10/0 and 9.5/0.5) (20 mm diameter and 30 mm height) stored at 5ºC for 4, 7, and 14 days. Frequency was set at 3 Hz, strain at 0.0033 and measurement temperature for E' and E'' values was done at 5°C intervals: ① increasing temperature of gels from 20 to 55°C, ② then decreasing from 55 to 20°C, and ③ finally increased again from 20 to 55°C. Values measured at 5°C intervals.

When the temperature cycling started, the E' and E'' values of the TS and TS/Xan gels decreased with increasing temperature on heating from 20 to 55°C (step ①, Fig. 3.2.4). The values increased slightly on cooling from 55 to 20°C (step ②) but decreased only slightly on reheating again from 20 to 55°C (step ③). However, the E' and E'' values at the end of cooling step ② (20°C) did not recover back to the initial values, indicating that the disintegrated structure cannot be recovered within a short time. While an initial stage of retrogradation is shown to be triggered by the gelation of amylose occurring within a short time, the restructuring of amylopectin takes a longer time (Miles et al, 1985). The present experimental time scale, measuring E' and E'' every 15 min on cooling, was much shorter for amylopectin molecules to recover

their initial structure before heating. As suggested by Nishinari et al. (1985) and Yoshimura et al. (1999), a strong cross linkage remained in the gels and weak cross linkages were broken by the thermal treatment. The main molecular forces stabilizing the network are secondary bonds such as hydrogen bonds (Nishinari et al., 1985). Therefore, the E' and E'' values on cooling (step ②) were lower than those on heating (step ①) revealing that a longer storage time is required to reestablish weak cross linkage in the TS and TS/Xan gels (Fig. 3.2.4). The retrogradation of starch molecules during storage proceeds in two crystallization stages: the rigidity of starch gels develops quickly by amylose gelation and the crystallinity develops slowly later by ordering of the amylopectin molecules (Miles et al., 1985). The long-term change was thermally reversible (Miles et al., 1985). Therefore, a strong cross linkage in the TS and TS/Xan gels was developed by the amylose gelation and a weak cross linkage was developed by amylopectin under storage at 5°C because after thermal treatment (heating-cooling) the E' and E'' values at 20°C were lower than those before starting heating (step ①) (Fig. 3.2.4). This conclusion was also revealed by Leloup et al. (1991) who reported that the main network of starch gels was formed by amylose with interspersing as an inactive polymeric filler by amylopectin. An increase in the elastic modulus after longer storage (7 and 14 days) is expected from the contribution of the amylopectin molecules in the gel formation since the initial value of the elastic modulus could not be recovered in a short time during the measurement on cooling.

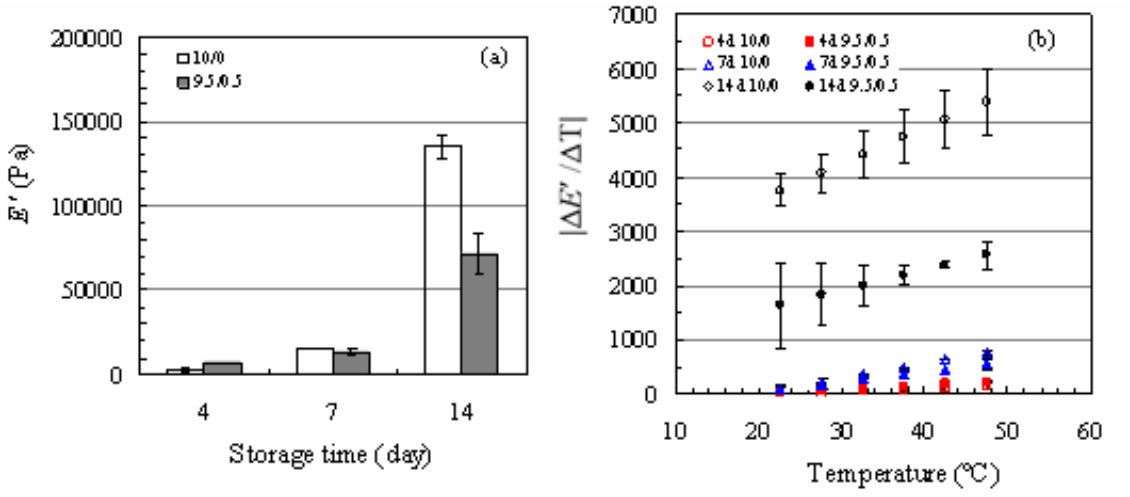


Fig. 3.2.5 Storage Young's moduli (E') (a) of 25% w/w TS/Xan gels (10/0 and 9.5/0.5) as a function of storage time before thermal treatment. The E' value measured at 20°C. Changes in $|\Delta E'/\Delta T|$ (the absolute value of $\Delta E'/\Delta T$) (slopes of Figs. 4a-c) as a function of increasing temperature in step ① of Figs. 4a-c for TS and TS/Xan gels kept for 4, 7, and 14 days, respectively (b).

Temperature dependence of $|\Delta E'/\Delta T|$ for TS and TS/Xan gels stored for 4, 7, and 14 days was plotted (Fig. 3.2.5b). The value of $\Delta E'/\Delta T = dE'/dT$ as a function of temperature on heating in step ① (Figs. 3.2.4a-4c) was calculated using E' value from the polynomial equation (n = 2) fitting of Fig. 4 (data not shown) to obtain the

smoothed plot for the differentiation operation (Nishinari et al., 1984). A longer storage time enhanced $|\Delta E'/\Delta T|$, indicating that the structure formation induced by the amylopectin association during longer storage time was thermally weaker which is in good agreement with the lower T_o value from the DSC determination (Table 3.2.1). The $|\Delta E'/\Delta T|$ values of the TS/Xan gels were lower than those of the TS gels after longer storage (7 and 14 days), indicating the contribution of Xan to the thermal stability of the systems.

The E' and E'' values of TS gel stored for 14 days (Figs. 3.2.4c, 4f) after heating in step ① were higher than those kept for 4 and 7 days (Figs. 3.2.4a-b, Figs. 4d-e). In addition, adding Xan in the TS gels retarded retrogradation of TS with a lower E' value from 20 to 45°C in step ① (Fig. 3.2.4c) and created higher thermal stability in TS gels with higher E' values than those of TS gels alone from cooling in step ② and reheating again from 20 to 55°C in step ③ (Fig. 3.2.4). The results were different with mixed gels of corn starch/konjac-glucomannan (Yoshimura et al., 1996) and corn starch/xyloglucan (Yoshimura et al., 1999) in which the E' and E'' values of starch/hydrocolloid gels were higher than for starch alone for all storage times as was expected from the difference in the starch type.

3.2.3 Changes in compression behaviors of cylindrical TS gels with and without Xan kept in cold storage

The changes in compression behaviors for 25% w/w TS and TS/Xan (9.5/0.5) cylindrical gels (20 mm diameter and 20 mm height) were evaluated. It was impossible to compress the TS and TS/Xan gels stored at 5ºC for 1-3 days because the cylindrical shape of the gel was not retained for the compression test. However, the TS/Xan gel kept for 4 days still showed small shrinkages after removal from the cylindrical Teflon mold. The stress-strain curves of the cylindrical TS and TS/Xan gels (Figs. 3.2.6a and 3.2.6b) were calculated from a force-deformation curve. The breaking stress ($\sigma_B = F_B/A_o$) and breaking strain ($\varepsilon_B = \Delta h_B/h_0$) of the TS/Xan gels (10/0 and 9.5/0.5) stored at 5°C for 4 days could not be calculated because the gel was not broken clearly but the gels were deformed with compression. Both the TS and TS/Xan gels showed smaller strain and larger stress at the breaking point with increasing storage time (Figs. 3.2.6a and 3.2.6b) (Keetels et al., 1996; Yoshimura et al., 1996).

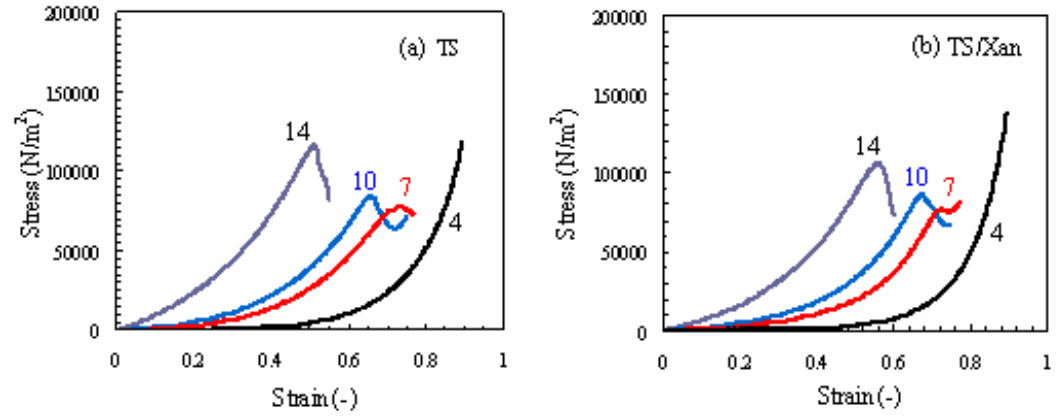


Fig. 3.2.**6** Typical stress-strain curve of 25% w/w TS (a) and TS/Xan (9.5/0.5) (b) cylindrical gels (20 mm diameter and 20 mm height) kept at 5°C for 4, 7, 10, and 14 days. Compression at 30 mm/min with a 50-mm diameter probe and at 25±2°C.

The σ_B values of the TS and TS/Xan gels increased with storage time but the TS/Xan gel revealed a lower value than that of the TS gel kept for 14 days. However, during longer storage times, the values of σ_B of the TS/Xan gels increased at a slower rate than those of the TS gel kept at 5°C (Fig. 3.2.7a). The σ_B value at the breaking point increased with a concurrent reduction in the value of ε_B with the storage time of the TS and TS/Xan gels (Fig 3.2.7b). The value of ε_B of the TS/Xan gel kept for 14 days was higher than that of the TS gel. The TS gels kept for longer storage times revealed a firmer and more brittle appearance than that of TS/Xan which showed good agreement with the results of higher σ_B and lower ε_B values for the TS gel than those of the TS/Xan gel. The results suggested that Xan retards retrogradation in TS gels from the amylose and amylopectin molecule association in the gel.

When Young's modulus (E) was estimated from an initial slope of the stress-strain plot ($E = \sigma/\varepsilon$ at small ε), the E values of the TS and TS/Xan gels increased with increasing storage time (Fig. 3.2.7c). As expected, the elastically active network chains were increased by the longer storage time with increasing E values (Lee, Kim, & Nishinari, 1998). The E values of the TS/Xan gels were higher than those of the TS gel in the initial stage of storage. After a longer storage time (14 days), the E values of the TS gels decreased with Xan substitution (Fig. 3.2.7c). The results suggested that Xan could retard the retrogradation of TS gels that had been kept for a longer time under cold storage. The E results corresponded well with those found in the complex Young's modulus test of cylindrical gels.

Since the changes in starch gel under cold storage are related to the retrogradation process, E was plotted as a function of the retrogradation ratio determined from the thermal and rheological properties of TS gels with and without Xan (Fig. 3.2.7d). The values of the retrogradation ratio were obtained from the regression equations of a polynomial fitting ($n = 2$) of Fig. 3.2.3 for the TS/Xan gels (mixing ratio = 10/0, 9.5/0.5). The results showed that, at the same retrogradation ratio, Xan addition enhanced the E value of the TS gels. The exponential equation was used to establish the relationship between E and the retrogradation ratio (Fig. 3.2.7d). The change in the E value of the TS gel (29.2) as a function of the retrogradation ratio was higher than that of the TS/Xan system (21.4). The equations can be used to estimate the E values of the TS and TS/Xan gels from the retrogradation ratio under cold storage conditions.

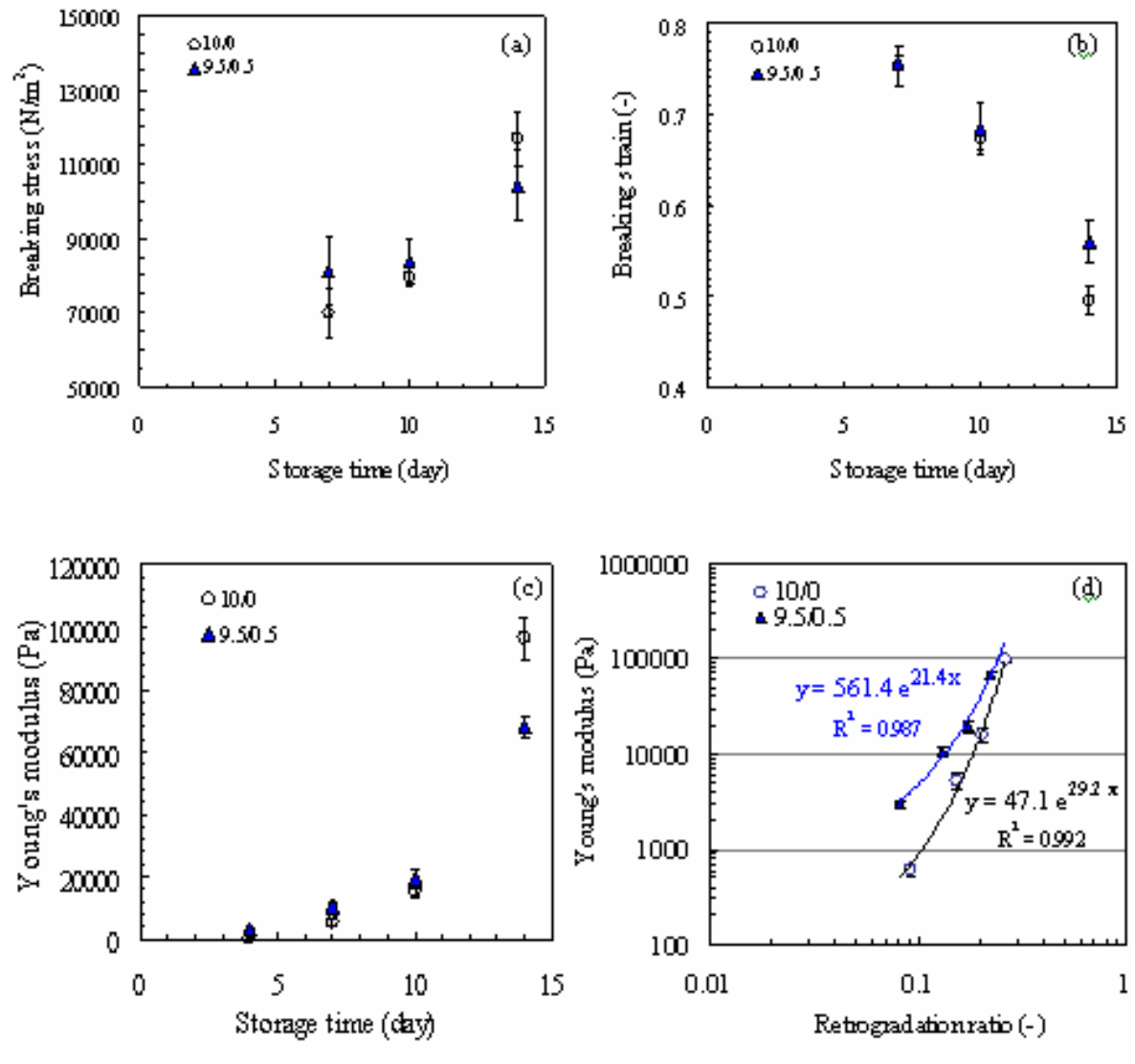


Fig. 3.2.7 Breaking stress (a), breaking strain (b) and Young's modulus (c) of 25% w/w gels with and without Xan (mixing ratio = 10/0 and 9.5/0.5) as a function of storage time. Storage temperature = 5ºC, measurement temperature = 25±2ºC and crosshead speed = 30 mm/min. The relationship between Young's modulus and retrogradation ratio from DSC is also shown (d).

3.3 Effect of heating time on the quality of tapioca starch and xanthan gum mixture

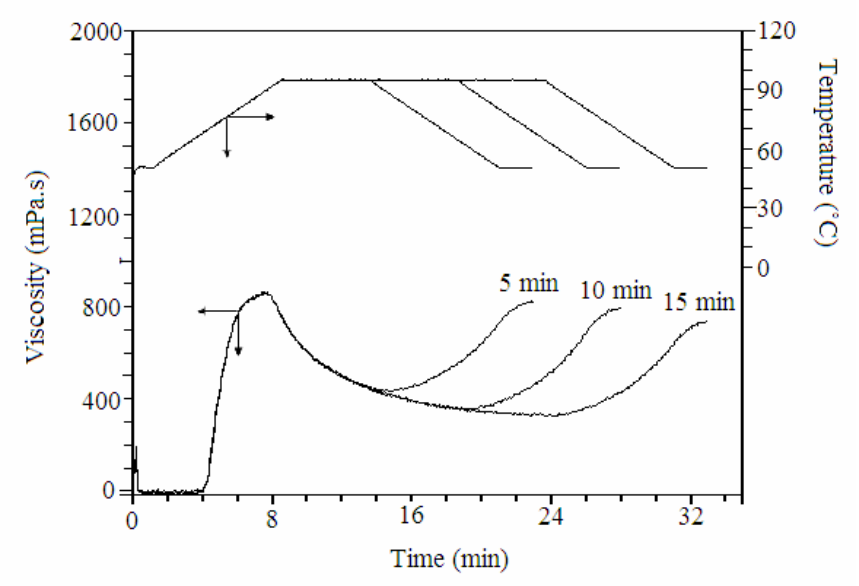
3.3.3 Pasting properties from rapid visco-analyser measurement

The rapid visco-analyser was used to investigate the effect of thermal treatment under constant shear on pasting properties of TS and TS/Xan (mixing ratio = 9/1) mixtures with heating at 95°C for 5-15 min. The pasting profiles of 5% w/w TS and TS/Xan mixtures at pH 7 were shown in Fig. 3.3.3. The profiles showed that the viscosities of the mixtures from initial pasting to peak (the highest apparent viscosity obtained) were almost identical among different holding time. Pasting temperatures of TS and TS/Xan mixtures with different heating time (5, 10 and 15 min) at 95°C were 68.6-69.3°C and 72.4-73°C whereas peak viscosities from these three heating times were about 851-861 mPa.s and 1476-1495 mPa.s for TS and TS/Xan mixtures, respectively. Pasting temperatures and peak viscosities for TS and TS/Xan mixtures compared within different heating time at 95°C were not different significantly ($p>0.05$) as expected due to the same heating profile for the first 13.5 min of each total RVA time. However, pasting temperatures and peak viscosities of TS/Xan mixtures were higher than those of TS alone due to the contribution of Xan in the continuous phase of the mixtures (Temsiripong *et al.*, 2005). When the system was maintained at 95°C, the mixtures were subjected to both thermal and shear stresses, leading to further disruption of the starch granules and leaching out of starch molecules. A greater decrease in viscosity was observed in the systems with higher holding time at 95°C. The breakdown values of TS and TS/Xan mixtures increased with heating time (Fig. 3.3.2a, $p<0.05$). The higher increase in breakdown of TS/Xan suspensions under the shear forces indicating the formed aggregates of xanthan molecules in the pastes through hydrogen bonding and polymer entanglement were disrupted with increasing heating time (Sworn, 2000; Pongsawatmanit and Srijunthongsiri, 2008).

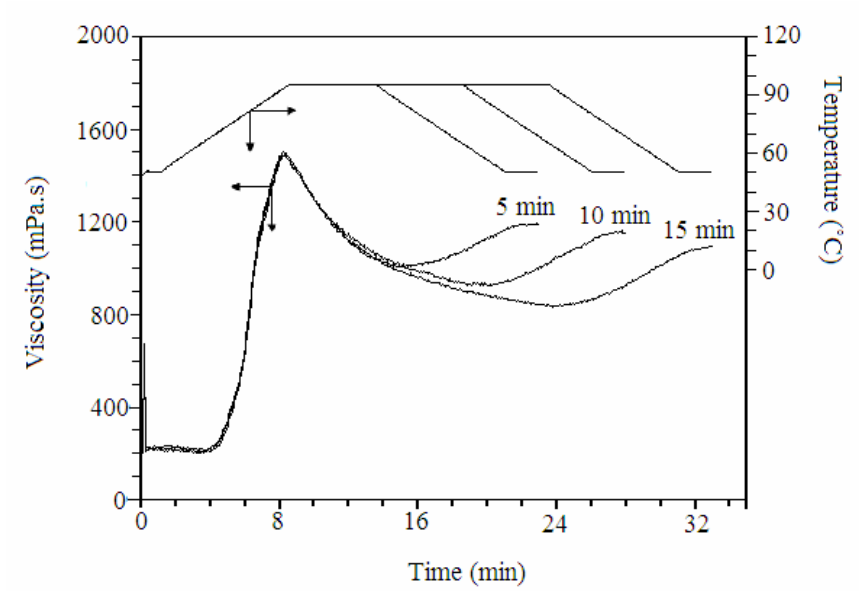
Final viscosities (the viscosity values at the end of RVA measurement) of TS/Xan were higher than those of TS pastes (Fig. 3.3.2b, $p<0.05$). The final viscosities of both TS and TS/Xan systems decreased with heating time from 5 min to 10 and 15 min ($p < 0.05$). The setback value of TS and TS/Xan pastes increased with increasing the holding time at 95°C from 5 min to 10 and 15 min (Fig. 3.3.2c, $p<0.05$) but addition of Xan resulted in a significant decrease in setback of TS/Xan pastes ($p<0.05$) compared with only TS pastes at the same holding time at 95°C. Usually, high setback is associated with syneresis during freeze–thaw cycles and is used to indicate the extent of short-term retrogradation (Pongsawatmanit and Srijunthongsiri, 2008). These results suggest that short-term retrogradation of TS/Xan mixtures under thermal stress can be depressed by Xan.

Considering the gelatinized TS or TS/Xan mixtures, the pastes were subjected to both thermal and shear stresses at holding temperature (95˚C) from 5, 10 and 15 min according to the RVA time at 13.5, 18.5 and 23.5 min, respectively. RVA profiles (Fig. 3.3.3) exhibited the lower viscosity with heating time indicated the higher breakdown of the starch molecules. We observed that the rate of starch breakdown at initial heating time at 95˚C was much higher than those heated after 3.5 min (Fig. 3.3.3). After plotting the viscosity of TS and TS/Xan pastes from all 3 heating time treatments (Fig. 3.3.3a), viscosity values of both TS and TS/Xan mixtures during heating at 95˚C from 3.5 min to 15 min were used to calculate the reaction rate of starch degradation under thermal and shear stresses. The kinetic of degradation exhibited pseudo-first- order reaction with respect to heating time. The plot indicates that TS pastes alone was more dependent on the heating time than those

from TS/Xan pastes evidenced by the reaction rate of TS and TS/Xan being 0.035 and 0.023, respectively (Fig. 3.3.3b). The results confirm the better thermal stability of Xan contributing to TS pastes



(a)



(b)

Fig. 3.3.3 RVA pasting profiles of 5% w/w TS (a) and TS/Xan = 9/1 (b) with pH 7 at different holding time at 95˚C (5, 10 and 15 min)

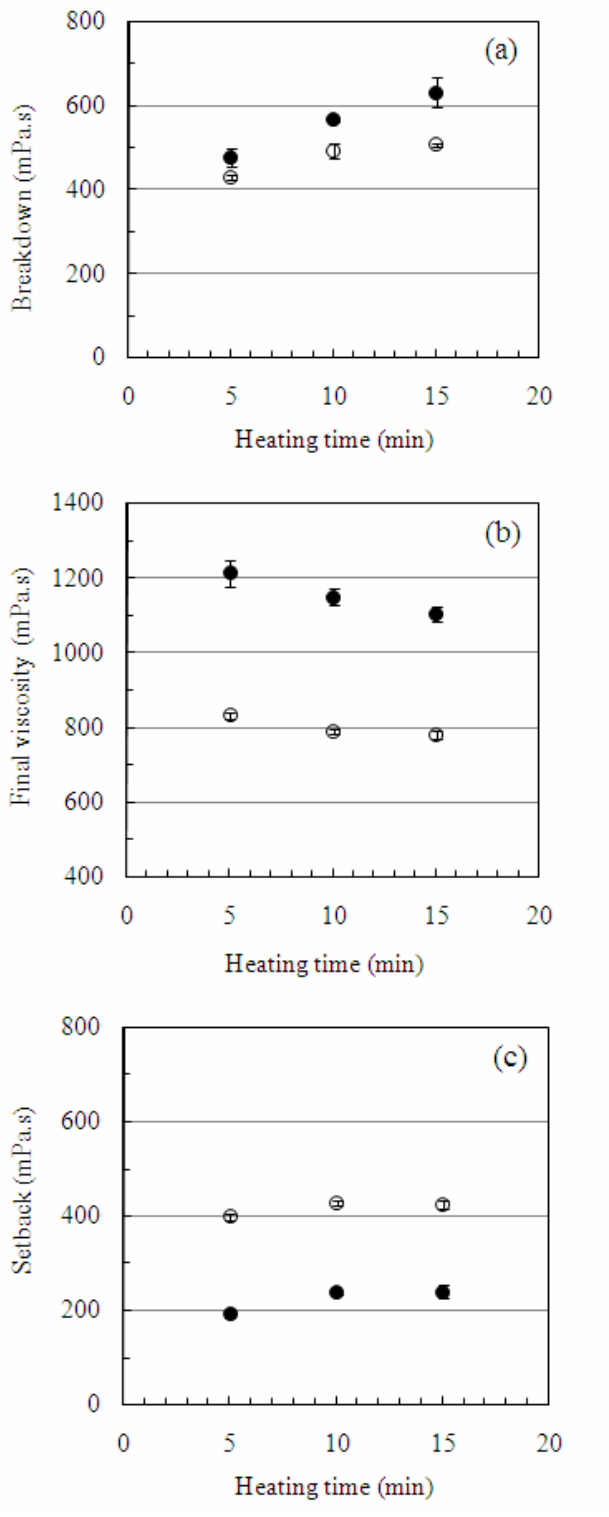
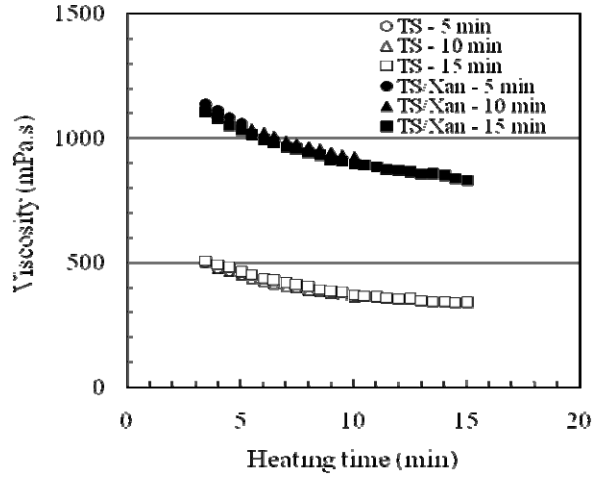
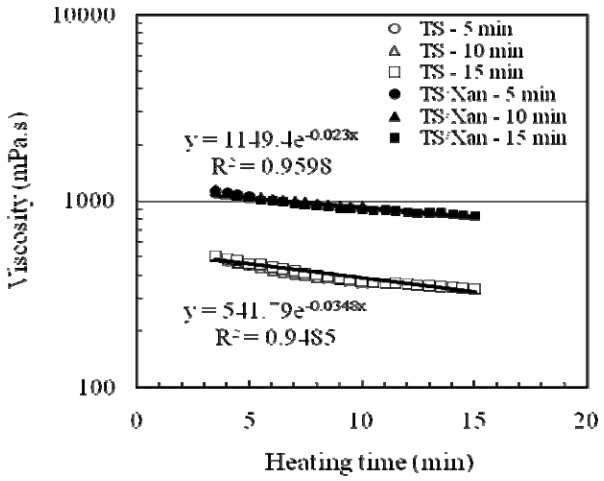


Fig. 3.3.2 Breakdown (a), final viscosity (b) and setback (c) of TS (○) and TS/Xan (●) as a function of RVA heating time at 95°C.



(a)

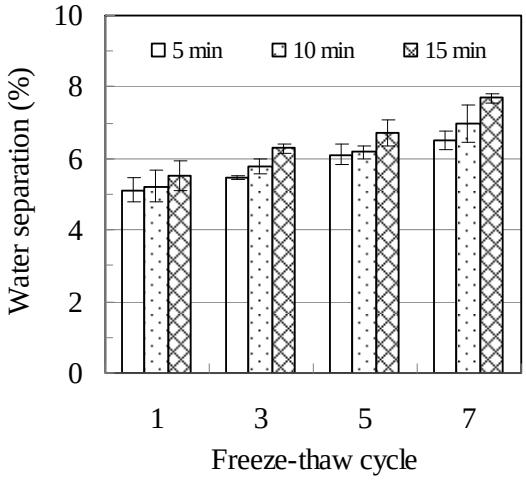


(b)

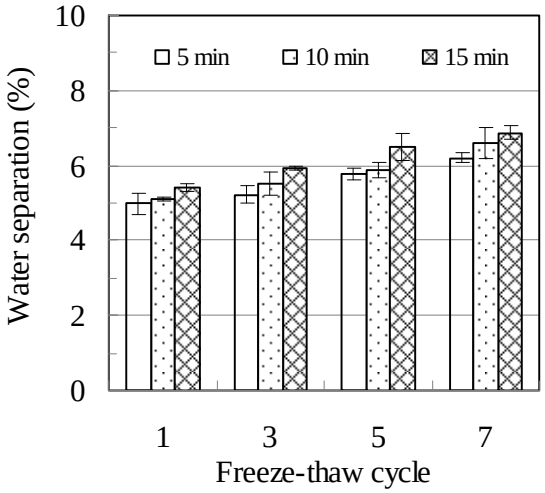
Fig. 3.3.3 Viscosity (a) and first order plot of viscosity (b) of 5% TS (open symbol) and TS/Xan (filled symbol) pastes as a function of RVA heating time at 95˚C

3.3.2 Freeze-thaw stability measurement

Freeze-thaw stability is important in the frozen food industry. It is the ability of a product to maintain its composition and integrity after repeated cycles between freezing and thawing. Thawed liquid within the product causes larger ice crystals after refreezing leading to the breakdown of a product structure. Water separation of TS and TS/Xan pastes increased with freeze-thaw cycle and heating time (Fig. 3.3.4), confirming the higher breakdown of starch molecules (Fig. 3.3.2) in the systems. However, TS pastes containing Xan exhibited the lower water separation ($p<0.05$) compared with those of TS pastes alone. The increase in water separation as a function of heating time from TS and TS/Xan pastes was characterized in terms of the difference values of water separation (%) from thawed pastes after repeated freeze–thaw cycle 7 and cycle 1 as ($W_7 - W_1$). The higher water separations at cycle 7 compared to cycle 1 ($W_7 - W_1$) of TS pastes were much higher than those of TS/Xan pastes with increasing RVA heating time at 95°C (Fig. 3.3.5). The change in ($W_7 - W_1$) of TS pastes (~0.076) as a function of heating time was higher than that of TS/Xan pastes (~0.0265). The results again confirm the better freeze–thaw stability of Xan contributing to TS pastes.



(a)



(b)

Fig. 3.3.4 Water separation of 5% w/w gelatinized TS (a) and TS/Xan = 9/1 (b) with pH 7 at different holding time at 95˚C (5, 10 and 15 min)

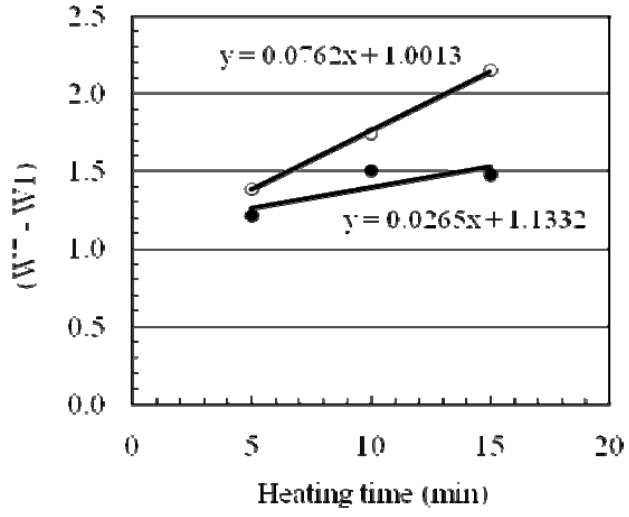


Fig. 3.3.5 The difference of water separation obtained from freeze-thaw cycle 7 and 1 of 5% TS (○) and TS/Xan (●) pastes as a function of RVA heating time.

3.4 Influence of sucrose on thermal and pasting properties of tapioca starch and xanthan gum mixtures

3.4.1 Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used as a thermal analysis technique and applied to determine the effect of sucrose on the gelatinization of starch in this study. Total polysaccharide concentration at 5% w/w of TS and Xan dispersions (at mixing ratios = 10/0, 9.5/0.5 and 9/1) containing 0 to 30% sucrose was prepared to investigate the changes in gelatinization process of the mixtures. The concentrations of Xan used in the study were ranged from 0 to 0.5% due to the common concentration range applied in food products (Sharma et al., 2006). Sucrose concentrations (0 to 30%) in TS/Xan mixtures were investigated for further application in real products such as chilli dipping sauces or plum sauces containing up to 30% sucrose. A single endothermic peak was observed (Fig. 3.4.1) due to the disintegration of the native starch structure at high water content (more than 60% w/w) (Biliaderis, 1990; Aee et al., 1998). Glass transition of the amorphous regions of starch granule that surround the crystalline zones to a mobile rubbery state, at a glass transition temperature (T_g), precedes gelatinization during heating have been reported (Biliaderis et al., 1986; Jacobs and Delcour, 1998). However, no change in heat capacity could be observed in the region that preceded the gelatinization endotherm from this study. The result is in agreement with the report of Ferrero and Zaritzky (2000).

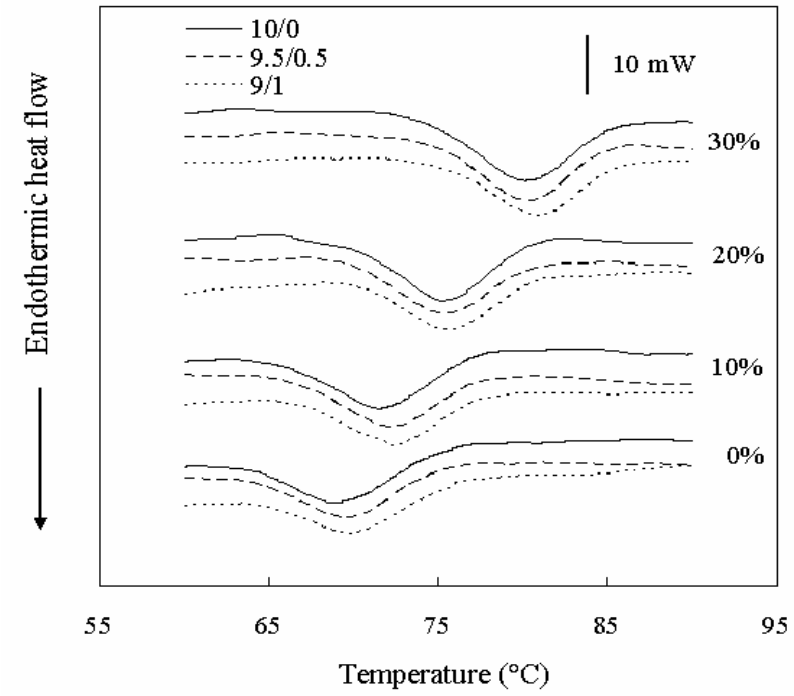


Fig. 3.4.1 DSC thermograms of 5% w/w TS and TS/Xan mixtures at various mixing ratios (10/0, 9.5/0.5 and 9/1) containing sucrose (0 to 30%).

The onset, peak and conclusion temperatures (T_o, T_p and T_c) of all TS/Xan dispersions without sucrose were about 64°C, 69°C and 74°C, respectively. The gelatinization temperatures (T_o, T_p and T_c) shifted significantly to higher temperatures with increasing sucrose concentration for all mixing ratios of TS and Xan ($p<0.05$, Table 3.4.1) due to the anti-plasticizing effect because the presence of sucrose

dissolving in the continuous phase enhances higher viscosity accompanied with the lower water mobility in the dispersion (Pongsawatmanit et al., 2007; Pongsawatmanit et al., 2002; Kohyama and Nishinari, 1991). However, at the same sucrose concentration, Xan did not affect each gelatinization temperature (T_o, T_p, T_c) of the TS/Xan dispersions ($p>0.05$, Table 3.4.1). These results are in agreement with those reported from previous studies of TS –xyloglucan mixtures (Pongsawatmanit et al., 2007) and maize starch – 0.5% guar gum (Tester and Sommerville, 2003).

Table 3.4.**1** Effect of sucrose on gelatinization temperatures and enthalpy of 5% w/w TS and TS/Xan mixtures.

DSC Gelatinization parameters	TS/Xan mixtures	Sucrose concentration (%)			
		0	10	20	30
T_o (°C)	10/0	63.7 ± 0.1^{Ad}	66.3 ± 0.1^{Ac}	69.7 ± 0.4^{Ab}	74.5 ± 0.8^{Aa}
	9.5/0.5	63.9 ± 0.1^{Ad}	66.6 ± 0.2^{Ac}	69.7 ± 0.2^{Ab}	74.8 ± 0.6^{Aa}
	9/1	64.0 ± 0.4^{Ad}	66.6 ± 0.3^{Ac}	70.2 ± 0.4^{Ab}	75.1 ± 0.3^{Aa}
T_p (°C)	10/0	69.2 ± 0.2^{Ad}	71.8 ± 0.1^{Ac}	75.3 ± 0.5^{Ab}	80.2 ± 0.4^{Aa}
	9.5/0.5	69.4 ± 0.2^{Ad}	71.8 ± 0.2^{Ac}	75.5 ± 0.3^{Ab}	80.3 ± 0.3^{Aa}
	9/1	69.5 ± 0.2^{Ad}	72.0 ± 0.1^{Ac}	75.8 ± 0.2^{Ab}	80.6 ± 0.1^{Aa}
T_c (°C)	10/0	74.6 ± 0.4^{Ad}	76.8 ± 0.3^{Ac}	80.3 ± 0.3^{Ab}	85.0 ± 0.1^{Aa}
	9.5/0.5	74.4 ± 0.2^{Ad}	76.6 ± 0.1^{Ac}	80.2 ± 0.4^{Ab}	84.8 ± 0.2^{Aa}
	9/1	74.0 ± 0.7^{Ad}	76.8 ± 0.3^{Ac}	80.4 ± 0.3^{Ab}	85.0 ± 0.4^{Aa}
ΔH (J/g dry starch)	10/0	13.6 ± 0.6^{Ac}	15.1 ± 0.1^{Ab}	16.2 ± 0.4^{Aa}	16.9 ± 0.5^{Aa}
	9.5/0.5	12.6 ± 0.2^{Bc}	13.8 ± 0.3^{Bb}	15.7 ± 0.8^{Aa}	15.9 ± 0.5^{Ba}
	9/1	12.5 ± 0.3^{Bb}	13.0 ± 0.9^{Bb}	15.0 ± 0.5^{Ba}	15.8 ± 0.2^{Ba}

Mean ± standard deviation values followed by different small and capital letters are significantly different ($p<0.05$) by Duncan's multiple range test within the same row (sucrose effect) and column (TS/Xan effect for each DSC parameter), respectively.

Endothermic enthalpy (ΔH) values for the gelatinization of TS/Xan/sucrose mixtures were evaluated from the areas under the single endothermic curves during heating. The transition enthalpy of TS dispersion indicated that the quantity of energy required to gelatinize the starch was 13.6 J/g dry starch; gelatinization enthalpies of TS reported in the literature are 12.4 J/g (Hung and Morita, 2005) and 16.0 J/g (Pongsawatmanit et al., 2007). Difference in gelatinization enthalpy is expected from differences in cassava cultivar and harvesting time which lead to the difference in physicochemical properties of TS (Sriroth et al., 1999). The gelatinization enthalpy values of TS alone increased from 13.6 to 16.9 J/g dry starch for the dispersions containing sucrose from 0 to 30% ($p<0.05$, Table 3.4.1), respectively. No exothermic or endothermic peak of Xan dispersions with and without sucrose was observed (data not shown). The enthalpy of 5% w/w TS/Xan increased with increasing sucrose concentration for each mixing ratio. At the same sucrose concentration, the enthalpy of TS showed a significant decrease with partial substitutions of TS with Xan ($p<0.05$, Table 3.4.1).

3.4.2 RVA pasting properties

RVA is used to observe the changes in pasting properties of starch during heating and cooling processes affecting the quality of final starch-based products. An addition of hydrocolloids and sugars can alter the pasting properties of starch. Pasting profiles of 5% w/w TS/Xan mixtures (mixing ratios = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) containing sucrose (0 to 30%) were investigated during RVA experiment. A strong influence of sucrose on pasting properties for each TS/Xan mixing ratio was observed as shown in the selected typical RVA pasting profiles of 5% w/w TS and TS/Xan (mixing ratio = 9/1) (Fig. 3.4.2). RVA pasting properties are related to the gelatinization and short-term retrogradation of starch-based samples during heating and cooling since no peak was observed in the mixture of 1% Xan containing 30% sucrose. Pearson's correlation coefficients © were analyzed to quantify the relationship between sucrose and RVA parameters. The r values revealed significant positive correlations (p<0.05, Table 3.4.2). Pasting temperatures of TS/Xan pastes increased significantly with sucrose concentration (p<0.05, Table 3.4.3). These results are in agreement with the DSC gelatinization temperatures (T_o, T_p and T_c) and suggest that sucrose reduces the available water in the system. The anti-plasticizing effect of sucrose leads to a lower amount of amylose leaching and causes a retardation in gelatinization of TS and TS/Xan mixtures (Ahmad and Williams, 1999; Kohyama and Nishinari, 1991) leading to higher pasting temperatures (Table 3) (Hirashima et al., 2005). Sucrose may play an important role in the inhibition of hydration for starch granules or the non-starch polysaccharide fraction (Yoshimura et al., 1996). Therefore, in systems containing higher concentrations of sugar, the competition between sucrose and Xan to be hydrated by water in the 5% w/w of total polysaccharides may lead to an increase in pasting temperatures of TS/Xan mixtures from 72-78°C to 82-90°C with increasing sucrose concentration from 0 to 30%, respectively (Table 3.4.3).

The viscosity at the peak of the RVA profile (peak viscosity) is considered as the equilibrium point between swelling and rupture of starch granules during heating, while final viscosity is the viscosity after cooling at the end of RVA experiment (23 min for this study). The addition of sucrose enhanced both the peak and final viscosities of the gum-starch pastes (p<0.05) and had a much greater influence than Xan substitution (Figs. 3.4.3a and 3.4.3b), indicating that the synergistic effect of sucrose and TS or TS/Xan systems is dominant.

After TS or TS/Xan dispersions were gelatinized, the pastes were subjected to both thermal and shear stresses at the holding temperature (95°C). Further disruption of starch granules and leaching out of starch molecules caused a decrease in viscosity. The resultant drop in viscosity from peak to a holding strength (minimum viscosity after the peak, occurring around the beginning of RVA cooling stage) was determined and defined as breakdown. Therefore, the breakdown measures the susceptibility of gelatinized starch to disintegration due to the loss of starch granule integrity and subsequent disruption, leading to a reduction of the paste viscosity (Christianson et al., 1981; Pongsawatmanit et al., 2007). The breakdown of TS/Xan pastes revealed almost constant values with increasing Xan substitution (p>0.05) at the same sucrose concentration. However, breakdown values of TS or TS/Xan pastes increased significantly with sucrose addition (p<0.05, Table 3.4.2, Fig. 3.4.3c) under the influence of applied shear to the mixtures. The results indicate that formed aggregates among polysaccharides and sucrose molecules in the pastes through hydrogen bonding and polymer entanglement are more sensitive to disruption under isothermal shear with increasing sucrose concentration.

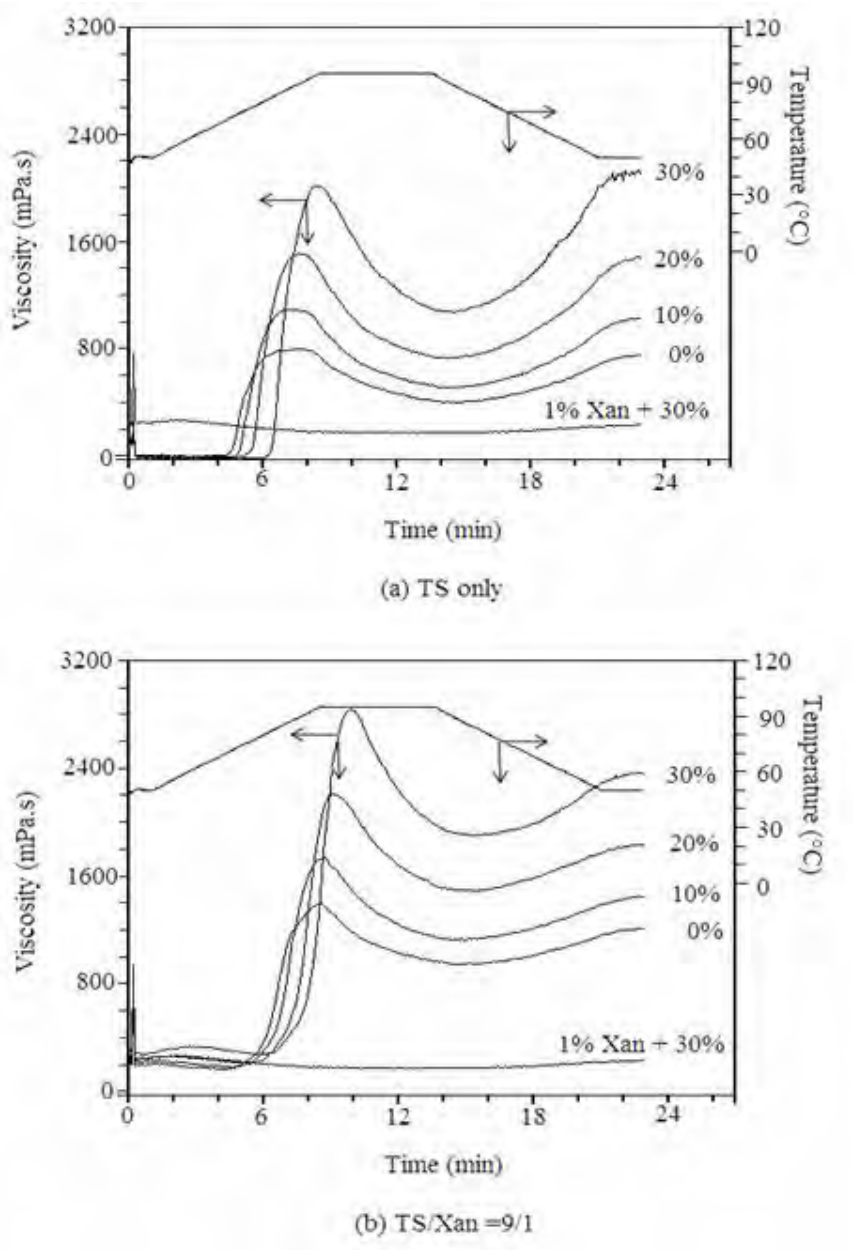


Fig. 3.4.2 Typical RVA pasting profiles of 5% w/w TS (a) and 5% w/w TS/Xan mixtures (mixing ratio = 9/1) (b) with sucrose ubstitu (0 to 30%). RVA profile of 1% xanthan gum containing 30% sucrose also included.

Table 3.4.**2** Pearson's correlation coefficients between selected RVA parameters of 5% TS/Xan mixtures and sucrose.

RVA parameters	Pearson's correlation coefficient
Pasting temperature	0.850*
Peak viscosity	0.903*
Breakdown	0.985*
Final viscosity	0.954*
Setback	0.723*

*$p<0.05$ (2-tailed).

Table 3.4.3 Pasting temperatures (°C) of 5% TS/Xan mixtures as affected by Xan and sucrose concentrations.

Xan concentration (%)	Sucrose concentration (%)			
	0	10	20	30
0.0	71.8 ± 0.22^{Ed}	73.5 ± 0.38^{Dc}	76.7 ± 0.03^{Db}	81.8 ± 0.29^{Ea}
0.125	72.7 ± 0.43^{Dd}	75.4 ± 0.31^{Cc}	78.8 ± 0.20^{Cb}	83.2 ± 0.42^{Da}
0.25	74.4 ± 0.52^{Cd}	77.2 ± 0.42^{Bc}	80.7 ± 0.43^{Bb}	85.0 ± 0.95^{Ca}
0.375	76.4 ± 0.52^{Bd}	78.8 ± 0.45^{Ac}	81.8 ± 0.80^{Ab}	87.7 ± 0.25^{Ba}
0.5	78.1 ± 0.59^{Ac}	79.3 ± 1.19^{Ac}	82.7 ± 0.68^{Ab}	90.5 ± 1.14^{Aa}

Mean ± standard deviation values followed by different small and capital letters are significantly different ($p < 0.05$) by Duncan's multiple range test within the same row and column, respectively.

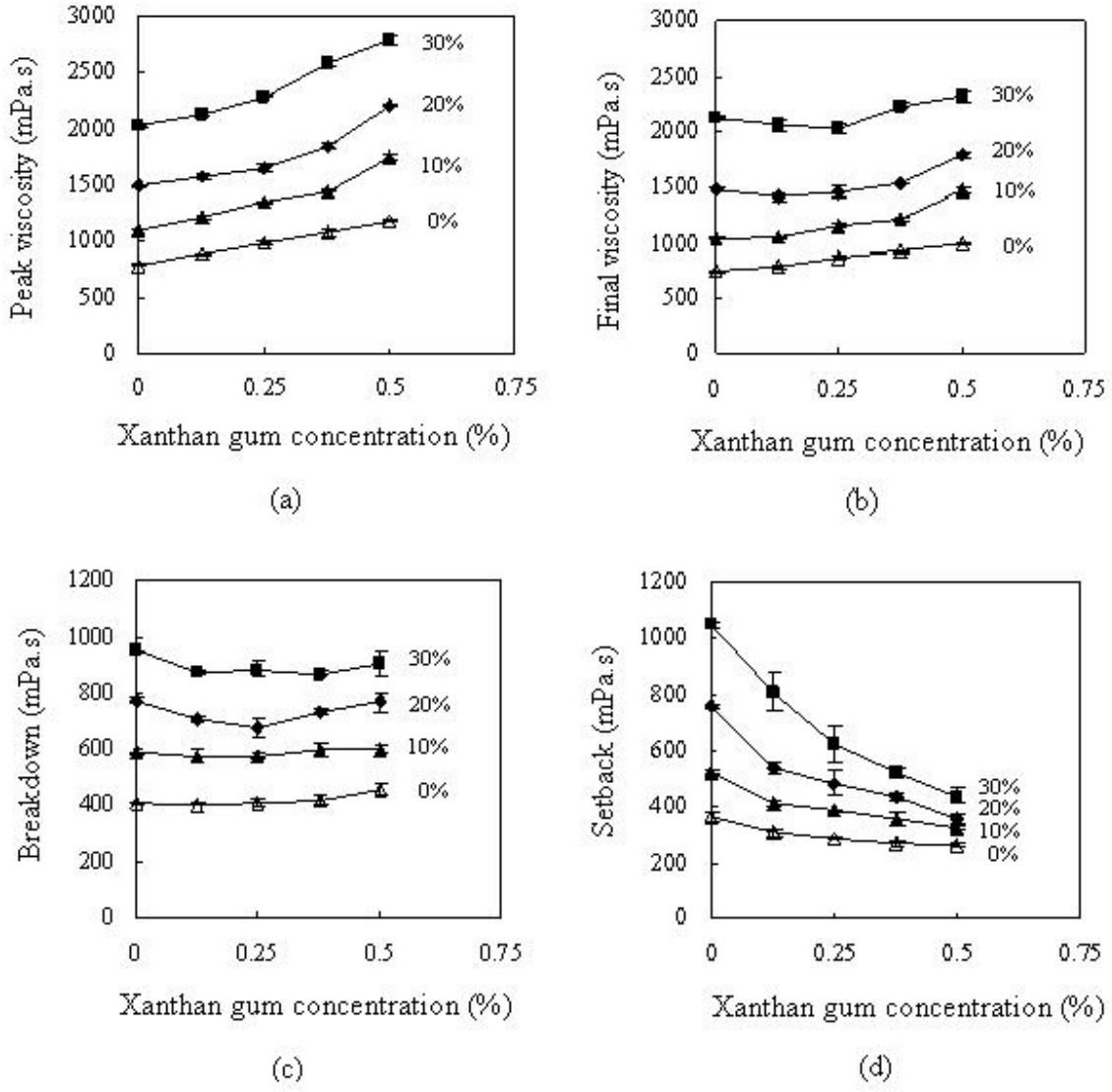


Fig. 3.4.3 Influence of sucrose on peak viscosity (a), final viscosity (b), breakdown (c) and setback (d) of 5% w/w TS/Xan mixtures at mixing ratios of 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75, and 9/1.

The RVA setback obtained from the measurement occurs not only due to the degree of reassociation of gelatinized starch (particularly amylose) molecules during cooling, but also due to the simple kinetic effect of cooling on viscosity. The setback value indicates short-term retrogradation of starch (Pongsawatmanit, et al., 2006). It was determined from the increase in viscosities of TS and TS/Xan pastes from holding strength value to final viscosity after cooling down to 50°C at 6°C/min. Setback increased with increasing sucrose concentration and decreased with increasing Xan substitution ($p<0.05$) (Fig. 3.4.3d). The effect of Xan on the extent of the decrease in setback values of TS/Xan pastes with and without sucrose was also observed. Setback values of 5% w/w TS and TS/Xan pastes (mixing ratio = 9/1) decreased from 1050 mPa.s to 440 mPa.s and from 360 mPa.s to 260 mPa.s for the pastes containing 30% and 0% sucrose, respectively. These results imply that for the TS-based formulation containing sucrose, Xan addition could reduce the setback of the TS pastes leading to lower syneresis (Pongsawatmanit and Srijunthongsiri, 2008).

3.4.3 Analysis of viscosity breakdown under RVA isothermal shear stress

During RVA heating at 95°C, viscosities of each TS/Xan mixture with and without sucrose from a RVA running time range (600 to 780 s) under isothermal shear were used to calculate the rate of viscosity breakdown from the slope of each curve. Rates of viscosity breakdown for each sucrose concentration were plotted against Xan concentration (Fig. 3.4.4). The rates of viscosity breakdown for TS/Xan mixtures (0% sucrose) increased only slightly with increasing Xan substitution (slope = 0.434) whereas relatively large increase in the value (slope = 3.17) was observed from TS/Xan mixtures containing 30% sucrose. The slopes obtained from each linear curve increased with increasing sucrose concentration, confirming that hydrogen bonding and polymer entanglement among polysaccharides and sucrose molecules in the pastes are more susceptible to disruption under isothermal shear with increasing sucrose content.

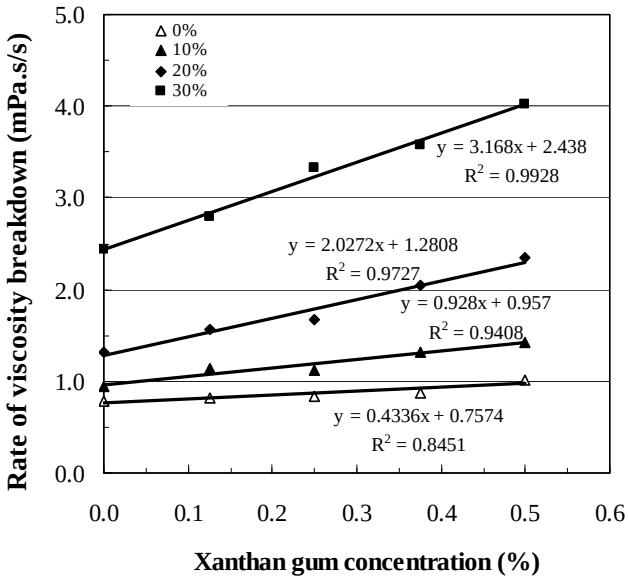


Fig. 3.4.4 Rate of viscosity breakdown calculated from RVA pasting profiles of 5% w/w TS/Xan mixtures (mixing ratios = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75, and 9/1) containing different sucrose contents under heating at 95 °C with RVA paddle speed at 160 rpm and running time from 600 to 780 s^{-1}.

3.4.4 Steady shear viscosity of TS/Xan pastes

Steady shear viscosity measurement was applied to characterize the properties of TS/Xan pastes with and without sucrose at 25°C and 50°C. Selected gelatinized TS and TS/Xan pastes at three mixing ratios (10/0, 9.75/0.25, 9.5/0.5) with and without sucrose (0% and 30%) from RVA experiments were used to evaluate the shear rate dependence of the steady shear viscosity after starch gelatinization. Since the TS/Xan mixture was agitated by the RVA paddle at the speed of 160 rpm during heating and cooling profiles, a homogeneous gelatinized TS/Xan mixture was obtained. In addition, air bubbles formed and trapped in TS/Xan pastes during heating and cooling were removed by centrifuging before shear viscosity measurement. The pasting properties imitating RVA analysis using the rheometer plate (cone and plate geometry) from this study were not appropriate for further investigating the shear viscosity due to the lack of mixing and air bubbles retained in the pastes. This seems to be supported by the observation of higher steady shear viscosities of TS/Xan pastes with and without sucrose compared with those prepared from RVA experiment (data not shown).

All gelatinized TS and TS/Xan pastes exhibited shear thinning behavior (Fig. 3.4.5). At 25°C, TS/Xan pastes showed lower viscosities than those of TS pastes at shear rates higher than 1 s^{-1} (Fig. 3.4.5a). The viscosity values of all TS and TS/Xan pastes containing sucrose (30%) (Fig. 3.4.5b) were higher than those without sucrose significantly at any given shear rate. Sucrose may have a greater access to the hydration layer of the starch chains and create a localized environment of increased viscosity producing a strong anti-platicizing effect compared to water alone (Kruger et al., 2003).

When the viscosity measurement of TS and TS/Xan pastes was carried out at higher temperature (50°C), shear thinning behaviors were also observed. However, the viscosities of only TS pastes were lower than those of pastes containing Xan in the studied shear rate range (Fig. 3.4.5c). Steady shear viscosities of all TS and TS/Xan pastes containing 30% sucrose were higher than those without sucrose (Fig. 3.4.5d). In these mixtures containing 30% sucrose, viscosities of TS/Xan pastes at shear rates less than 1 s^{-1} were also higher than those of TS pastes significantly at higher temperature, indicating the contribution of thermal stability of Xan to TS pastes.

3.4.5 Regression model and model validation of final viscosity

Final viscosity plays an important role in colloidal system stabilization and product handling in the food industry. The final viscosity of TS paste depends on both Xan and sucrose concentrations in the system as discussed in the previous sections. Therefore, the experimental RVA final viscosity from TS and TS/Xan pastes was plotted as a function of Xan and sucrose concentrations (data not shown). Since the mechanism for explaining the final viscosity depends on the amount of hydrocolloid and sucrose in the TS/Xan/sucrose mixtures, linear regression was conducted to relate the RVA final viscosity with Xan and sucrose to predict response/dependent variable (*Y: final viscosity*) from a set of explanatory/independent variables (*X: xanthan gum and sucrose*). The linear regression analysis yielded equation (3.4.1) for predicting final viscosity (mPa.s):

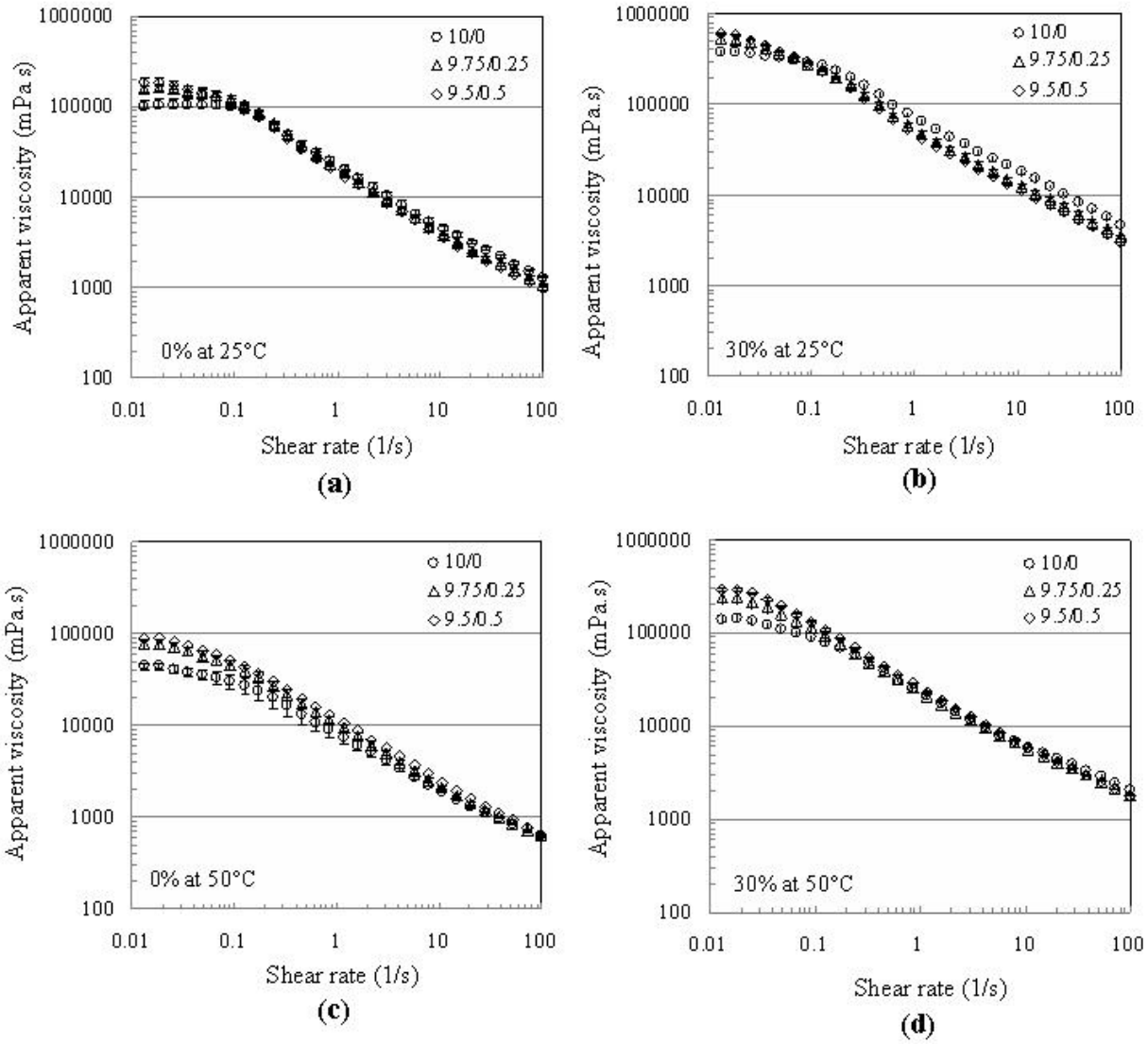


Fig. 3.4.5 Shear rate dependence of the steady shear viscosity for 5% w/w gelatinized TS/Xan mixtures (mixing ratios = 10/0, 9.75/0.25, 9.5/0.5) at 25°C without sucrose (a), 25°C with 30% sucrose (b), 50°C without sucrose (c) and 50°C with 30% sucrose (d). The vertical bar represents the standard deviation

$$\text{Final viscosity} = 712.417 + 355.267\,(\text{Xan}) + 42.303\,(\text{Sucrose}) \qquad (3.4.1)$$

Where Xan = xanthan gum concentration (0 to 0.5%) and Sucrose = sucrose concentration (0 to 30%).

To test the model performance from Equation (3.4.1), another group of RVA experiments was performed with newly prepared different TS/Xan/Sucrose pastes (TS/Xan = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1, sucrose content = 0 to 30%) to determine the final viscosity. Final viscosity values were plotted against those calculated from Eq. (3.4.1) using the different Xan and sucrose concentrations. A good predictability of the viscosity at various sucrose and Xan concentrations between the modeling dataset and testing dataset was achieved, indicated by the corresponding correlation coefficient (r = 0.980) and small value of the root mean square error (RMSE = 84.4) between them as shown in the Fig. 3.4.6.

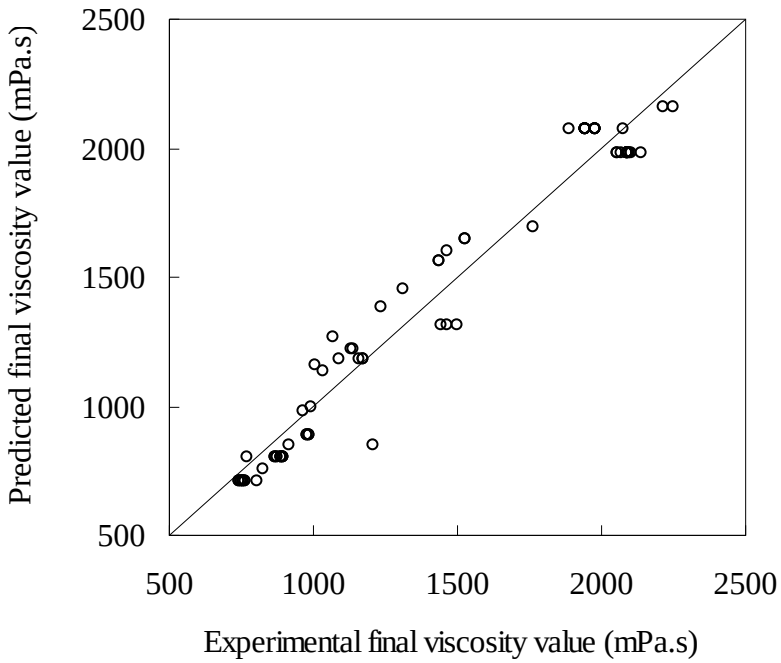


Fig. 3.4.6 Predicted final viscosity value using Eq. (1) against experimental RVA final viscosity from 5% w/w TS/Xan pastes at different mixing ratios (10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) containing sucrose concentrations (0 to 30%) (r = 0.980, RMSE = 84.4).

3.5 Effect of NaCl on physical properties of TS containing Xan

3.5.1 Rapid visco-analyser (RVA) measurement

The pasting properties of 5% w/w TS/Xan mixtures (mixing ratios = 10/0, 9.5/0.5 and 9/1) with and without 400 mM NaCl were determined by RVA. The typical RVA pasting profiles are shown in Fig. ***3.5.1***. Addition of 400 mM NaCl to TS dispersion resulted in an increase in pasting temperature significant ($p \leq 0.05$) compared with that of TS without NaCl, indicating NaCl could enhance the pasting temperature of TS as shown in Table 3.5.1. The ability of the salts to modify the gelatinization temperature of starch was expected to be the strongly hydrated ions of NaCl modify the structural order of water leading to a decrease in starch gelatinization. The peak viscosity referred to the equilibrium point between swelling and rupture of starch granules during heating from RVA profile, slightly increased due to starch/salt interactions leading to higher viscosity. After peak viscosity, the pastes were further subjected to both thermal and shear stresses at a holding temperature (95°C). Further disruption of starch granules and leaching out of starch molecules caused a decrease in viscosity. Breakdown was determined from the resultant drop in viscosity from peak to a holding strength (minimum viscosity after peak). The breakdown values of TS pastes decreased with NaCl addition (from 329 to 273 mPa s). The NaCl reduced breakdown value of TS suggesting the improvement of starch paste stability which is corresponding to the report of Jyothi et al. (2005). The stability of cassava flour was improved by NaCl and sodium sulphate addition whereas the latter exhibited the better than NaCl. Final viscosity referred to the viscosity at the end of RVA experiment after cooling and holding at 50ºC. The final viscosity of TS pastes increased with Xan and NaCl addition. However, when TS/Xan was 9/1, the final viscosity exhibited no significant difference with and without NaCl ($p<0.05$).

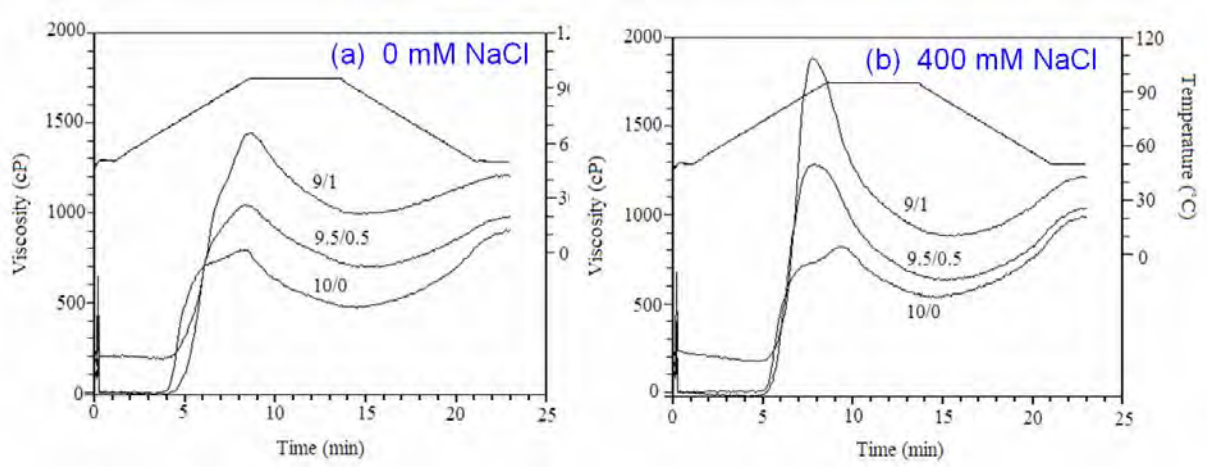


Fig.3.5.1 Typical RVA pasting profiles of 5% w/w TS/Xan mixtures at different mixing ratios of 10/0, 9.5/0.5, and 9/1 without (a) and with 400 mM. NaCl (b).

Table 3.5.1 Pasting properties of 5% TS/Xan mixtures (10/0, 9.5/0.5 and 9/1) with or without 400 mM NaCl.

NaCl (mM)	TS/Xan	Pasting temperature (˚C)	Peak viscosity (mPa s)	Breakdown (mPa s)	Final viscosity (mPa s)	Setback (mPa s)
0	10/0	68.9±0.5d	793±4e	329±7e	882±14d	419±10b
	9.5/0.5	72.8±0.2c	1061±38d	374±40d	969±11c	282±4e
	9/1	73.2±0.4c	1498±13b	474±13c	1250±11[a]	226±17f
400	10/0	75.8±0.3b	814±6e	274±10f	985±5c	445±11a
	9.5/0.5	76.2±0.3b	1286±8c	652±7b	1031±6b	397±9c
	9/1	78.3±0.8a	1919±38a	1019±15a	1248±32a	348±10d

Mean ± standard deviation values followed by different letters within the same column are significantly different ($p<0.05$) by Duncan's multiple range test.

Setback is an increase in viscosity from holding strength value to final viscosity. Table 4 revealed the setback values of TS with and without NaCl addition decreased with Xan. In the TS/Xan containing NaCl showed the higher setback at the same mixing ratios of TS/Xan. The changes in pasting properties may explain from the a disorder to order conformation of Xan molecules which affected the solution viscosity containing salts.

3.5.*2 Texture profile analysis (TPA) measurement*

Texture measurement is a rheological method used for examining food textural properties and evaluating changes in mechanical properties of biopolymer gel (Bourne, 2000) using single or double compression tests. The typical texture profile analysis curve of 25% w/w TS/Xan (mixing ratios of 10/0, 9.5/0.5 and 9/1) with and without NaCl addition (400 Mm) after keeping at 5°C for 24 h were shown in Fig. ***3.5.2***.

TPA parameters were determined from the TPA profiles. Hardness is the maximum force during the first compression cycle as shown in Fig. **3.5.*2***. The hardness of TS gels decreased with Xan and NaCl addition (Table **3.5.**2). Cohesiveness is the ratio of the positive force areas under the first and second compressions (A_2/A_1). Springiness (ubstituti) is the distance of the detected height of the product on the second compression (Length 2), divided by the original compression distance (Length 1) whereas chewiness refers to the energy required to masticate a solid food product and is calculated from the terms of (hardness × cohesiveness × springiness). The cohesiveness and chewiness of gels without NaCl increased with Xan concentration whereas in the presence of NaCl, the values of both TS and TS/Xan gels exhibited no significant difference ($p>0.05$).

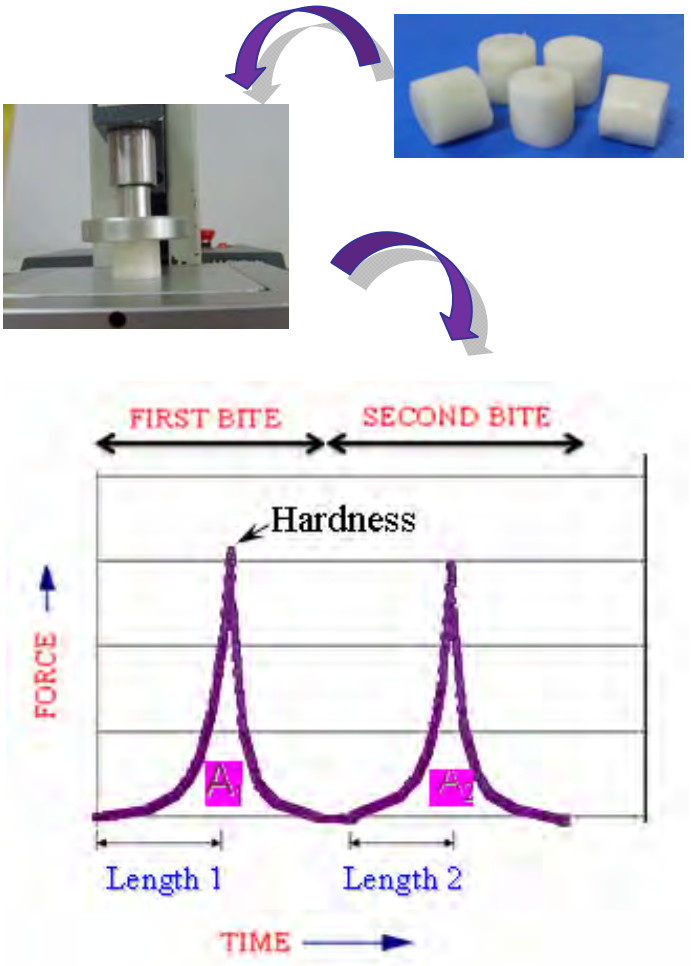


Fig. 3.5.2 TPA profile of 25% w/w TS/Xan gel sample.

Table 3.5.2 TPA of 25% TS/Xan gels (10/0, 9.875/0.125 and 9.75/0.25) with or without 400 mM NaCl.

NaCl (mM)	TS/Xan	Hardness (N)	Cohesiveness (-)	Springiness (-)	Chewiness (Nm)
0	10/0	9.67±0.47a	0.34±0.03b	0.83±0.02b	0.03±0.00b
	9.875/0.125	8.14±0.06b	0.59±0.01a	0.85±0.01b	0.04±0.00a
	9.75/0.25	7.59±0.14bc	0.57±0.00a	0.84±0.01b	0.04±0.00a
400	10/0	8.35±0.32b	0.45±0.08ab	0.85±0.01b	0.03±0.01b
	9.875/0.125	7.03±0.59cd	0.46±0.10ab	0.92±0.01a	0.03±0.01b
	9.75/0.25	6.20±0.08d	0.47±0.05ab	0.87±0.03b	0.03±0.00b

Mean ± standard deviation values followed by different letters are significantly different ($p<0.05$) by Duncan's multiple range test within the same column.

3.6 **Effect of acidulents on pasting properties and freeze-thaw stability of tapioca starch with and without xanthan gum**

3.6.1. Effect of acidulents concentration on pH of TS/Xan mixtures

The pH values of 5% w/w TS/Xan mixtures (TS/Xan = 10/0, 9.5/0.5 and 9/1) with acetic acid or citric acid or lactic acid addition (concentration = 0, 1, 5 and 10 mM) were showed in Table 3.6.1. The acidity of the TS/Xan mixtures decreased with increasing acid concentration. Citric acid provided the highest acidity in TS/Xan mixtures among the selected acidulants. The TS containing higher Xan content revealed a higher pH value (decreasingthe acidity of the system).

Table 3.6.1 The pH values of 5% w/w TS/Xan pastescontaining different concentration of acetic acid, citric acid and lactic acid after RVA experiment.

TS/Xan	Conc. (mM)	Acetic acid		Citric acid		Lactic acid	
		Conc. (%)	pH	Conc. (%)	pH	Conc. (%)	pH
10/0	0	0	5.88±0.02	0	5.88±0.02	0	5.88±0.02
	1	0.006	4.22±0.02	0.021	3.23±0.02	0.009	3.54±0.02
	5	0.030	3.62±0.02	0.105	2.76±0.02	0.045	3.08±0.02
	10	0.060	3.42±0.02	0.210	2.58±0.02	0.090	2.90±0.02
9.5/0.5	0	0	5.84±0.02	0	5.84±0.02	0	5.84±0.02
	1	0.006	4.65±0.02	0.021	3.84±0.02	0.009	4.23±0.02
	5	0.030	4.13±0.02	0.105	3.10±0.02	0.045	3.55±0.02
	10	0.060	3.89±0.02	0.210	2.86±0.02	0.090	3.29±0.02
9/1	0	0	5.82±0.02	0	5.82±0.02	0	5.82±0.02
	1	0.006	4.98±0.02	0.021	4.30±0.02	0.009	4.50±0.02
	5	0.030	4.33±0.02	0.105	3.56±0.02	0.045	3.74±0.02
	10	0.060	4.06±0.02	0.210	3.32±0.02	0.090	3.55±0.02

Mean ± standard deviation values.

3.6.2. RVA pasting parameter of TS/Xan mistures with and without acidulants

RVA pasting properties of TS/Xan mistures with and without acidulants were determined and shown in Table 3.6.1, 3.6.2 and 3.6.3 for the systems containing acetic acid, citric acid and lactic acid, respectively. The peak and final viscosities, setback of TS decreased with increasing acid concentration in the systems. The addition of Xan retarded the degree of reduction of those parameters. Pasting temperatures revealed the higher values in the TS system containing Xan.

Table 3.6.2 Effect of acetic acid on pasting properties for 5% w/w TS/Xan mixtures

TS/Xan	Acetic acid (mM)	Pasting temperature (°C)	Peak viscosity (mPa.s)	Breakdown (mPa.s)	Final viscosity (mPa.s)	Setback (mPa.s)
10/0	0	68.6±0.2f	770.0±9.9e	313.0±7.1d	841.0±1.4d	384.0±4.2a
	1	68.8±0.0f	725.5±16.3ef	327.0±7.1d	705.5±13.4e	307.0±4.2b
	5	68.6±0.3f	704.5±16.3f	386.0±9.9c	543.0±15.6f	224.5±9.2de
	10	68.8±0.1f	695.5±24.7f	399.0±14.1bc	469.0±22.6g	172.5±12.0g
9.5/0.5	0	72.7±0.1c	1098.0±14.1c	332.5±3.5d	1023.5±13.4b	258.0±2.8c
	1	72.1±0.3cd	1033.0±45.3d	339.5±19.3d	924.0±39.6c	230.5±13.4d
	5	71.3±0.8de	1025.5±34.6d	388.5±16.3c	806.0±31.1d	169.0±12.7g
	10	70.9±0.3e	989.5±23.3d	419.5±3.5b	734.0±41.0e	164.0±14.1g
9/1	0	73.1±0.5bc	1383.5±10.6a	412.5±4.9bc	1179.0±19.8a	208.0±4.2ef
	1	72.9±0.8bc	1344.0±7.1ab	415.5±19.1bc	1123.0±24.0a	194.5±2.1f
	5	73.9±0.6ab	1337.5±7.8ab	479.0±24.0a	997.5±27.6b	139.0±4.2h
	10	74.5±0.3a	1304.5±30.4b	488.5±0.7a	932.0±31.1c	116.0±0.0i

Mean ± standard deviation values followed by different lower case letter are significantly different ($p<0.05$) by Duncan's multiple range test within the same column.

Table 3.6.3 Effect of citric acid on pasting properties for 5% w/w TS/Xan mixtures

TS/Xan	Citric acid (mM)	Pasting temperature (°C)	Peak viscosity (mPa.s)	Breakdown (mPa.s)	Final viscosity (mPa.s)	Setback (mPa.s)
10/0	0	68.6±0.2e	770.0±9.9g	313.0±7.1j	841.0±1.4d	384.0±4.2a
	1	68.6±0.3e	673.5±2.1h	448.5±2.1g	336.0±7.1i	111.0±2.8h
	5	68.5±0.3e	660.5±2.1hi	563.5±0.7e	128.5±2.1k	31.5±0.7j
	10	68.9±0.3e	654.0±7.1i	590.5±3.5d	81.5±3.5l	18.0±0.0k
9.5/0.5	0	72.7±0.1bc	1098.0±14.1d	332.5±3.5i	1023.5±13.4b	258.0±2.8b
	1	70.9±0.3d	1015.5±0.7e	415.0±12.7h	764.0±7.1f	163.5±6.4e
	5	70.6±0.8d	956.0±4.2f	613.0±11.3c	467.5±6.4h	124.5±9.2g
	10	70.2±0.2d	1026.0±2.8e	800.5±3.5b	279.0±0.0j	53.5±2.1i
9/1	0	73.1±0.5ab	1383.5±10.6a	412.5±4.9h	1179.0±19.8a	208.0±4.2c
	1	74.0±0.0a	1333.0±5.7b	469.5±9.2f	997.0±1.4c	133.5±2.1f
	5	73.3±0.3ab	1208.0±1.4c	575.0±2.8e	821.0±5.7e	188.0±1.4d
	10	72.3±0.5c	1345.5±3.5b	865.0±0.0a	592.0±5.7g	111.5±2.1h

Mean ± standard deviation values followed by different lower case letter are significantly different ($p<0.05$) by Duncan's multiple range test within the same column.

Table 3.6.4 Effect of lactic acid on pasting properties for 5% w/w TS/Xan mixtures

TS/Xan	Lactic acid (mM)	Pasting temperature (°C)	Peak viscosity (mPa.s)	Breakdown (mPa.s)	Final viscosity (mPa.s)	Setback (mPa.s)
10/0	0	68.6±0.2f	770.0±9.9h	313.0±7.1e	841.0±1.4e	384.0±4.2a
	1	68.5±0.4f	704.0±7.1i	395.0±2.8cd	506.5±6.4h	197.5±2.1d
	5	68.5±0.2f	667.0±1.4j	472.5±2.1b	281.5±2.1i	87.0±1.4h
	10	68.9±0.3f	658.0±1.4j	544.0±52.3a	213.0±11.3j	57.5±6.4i
9.5/0.5	0	72.7±0.1c	1098.0±14.1e	332.5±3.5e	1023.5±13.4c	258.0±2.8b
	1	71.7±0.2d	1026.5±2.1f	368.0±1.4d	842.5±7.8e	184.0±4.2f
	5	70.6±0.3e	931.5±3.5g	451.5±4.9b	674.0±7.1f	194.0±5.7de
	10	70.3±0.0e	926.5±6.4g	532.0±0.0a	559.0±7.1g	164.5±0.7g
9/1	0	73.1±0.5bc	1383.5±10.6a	412.5±4.9c	1179.0±19.8a	208.0±4.2c
	1	74.7±0.0a	1353.0±2.8b	458.0±11.3b	1062.5±9.2b	167.5±0.7g
	5	73.3±0.3bc	1242.5±6.4c	543.5±2.1a	886.5±2.1d	187.5±6.4ef
	10	73.7±0.3b	1176.0±2.8d	525.0±1.4a	842.5±4.9e	191.5±3.5def

Mean ± standard deviation values followed by different lower case letter are significantly different ($p<0.05$) by Duncan's multiple range test within the same column.

3.6.3. Freeze-thaw stability

Water separation of TS pastes increased with increasing the numbers of repeated freeze-thawed cycle (Fig. 3.6.1). The citric acid showed the highest influence on water separation among the studied acidulants. The addition of Xan in TS pastes revealed significant lower water separation compared with those of TS alone. The results suggest that Xan could be used to enhance the viscosity and freeze-thaw stability of TS pastes.

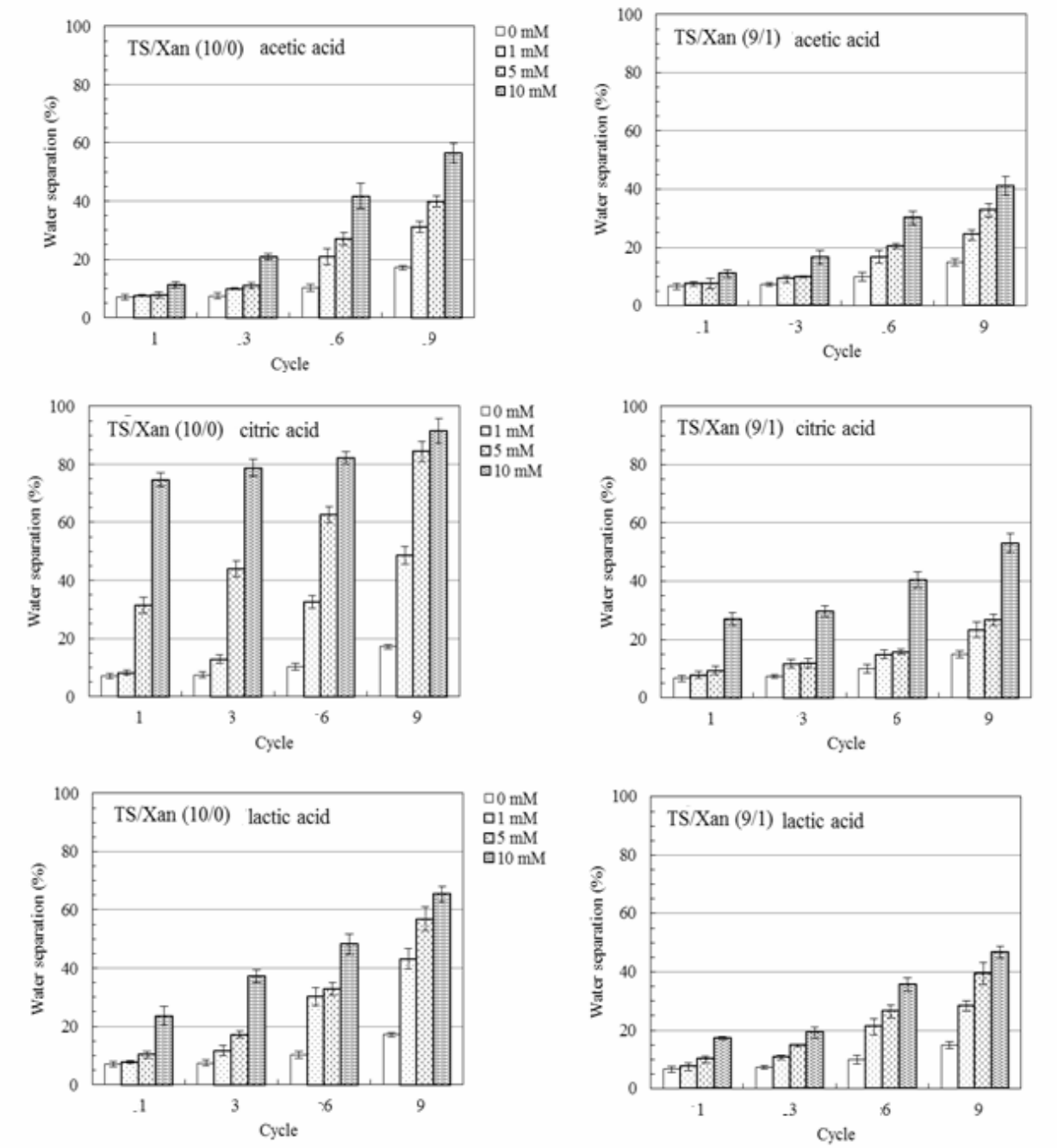


Fig. 3.6.1 Effect of acidulents (acetic acid, citric acid and lactic acid) on water separation for TS/Xan pastes (10/0 and 9/1) at various freeze-thaw cycles.

3.7 Effect of xanthan gum on the quality of syrup thickened by modified starch during heating and storage

3.7.1 Effect of heating time on quality of blueberry syrup

The apparent viscosity as a function of shear rate of blueberry syrups with different mixing ratios of MTS and Xan (4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3) after heating for 20 to 80 min at 90ºC was investigated at 25ºC (Fig. 3.7.1). The viscosity values of blueberry syrups increased with increasing Xan contents ($p<0.05$) at the same shear rate and the values were higher than those of the syrup without Xan (MTS/Xan = 4.0/0.0). The syrup without Xan revealed a lower viscosity value with higher heating time. All syrups with and without Xan exhibited a shear thinning fluid because the apparent viscosity decreased with increasing shear rate.

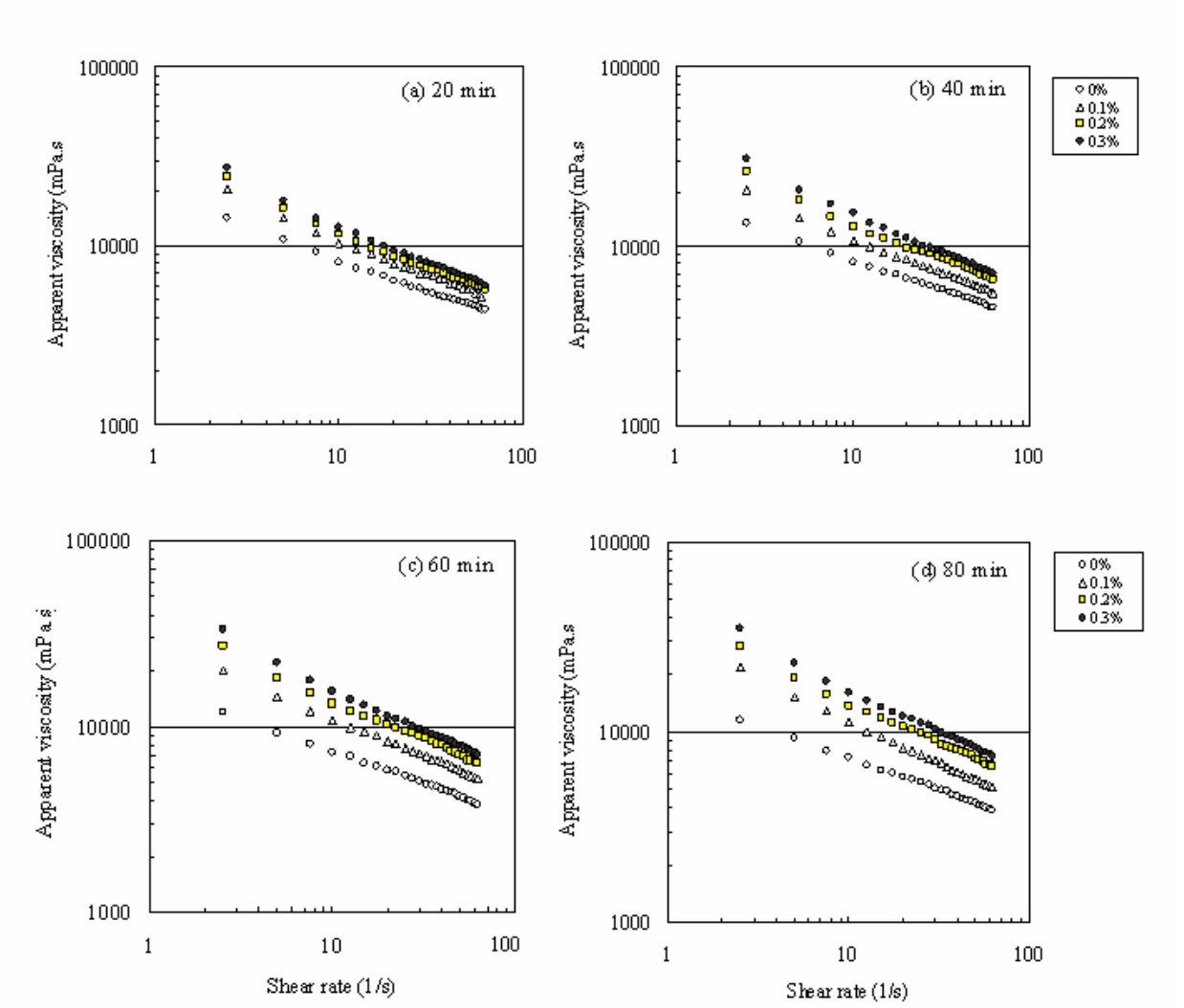


Fig. 3.7.1 Apparent viscosity of blueberry syrups stabilized by MTS and Xan mixtures with different mixing ratios prepared from heating at 90°C for 20 min (a), 40 min (b), 60 min (c) and 80 min (d): measurement was performed at 25°C

The condition of heating at 90ºC for 40 min was selected for further investigating the effect of Xan on syrup quality due to the similar condition of hot-fill process found in food manufacturer. The data of shear stress and shear rate of syrups (MTS/Xan = 4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3) were plotted to describe the behavior of non-Newtonian fluids using the Herschel-Bulkley, power law and Bingham models (data not shown). Coefficients of determination (r^2) indicated that the power law equation (r^2 = 0.996-0.999) provided the best model of the experimental data (Steffe, 1996). Then, the power law model was used to calculate the power law parameters as shown in Equation (3.7.1)

$$\tau = K\dot{\gamma}^n \qquad (3.7.1)$$

where τ = shear stress (Pa), $\dot{\gamma}$ = shear rate (s^{-1}), K = consistency coefficient ($Pa.s^n$), and n = flow behavior index.

For all syrup formulations with different mixing ratios of MTS and Xan, the consistency coefficient value (K) of syrup thickened by only MTS (15.6 $Pa.s^n$) was lower than those containing Xan (25-52 $Pa.s^n$) (Table 3.7.1) and increased with Xan substitution. The flow behavior index (n) of all syrups was below 1 as expected for shear thinning liquids (Steffe, 1996). The substitution of Xan for MTS in the syrups also altered the flow behavior index (n) of the syrups from 0.7 to be 0.61, 0.54 and 0.48 for 0.1, 0.2 and 0.3% Xan substitution (Table 3.7.1), respectively. The n values decreased with increasing Xan substitution. The results suggest that the syrups containing Xan enhanced the viscosity of the systems and exhibited more pronounced non-Newtonian behavior due to the flow behavior index more deviated from n value = 1 of Newtonian fluid.

Total soluble solid (TSS), pH values and water activity of the syrups with and without Xan are not significantly different ($p>0.05$). The TSS and pH values of syrups were about 55.6-56.0°Brix and 2.45-2.48, respectively whereas water activity of all syrups was found to be about 0.92.

Table 3.7.1 Power law constants (K = consistency coefficient, n = flow behavior index) of the syrups with and without Xan determined from the shear rate range of 2.5-62.5 s^{-1} at 25ºC prepared from further heating 40 min at 90°C.

Xan substitution (%)	K ($Pa.s^n$)	n (-)	r^2
0	15.9±0.1d	0.695±0.001a	0.996
0.1	25.6±0.5c	0.607±0.001b	0.999
0.2	36.7±0.2b	0.545±0.000c	0.999
0.3	52.3±0.3a	0.481±0.001d	0.996

Mean ± standard deviation values followed by different small letters are significantly different ($p<0.05$) by Duncan's multiple range test within the same column.

The quality of the syrups was assessed by sensory evaluation using 9 point hedonic scale. The result showed that overall liking scores of the blueberry syrup containing 0.2%Xan was the highest among other samples in terms of thickness and overall liking ($p<0.05$, Table 3.7.2). Therefore, according to these results, the blueberry syrup containing 0.2%Xan (MTS/Xan = 3.8/0.2) was selected for storage studies and compared to the syrup without Xan (4%MTS) as a control sample.

Table 3.7.**2** Mean sensory scores of blueberry syrups with and without Xan prepared from heating 40 min at 90°C.

Xan substitution (%)	Appearance	Color	Odor	Thickness	Overall liking
0.0	6.6±0.7a	6.5±0.8a	6.2±1.0a	6.5±1.0b	6.1±1.0c
0.1	6.6±0.7a	6.4±0.7a	6.0±1.0a	6.8±1.1ab	6.6±0.9b
0.2	6.7±0.7a	6.5±0.7a	6.2±0.7a	7.4±0.6a	7.1±0.9a
0.3	5.5±0.9b	6.3±0.6a	5.9±1.0a	5.8±1.4c	5.9±0.9c

Mean ± standard deviation values followed by different small letters are significantly different ($p<0.05$) by Duncan's multiple range test within the same column.

3.7.2 Quality change of blueberry syrup during storage

Each batch (20 kg) of blueberry syrups containing 4% MTS and 4% MTS/Xan (mixing ratio = 3.8/0.2) was prepared for storage stability test. After heating the syrups to 90°C with further 40 min heating, hot filling into OPA bag (500 g), hermetically sealing and cooling, the syrups with and without Xan were kept at ambient temperature (average temperature 30±3ºC). The product samples were tested over 16 weeks of storage for viscosity and other quality measurements. The viscosity at shear rate 10 s^{-1} of blueberry syrups with and without Xan decreased with storage time (Fig. 9). The rate of viscosity reduction of syrup containing 0.2% Xan was lower than that of syrup without Xan addition evidenced by the slope values of both syrups with and without Xan about 19 and 41 mPa.s/day , respectively. The results indicate that Xan addition enhances the viscosity stability of the syrup during storage at ambient temperature. The change of the syrup viscosity during storage (Fig. 3.7.2) were found to follow zero-order kinetics at ambient temperature (30±3ºC) with r^2 >0.98. Therefore, the viscosity (mPa.s) at shear rate 10 s^{-1} as a function of storage time for both syrups can be determined using the Equations (3.7.2) and (3.7.3) as follow:

For syrup with 4% MTS; $\eta = -18.73\ t + 15493$ (3.7.2)
For syrup with 4% MTS/Xan; $\eta = -41.202t + 13434$ (3.7.3)

Where η = viscosity (mPa.s) and t = storage time (day)

Since the shelf life can be defined as the length of time that a product may be stored at a specified condition without becoming unsuitable for use or consumption, for syrup, the viscosity plays an important role for determining the ending quality of the product. Then, we can estimate the shelf life of blueberry syrup kept at ambient temperature from the Equations (3.7.2) and (3.7.3), if a criteria for specifying the ending of shelf life is provided. For example, if the viscosity of syrup below 9000 mPa.s is used as the end point of quality to be accepted, the shelf life values of syrups with and without Xan were 346 and 107 days using Equations (3.7.2) and (3.7.3), respectively. The results suggest that addition of 0.2% Xan in the blueberry syrup can enhance the shelf life of the product in terms of viscosity.

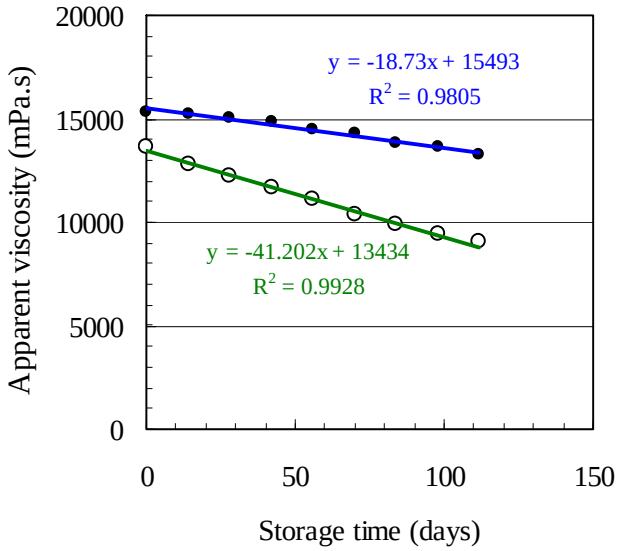


Fig. 3.7.2 Apparent viscosity at shear rate 10 $s^{-1}$of blueberry syrups thickened by the combination of 4% MTS (○) and 4% MTS/Xan (3.8/0.2) (●) and heated for 40 min at 90ºC during storage for 4 months at ambient temperature

Shear stress and shear rate data of fresh and stored blueberry syrups containing 4% MTS and 4% MTS/Xan were also fit to a power law model with the values of coefficient of determination (r^2) about 0.997-0.999 (Table 3.7.3). The consistency coefficient value (*K*) of stored syrup thickened by MTS only (12 Pa.s^n) was lower than that of fresh sample (17 Pa.s^n) significantly ($p<0.05$) during the storage due to the degradation or hydrolysis of MTS at low pH in the system. However, addition of Xan in the syrup revealed that the *K* values for fresh (33 Pa.s^n) and stored (32 Pa.s^n) products exhibited no significant difference ($p>0.05$, Table 3.7.3). The flow behavior index (*n*) of the syrups without Xan altered *n* value of fresh sample from 0.591 to 0.622 (Table 5) after storage for 16 weeks whereas *n* value of syrup containing 0.2% Xan changed from 0.514 to 0.496 with no significant difference ($p>0.05$, Table 3.7.3). The difference in power law constants of syrups with and without 0.2%Xan in Table 3.7.3 and Table 3.7.1 is expected to be the effect of production scale.

Table 3.7.3 Power law constants of blueberry syrups with and without Xan packed in OPA film for 0 and 16 weeks of storage.

Xan substitution (%)	Storage (weeks)	K (Pa.s^n)	n (-)	r^2
0	0	17.1±1.4b	0.591±0.028b	0.998
0	16	12.1±0.3c	0.622±0.006a	0.999
0.2	0	33.2±0.2a	0.514±0.001c	0.999
0.2	16	31.9±0.3a	0.496±0.003c	0.997

Mean ± standard deviation values followed by different small letters are significantly different ($p<0.05$) by Duncan's multiple range test within the same column.

The TSS and pH values of both syrup formulations were about 55.4-56.0 ºBrix and 2.42-2.48, respectively over 16 weeks of storage and showed no significantly differences ($p>0.05$). In this study, the syrup was prepared as the hot-filled product, 1000 ppm sorbic acid addition was used as an antimicrobial agent. Total plate count (TPC) and yeast/mold counts of syrups with and without Xan sampled out before and after storage (16 weeks) were found to be < 10 cfu/g.

The sensory evaluation of fresh blueberry syrups containing 0.2% Xan (MTS/Xan = 3.8/0.2) before storage exhibited the higher overall liking score than that of syrup without Xan addition (Table 3.7.4). After 16 weeks storage, the syrup with 0.2% Xan (MTS/Xan = 3.8/0.2) did not show any significant difference in overall liking ($p>0.05$) between the fresh and stored samples. The results suggest that blueberry syrup obtained from 3.8%MTS and 0.2%Xan combination was more stable than those syrups without Xan in terms of viscosity and overall liking after storage for 16 weeks

Table 3.7.4 Mean sensory scores of blueberry syrups with and without Xan packed in OPA film for 0 and 16 weeks of storage.

Xan substitution (%))	Storage (weeks)	Appearance	Color	Odor	Thickness	Overall liking
0	0	7.0±0.65b	6.8±0.62a	6.7±0.74a	7.0±0.47bc	7.0±0.59b
0	16	6.7±0.52c	6.5±0.57a	6.6±0.67a	6.7±0.81d	6.7±0.55c
0.2	0	7.5±0.57a	6.8±0.55a	6.7±0.48a	7.4±0.50a	7.6±0.50a
0.2	16	7.3±0.59a	6.7±0.48a	6.6±0.50a	7.3±0.44ab	7.4±0.50a

Mean ± standard deviation values followed by different small letters are significantly different ($p<0.05$) by Duncan's multiple range test within the same column.

3.8 Quality of batter and sponge cake prepared from wheat-tapioca flour blends

3.8.1 Quality of cake batter with and without tapioca starch

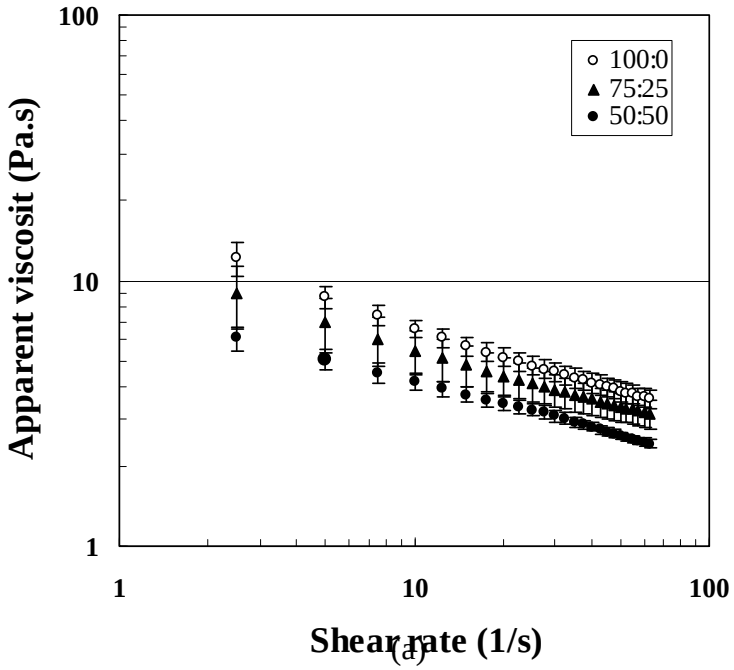
Table 3.8.1 shows the ingredients and formulation for spongy cake preparation.

Table 3.8.1 Percentage of ingredients in sponge cake formulations (100 g) containing different mixing ratios of wheat flour (WF) and tapioca starch (TS).

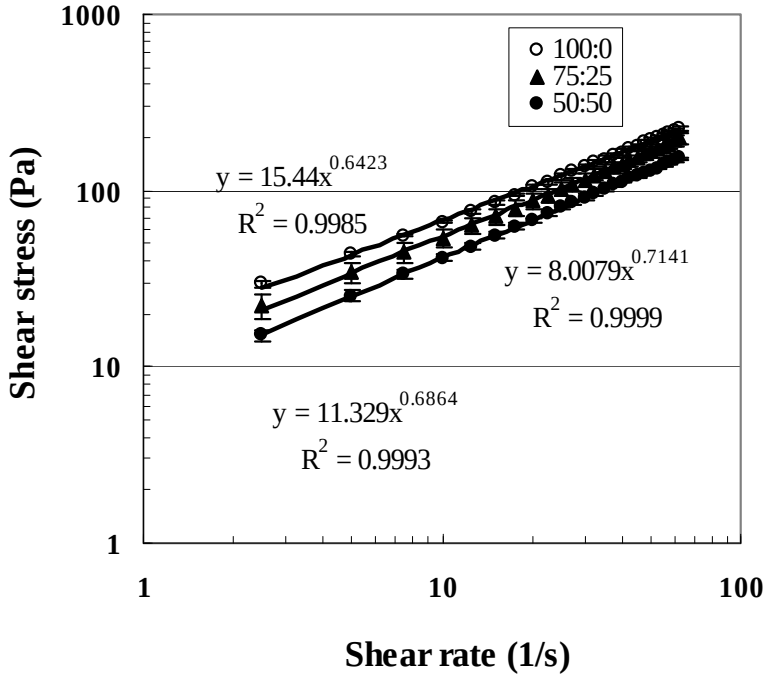
Ingredients	Flour blend (WF:TS) (%)		
	100:0	**75:25**	**50:50**
Wheat flour (for cake)	20.0	15.0	10.0
Tapioca starch	0	5.0	10.0
Liquid whole egg	28.0	28.0	28.0
Whole milk powder	2.0	2.0	2.0
Baking powder	0.4	0.4	0.4
Water	8.0	8.0	8.0
Emulsifier (SP®)	1.6	1.6	1.6
Sugar	24.0	24.0	24.0
Butter (1.5 % salt)	16.0	16.0	16.0
Total	**100.00**	**100.00**	**100.00**

The flow curves of the cake batters containing different mixing ratios of WF and TS (100:0, 75:25, 50:50) were determined from steady shear measurements at 25°C. All batters with and without TS exhibited a pseudoplastic behavior. The apparent viscosity of the batters decreased with increasing shear rate and TS substitution for WF (Fig. 3.8.1a). The results obtained were in good agreement with the results obtained from batters containing WF and TS mixtures for fried products (Ketjarut *et al.*, 2010). Therefore, the WF content in the cake batter plays a predominant role in increasing the batter viscosity due to the wheat protein being the main cause of batter viscosity development during mixing (Loewe, 1993).

Since the shear-thinning behavior was exhibited in the middle region, the apparent viscosity decreased with increasing shear rate for the shear thinning fluid. Thus, the power law equation (Equation 1) described the flow behaviors of all cake batter formulations with different mixing ratios of WF and TS (R^2 = 0.998–1.000; Table 3.8.2; Fig. 3.8.1b). The consistency index (*K*) of all batters decreased with increasing TS substitution from 15.4 to 8.0 for batters without TS and with 50 % TS substitution for WF (Table 3.8.2), respectively. The addition of TS in the batters significantly altered the flow behavior index of the batters from 0.64 to 0.71 for the samples without and with TS, respectively (Table 3.8.2) suggesting that the batters containing TS had more pronounced Newtonian behavior due to the value of *n* approaching close to one.



(a)



(b)

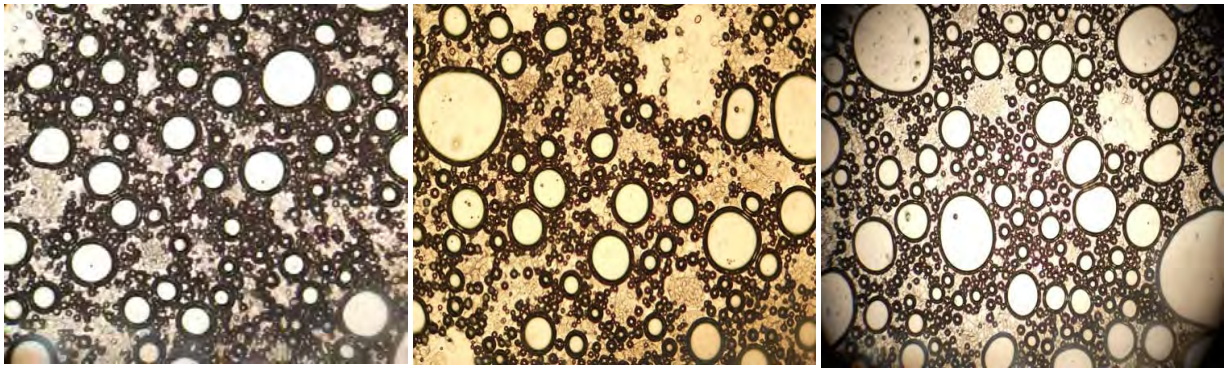
Fig. 3.8.1 Apparent viscosity shown as mean ± standard deviation bars (a) and rheogram with power law model (b) of cake batters prepared from flour blends with different mixing ratios of WF and TS (100:0, 75:25 and 50:50) determined at 25 ºC. The equations in the plot follow Equation (1): $\tau = K\dot{\gamma}^n$.

Table 3.8.2 Power law constants and density of batters prepared from flour blends of wheat flour (WF) and tapioca starch (TS) with different mixing ratios.

Flour blend (WF:TS)	K (Pa.s^n)	n (no unit)	r^2	Batter density (g/cm^3)
100:0	15.4±0.4a	0.64±0.01b	0.998	0.488±0.015a
75:25	11.4±2.1b	0.70±0.02a	0.999	0.467±0.009ab
50:50	8.0±0.9c	0.71±0.03a	1.000	0.459±0.037b

Mean ± standard deviation values (n = 9) followed by a different lower-case letter within the same column are significantly different ($P < 0.05$) by Duncan's multiple range test.

In general, the methods used to characterize cake batters are mainly based on the measurement of the viscosity and the density. Density is a key measurement used in the industry to characterize aeration. It is generally measured by weighing a known volume of batter (Fox *et al.*, 2004). Then, the batter density can be related to the amount of air incorporated in the batter during the mixing process and applied to determine the expected quality of the final baked cake. The present study found that the batter density decreased with increasing TS substitution (Table 3.8.2), indicating there was a higher amount of air incorporated into the batter. The lower viscosity was expected to have lower resistance to the applied shear during the mixing process leading to a higher amount of air being incorporated. The batter without TS (100 % WF) showed the highest batter density values (0.488 g/cm^3) but was not significantly different to the batter containing 25 % TS substitution for WF (0.467 g/cm^3), whereas the batter density was significantly different to that containing 50 %TS substitution (0.459 g/cm^3) as shown in Table 3.8.2. To confirm the explanation of the relationship between the batter density and bubble size and distribution, images of the cake batters are shown in Fig. 3.8.2a–3.8.2c. The bubble size distribution was dependent on the batter density as well as on the level of TS substitution for WF. The smaller bubble size with more uniform appearance was observed in the batter samples prepared from WF only, due to the higher batter viscosity with higher WF content (Table 3.8.2). The bubbles in the batters containing TS with lower batter density (0.467–0.459 g/cm^3) exhibited a wide variation in bubble size distribution due to the low viscosity of the batter containing TS having lower gluten content which affected the larger number of air cells initially incorporated during mixing (Sahi and Alava, 2003). A higher number of larger air bubbles was observed in the photomicrographs of cake batters containing higher TS contents. The larger air bubble sizes that existed in the batters containing TS with lower viscosity were expected to reveal evidence of coalescence where two or more bubbles had merged to form a larger bubble (Irene *et al.*, 2006) during the aeration stage before baking.



(a) (b) (c)

Fig. 3.8.2 Images of aerated cake batters (a-c) (10x magnification) prepared from different mixing ratios of WF and TS. (a) 100:0; (b) 75:25; (c) 50:50.

3.8.2 Quality of cakes containing tapioca starch

The specific volume of baked cake indicates the amount of air that can remain in the final product. A higher gas retention and higher expansion of the product (Gomez *et al.,* 2008) leads to a higher specific volume. After baking at 175 ºC for 20 min, the specific volumes of cake with and without TS were determined and showed a significantly higher value with increasing TS content indicating a higher amount of air remained in the cake. When the specific volume of baked cake as a function of batter density was plotted (Fig. 3.8.3), a linear relationship was observed. Cake batters containing TS with lower batter density exhibited higher gas retention resulting in a higher specific volume, due to the expansion of gas retained in the batter. The air entrapped in the system that related to final cake volume could be explained by the changes in batter viscosity during baking.

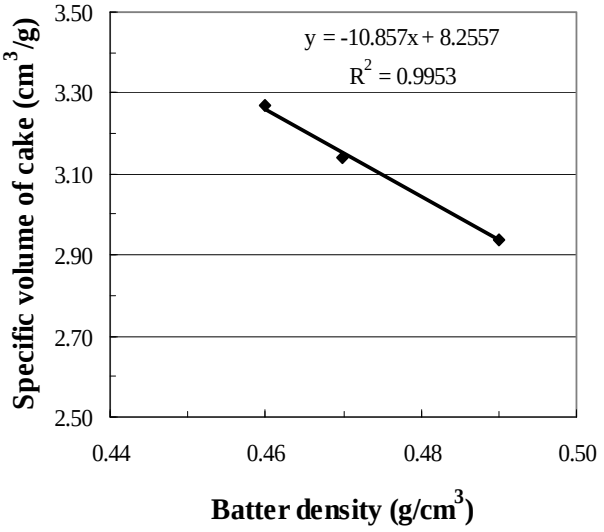


Fig. 3.8.3 Specific volume of cake as a function of batter density prepared from flour blends with different mixing ratios of WF and TS (100:0, 75:25 and 50:50).

According to a preliminary rapid visco analyzer (RVA) experiment for monitoring the heating profile of the cake batter (data not shown), the viscosity of the batters increased after being subjected to the pasting temperature due to the starch gelatinization and protein denaturation (Wilderjans *et al*., 2008). The cake batter viscosity increased earlier in the samples containing higher TS contents. Peak viscosity increased with increasing TS content along with the earlier increase in viscosity, leading to air bubbles created during whipping being retained in the cake crumb. Thus the changes of batter viscosity during baking with different mixing ratios of WF and TS were expected to modify the cake structure (the data not shown). However, the baked cakes prepared from 100 % TS had a very low volume with a dense, gummy layer at the bottom. Therefore, the relationship between specific volume and batter density as shown in Fig. 3.8.3 could explain the batters prepared from the WF and TS within the studied mixing ratios.

Texture profile analysis is a very useful technique for investigating food products. In the present study, the TPA parameters of cake with and without TS substitution were determined from the texture analyzer using double compression tests and are shown in Table 3. Hardness was defined as the maximum force of the first compression of the product at the point of 50 % compression (12.5 mm) of the original sample height. The hardness values of baked cakes decreased significantly with increasing TS substitution up to 50 % (Table 3.8.3) from about 4.5 to 3.4 N in the cakes containing only WF and 50 % TS substitution, respectively. However, cohesiveness determined from the area of work during the second compression divided by the area of work during the first compression (Borne, 2002) ranged between about 0.52 and 0.56 with no significant difference between any samples with and without TS. Springiness was defined as the distance to which the sample recovered in height during the time that elapsed between the end of the first compression cycle and the start of the second compression cycle. The springiness of baked cakes with and without TS exhibited no significant difference (Table 3.8.3). Gumminess was calculated by the product of (that is by multiplying) hardness and cohesiveness, whereas chewiness, defined as the energy required to masticate solid food to a state of readiness for swallowing (Karaoglu and Kotancilar, 2009) was obtained from the product of hardness, cohesiveness and springiness. Chewiness and gumminess values in cakes with and without TS exhibited a similar trend with the hardness values, as shown in Table 3.8.3. Significantly lower chewiness and gumminess were found in the cake samples containing 50 % TS substitution (Table 3.8.3). The results suggest that partial (50 %) TS substitution for WF in cakes increased the cake volume and softened the texture (as shown by lower values of hardness, chewiness and gumminess).

The sensory evaluation was carried out by rating the liking of the sensory attributes of cakes with and without TS substitution for appearance, color, odor, tenderness and overall liking using a 9-point hedonic scale. There was no significant difference among the samples with and without TS substitution for the liking scores of appearance, color and odor exhibited (Table 3.8.4). However, the mean scores of cakes evaluated in terms of tenderness and overall liking were higher with higher TS content in the cake and significantly different (Table 3.8.4). The overall liking score of the cake with 50 % TS substitution was about 7.0 (like moderately) and was significantly different from the cake prepared from 100 % WF (Table 3.8.4). It was observed that the higher tenderness scores with higher TS substitution resulted in an increase in the overall liking values.

Table 3.8.3 TPA parameters of sponge cakes prepared from different mixing ratios of WF and TS.

Flour blend (WF:TS)	Hardness (N)	Cohesiveness (-)	Springiness (mm)	Gumminess (N)	Chewiness (Nm)
100 : 0	4.49±0.70a	0.523±0.053a	10.8±1.0a	2.366±0.551a	0.026±0.008a
75 : 25	4.69±0.31a	0.559±0.112a	10.5±0.8a	2.604±0.387a	0.027±0.003a
50 : 50	3.39±0.37b	0.529±0.046a	10.9±0.9a	1.797±0.273b	0.020±0.003b

Mean ± standard deviation values (n = 30) followed by a different lower-case letter within the same column are significantly different (P<0.05) by Duncan's multiple range test.

Table 3.8.4 Sensory scores of sponge cakes prepared from different ratios of WF and TS*

Flour blend (WF:TS)	Appearance	Color	Odor	Tenderness	Overall liking
100 : 0	6.7±1.3a	6.7±1.4a	6.7±1.4a	6.4±1.6b	6.3±1.3b
75 : 25	6.5±1.2a	6.7±1.5a	6.6±1.5a	6.8±1.6ab	6.6±1.3ab
50 : 50	6.2±1.5a	6.6±1.6a	6.5±1.4a	7.4±1.2a	7.0±1.3a

Mean ± standard deviation values (n = 30) followed by a different lower-case letter within the same column are significantly different ($P < 0.05$) by Duncan's multiple range test.

- = Sensory scores are based on a 9-point hedonic scale ranging from 1 = dislike extremely to 9 = like extremely.

4. Conclusions

The influence of Xan on pasting and rheological properties of TS was observed by increasing gelatinization temperature, peak and final viscosity, and breakdown but decreasing setback values. G' and G'' of TS dispersions and pastes depended on Xan concentration. Thermal stability of TS paste in terms of steady shear viscosity was obtained by adding Xan. Freshly prepared TS pastes containing Xan showed larger G' compared with TS pastes and G' increased with increasing Xan for both on cooling and heating. Holding TS/Xan pastes for 10 h after cooling to 10ºC enhanced the structure formation between leached amylose and amylose-Xan reassociation leading to much larger G' on reheating from 10 to 90ºC than those without holding time.

For 25% w/w TS and TS/Xan mixtures, gelatinization shifted to higher temperatures with increasing Xan content. Xan enhanced the retrogradation and the E' and E'' values of the TS gels in the initial stage of storage at 5°C but retarded the retrogradation of the TS gels after longer storage. The influence of Xan on retarding the reassociation of starch molecules on retrogradation and contributing to the thermal stability and to the more elastic appearance of TS mixtures is useful for modifying TS-based food products under cold storage in terms of product texture and process development in food production

At a total polysaccharide concentration of 5% w/w TS and TS/Xan mixtures, the longer heating time at 95°C under a constant shear stress increased the breakdown but decreased the final viscosity of the system. TS pastes containing Xan exhibited better thermal stability with lower setback of starch molecules leading to the better freeze-thaw stability than those of TS pastes. This study has provided information that may help improve our understanding of the role that Xan play in determining the stability of TS paste at pH 7 during heating and repeated freeze-thaw process.

The strong influence of sucrose on the thermal and pasting properties of 5%w/w TS and TS/Xan mixtures was observed by increasing gelatinization temperatures and enthalpy, peak and final viscosities, breakdown and setback values. Partial substitution of TS with Xan imparted more stability to the gelatinized TS pastes in terms of setback reduction and viscosity change due to temperature, especially in the case of pastes containing sucrose. Addition of 400 mM NaCl alter the pasting properties and hardness of TS and TS/Xan mixtures due to the change in hydrodynamic volume of biopolymers in the systems. Xan could be used to enhance the viscosity and freeze-thaw stability of TS pastes under acidic condition of food product.

For food model, apparent viscosities of the blueberry syrups containing Xan were higher than those without Xan (MTS/Xan = 4/0) for all heating time at 90ºC. The syrup containing 0.2%Xan (MTS/Xan = 3.8/0.2) prepared from heating at 90ºC for 40 min revealed the highest overall liking score. The lower rate of viscosity reduction was found in the syrup containing 0.2%Xan. Overall liking scores of the syrup with 0.2% Xan for both fresh and stored samples were not significantly different and exhibited higher values than those without Xan. The other application in spongy cake was investigated by substitution of WF by TS. The batter viscosity decreased with decreasing batter density indicating more air was incorporated into the cake batter during mixing. The higher specific volume in baked cakes containing TS was expected from the retention of air bubbles during baking leading to lower hardness of the cake after baking. TS substitution up to 50 % for WF could be used in cake preparation for modifying textures in the bakery industry.

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Output from the project

1. Publications in international journal

1. Pongsawatmanit P, Chantaro P, Nishinari K. *Thermal and rheological properties of tapioca starch gels with and without xanthan gum under cold storage*. Journal of Food Engineering, **2013**, 117: 333-341.
2. Chantaro P, Pongsawatmanit P, Nishinari K. *Effect of heating-cooling on rheological properties of tapioca starch paste withand without xanthan gum.* Food Hydrocolloids, **2013**, 31: 183-194.
3. Chaiya B, Pongsawatmanit R. *Quality of batter and sponge cake prepared from wheat-tapioca flour blends*. Kasetsart Journal (Natural Science), **2011**, 45: 305-313.
4. Pongsawatmanit R, Yakard N, Suwonsichon T. *Effect of xanthan gum on the quality of syrup thickened by modified starch during heating and storage***.** Kasetsart Journal (Natural Science), **2011,** 45: 128-135.
5. Chantaro P, Pongsawatmanit P. *Effect of heating time on the quality of tapioca starch and xanthan gum mixture.* Kasetsart Journal (Natural Science), **2010**, 44: 1183-1190.
6. Chantaro P, Pongsawatmanit P. *Influence of sucrose on thermal and pasting properties of tapioca starch and xanthan gum mixtures*. Journal of Food Engineering, **2010**, 98: 44–50.

The oral/poster presentations at various conferences

Chantaro, P. and Pongsawatmanit, R. 2010. Changes in pasting properties and freeze-thaw stability of tapioca starch-xanthan gum mixtures containing different pH. In: Proceeding of The 10th International Hydrocolloids Conference (10th IHC). 20-24 June 2010. Shanghai Jiao Tong University, Shanghai, China.

Chaiya, B., P. Chantaro and R. Pongsawatmanit. 2010. Influence of tapioca starch on quality of wheat flour based sponge cake. The 10th International Hydrocolloids Conference (10th IHC). Shanghai Jiao Tong University, Shanghai, China, June 20-24, 2010.

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Chantaro, P., Pongsawatmanit, R., and Nishinari, K. 2011. Gelatinization and retrogradation of tapioca starch with and without xanthan. In: Proceeding of International Symposium on Food Hydrocolloids. 20 January 2011, OCU Academic Extension Center, Osaka, Japan.

Chantaro, P., Nishinari, K., and Pongsawatmanit, R. 2011. Influence of sodium chloride on pasting and thermal properties of tapioca starch and xanthan gum mixtures. In: Proceeding of Commission on Higher Education Congress IV: University Staff Development Consortium. 14-16 September 2011. The Zign Hotel, Chonburi, Thailand, *Organized by* Commission on Higher Education, Thailand.

Chantaro, P., Pongsawatmanit, R. and Nishinari, K. 2012. Rheological properties of tapioca starch and xanthan gum mixtures as affected by heating-cooling. The 11th International Hydrocolloids Conference. 15-17 May 2012. Whistler Center for Carbohydrate Research, Purdue University West Lafayette, USA.

Chantaro, P., Pongsawatmanit, R. and Nishinari, K. 2012. Effect of xanthan gum on retrogradation of tapioca starch gels under cold storage. IFT 12 Annual Meeting and Food Expo. 28-28 June, 2012. Las Vegas Convention Center, Las Vegas, Nevada, USA.

Appendices

(Reprint and บทความสำหรับการเผยแพร่)

บทความสำหรับการเผยแพร่

ในอุตสาหกรรมอาหาร มักมีการเติมส่วนประกอบต่างๆ เพื่อให้ผลิตภัณฑ์มีสมบัติและเนื้อสัมผัสที่เป็นลักษณะเฉพาะของผลิตภัณฑ์ที่เป็นที่ยอมรับของผู้บริโภค แป้งเป็นส่วนประกอบของอาหารที่มีการใช้เพื่อให้ความหนืดหรือทำให้เกิดเป็นเจลในผลิตภัณฑ์อาหาร รวมทั้งความคงตัวแก่ผลิตภัณฑ์ที่มีแป้งเป็นส่วนประกอบ ประเทศไทยมีการผลิตแป้งมันสำปะหลังเป็นอันดับต้นๆ ของโลก ในอุตสาหกรรมอาหารมีการใช้แป้งมันสำปะหลังเป็นส่วนประกอบหลักเพื่อทำให้เป็นเจลหรือใช้เป็นส่วนประกอบรองเพื่อทำหน้าที่เป็นสารให้ความหนืดในผลิตภัณฑ์อาหารใน เนื่องจากสมบัติทางด้านความหนืดที่ต้องการและมีราคาถูก เช่น ซอส น้ำจิ้มไก่ เป็นต้น หรือมีการใช้แป้งมันสำปะหลังทดแทนแป้งอื่นในการทำให้เป็นเจล อย่างไรก็ตาม การใช้แป้งในการทำหน้าที่ให้ความหนืดหรือเกิดเป็นเจลมักมีข้อเสียในด้านการนำไปใช้โดยเฉพาะความคงตัวของผลิตภัณฑ์ระหว่างการเก็บ เช่น ความหนืดลดลงเมื่อเก็บนานขึ้นซึ่งมีผลให้เกิดการนอนก้นของส่วนประกอบอาหารอื่น หรือลักษณะเนื้อสัมผัสของเจลในผลิตภัณฑ์ที่ใช้แป้งเป็นส่วนประกอบหลักมักเกิดการเปลี่ยนแปลงจากกระบวนการรีโทรกราเดชันส่งผลให้เนื้อสัมผัสเปลี่ยนแปลงจากเหนียวนุ่มเป็นแข็งแต่เปราะแตกง่ายขึ้น ลักษณะปัญหาเช่นนี้ ในทางอุตสาหกรรมอาหารสามารถใช้ไฮโดรคอลลอยด์ (หรือเรียกว่า กัม) ร่วมกับแป้งเพื่อเพิ่มความหนืดหรือทำให้เกิดลักษณะเจลที่ต้องการในอาหารส่งผลให้ผลิตภัณฑ์มีความคงตัวมากขึ้น ดังนั้น อันตรกิริยาของส่วนประกอบต่างๆ ระหว่างแป้งมันสำปะหลังและไฮโดรคอลลอยด์ (หรือพอลิแซคคาไรด์ที่ไม่ใช่แป้ง) ที่เกี่ยวข้องกับเจลาติไนเซชันและรีโทรกราเดชันระหว่างการให้ความร้อนและทำให้เย็น จึงมีบทบาทต่อการกำหนดคุณภาพสุดท้ายของผลิตภัณฑ์ที่มีแป้งเป็นส่วนประกอบ นอกจากนี้ ในการเตรียมสูตรอาหาร มักมีการเติมน้ำตาล เกลือ หรือกรด ล้วนมีผลต่อการเปลี่ยนแปลงสมบัติทางกายภาพของระบบแป้งมันสำปะหลังที่มีและไม่มีไฮโดรคอลลอยด์

แซนแทนกัมนิยมใช้ในอุตสาหกรรมอาหารเพื่อปรับปรุงความคงตัวของผลิตภัณฑ์อาหาร เนื่องจากเป็นไฮโดรคอลลอยด์ที่ให้ความคงตัวที่ดีเยี่ยมในระบบที่มีการเปลี่ยนแปลงอุณหภูมิและความเป็นกรด โดยแซนแทนกัมมีพฤติกรรมเป็น weak gel ที่อัตราเฉือนต่ำและให้ความหนืดสูงแก่ระบบ แต่ความหนืดจะลดลงอย่างมากเมื่อมีการเขย่าหรือกวนหรือการเท ซึ่งลักษณะนี้เป็นที่ต้องการสำหรับการทำหน้าที่เป็นสารให้ความคงตัว

จากการศึกษาผลของแซนแทนกัม (Xan) ต่อพฤติกรรมเพสติงและเจลาติไนเซชันของระบบแป้งมันสำปะหลัง (TS) ที่มีความเข้มข้นต่ำ (5%) ที่ทำหน้าที่ในการให้ความหนืดแก่ระบบ พบว่า การเตรียมตัวอย่างและสภาวะของการวัดค่ามีผลต่อสมบัติทางรีโอโลจีของของผสม TS/Xan ซึ่งมีความสำคัญต่อกระบวนการแปรรูปในอุตสาหกรรม เมื่อวิเคราะห์การเปลี่ยนแปลงสมบัติความร้อนและรีโอโลจีของเจล TS และ TS/Xan ซึ่งเป็นระบบมีความเข้มข้นสูง (25 % w/w) เก็บที่อุณหภูมิต่ำ (5°C) พบว่า ค่า storage Young's moduli (ค่าที่ระบุ solid-like properties) ของเจล TS และ TS/Xan เพิ่มขึ้นเมื่อเก็บนานขึ้นและการเปลี่ยนแปลงอุณหภูมิมีผลต่อค่านี้มากในเจล TS เมื่อเก็บนานขึ้น เนื่องจากการเชื่อมโยงข้ามที่เปราะบางของอะไมโลเพ

กทิน แต่ผลของอุณหภูมิลดน้อยลงในเจล TS/Xan ดังนั้น Xan สามารถยับยั้งการเกิดรีโทรกราเดชันของเจล TS ที่เก็บที่ 5°C เป็นเวลานานขึ้น การให้ความร้อนเป็นขั้นตอนสำคัญสำหรับการเตรียมผลิตภัณฑ์ที่มีแป้งเป็นส่วนประกอบและมีผลต่อคุณภาพผลิตภัณฑ์เนื่องจากการแตกสลายของโมเลกุลแป้ง โดยเลือกที่ pH = 7 เพื่อให้สามารถนำไปประยุกต์กับผลิตภัณฑ์อาหารบางชนิดที่มีความเป็นกลาง เช่น กะทิ นมถั่วเหลืองหรือซุปผักบางชนิดที่ใช้แป้งมันสำปะหลังและ/หรือไฮโดรคอลลอยด์ทำหน้าที่ให้เกิดความคงตัวในการพัฒนาผลิตภัณฑ์ การแทนที่แป้งมันสำปะหลังบางส่วนด้วยแซนแทนกัมช่วยปรับปรุงสมบัติเพสติงและความคงตัวทางด้านการแช่แข็งและละลายของระบบ TS ที่ผ่านการให้ความร้อน การเติมซูโครส (10-30%) ในเพสต์ของ TS/Xan เพิ่มอัตรา viscosity breakdown ระหว่างการให้ความร้อนที่อัตราการเฉือนและอุณหภูมิคงที่หนึ่งๆ การเติมเกลือ (NaCl) มีผลทำให้อุณหภูมิเพสติง setback และความหนืดสุดท้ายของของผสม TS และ TS/Xan เพิ่มขึ้นแต่ค่า breakdown ของ TS ลดลง นอกจากนี้ ยังพบว่า Xan สามารถเพิ่มความหนืดและความคงตัวทางด้านการแช่แข็งและละลายของเพสต์ TS ในอาหารที่มีความเป็นกรด สุดท้ายจากความรู้พื้นฐานที่ได้ มีการนำไปประยุกต์ใช้ในโมเดลอาหาร พบว่า การทดแทนแป้งสาลีบางส่วนด้วย TS สามารถใช้ในการเตรียมสปองจ์เค้กเพื่อดัดแปลงเนื้อสัมผัสในอุตสาหกรรมขนมอบที่มีความนุ่มและผู้ทดสอบให้คะแนนความชอบมากกว่าการเตรียมสปองจ์เค้กจากแป้งสาลีเพียงอย่างเดียว นอกจากนี้ Xan สามารถใช้ในน้ำเชื่อมผลไม้ที่ใช้เป็น topping ในผลิตภัณฑ์ต่างๆ เช่น ไอศกรีม หรือไส้ขนมอบ เป็นต้น โดยเพิ่มคุณภาพและความคงตัวในด้านความหนืดระหว่างการให้ความร้อนและการเก็บ โดยผู้ทดสอบสามารถให้คะแนนความชอบของน้ำเชื่อมผลไม้ที่เติมแป้งมันสำปะหลังและ Xan มากกว่าที่ใช้แป้งมันสำปะหลังเป็นสารให้ความคงตัวเพียงอย่างเดียว

ด้วยเหตุนี้ ผลงานวิจัยที่ได้ก่อให้เกิดความเข้าใจและสามารถวิเคราะห์สมบัติทางกายภาพของสารผสมระหว่างแป้งมันสำปะหลังและไฮโดรคอลลอยด์ที่มีส่วนประกอบอาหารอื่นเพื่อการพัฒนาผลิตภัณฑ์ในอุตสาหกรรมอาหารต่อไป

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Thermal and rheological properties of tapioca starch gels with and without xanthan gum under cold storage

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ABSTRACT

Changes in the thermal and rheological properties of tapioca starch (TS) with and without xanthan gum (Xan) (total polysaccharide concentration = 25% w/w) were investigated using a differential scanning calorimeter, Rheolograph Gel and Texture Analyser. The gelatinization temperatures of TS shifted to higher values with the Xan concentration. Xan enhanced the retrogradation of TS during the initial stage of storage but retarded the process for a further storage time at 5 °C. The onset temperature of all reheated TS/Xan gels decreased with increasing storage time indicating thermally unstable structure formation after a longer storage time. Storage Young's moduli (E') of the TS and TS/Xan gels stored at 5 °C increased with increasing storage time. The E' values became more temperature dependent with storage time due to the weak cross-linkage of amylopectin molecules in the gels but became less dependent in the system containing Xan. TS/Xan gels kept for 14 days showed lower Young's moduli than TS gels from the compression test confirming retardation of the retrogradation process by Xan. The results suggested that Xan could retard the retrogradation of TS gels for longer storage times.

1. Introduction

Starch composed of amylose and amylopectin has been widely used not only as a main ingredient in many products such as noodles and bakery products but also as a thickener, stabilizer, or gelling ingredient in food products. Starch used for food gel preparation plays an important role in product development especially for modifying the texture or shape setting. At high concentrations of starch, three-dimensional networks are obtained after starch dispersions are heated and cooled. Heating starch dispersions above a certain temperature leading to swelling and disintegration of starch granules is known as gelatinization. Then, upon cooling, starch gels are formed if the concentration of the starch paste is high enough (normally >6%) (Clark and Ross-Murphy, 1987; Miles et al., 1985) as a consequence of the aggregation of amylose chains forming ordered junction zones. The starch gelation process is also described as occurring after a hot paste containing amylose is cooled and becomes more elastic with solid-like characteristics (BeMiller, 2011). The starch gel, a thermodynamically unstable system, is generally regarded as composed of composite networks in which swollen starch granules are embedded in a continuous three-dimensional network of aggregated amylose chains with junction zone formation (Ring, 1985) or entanglements called the initial phase of retrogradation. Further reorganization proceeds in starch gels during storage resulting in an increase in the rigidity of the gel by amylopectin (Biliaderis, 1991; Miles et al., 1985; Temsiripong et al., 2005; Yoshimura et al., 1996) depending on many factors such as the type of starch, the starch paste concentration, the heating and cooling conditions, the pH, and the presence of solutes such as salts and sugars (Swinkels, 1985).

Storage of starch-based gels with high moisture content at low temperature is one method to increase shelf life. However, this could enhance retrogradation in the products leading to changes in quality, especially in the texture of the stored product. Hydrocolloids have been widely used in food formulation to improve or to maintain the overall quality during distribution and storage by modifying the rheological and textural properties of foods. Many studies have reported the effect of hydrocolloids on starch paste and/or gel properties (Chen et al., 2009; Christianson et al., 1981; Kim and Yoo, 2006; Mandala and Bayas, 2004; Shi and BeMiller, 2002; Yoshimura et al., 1998). Tapioca starch (TS), produced from cassava roots, is differentiated from other starches because it contains about 17–20% amylose with very low protein and lipid contents (Breuninger et al., 2009). It is widely used in many products (Pongsawatmanit et al., 2007) because of the high viscosity, clear appearance, and low production cost, compared to other starches, especially in Southeast Asia (Biliaderis, 2009; Rapaille and Vanhemelrijck, 1997; Temsiripong et al., 2005). Xanthan gum

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(Xan) is a heteropolysaccharide produced by *Xanthomonas campestris* and provides excellent stability in thermal and acid systems. However, most reports on the thermal and rheological properties of the TS/Xan were investigated in a system with the total polysaccharide concentration at about 6% or lower (Chaisawang and Suphantharika, 2006; Chantaro and Pongsawatmanit, 2010a,b; Pongsawatmanit and Srijunthongsiri, 2008; Pongsawatmanit et al., 2011; Sikora et al., 2008). Sae-kang and Suphantharika (2006) investigated the thermal properties of a 24.0% TS/Xan mixture using differential scanning calorimetry (DSC) but the hardness and rupture strength were determined at 6.0% TS/Xan after repeated freeze–thaw cycles. For application in the food industry, both the thermal and rheological properties should be investigated at the same high total polysaccharide concentration to gain knowledge for further application in TS-based products such as pudding, jelly, and steamed layer dessert during manufacturing and storage.

Therefore, in this study, 25% w/w TS and TS/Xan systems were used to enhance the reassociation of starch molecules under low temperature storage. The effect of Xan on the gelatinization and retrogradation of the TS gel was evaluated using DSC. Changes in the rheological properties of cylindrical TS gels with and without Xan after storing at 5 °C were also investigated by observing the dynamic viscoelasticity and compression behaviors. The relationship between the thermal and rheological properties of TS and TS/Xan mixtures was established using the retrogradation parameter and Young's modulus. The results of this study are expected to be useful for TS-based product development in the food industry.

2. Materials and methods

2.1. Materials

Tapioca starch (TS) (Siam Modified Starch, Pathum Thani, Thailand) and xanthan gum (Xan) (Keltrol F, CP Kelco, San Diego, CA, USA) were used in the experiments. The moisture content of the TS and Xan was 11.1% and 8.6%, respectively, determined by a hot air oven method at 105 °C (AOAC, 2000). The amylose content of TS was 18.0% determined according to the method of Juliano (1971). The concentrations of both polysaccharides were calculated based on a dry basis and used without any further purification. Silicone oil with a viscosity of about 0.65–1 $\times$ 10^6 mPa s was used as the heating medium to control the temperature and prevent water loss during measurement of the dynamic viscoelasticity.

2.2. Preparation of gels

Gel preparation and measurement procedures were performed according to Yoshimura et al. (1996) with a slight modification. Powders of TS or of the TS and Xan mixture were calculated and weighed for gel preparation of 25% w/w TS and TS/Xan (mixing ratio of 9.5/0.5 = 23.75% TS and 1.25% Xan, respectively). TS was dispersed in preweighed distilled water in a separable flask to achieve a total weight of 200 g using a motorized stirrer with a mixing blade (propeller shape with 40 mm diameter) at 340 rpm for 30 min at room temperature. In the case of the TS/Xan mixture, a precalculated amount of Xan was added to the preweighed distilled water and stirred for at least 6 h with a magnetic stirrer to ensure complete hydration of the polysaccharide before TS addition in a separable flask. The dispersion (TS or TS/Xan) was heated in an oil bath to 95 °C and heated further by holding at 95–98 °C for 30 min with continuous stirring at 340 rpm. Boiled hot distilled water was added into the hot mixtures for adjusting the total polysaccharide concentration to 25% w/w TS or TS/Xan dispersions and then mixed immediately. Hot mixtures were poured into cylindrical Teflon molds with 20 mm diameter (20 mm or 30 mm height for the compression test and dynamic measurement, respectively), placed under a glass cover and packed in plastic bags before cooling in an ice-bath for 20 min. To prevent water evaporation, the gels were kept within the Teflon mold and covered with plastic film and finally packed in plastic bags before placing in a refrigerator at 5 °C. Samples were taken after 4, 7, 10, and 14 days for dynamic viscoelasticity measurement and a uniaxial compression test.

2.3. Determination of gelatinization and retrogradation of TS and TS/Xan mixtures using differential scanning calorimetry

The thermal properties of 25% w/w TS and TS/Xan mixtures with mixing ratios of 10/0, 9.875/0.125, 9.75/0.25 and 9.5/0.5 were measured using a differential scanning calorimeter (DSC822^e, Mettler-Toledo GmbH, Greifensee, Switzerland). Precalculated amounts of Xan were added to preweighed distilled water and allowed to disperse throughout the sol for at least 6 h at room temperature using a magnetic stirrer to ensure full hydration of the polysaccharide. TS was added into the dispersions with continued stirring for a further 30 min. About 15 mg of the dispersions were weighed directly into a 40-μL aluminum DSC pan and the pan was hermetically sealed. Gelatinization behaviors of TS/Xan mixtures were investigated by heating the pans from 25 °C to 110 °C at a heating rate of 5 °C/min. Another empty DSC pan was used as a reference. The onset temperature (T_0), peak temperature (T_p) and conclusion temperature (T_c) were determined based on DSC thermograms. The sharpness of the transition peak was measured as the width at the half-peak height (the "half width", $\Delta T_{1/2}$). Gelatinization enthalpy (ΔH_1) expressed as J/g dry starch was evaluated based on the area of the main endothermic peak. After the first-run heating, the gelatinized TS and TS/Xan pastes were cooled down to 25 °C with a cooling rate of 10 °C/min and kept at 5 °C for 1, 4, 7, 14, 21, and 28 days. The stored samples were then reheated again to study the effect of Xan on the retrogradation of TS using the parameter of the retrogradation ratio determined by dividing the enthalpy of disintegration of the ordered structure (ΔH_2) in the second-run heating by the gelatinization enthalpy in the first-run heating (ΔH_1). Each sample pan was weighed before and after measurement to ensure that no weight was lost during the measurement. Four independent sets of samples were prepared and the average value was reported.

2.4. Dynamic viscoelasticity measurement of cylindrical TS/Xan gels kept under cold storage

The dynamic viscoelasticity of 25% w/w TS and TS/Xan (mixing ratio = 9.5/0.5) gels (cylindrical shape with 20 mm diameter and 30 mm height) were measured using a Rheolograph Gel (Toyo Seiki Seisakusho Ltd., Tokyo, Japan). The storage (E') and loss (E'') Young's moduli of TS and TS/Xan gels were determined as a function of the storage time according to Nishinari et al. (1980) and Yoshimura et al. (1996) with a slight modification. The temperature dependence of the E' and E'' values for 25% w/w TS and TS/Xan gels stored at 5 °C for 4, 7, and 14 days were also measured by increasing the temperature of the gels from 20 °C to 55 °C (step ①), then decreasing from 55 °C to 20 °C (step ②), and finally increasing again from 20 °C to 55 °C (step ③). The E' and E'' values were determined at 5 °C intervals. The measurement conditions were set within a linear viscoelastic regime as follows: longitudinal vibrations with frequency at 3 Hz, amplitude at 100 μm and applied strain with a value of 0.0033. The measurement temperature was controlled in a silicon oil bath. Gels were held at each measured temperature for 15 min before starting the measurement process at each set temperature.

2.5. Compression test of TS/Xan cylindrical gels stored in cold storage

Prepared cylindrical gels (20 mm diameter and 20 mm height) of 25% w/w TS and TS/Xan (mixing ratio = 9.5/0.5) were evaluated after storing at 5 °C for 4, 7, 10, and 14 days for a compression test using a Texture Analyser (TA.XT plus, Stable Micro Systems, London, UK.) with a 50-kg loading cell. The gels were held at room temperature (25 ± 2 °C) for about 2 h before measurement. A program of compression tests was used to compress the TS or TS/Xan gels by a distance of 18 mm (90% compression of the original sample height according to a preliminary test) at a speed of 30 mm/min using a 50-mm diameter probe. The breaking stress (σ_B) and breaking strain (ε_B) of the gels were determined from a force–deformation curve according to the method of Yoshimura et al. (1996). The value of σ_B defined as F_B/A_0, was estimated by the force at which a gel was broken (F_B) divided by the initial cross sectional area (A_0). The value of ε_B defined as $\Delta h_B/h_0$ was estimated by the deformation at which a gel was broken (Δh_B) divided by the initial height (h_0) of the sample. Then, Young's modulus (E) was estimated from an initial slope of the stress–strain plot ($E = \sigma/\varepsilon$ at small ε). At least 15 cylindrical gels were tested to obtain an average value and standard deviation of measurement.

2.6. Statistical analysis

Each measurement was carried out using at least two fresh, independently prepared samples. The results were reported as the mean value and standard deviation. The data were subjected to analysis of variance (ANOVA) using the SPSS V.12 statistical software package (SPSS (Thailand) Co., Ltd., Bangkok, Thailand). Duncan's multiple range test was also applied to determine the difference of means from the ANOVA, using a significance test level at 5% ($p < 0.05$).

3. Results and discussion

3.1. Gelatinization and retrogradation of TS and TS/Xan gels using differential scanning calorimetry

Differential scanning calorimetry (DSC) was used as a thermal analysis technique to determine the effect of Xan on the gelatinization and retrogradation of TS in this study. DSC thermograms of 25% w/w TS/Xan mixtures at different mixing ratios (10/0, 9.875/0.125, 9.75/0.25 and 9.5/0.5) showed single large endothermic DSC peaks (Fig. 1) on the first-run heating from 25 °C to 110 °C indicating the disintegration of the native starch structure (Zobel and Stephen, 1995). Dispersions of individual Xan (0.625% and 1.25%) alone with a concentration equivalent to those in the TS/Xan mixtures (= 9.75/0.25 and 9.5/0.5) and with a high concentration of 10% Xan did not show any exothermic or endothermic peak using the DSC equipment with a heating rate at 5 °C/min. The gelatinization temperatures of TS with and without Xan under the endothermic DSC peaks were about 56–76 °C implying the temperatures required to disrupt the cluster of amylopectin chains (Taggart and Mitchell, 2009). The onset temperatures (T_0), peak temperatures (T_p), and conclusion temperatures (T_c) of all examined TS/Xan mixtures ranged from 56.4 ± 0.4 to 57.1 ± 0.4 °C, 65.9 ± 0.1 to 66.8 ± 0.1 °C and 74.7 ± 0.2 to 75.8 ± 0.1 °C, respectively, with increasing Xan content in the system from 0% to 1.25%. The gelatinization temperature slightly shifted to higher temperatures with an increasing Xan content ($p < 0.05$) indicating that Xan alters the gelatinization temperatures of TS. Three possible mechanisms were expected. The first mechanism involved the interaction of the starch with Xan leading to a more stable structure (Yoshimura et al., 1996). The second mechanism involved an

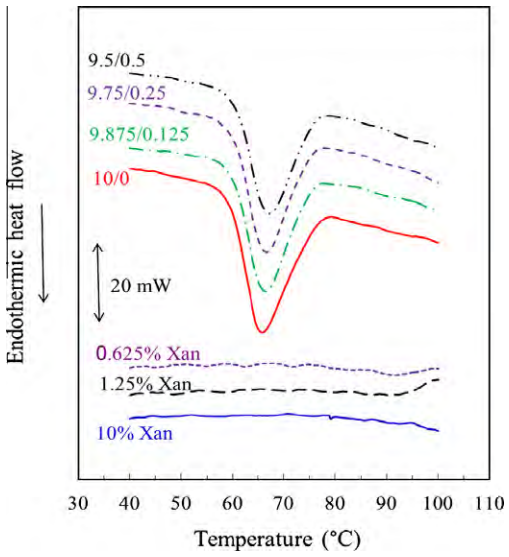

Fig. 1. Typical DSC thermograms of 25% w/w TS and TS/Xan mixtures at various mixing ratios (10/0, 9.875/0.125, 9.75/0.25 and 9.5/0.5). Thermograms of Xan dispersions (0.625%, 1.25% and 10%) are also shown. Heating rate = 5 °C/min.

increase in the effective concentration of TS since the water required for gelatinization is taken by Xan substitution. The estimation of an increase in effective concentration of TS is not easy because it is difficult to estimate the amount of water taken by Xan. In addition, the gelatinization temperature was reported to be independent of the starch concentration below 35% (Biliaderis et al., 1986; Yoshimura et al., 1996). Finally, the third mechanism involved lower heat transfer rates (Krüger et al., 2003) due to the higher viscosity contributed from the hydrocolloid. Since a high concentration of Xan (1.25%) in the TS/Xan mixture (mixing ratios = 9.5/0.5) was used, available water for gelatinization was reduced due to an increase in the hydration of Xan assumed to be located in the continuous phase leading to the higher pasting temperatures (Hirashima et al., 2005; Pongsawatmanit and Srijunthongsiri, 2008). The results showed a good agreement with those reported in previous studies of the system of TS and xyloglucan mixtures (Temsiripong et al., 2005), corn starch–konjac-glucomannan mixtures (Yoshimura et al., 1996), or corn starch–xyloglucan mixtures (Yoshimura et al., 1999). The difference in the gelatinization temperatures of TS alone from the present report and those of Temsiripong et al. (2005) was anticipated from the difference in the cassava cultivar used for the TS preparation and the time of conditions at harvest leading to the differences in the physicochemical properties of TS (Sriroth et al., 1999).

The gelatinization enthalpy of all TS and TS/Xan dispersions, indicating the energy required to gelatinize starch granules, was evaluated from the area under the single, large endothermic DSC curve observed during the first-run heating and defined as ΔH_1. The ΔH_1 values of all TS/Xan mixtures were similar to those of TS dispersion being about 13.3–13.5 J/g dry starch ($p > 0.05$), suggesting that Xan did not associate synergistically with the TS molecules. Similar results were observed in the case of corn starch mixed with xyloglucan (Yoshimura et al., 1999). The temperatures at half width ($\Delta T_{1/2}$) indicating the sharpness of the transition DSC thermogram and the (T_p–T_0) values of TS/Xan mixtures were similar to those of TS with the values ranging about 8.6–8.7 °C and 9.4–9.7 °C, respectively ($p > 0.05$), suggesting that Xan (<1.25% w/w) exhibited no influence on the gelatinization process of TS for a total polysaccharide concentration of 25% w/w.

Starch granules consist of crystalline and amorphous regions. Gelatinization is a process in which the crystalline region in the starch granules is changed into an amorphous region. To investi-

gate the extent of retrogradation in this study, the reheating DSC endothermic peak was used to estimate the disintegration of the ordered structures during retrogradation (Kohyama and Nishinari, 1991) by again reheating to 110 °C the TS and TS/Xan pastes that had been kept at 5 °C. Fig. 2 shows the typical reheating DSC curves of stored gelatinized TS and TS/Xan (=9.5/0.5) gels with different storage times. The reheating DSC curves revealed smaller endothermic peaks compared with those of the first-run heating. The area under the peak increased with increasing storage time indicating a higher association extent of the amylose/amylopectin molecules under cold storage due to retrogradation. In the present work, the term "retrogradation ratio" [$=(\Delta H_2)/(\Delta H_1)$] is used to express the extent of retrogradation in the sample (Kohyama and Nishinari, 1991). The gelatinization enthalpy (ΔH_1) was obtained from the first-run heating. The reheating enthalpy (ΔH_2) determined from the area under the peak of the second-run heating can be considered as the heat required for disintegration of the reassociated starch structure after retrogradation. At the same storage time after 7 days, the retrogradation ratio decreased with increasing Xan content in the TS system (Fig. 3a). The TS/Xan gels exhibited a lower rate of retrogradation than those of TS indicating Xan retarded the reassociation of amylose and amylopectin at low temperatures. The results revealed a good agreement with those previous reports on retrogradation in starch containing hydrocolloids. Substitution of a small portion of starch with either konjac glucomannan or xyloglucan increased the retrogradation ratios in the initial stage of storage but both hydrocolloids retarded an increase in the retrogradation ratio of the starch over longer storage (Temsiripong et al., 2005; Yoshimura et al., 1996; 1999). Xanthan is a branched, ionic polysaccharide, and the primary backbone consists of a repeating unit of 1,4-linked β-D-glucose as in cellulose. A trisaccharide side chain, α-D-mannose, β-D-glucuronic acid, and β-D-mannose is attached to every second glucose residue of the main chain. The side chain may play an important role in retarding the TS gel development during longer storage. The results suggest that Xan could retard the retrogradation of TS which is useful for application in chilling TS-based products. The first order reaction was applied in the present study to explain how fast the retrogradation process proceeds as a function of storage time as shown in the following equation:

$$R(t) = R_{sat}(1 - e^{-k(t-t_0)}) \quad (1)$$

When t_0 = initial storage time = 0, Eq. (2) was obtained:

$$ln[1 - R(t)/R_{sat}] = -kt \quad (2)$$

where $R(t)$ = the retrogradation ratio at storage time t, R_{sat} = the retrogradation ratio at the saturation value, k = the kinetic rate constant for the first order reaction ($n = 1$). Fig. 3b presents the first order reaction of retrogradation using Eq. (2) with $R^2 > 0.973$ and the kinetic rate constants (k) of the retrogradation process obtained from the slopes of the plots. The retrogradation ratio value after 28 storage days was obtained from the regression equation using a polynomial equation ($n = 2$, $R^2 > 0.99$, data not shown) and used as R_{sat} for each mixing ratio. When the rate constant (k) of each TS/Xan mixing ratio was plotted as a function of the Xan concentration (Fig. 3c), the results revealed that adding Xan retarded the retrogradation process of TS gel.

However, the onset temperature (T_0) values of the disintegration of reassociated starch structure after retrogradation of stored TS and TS/Xan pastes (Table 1) were about 36–48 °C and lower than those of the first-run heating (56.4–57.1 °C). The observed T_0 values for both TS and TS/Xan gels from the second-run heating decreased with increasing storage time (Table 1, $p < 0.05$) but the TS/Xan gels (especially with mixing ratio = 9.5/0.5) revealed higher T_0 values for the same storage time. The results implied that the structure formed after a longer storage time was thermally unstable and could be disintegrated at lower temperatures in the second-run heating. In addition, the peak temperatures (T_p) of the second-run heating of TS with and without Xan were almost constant (52–56 °C) and lower than those of the first-run heating (65.9–66.8 °C). The conclusion temperatures (T_c) of the second-run heating (60–63 °C) were also lower than those obtained from the first-run gelatinization (74.7–75.8 °C). The ΔH_2 values for all TS and TS/Xan mixtures from the DSC second-run heating increased with increasing storage time confirming that reassociation of amylose/amylopectin molecules in the retrogradation process was enhanced during longer storage but was thermally unstable with lower values of T_0, T_p, and T_c. The ΔH_2 values of TS containing Xan were lower than those of TS alone indicating that Xan retarded the reassociation of amylose and amylopectin during storage.

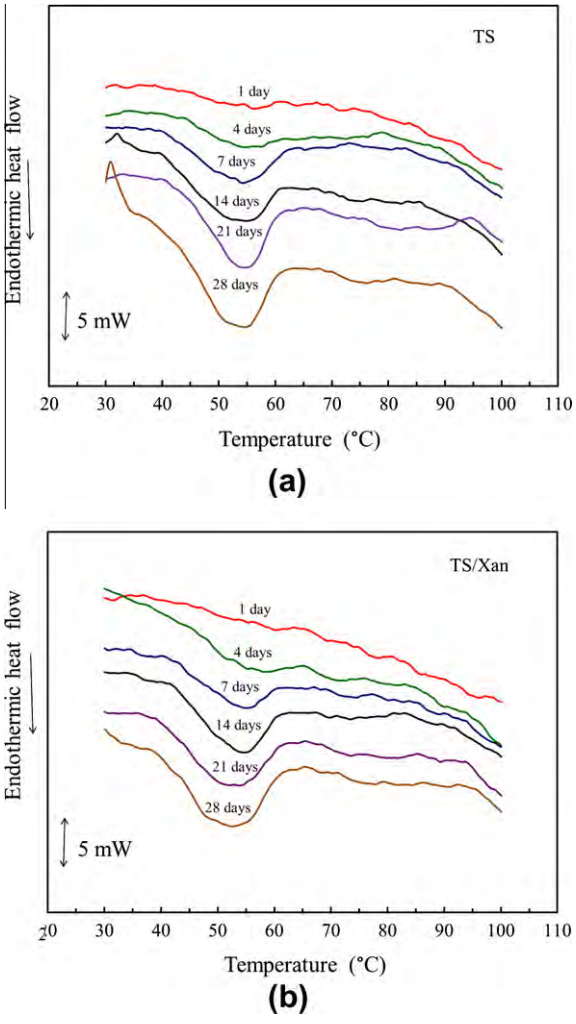

Fig. 2. Typical reheating DSC thermograms of 25% w/w TS (a) and TS/Xan (mixing ratio = 9.5/0.5 with 23.75% TS and 1.25% Xan) and (b) after storing at 5 °C for 1, 4, 7, 14, 21, and 28 days and reheating to 110 °C. Heating rate = 5 °C/min.

3.2. Dynamic viscoelasticity of cylindrical TS gels with and without Xan under cold storage

The TS/Xan mixture revealed a significant difference in gelatinization temperatures without any changes in the TS gelatinization enthalpy and transition peak indicating no interaction of TS and Xan during the disintegration of the native starch structure (Section 3.1). Therefore, the TS/Xan mixture (mixing ratio = 9.5/0.5

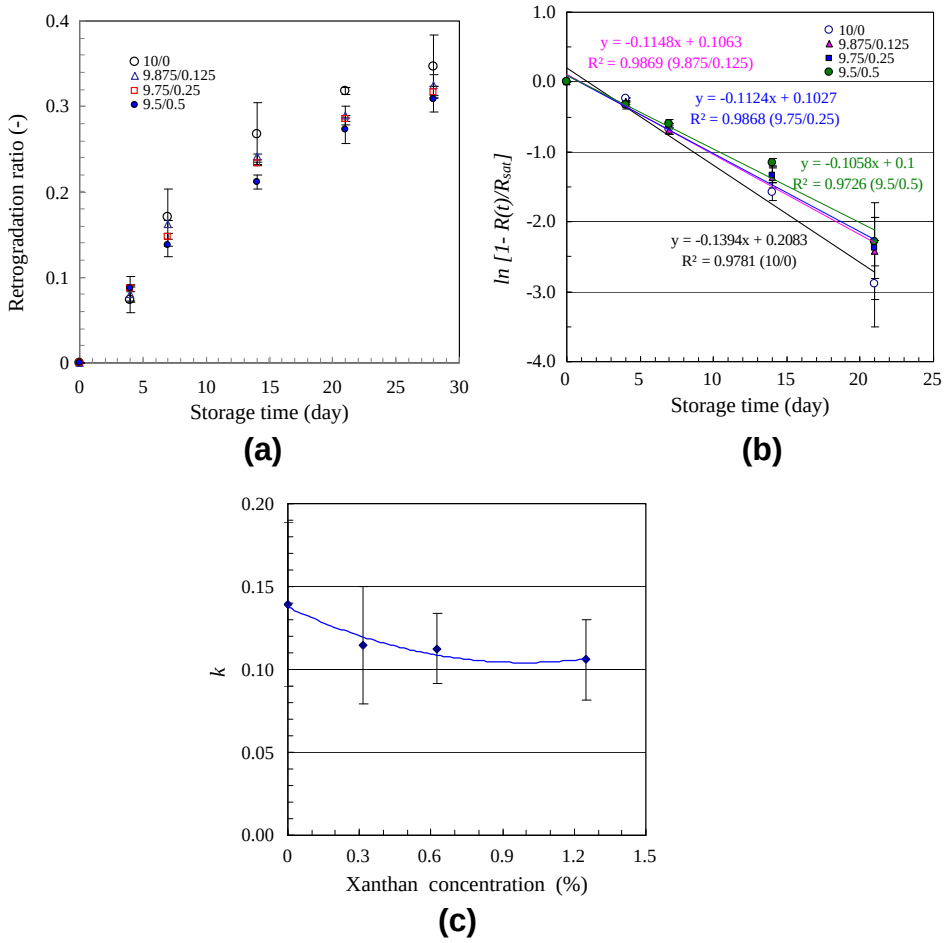

Fig. 3. Retrogradation ratio ($\Delta H_2/\Delta H_1$) of 25% w/w TS/Xan mixtures (mixing ratios = 10/0, 9.875/0.125, 9.75/0.25 and 9.5/0.5) as a function of storage time at 5 °C (a), with DSC reheating rate at 5 °C/min. The kinetic rate constants of the first order reaction were determined from the slope of plots (b) and are presented as a function of Xan concentration in the TS/Xan mixtures (c).

Table 1
DSC onset temperatures (T_0) (based on deviation from base line) and enthalpy of disintegration of ordered structure from the second-run heating of 25% w/w TS/Xan pastes (mixing ratios = 10/0, 9.875/0.125, 9.75/0.25, and 9.5/0.5) after storing for 1 to 28 days at 5 °C and reheating to 110 °C with heating rate 5 °C/min.

Storage time (day)	T_0 (°C) of TS/Xan gels at mixing ratio				ΔH_2 (J/g dry starch) of TS/Xan gels			
	10/0	9.875/0.125	9.75/0.25	9.5/0.5	10/0	9.875/0.125	9.75/0.25	9.5/0.5
1	43.5 ± 0.6^{aB}	47.0 ± 0.7^{aA}	47.5 ± 1.0^{aA}	47.8 ± 0.6^{aA}	0.02 ± 0.01^{eA}	0.02 ± 0.00^{fAB}	0.02 ± 0.00^{dAB}	0.01 ± 0.00^{fB}
4	41.9 ± 1.1^{bC}	42.7 ± 0.7^{bC}	45.5 ± 0.6^{bAB}	47.4 ± 1.2^{aA}	0.99 ± 0.04^{dA}	1.06 ± 0.11^{eA}	1.15 ± 0.03^{eA}	1.16 ± 0.19^{eA}
7	40.0 ± 0.2^{cB}	41.3 ± 0.6^{cA}	41.4 ± 1.0^{cA}	41.5 ± 0.5^{bA}	2.28 ± 0.21^{cA}	2.13 ± 0.08^{dA}	1.99 ± 0.05^{dBC}	1.84 ± 0.16^{dC}
14	39.5 ± 0.8^{cB}	40.4 ± 0.8^{cdAB}	41.1 ± 0.9^{cA}	40.9 ± 1.0^{bA}	3.72 ± 0.44^{bA}	3.33 ± 0.26^{cAB}	3.21 ± 0.23^{cB}	2.98 ± 0.25^{cB}
21	39.0 ± 0.8^{cA}	39.6 ± 0.8^{dA}	39.2 ± 0.4^{dA}	39.5 ± 0.5^{cA}	4.40 ± 0.26^{aA}	3.98 ± 0.29^{bB}	3.86 ± 0.14^{bB}	3.79 ± 0.24^{bB}
28	36.3 ± 0.8^{dC}	38.0 ± 0.9^{eB}	38.2 ± 0.4^{dAB}	39.3 ± 0.5^{cA}	4.55 ± 0.44^{aA}	4.50 ± 0.14^{aA}	4.34 ± 0.09^{aA}	4.22 ± 0.20^{aA}

Mean ± standard deviation values of T_0 and ΔH_2 ($n = 4$) within the same column followed by different lower case superscript letters ($^{a-f}$) for different storage time and within the same row by different upper case superscript letters ($^{A-B}$) for different TS/Xan mixing ratios are significantly different ($p < 0.05$) by Duncan's multiple range test.

consisting of 23.75% TS and 1.25% Xan) was selected for evaluating changes in the rheological properties of TS gels with and without Xan during storage at 5 °C.

The changes in the E' and E'' values of 25% w/w TS and TS/Xan cylindrical gels (20 mm diameter and 30 mm height) after storage at 5 °C for 4, 7, and 14 days as a function of temperature are shown in Fig. 4. Cylindrical gels could not form and be taken out of the Teflon mold before storage. The temperature increased up to 55 °C because the cylindrical shape of the TS/Xan gels was deformed when the temperature was raised to higher temperatures above 55 °C.

Before starting the temperature cycling, the E' and E'' values of all TS gels with and without Xan substitution were recorded at 20 °C. The E' values, indicating the solid-like properties, increased with increasing storage time (Fig. 5a) at 5 °C. E'' values of TS gel also increased from 1350 to 5550 Pa for storage of 4 and 14 days, respectively, whereas those of TS/Xan (9.5/0.5) increased from 2250 to 4950 Pa. The E' values of the TS/Xan gels were lower than those of TS after 7 and 14 days of storage (Fig. 5a). The results suggested that partial substitution of TS with Xan could retard the retrogradation process of the TS gel. It was observed that the E' value of the TS/Xan gel was higher than that of the TS gel alone after stor-

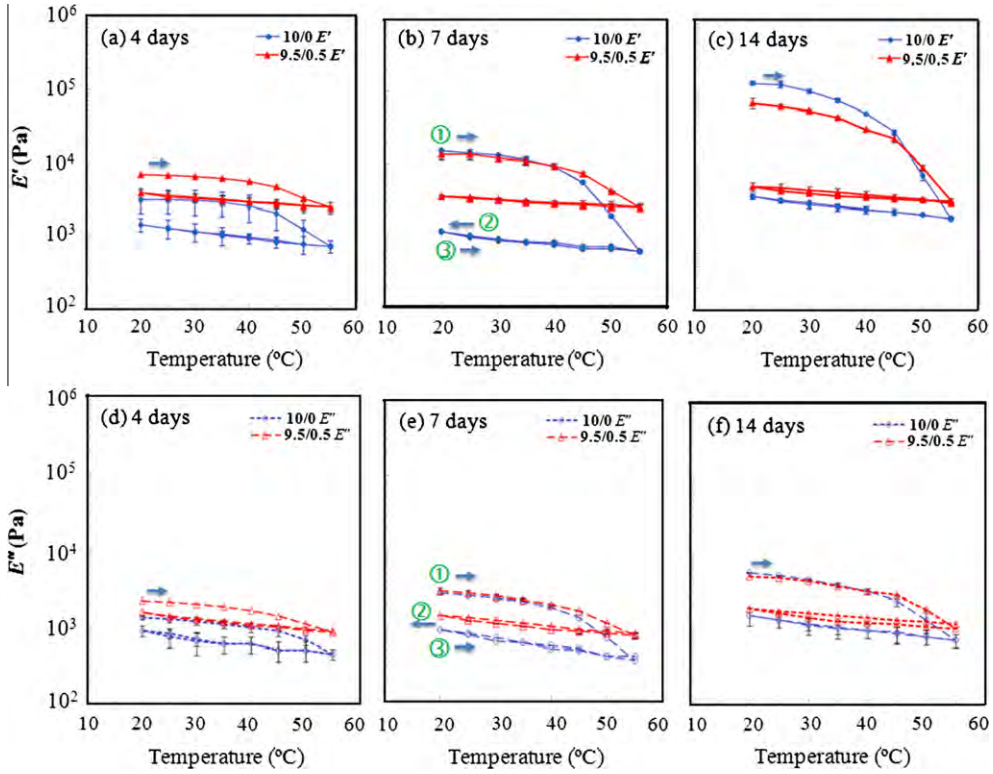

Fig. 4. Temperature dependence of storage (E') and loss (E'') Young's moduli of 25% w/w TS/Xan gels (10/0 and 9.5/0.5) (20 mm diameter and 30 mm height) stored at 5 °C for 4, 7, and 14 days. Frequency was set at 3 Hz, strain at 0.0033 and measurement temperature for E' and E'' values was done at 5 °C intervals: ①increasing temperature of gels from 20 °C to 55 °C, ②then decreasing from 55 °C to 20 °C, and ③ finally increased again from 20 °C to 55 °C. Values measured at 5 °C intervals.

age for 4 days. The result was in good agreement with the DSC retrogadation result. The structure of Xan plays a dominant role in the structure contributing to solid-like properties in the TS gel in the initial stage of storage. For a longer storage time, the reassociation of amylose/amylopectin molecules on retrogradation contributed to the higher solid-like properties indicated by the higher E' (Fig. 5a) and ΔH_2 (Table 1) values.

When the temperature cycling started, the E' and E'' values of the TS and TS/Xan gels decreased with increasing temperature on heating from 20 °C to 55 °C (step①, Fig. 4). The values increased slightly on cooling from 55 °C to 20 °C (step ②) but decreased only slightly on reheating again from 20 °C to 55 °C (step ③). However, the E' and E'' values at the end of cooling step ② (20 °C) did not recover back to the initial values, indicating that the disintegrated structure cannot be recovered within a short time. While an initial stage of retrogradation is shown to be triggered by the gelation of amylose occurring within a short time, the restructuring of amylopectin takes a longer time (Miles et al., 1985). The present experimental time scale, measuring E' and E'' every 15 min on cooling, was much shorter for amylopectin molecules to recover their initial structure before heating. As suggested by Nishinari et al. (1985) and Yoshimura et al. (1999), a strong cross linkage remained in the gels and weak cross linkages were broken by the thermal treatment. The main molecular forces stabilizing the network are secondary bonds such as hydrogen bonds (Nishinari et al., 1985). Therefore, the E' and E'' values on cooling (step ②) were lower than those on heating (step①) revealing that a longer storage time is required to reestablish weak cross linkage in the TS and TS/Xan gels (Fig. 4). The retrogradation of starch molecules during storage proceeds in two crystallization stages: the rigidity of starch gels develops quickly by amylose gelation and the crystallinity develops slowly later by ordering of the amylopectin molecules (Miles et al., 1985). The long-term change was thermally reversible (Miles et al., 1985). Therefore, a strong cross linkage in the TS and TS/Xan gels was developed by the amylose gelation and a weak cross linkage was developed by amylopectin under storage at 5 °C because after thermal treatment (heating–cooling) the E' and E'' values at 20 °C were lower than those before starting heating (step①) (Fig. 4). This conclusion was also revealed by Leloup et al. (1991) who reported that the main network of starch gels was formed by amylose with interspersing as an inactive polymeric filler by amylopectin. An increase in the elastic modulus after longer storage (7 and 14 days) is expected from the contribution of the amylopectin molecules in the gel formation since the initial value of the elastic modulus could not be recovered in a short time during the measurement on cooling.

Temperature dependence of $|\Delta E'/\Delta T|$ for TS and TS/Xan gels stored for 4, 7, and 14 days was plotted (Fig. 5b). The value of $\Delta E'/\Delta T = dE'/dT$ as a function of temperature on heating in step ① (Fig. 4a–c) was calculated using E' value from the polynomial equation ($n = 2$) fitting of Fig. 4 (data not shown) to obtain the smoothed plot for the differentiation operation (Nishinari et al., 1984). A longer storage time enhanced $|\Delta E'/\Delta T|$, indicating that the structure formation induced by the amylopectin association during longer storage time was thermally weaker which is in good agreement with the lower T_0 value from the DSC determination (Table 1). The $|\Delta E'/\Delta T|$ values of the TS/Xan gels were lower than those of the TS gels after longer storage (7 and 14 days), indicating the contribution of Xan to the thermal stability of the systems.

The E' and E'' values of TS gel stored for 14 days (Fig. 4c and f) after heating in step ① were higher than those kept for 4 and 7 days (Fig. 4a, b, d and e). In addition, adding Xan in the TS gels retarded retrogradation of TS with a lower E' value from 20 °C to 45 °C in step ① (Fig. 4c) and created higher thermal stability in TS gels with higher E' values than those of TS gels alone from cooling in step ② and reheating again from 20 °C to 55 °C in step ③

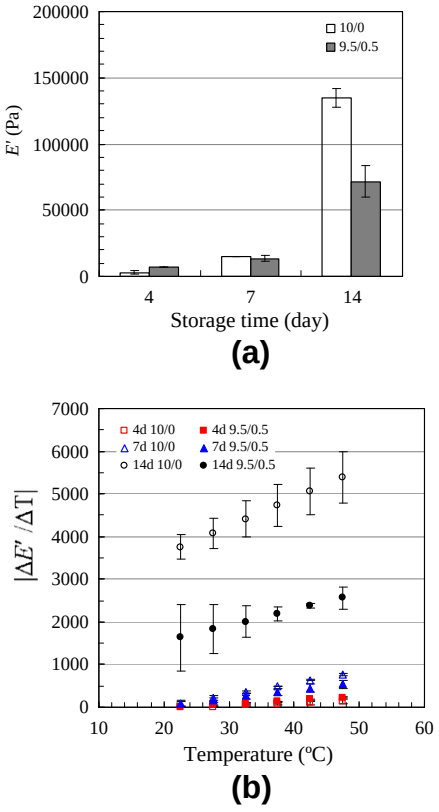

Fig. 5. Storage Young's moduli (E') (a) of 25% w/w TS/Xan gels (10/0 and 9.5/0.5) as a function of storage time before thermal treatment. The E' value measured at 20 °C. Changes in $|\Delta E'/\Delta T|$ (the absolute value of $\Delta E'/\Delta T$) (slopes of Fig. 4a–c) as a function of increasing temperature in step ① of Fig. 4a–c for TS and TS/Xan gels kept for 4, 7, and 14 days, respectively and (b).

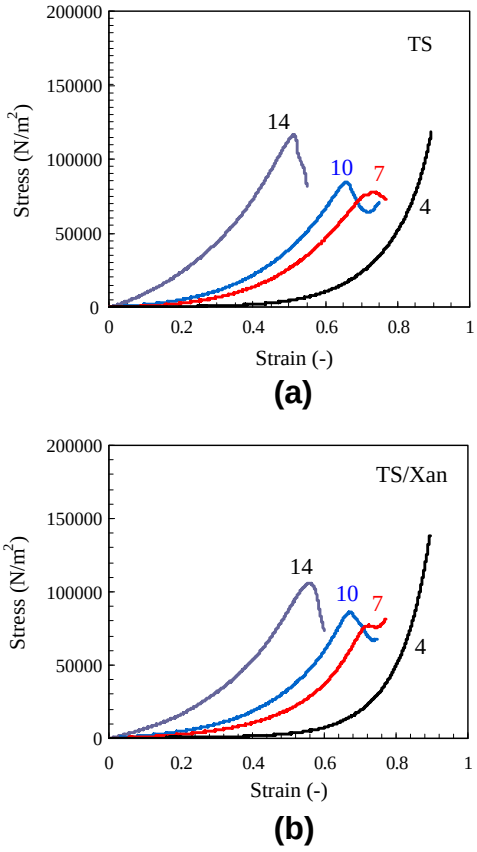

Fig. 6. Typical stress–strain curve of 25% w/w TS (a) and TS/Xan (9.5/0.5) and (b) cylindrical gels (20 mm diameter and 20 mm height) kept at 5 °C for 4, 7, 10, and 14 days. Compression at 30 mm/min with a 50-mm diameter probe and at 25 ± 2 °C.

(Fig. 4). The results were different with mixed gels of corn starch/konjac-glucomannan (Yoshimura et al., 1996) and corn starch/xyloglucan (Yoshimura et al., 1999) in which the E' and E'' values of starch/hydrocolloid gels were higher than for starch alone for all storage times as was expected from the difference in the starch type.

3.3. Changes in compression behaviors of cylindrical TS gels with and without Xan kept in cold storage

The changes in compression behaviors for 25% w/w TS and TS/Xan (9.5/0.5) cylindrical gels (20 mm diameter and 20 mm height) were evaluated. It was impossible to compress the TS and TS/Xan gels stored at 5 °C for 1–3 days because the cylindrical shape of the gel was not retained for the compression test. However, the TS/Xan gel kept for 4 days still showed small shrinkages after removal from the cylindrical Teflon mold. The stress–strain curves of the cylindrical TS and TS/Xan gels (Fig. 6a and b) were calculated from a force–deformation curve. The breaking stress ($\sigma_B = F_B/A_0$) and breaking strain ($\varepsilon_B = \Delta h_B/h_0$) of the TS/Xan gels (10/0 and 9.5/0.5) stored at 5 °C for 4 days could not be calculated because the gel was not broken clearly but the gels were deformed with compression. Both the TS and TS/Xan gels showed smaller strain and larger stress at the breaking point with increasing storage time (Fig. 6a and b) (Keetels et al., 1996; Yoshimura et al., 1996).

The σ_B values of the TS and TS/Xan gels increased with storage time but the TS/Xan gel revealed a lower value than that of the TS gel kept for 14 days. However, during longer storage times, the values of σ_B of the TS/Xan gels increased at a slower rate than those of the TS gel kept at 5 °C (Fig. 7a). The σ_B value at the breaking point increased with a concurrent reduction in the value of ε_B with the storage time of the TS and TS/Xan gels (Fig 7b). The value of ε_B of the TS/Xan gel kept for 14 days was higher than that of the TS gel. The TS gels kept for longer storage times revealed a firmer and more brittle appearance than that of TS/Xan which showed good agreement with the results of higher σ_B and lower ε_B values for the TS gel than those of the TS/Xan gel. The results suggested that Xan retards retrogradation in TS gels from the amylose and amylopectin molecule association in the gel.

When Young's modulus (E) was estimated from an initial slope of the stress–strain plot ($E = \sigma/\varepsilon$ at small ε), the E values of the TS and TS/Xan gels increased with increasing storage time (Fig. 7c). As expected, the elastically active network chains were increased by the longer storage time with increasing E values (Lee et al., 1998). The E values of the TS/Xan gels were higher than those of the TS gel in the initial stage of storage. After a longer storage time (14 days), the E values of the TS gels decreased with Xan substitution (Fig. 7c). The results suggested that Xan could retard the retrogradation of TS gels that had been kept for a longer time under cold storage. The E results corresponded well with those found in the complex Young's modulus test of cylindrical gels.

Since the changes in starch gel under cold storage are related to the retrogradation process, E was plotted as a function of the retrogradation ratio determined from the thermal properties of TS gels with and without Xan (Fig. 7d). The values of the retrogradation ratio were obtained from the regression equations of a polynomial fitting ($n = 2$) of Fig. 3 for the TS/Xan gels (mixing ratio = 10/0, 9.5/0.5). The results showed that, at the same retrogradation ratio, Xan addition enhanced the E value of the TS gels. The exponential equation was used to establish the relationship between E and the

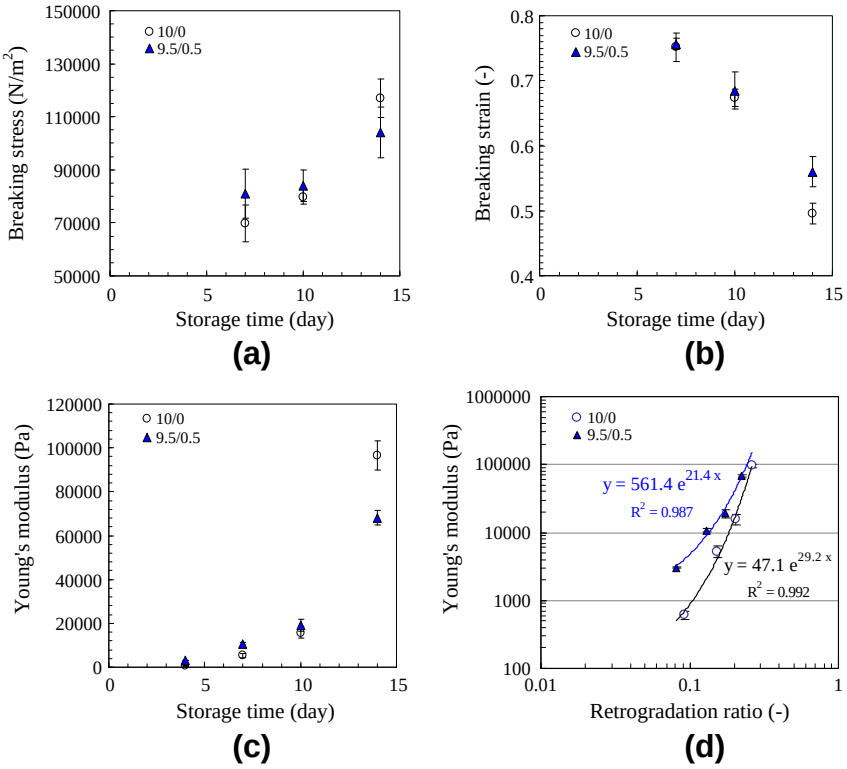

Fig. 7. Breaking stress (a), breaking strain (b) and Young's modulus (c) of 25% w/w gels with and without Xan (mixing ratio = 10/0 and 9.5/0.5) as a function of storage time. Storage temperature = 5 °C, measurement temperature = 25 ± 2 °C and crosshead speed = 30 mm/min. The relationship between Young's modulus and retrogradation ratio from DSC is also shown (d).

retrogradation ratio (Fig. 7d). The change in the E value of the TS gel (29.2) as a function of the retrogradation ratio was higher than that of the TS/Xan system (21.4). The equations can be used to estimate the E values of the TS and TS/Xan gels from the retrogradation ratio under cold storage conditions.

4. Conclusion

For 25% w/w TS and TS/Xan mixtures, gelatinization shifted to higher temperatures with increasing Xan content. Xan addition into the TS mixture did not change the gelatinization enthalpy and transition sharpness of the DSC thermogram. Xan enhanced the retrogradation and the E' and E'' values of the TS gels in the initial stage of storage at 5 °C but retarded the retrogradation of the TS gels after longer storage. The influence of Xan on retarding the reassociation of starch molecules on retrogradation and contributing to the thermal stability and to the more elastic appearance of TS mixtures is useful for modifying TS-based food products under cold storage in terms of product texture and process development in food production.

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Effect of heating–cooling on rheological properties of tapioca starch paste with and without xanthan gum

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ABSTRACT

The effect of xanthan gum (Xan) on pasting and gelatinization behavior of tapioca starch (TS) was investigated. Rheological measurements of TS/Xan mixtures with 5% w/w total polysaccharide concentration at different mixing ratios (10/0, 9.5/0.5, 9/1 and 8.5/1.5) were performed to understand the pasting and gelatinization behavior of TS with and without Xan on heating–cooling cycle using a Rapid Visco Analyzer (RVA) and conventional rheometers. Xan increased storage modulus (G') and loss modulus (G'') of TS dispersions during gelatinization process. Pastes of TS/Xan tended to be more solid-like, i.e., G' larger than G'', with increasing Xan. The G' of TS/Xan paste increased when kept at 10 °C indicating the network formation. Pasting temperatures, peak viscosity, final viscosity and breakdown values of TS increased with increasing Xan content but the opposite result was observed in setback value from RVA measurement. Temperature dependence of steady shear viscosity became less pronounced with increasing Xan content on both cooling and reheating indicating that Xan made the mixture more thermally stable. All the results suggest that the sample preparation and measuring conditions influence the rheological properties of TS/Xan mixtures, which should be taken into account in food application.

1. Introduction

Polysaccharides are often used in certain food products mainly for their thickening and gelling properties. A small amount of polysaccharide can bind a large amount of water, bringing about a desirable change in the texture of food products. Especially, starches are the most widely used food ingredients for textural modification because they are not expensive, natural and safe.

Tapioca starch (TS) can be produced with low production cost especially in Thailand. When gelatinized, TS forms a clear paste with a bland taste and high viscosity and is used in many food applications (Muadklay & Charoenrein, 2008; Pongsawatmanit, Temsiripong, Ikeda, & Nishinari, 2006). However, starch based formulations are subjected to different processing conditions leading to changes in structural and rheological properties during heating and cooling. Hydrocolloids are widely used in starch-based product formulations for improving the final quality of foods, induced by the differences in the gelatinization and viscoelastic properties of starch (BeMiller, 2011; Funami, 2009). Therefore, starch and hydrocolloids are often mixed and used in food systems to control moisture and water mobility, provide a proper texture, improve overall product quality and stability, facilitate processing and reduce cost of production (Mandala, Michon, & Launay, 2004; Yoshimura, Takaya, & Nishinari, 1996). Many researchers investigated the effects of blending of starch and hydrocolloids to modify and control the pasting properties, rheological properties, thermal properties and freeze–thaw stability of starch such as corn starch/xyloglucan mixtures (Yoshimura, Takaya, & Nishinari, 1999), corn starch/konjac–glucomannan mixtures (Yoshimura et al., 1996), TS/xyloglucan mixtures (Pongsawatmanit et al., 2006; Temsiripong, Pongsawatmanit, Ikeda, & Nishinari, 2005), cassava, corn, oat and potato starch/Xan mixtures (Sikora, Kowalski, & Tomasik, 2008), wheat starch/Xan, guar gum and cellulose gum mixtures (Christianson, Hodge, Osborne, & Detroy, 1981), rice starch/gellan, carrageenan and glucomannan mixtures (Huang, Kennedy, Li, Xu, & Xie, 2007), cereal starch/galactomannan mixtures (Alloncle, Lefebvre, Llamas, & Doublier, 1989), corn starch/guar gum mixtures (Sudhakar, Singhal, & Kulkarni, 1995), rice starch/xanthan gum mixtures (Viturawong, Achayuthakan, & Suphantharika, 2008). The viscoelastic properties are important in the processing

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of starch foods, and the processing conditions such as stirring and extrusion sometimes play a key role on the final texture of starch products (Tsutsui et al., 2006).

Xanthan gum (Xan), anionic microbial heteropolysaccharide, is produced by *Xanthomonas campestris*. The main chain consists of β-D-(1,4)-linked glucose, which is the same as in cellulose. A trisaccharide side chain, consisting of α-D-mannose, β-D-glucuronic acid, and β-D-mannose is attached to every second glucose residue of the main chain. There have been many studies on the conformation of Xan (Morris, 2006), and it is well established that the double helical conformation changes into coil conformation on heating, and disordered coils return into helices on cooling but this renaturation process is still a matter of debate (Matsuda, Biyajima, & Sato, 2009). The midpoint transition temperature is reported to be 40–50 °C depending on the ionic strength. Xan dispersions are known to show a weak gel behavior at low shear rates where they show a high viscosity and the weak gel structure is disrupted on application of shear (Morris, 2006; Ross-Murphy, Morris, & Morris, 1983). Because of these unique and useful properties, Xan is widely used in food industry. It is soluble in hot or cold water and the solutions exhibit high viscosities even at low concentrations with high pseudoplastic behavior. At low concentrations, Xan produces a high viscosity permitting suspension of particulates, and inhibition of emulsion droplet association. Upon shaking, stirring or pouring (shearing) the viscosity decreases markedly (shear-thinning) but recovers completely upon removal of shear. The viscosity is retained over the wide range of pH, temperature and ionic strength (Morris, 2006; Sworn, 2009). These characteristics satisfy requirements for a thickening and suspending agent.

There are some studies reporting the influence of Xan on pasting and rheological properties of native TS (Chaisawang & Suphantharika, 2005, 2006; Chantaro & Pongsawatmanit, 2010) and freeze–thaw stability of TS paste (Pongsawatmanit & Srijunthongsiri, 2008). The TS/Xan mixed system is a composite system consisting of a dispersion medium (continuous phase) and a disperse phase: the former consists of Xan-phase (+dispersed leached amylose) and the latter dispersed water-swollen TS granules. Xanthan solution is known to be shear thinning, but shear and heat stable as mentioned above, i.e. there is no effect of previous shear and thermal history, e.g. in blend preparation. Starch paste is also shear thinning, but shear and heat labile, i.e. highly dependent on previous shear and thermal history: swollen starch granules can be irreversibly disrupted (Taggart & Mitchell, 2009). This implies that the rheology of TS/Xan composites is strongly dependent both on sample preparation and on shear conditions during testing. Therefore, the objective of this work was to investigate the pasting and gelatinization properties of TS with and without Xan substitution using a Rapid Visco Analyzer (RVA) and conventional rheometers. In addition, steady shear viscosity and changes in dynamic rheological properties of gelatinized TS/Xan pastes under cooling and reheating cycle were also studied for further process development in food industry.

2. Materials and methods

2.1. Materials

Tapioca starch (TS) (Siam Modified Starch, Pathumthani, Thailand) and xanthan gum (Xan) (CP Kelco, San Diego, USA) were used without any further purification. The moisture content of the TS and Xan was 11.1 and 8.6%, respectively determined by the hot air oven method at 105 °C (AOAC, 2000). Both polysaccharides were mixed on a dry basis. Silicone oil or mineral oil was used to prevent water loss during measurement for a Haake Rheostress-600 and a Physica MCR 300, respectively.

2.2. Dynamic viscoelastic measurement of TS/Xan mixtures during gelatinization

A Haake Rheostress-600 (Thermo Electron, Karlsruhe, Germany) equipped with a C60/2Ti cone and plate geometry (60 mm diameter, 2° cone angle and 0.105 mm gap) was used to investigate storage (G') and loss (G'') moduli of 5% w/w TS/Xan mixtures at different mixing ratios (9.5/0.5, 9/1 and 8.5/1.5) under heating for gelatinization. A dispersion of TS alone (10/0) was not prepared for the small deformation oscillatory measurement due to the sedimentation of starch granules. Precalculated amounts of Xan were added to preweighed distilled water and allowed to disperse throughout the sol for at least 6 h at room temperature using a magnetic stirrer to ensure the complete hydration of the polysaccharide. Then, TS was added into the dispersions with stirring for a further 30 min. Each TS/Xan suspension was loaded on the plate of the rheometer and covered with a thin layer of silicone oil (viscosity about 0.65×10^6 to 1×10^6 mPa s) to minimize evaporation loss. The angular frequency was fixed at 1.0 rad/s and 5% strain was set to obtain the data within the linear viscoelastic strain region. The TS/Xan samples were heated from 10 to 95 °C at a heating rate of 1 °C/min.

2.3. Effect of cooling and reheating on storage and loss moduli of TS/Xan pastes

The changes in dynamic rheological properties of gelatinized TS/Xan pastes were studied during cooling and reheating cycle using a C60/2Ti cone and plate geometry (60 mm diameter, 2° cone angle and 0.105 mm gap). The 5% w/w TS/Xan suspensions (10/0, 9.5/0.5, 9/1 and 8.5/1.5) were heated at 92 °C for 30 min in a water bath and stirred at constant rate during heating with a magnetic stirrer. Immediately after cooking, TS/Xan pastes were poured on the plate of the rheometer which had been pre-heated at 90 °C and covered with silicone oil immediately. The measurements were carried out by cooling from 90 to 10 °C and subsequently heating from 10 to 90 °C at the rate of 1 °C/min with angular frequency at 1 rad/s and 5% strain. The effect of short term storage at low temperature on the storage and loss moduli was evaluated by holding at 10 °C for 10 h after cooling the freshly gelatinized TS/Xan pastes to 10 °C, and then reheating again to 90 °C at the rate of 1 °C/min (modified from Singh, Inouchi, & Nishinari, 2006).

2.4. Pasting properties of TS/Xan mixtures using a Rapid Visco Analyzer

Pasting properties of 5% w/w TS and Xan mixtures at different mixing ratios (TS/Xan = 10/0, 9.5/0.5, 9/1 and 8.5/1.5) were observed using a Rapid Visco Analyzer (RVA) (RVA-4, Newport Scientific, Narrabeen, Australia). For each mixture of TS/Xan, precalculated amounts of Xan were added to preweighed distilled water in RVA canisters and allowed to disperse throughout the sol for at least 6 h. TS was added to achieve a total weight of 28 g for preparing 5% w/w TS/Xan pastes. The dispersions were kept at room temperature for a further 30 min to hydrate the starch. Each suspension was stirred manually to disperse the sample uniformly before measurement. The pasting profile of the sample and agitation speeds of the paddle were monitored during thermal treatment according to the method of Pongsawatmanit et al. (2006) as follows: equilibrating the starch slurry at 50 °C for 1 min, increasing the temperature to 95 °C at a heating rate of 6 °C/min, holding the temperature at 95 °C for 5 min, decreasing the temperature to 50 °C at 6 °C/min, and holding at 50 °C for the remainder of the run. The total run time was 23 min. Agitation of paddle was started at 960 rpm for the first 10 s and kept constant at 160 rpm until the end

of the experiment. Pasting profiles were evaluated in triplicate and the average values of pasting parameters were reported.

2.5. Temperature dependence of steady shear viscosity of TS/Xan mixtures

Temperature dependence of steady shear viscosity measurement for 5% w/w TS/Xan mixtures at different mixing ratios (TS/Xan = 9.95/0.05, 9.5/0.5, 9/1 and 8.5/1.5) were determined using a rheometer (Physica MCR 300, Anton Paar GmbH, Stuttgart, Germany) with cone and plate geometry (50 mm diameter, 1° cone angle and 0.05 mm gap) at a shear rate of 10 s^{-1}. Sedimentation of native starch granules during the measurement is sufficiently retarded by adding a small amount of Xan (0.025%) for TS substitution. TS/Xan dispersions were prepared using the same method described in 2.2, then placed on the plate and covered with mineral oil to prevent water loss during heating–cooling cycle. The TS/Xan dispersions were heated from 10 to 95 °C, subsequently cooled from 95 to 10 °C, then reheating from 10 to 95 °C. The same scan rate (1 °C/min) was used for heating and cooling.

2.6. Steady shear viscosity measurement of TS/Xan pastes

Gelatinized TS/Xan mixtures (10/0, 9.5/0.5, 9/1 and 8.5/1.5) obtained from the RVA experiment were used for steady shear viscosity measurement. The pastes in RVA canisters (at temperature about 50 °C) were removed, kept in controlled temperature chamber at 50 °C and measured within 1 h. Cone and plate fixture (50 mm diameter, 1° cone angle and 0.05 mm gap) was used in a rheometer Physica MCR 300. Each TS/Xan paste was placed onto the measuring plate preset at 25 and 50 °C for at least 2 min and immediately covered with a small amount of mineral oil to prevent water loss during measurement. The shear rate was increased stepwise from 0.01 to 100 s^{-1} (test duration was 15 min). Shear stress and viscosity values were obtained as a function of shear rate.

Flow behaviors of the TS/Xan pastes were analyzed using a power law model as shown in equation (1):

$$\tau = K(\mathrm{d}\gamma/\mathrm{d}t)^n, \quad (1)$$

where τ = shear stress (Pa), $\mathrm{d}\gamma/\mathrm{d}t$ = shear rate (s^{-1}), K = consistency coefficient (Pa s^n), and n = flow behavior index. Shear stress and shear rate data were fitted to a power law model and the consistency coefficient and flow behavior index were calculated (Ketjarut, Suwonsichon, & Pongsawatmanit, 2010).

2.7. Statistical analysis

Each measurement was carried out using at least two freshly independently prepared samples. The results were reported as mean and standard deviation. Statistical analysis was performed using SPSS V.12 statistical software (SPSS (Thailand) Co., Ltd.).

3. Results and discussion

3.1. Temperature dependence of storage and loss moduli on heating for TS/Xan mixtures

The thermal scanning rheological measurements of 5% w/w dispersions of TS and Xan mixtures were performed by a Haake Rheostress-600. It should be noted that swollen starch granules are almost fully intact before heating. The samples were subjected to small oscillatory strains in the linear viscoelastic region and G' and G'' of the mixtures as a function of temperature are shown in Fig. 1. Changes in G' and G'' values of Xan alone (0.25, 0.5 and 0.75%) were

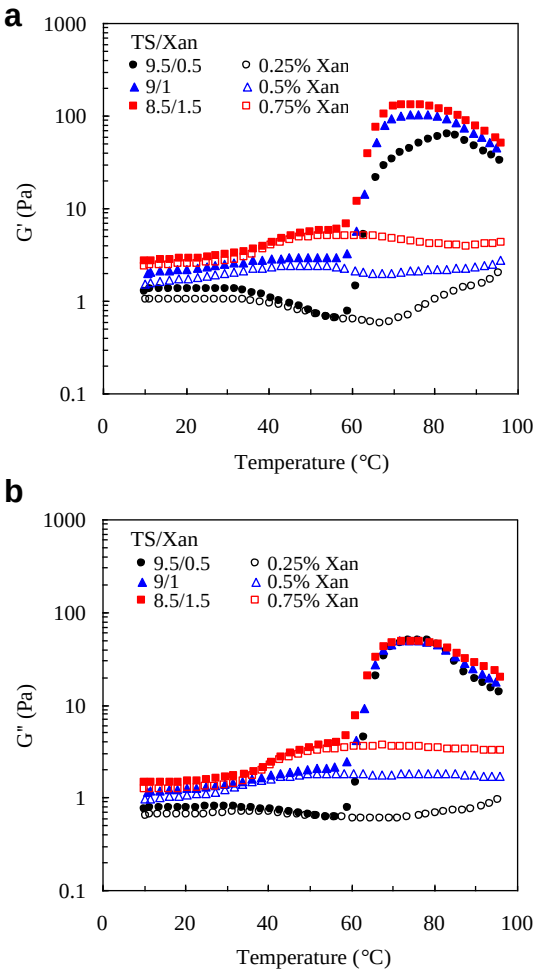

Fig. 1. Temperature dependence of the storage (a) and loss (b) moduli on heating of 5% w/w TS/Xan dispersions (9.5/0.5, 9/1 and 8.5/1.5) (solid) and Xan dispersions (0.25, 0.5 and 0.75%) (open) during heating from 10 to 95 °C (angular frequency: 1 rad/s, scan rate: 1 °C/min, 5% strain).

almost negligible compared with those of TS/Xan mixtures (Fig. 1). The G' and G'' of 0.75% Xan dispersions exhibited the same trend as those of RVA at temperatures below 60 °C (Fig. 5, Section 3.4). At a low concentration (0.25% Xan), G' was almost constant from 10 °C to 35 °C, then started to decrease until 65 °C with the lowest value, and finally increased with heating to higher temperatures. In the case of higher Xan concentration, G' of 0.5 and 0.75% Xan increased slightly with increasing temperature until 55 and 60 °C, respectively, and then slightly decreased. In a 0.25% Xan dispersion, Xan molecule existing as a helical structure converts to a coil conformation with a lower viscosity under elevated temperature conditions and low ionic strength. The midpoint transition temperature of the Xan was reported to be about 55 °C depending on ionic strength (Craig, Kee, Tamburic, & Barnes, 1997). In 0.5 and 0.75% Xan, an initial increase in G' and G'' occurred due to an initial entanglement of the coils during the transition process in the temperature range of 35–80 °C (Craig et al., 1997) or the helix-coil transformation (Westra, 1989) whereas G' and G'' decreased with increasing temperature due to the breaking down of the helix to the random coil conformation.

The G' and G'' of TS/Xan dispersions were higher than those of Xan alone due to the contribution of water-swollen starch granules. Increase in the G' and G'' is mainly caused by the gelatinization of starch because Xan did not show a steeper increase in the moduli

above 60 °C. Starting at a certain temperature range, the starch granules undergo an irreversible process known as gelatinization, which is marked by the crystalline melting, loss of birefringence, granule swelling and partial solubilization. At these temperatures, the starch granules begin to swell and disintegrate, then amylose chains release out from the granules leading to an increase in G' and G''. The increase in both G' and G'' of TS/Xan suspensions was promoted by increasing Xan concentration (Fig. 1). However, the patterns for thermal and rheological behaviors of TS/Xan dispersions before starch gelatinization are dominated by the Xan phase. During heating, the starch granules swell followed by leaching of small amylose molecules leading to an increase in G' and G'' to maximum values and then the moduli decreased indicating disruption of the starch granule. G' of all TS/Xan mixtures was larger than G'' and both moduli increased with increasing content of Xan (Fig. 1). The maximum G' increased with increasing Xan content but the maximum of G'' was not so dependent on Xan content. After heating at 95 °C, a three-fold increase in Xan content (from 0.25% to 0.75%) has only rather small effect on G' (2.0–4.2 Pa) whereas G' of TS/Xan dispersions is largely dominated by the starch phase with the values of 32.5–49.8 Pa for mixing ratios of 9.5/0.5 to 8.5/1.5, respectively (Table 1). The results also showed that the difference between G' and G'' tended to be larger with increasing Xan concentration. When tan δ ($=G''/G'$) values were plotted against the temperature (data not shown), tan δ of TS/Xan dispersions revealed almost constant values in the temperature range of 10 °C–35 °C, then started to increase. An increase in tan δ between 35 and 60 °C was most likely due to a conformational transition in Xan because starch swelling and gelatinization happen only at temperatures higher than 60 °C. At the end of the heating treatment at 95 °C, solid-like characteristics ($G' > G''$) were obtained.

3.2. Effect of cooling and reheating on viscoelastic properties of TS/Xan pastes

Influence of cooling (from 90 to 10 °C) and immediately reheating (from 10 to 90 °C) on G' and G'' of 5% w/w TS/Xan pastes (mixing ratio = 10/0, 9.5/0.5, 9/1 and 8.5/1.5) was examined using a Rheostress 600. All TS/Xan pastes were prepared by heating at 92 °C for 30 min for gelatinization of starch. Results are shown in Fig. 2 and Table 2. Moduli of TS/Xan at 90 °C were very strongly and irreversibly reduced (by a factor 10 or more) by shear conditions during hot magnetic stirring compared with the values in Fig. 1. Values of G' of TS/Xan pastes were about 1.3 and 4.9 Pa at 90 °C for mixing ratios of 9.5/0.5 and 8.5/1.5, respectively, and those of mixtures used in the previous Section 3.1 were about 32.5–49.8 Pa, due to starch degradation during preparation from thermal and shear effect (Table 2). While the G' of Xan did not decrease so much as shown in Table 2, G' (95 °C) = 32.5 (Table 1) and G' (90 °C) = 1.28 (Table 2) were obtained for TS/Xan at mixing ratio = 9.5/0.5, and the large decrease of G' was attributed mainly to that caused by starch phase. The G' and G'' of all TS/Xan pastes increased with decreasing temperature from 90 to 10 °C (Fig. 2a–d). The pastes of TS alone (Fig. 2a) showed G'' slightly larger than G'. Both moduli increased slightly with decreasing temperature caused by the short term retrogradation, but this slight increase was much smaller than the increase for TS/Xan pastes (Fig. 2b–d). In TS pastes containing Xan, G' was larger than G'' especially at lower temperatures where the structural formation was enhanced. At the same temperature, both G' and G'' of TS pastes increased with increasing Xan content. This is in a good agreement with the above mentioned thermal stability of Xan. However, the G' values became much higher than G'' in TS/Xan with increasing Xan content. The ratio G'(10 °C)/G'(90 °C) increased with increasing Xan content as shown in Table 2. The increase in G' of TS/Xan on cooling was induced by the formation of a solid-like network structure. This is opposite what is found by the steady shear viscosity measurement as will be shown in Fig. 6. The main reason for this observation originates from the conspicuous shear thinning behavior of Xan. With increasing Xan content, this shear thinning behavior becomes more apparent. The structure being formed on cooling is not destroyed in Fig. 2a–d because the G' was observed at a small deformation whilst in Fig. 6a–d, the steady shear viscosity was measured at a shear rate 10 s^{-1} and the structure being formed on cooling was destroyed at such a large deformation experiment. This short term retrogradation of starch is triggered by the gelation of amylose in starch alone as reported by Miles, Morris, Orford, and Ring (1985). Xan enhances the formation of network structure in our TS and appeared as an increase in G' as shown in Fig. 2a–d, but when the steady shear viscosity was measured, this structure formation was inhibited by a shear strong enough to destroy the structure being formed. In addition, the G' at 10 °C for TS/Xan samples is much larger than that for Xan alone and that for TS alone, indicating the enhancement of some structural formation in TS and Xan mixture at non-destructive small deformation. This structural formation is promoted by Xan which increases the effective concentration of starch (Kim & Yoo, 2006; Yoshimura, Takaya, & Nishinari, 1998). This is caused by the phase separation or mutual exclusion of unlike molecules (Eidam & Kulicke, 1995; Mandala & Bayas, 2004).

Whilst the G' of 0.5 and 0.75% Xan increased with increasing temperature from 10 to 95 °C in Fig. 1 and Table 1, G' of these samples increased with lowering temperature from 90 °C to 10 °C in Fig. 2 and Table 2. The so-called renaturation process of Xan has attracted much attention, but it is not so well understood. Once the double helices of Xan were denatured into coils on heating, it is believed that the original helices were not completely reproduced on cooling. It is still a matter of debate that the double helices are separated completely into two random coils simply by heating in water and not in DMSO or alkaline solvents (Matsuda et al., 2009). The interaction of Xan with amylose in the present mixture should be studied further.

After lowering the temperature to 10 °C, it was immediately raised from 10 to 90 °C. Then, G' and G'' of the pastes decreased on reheating. Once the network structure was formed on cooling, the structure was maintained at low temperatures. The G' values during reheating were higher than those during cooling, indicating that freshly gelatinized paste forms an initial inter-connected amylose network between the swollen granules and Xan during cooling. It is obvious that Xan plays an important role in creating the solid-like properties (Fig. 2) and enhances the viscosity of TS/Xan pastes (Fig. 6), suggesting that the rheological behaviors of 5% w/w TS during cooling and reheating could be modified with Xan.

Dispersions of Xan alone (0.5% and 0.75%) were also prepared by heating at 92 °C for 30 min for determining the changes of G' and G'' (Fig. 2e–f) under the same cooling and heating condition as those of TS/Xan pastes. The G' and G'' of 0.5% and 0.75% Xan dispersions increased with decreasing temperatures from 90 to 10 °C and

Table 1
Storage modulus of TS/Xan mixtures (prepared by magnetic stirring at room temperature for 30 min) in the heating process at 1 °C/min.

Sample (TS/Xan)	G' (10 °C) (Pa)	G' peak (Pa)	G' (95 °C) (Pa)
9.5/0.5		62.3 ± 1.36	32.50 ± 0.77
9/1		103.7 ± 1.13	45.13 ± 1.14
8.5/1.5		131.4 ± 1.27	49.80 ± 0.04
0.25%Xan	1.02 ± 0.03		1.97 ± 0.18
0.5% Xan	1.51 ± 0.03		2.81 ± 0.18
0.75% Xan	2.34 ± 0.08		4.20 ± 0.26

Mean ± standard deviation values.

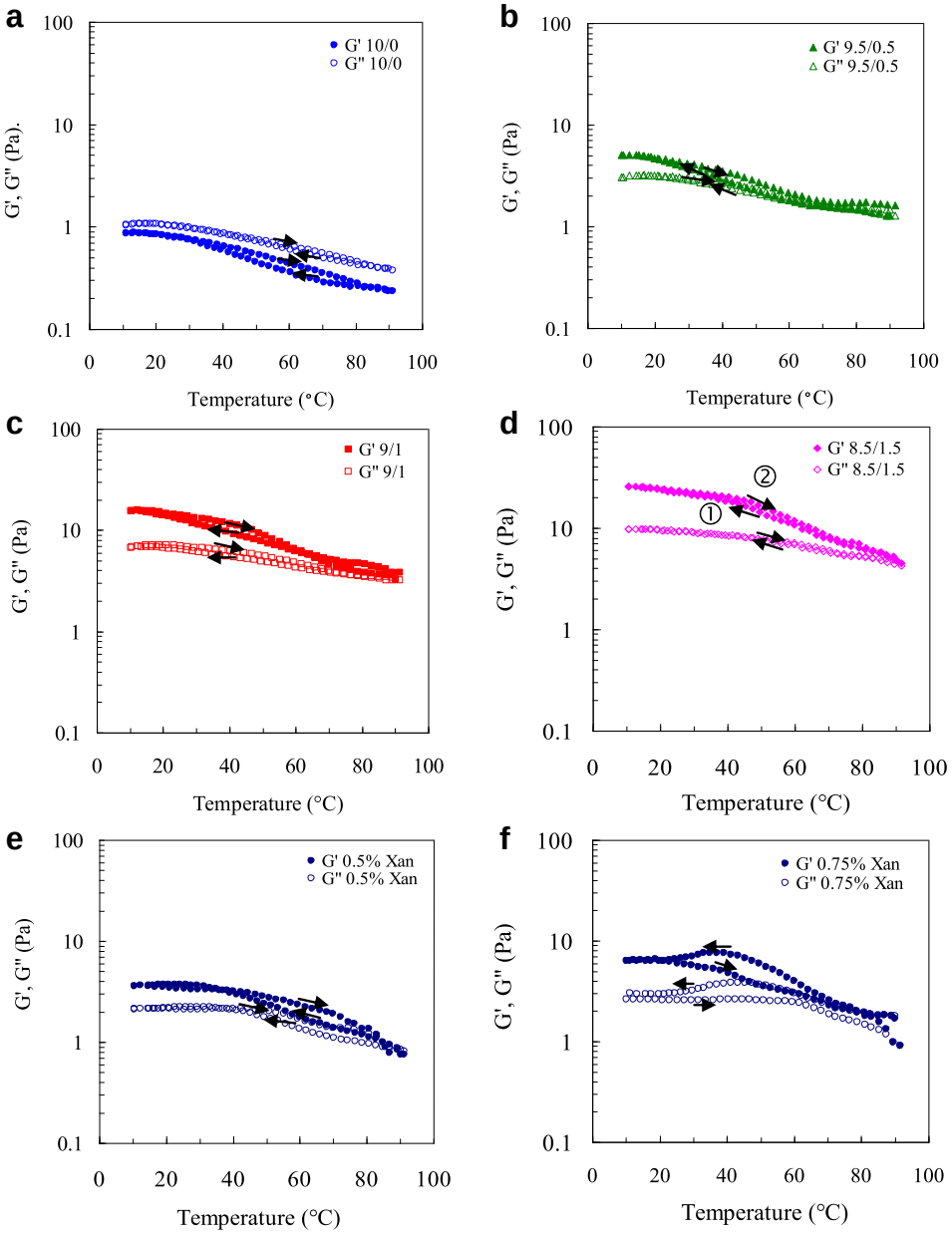

Fig. 2. Changes in G' and G'' of 5% w/w TS/Xan pastes at different mixing ratios; 10/0 (a), 9.5/0.5 (b), 9/1 (c) and 8.5/1.5 (d) on ① cooling from 90 to 10 °C and ② subsequently heating from 10 to 90 °C. 0.5% Xan (e) and 0.75% Xan (f) were also measured (angular frequency: 1 rad/s, scan rate at 1 °C/min, 5% strain).

showed the highest G' and G'' on cooling in the temperature range about 25 and 35–40 °C, respectively. After lowering the temperature to 10 °C, it was immediately raised from 10 to 90 °C. The G' and G'' decreased when reheating from 10 to 90 °C. Both Xan dispersions (0.5 and 0.75%) exhibited solid like property (so-called weak gel behavior) more than liquid like property when dissolved in water, i.e., $G' > G''$ on cooling and reheating (Morris, 2006). We observed the opposite phenomena from those of TS/Xan that both moduli of 0.75% Xan on cooling from 90 to 10 °C were higher than those on reheating from 10 to 90 °C. On heating above transition temperatures, the ordered structure, i.e. double helix of Xan changes into disordered structure and it returns to the ordered state upon cooling, but not completely to the same original state, depending on Xan concentration (Lee & Brant, 2002; Norton, Goodall, Frangou, Morris, & Rees, 1984).

Table 2
Storage modulus of TS/Xan mixtures (prepared by magnetic stirring at 92 °C for 30 min) measured at temperature 90 °C and cooling to 10 °C at 1 °C/min.

Sample (TS/Xan)	G' (90 °C) (Pa)	G' (10 °C) (Pa)	G' (10 °C)/G' (90 °C)
10/0	0.24 ± 0.03	0.86 ± 0.15	3.66 ± 0.20
9.5/0.5	1.28 ± 0.01	5.07 ± 0.07	3.96 ± 0.03
9/1	3.23 ± 0.11	15.59 ± 0.30	4.83 ± 0.26
8.5/1.5	4.92 ± 0.25	26.00 ± 0.16	5.29 ± 0.30
0.5% Xan	0.75 ± 0.07	3.59 ± 0.04	4.79 ± 0.49
0.75% Xan	1.70 ± 0.06	6.30 ± 0.28	3.71 ± 0.23

Mean ± standard deviation values.

3.3. Effect of storage at a low temperature on viscoelastic properties of TS/Xan pastes

In food preparation, many starch based sauces or soups are kept for a certain time after heating (including gelatinization) and

cooling before reheating. Then, in this section, the effects of storage time on G' and G'' at low temperature (10 °C) before reheating were investigated for developing further application in food product. The prepared TS/Xan pastes at 90 °C were cooled from 90 to 10 °C, then held for 10 h at 10 °C, and reheated to 90 °C. The changes in G' upon cooling and reheating process of 5% w/w TS/Xan pastes at various ratios (10/0, 9.5/0.5, 9/1 and 8.5/1.5) were recorded and plotted by comparing the values with and without holding at 10 °C for 10 h (Fig. 3). The G' values of Xan alone (0.5 and 0.75%) were also investigated for comparison. G' at 10 °C increased by a factor equal to or less than 2 (Table 3) indicating effect of storage at 10 °C for 10 h is rather limited. This is probably due to the limited contribution of the starch phase to the modulus. When the ratios of G'(10 h)/G'(0 h) of each TS/Xan paste were calculated (Table 3), the values decreased with increasing Xan (1.89, 1.27 and 1.22 for the mixtures of 9.5/0.5, 9/1 and 8.5/1.5, respectively) whereas the ratios of G'(10 h)/G'(0 h) of TS were about 1.03. This suggests that Xan dominates the composite rheology, and the increase in modulus on cooling is largely an effect of Xan. The G' of TS/Xan pastes (9.5/0.5, 9/1, 8.5/1.5) increased conspicuously during holding at 10 °C for 10 h (Fig. 3b). To observe the rate of network formation in TS/Xan pastes, changes in G' and G'' of all TS/Xan pastes and 0.5% and 0.75% Xan during holding at 10 °C as a function of time up to 10 h are presented in Fig. 4. For individual polysaccharide, the G' and G'' of TS alone (10/0) was not changed and only slightly increased in the 0.5% and 0.75% Xan (Fig. 4). However, during holding the pastes of TS/Xan (9.5/0.5, 9/1 and 8.5/1.5) at 10 °C for 10 h, G' and G'' increased obviously and this increase was promoted with increasing Xan content (Fig. 4) suggesting that Xan enhanced the structural formation of TS during the holding time at 10 °C. However, types of starch and hydrocolloid influence on the structure formation of starch. Yoshimura et al. (1999) reported that xyloglucan inhibits the formation of three dimensional network structure of corn starch and the phase arrangement of the two components in the system is not bi-continuous arrangement leading to a composite gel formed by only one component (corn starch) without the contribution from xyloglucan to the network formation. These were in agreement with the previous report for the mixtures of Xan and locust bean gum (Craig et al., 1997).

Table 3
Effect of storage at 10 °C on storage modulus of TS/Xan pastes (prepared by magnetic stirring at 92 °C for 30 min) with cooling to 10 °C at 1 °C/min and further holding at 10 °C for 10 h.

Sample (TS/Xan)	G' (90 °C) (Pa)	G' (10 °C, 0 h) (Pa)	G' (10 °C, 10 h) (Pa)	G' (10 h)/G' (0 h) at 10 °C
10/0	0.26 ± 0.01	1.13 ± 0.01	1.16 ± 0.03	1.03 ± 0.03
9.5/0.5	1.36 ± 0.04	4.57 ± 0.04	8.65 ± 0.28	1.89 ± 0.04
9/1	3.29 ± 0.02	15.49 ± 0.42	19.7 ± 0.16	1.27 ± 0.05
8.5/1.5	4.98 ± 0.17	25.69 ± 0.29	31.44 ± 0.08	1.22 ± 0.01

Mean ± standard deviation values.

After holding at 10 °C, the TS/Xan pastes were reheated to 90 °C at 1 °C/min heating rate. The larger hysteresis loops between cooling and reheating curves of TS/Xan pastes (9.5/0.5, 9/1, 8.5/1.5) were observed (Fig. 3b) compared with those without holding at 10 °C for 10 h (Fig. 3a). In addition, the loop areas (linear plot of Fig. 3 not shown) of TS/Xan pastes increased with increasing Xan concentration confirming the enhancement of network structure

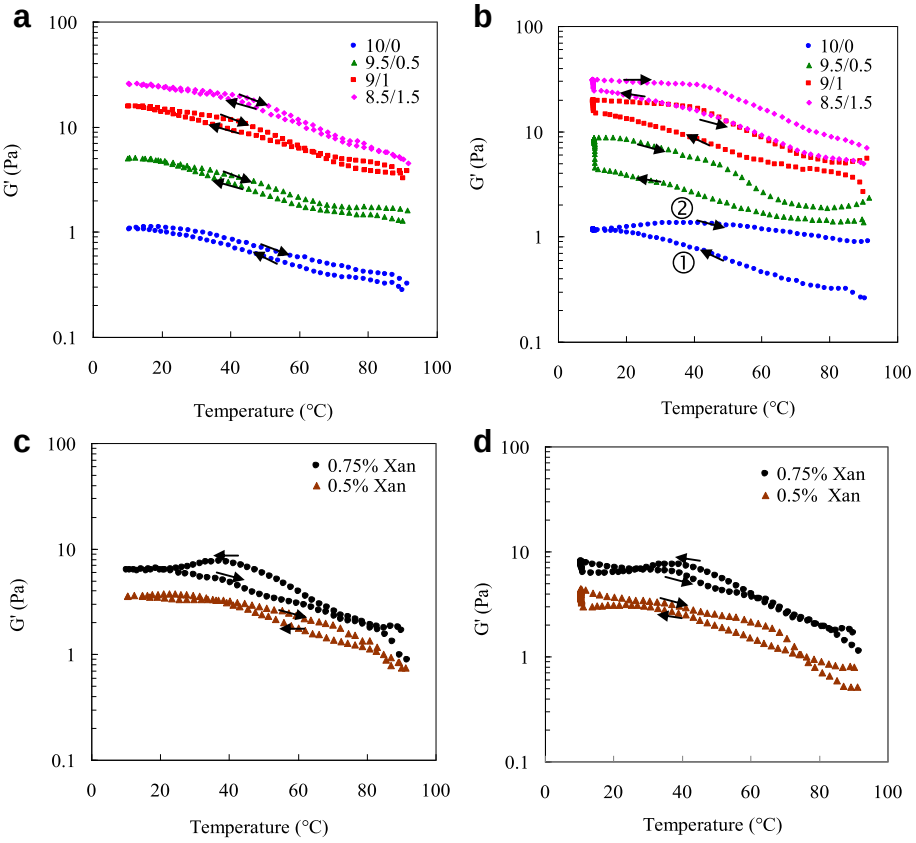

Fig. 3. Changes in G' on cooling and reheating process of 5% w/w TS/Xan pastes (10/0, 9.5/0.5, 9/1 and 8.5/1.5) (a, b) and 0.5% and 0.75% Xan (c, d). The cooling–heating cycle: (a, c) ① cooling from 90 to 10 °C and subsequently ② heating from 10 to 90 °C; and (b, d) ① cooling from 90 to 10 °C, holding at 10 °C for 10 h and ② reheating from 10 to 90 °C (angular frequency: 1 rad/s, scan rate at 1 °C/min, 5% strain).

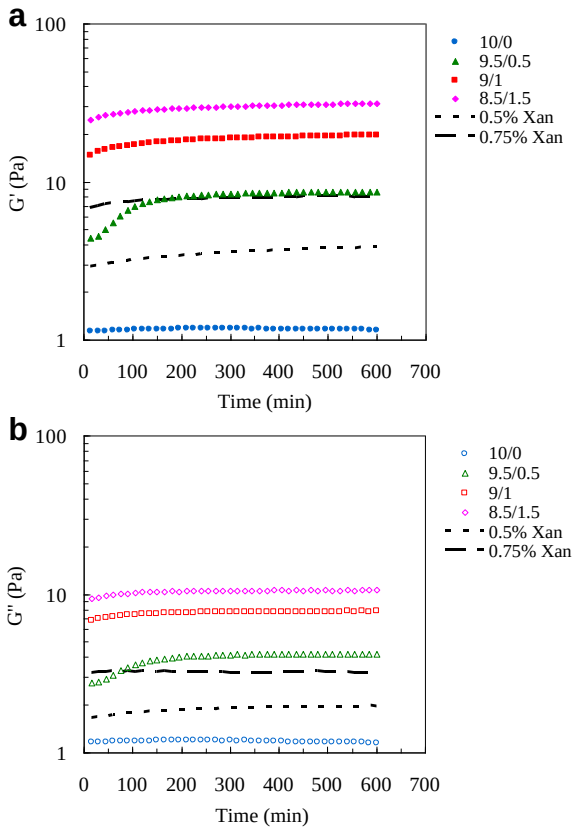

Fig. 4. Changes in G' (a) and G'' (b) of 5% w/w TS/Xan pastes (mixing ratios = 10/0, 9.5/0.5, 9/1 and 8.5/1.5) at 10 °C for 10 h after cooling to 10 °C from 90 °C. The pastes were heated at 92 °C for 30 min followed by cooling to 10 °C at 1 °C/min and holding for 10 h (angular frequency: 1 rad/s, scan rate at 1 °C/min, 5% strain).

formation induced by increasing effective concentration of TS, phase separation, and/or mutual exclusion.

3.4. RVA pasting properties

Typical pasting curves of 5% w/w TS/Xan mixtures (mixing ratios = 10/0, 9.5/0.5, 9/1 and 8.5/1.5) using RVA are shown in Fig. 5. The viscosity of Xan dispersion (0.75%) observed by RVA showed a normal temperature dependence in the range from 50 to 95 °C; it decreased gradually with increasing temperature and then showed a constant value at 95 °C, then increased gradually with decreasing temperature. In this temperature range, Xan is believed to be in disordered conformation and does not show order–disorder conformational change. However, addition of Xan resulted in a significant alteration on RVA pasting properties of TS (Fig. 5).

At temperatures below 50 °C, the native starch granules are insoluble in water leading to very low viscosities in starch suspensions at the beginning of pasting measurement. The viscosity of TS/Xan suspensions increased with increasing Xan content due to the thickening function of Xan except that of TS/Xan suspension at mixing ratio = 9.5/0.5 due to the limited sensitivity of the instrument. When starch granules are further heated in excess water, they adsorb a large amount of water. Pasting temperature (PT), the temperature at which viscosity shows a steep increase, of TS increased significantly from 68.9 to 73.2 °C with an increase in Xan concentration from 0 to 0.5% (Table 4) which is in a good agreement with a previous report (Pongsawatmanit & Srijunthongsiri, 2008). The PTs from the present experiment were lower than previously observed data due to the harvesting time

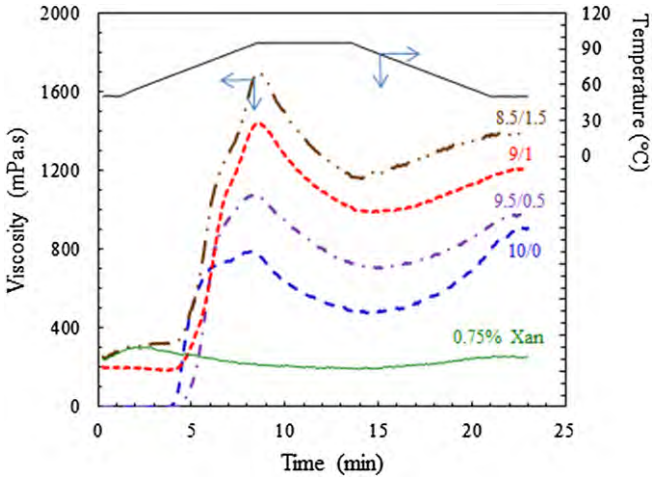

Fig. 5. Typical RVA pasting profiles of 5% w/w TS/Xan mixtures (mixing ratio = 10/0, 9.5/0.5, 9/1 and 8.5/1.5). Heating and cooling rate: 6 °C/min. Rotation speed of the paddle: 960 rpm for 10 s and then kept at 160 rpm throughout the experiment time.

leading to the difference in physicochemical properties of TS (Sriroth et al., 1999). The PT of TS decreased when Xan concentration in the mixture was higher than 0.75% (Table 4). It is important to note that the PT observed by RVA or a similar apparatus is dependent on instrument sensitivity: a gelatinization onset is recorded as soon as a minimum torque is exceeded. This is the reason why a pasting temperature determined by viscometry shifts to lower temperatures with increasing starch concentration. At low Xan additions (<0.75%) the positive effect of Xan on gelatinization onset temperature dominates, whereas at higher Xan dosages the onset temperature is reduced again by the increased viscosity of the medium.

As the temperature of the mixture increases further from PT, the viscosity increases to peak viscosity (PV) defined as the equilibrium point between swelling and polymer leaching. PV also indicates the water-binding capacity of the starch or mixture and often is correlated with quality of the final product, including the viscous load for a mixing cooker (Newport Scientific, 1995). The addition of Xan in the range from 0 to 0.75% enhanced the PV of the TS pastes from 793 mPa s to 1677 mPa s. This result can be interpreted by assuming that the system is a dispersed system consisting of starch granules dispersed in hydrocolloids which are dissolved in the continuous phase (Temsiripong et al., 2005). The effective concentration of hydrocolloids would then increase as the volume of the phase accessible to the hydrocolloids was reduced due to swelling of the starch granules during pasting. This resulted in a pronounced increase in the viscosity of the continuous phase (Alloncle et al., 1989). The increase in the viscosity of this suspension may be also explained as the increase of the volume fraction of the dispersed phase (starch granules) due to swelling. However, the contribution of the increase in volume fraction before the rupture of starch granules may be much smaller than the contribution from the increase in the viscosity of the continuous phase.

When the starch granules are held at a high temperature (usually 95 °C in RVA measurements) and mechanical shear stress, swollen granules break up and amylose molecules leach out into solution and undergo alignment resulting in a decrease in viscosity. The difference of the PV and minimum viscosity of RVA profile is defined as breakdown (BD). In the present experiment, BD of TS/Xan pastes increased from 329 mPa s to 529 mPa s with increasing Xan content from 0 to 0.75% (Table 4). The rate of viscosity reduction depends on the temperature and degree of mixing or shear stress applied to the mixture and the nature of material itself.

Table 4
RVA pasting properties of 5% w/w TS/Xan mixtures at various mixing ratios of 10/0, 9.5/0.5, 9/1 and 8.5/1.5.[a]

TS/Xan	PT (°C)	PV (mPa s)	BD (mPa s)	BD/PV	FV (mPa s)	SB (mPa s)	SB/FV
10/0	68.9 ± 0.5c	793±5d	329±7c	0.42 ± 0.01a	882 ± 14d	419 ± 10a	0.47 ± 0.01a
9.5/0.5	72.8 ± 0.2a	1053 ± 24c	361 ± 17c	0.34 ± 0.01b	972 ± 13c	280±2b	0.29 ± 0.01b
9/1	73.2 ± 0.4a	1498 ± 13b	473 ± 13b	0.32 ± 0.01c	1250 ± 11b	226 ± 17c	0.18 ± 0.01c
8.5/1.5	71.2 ± 0.2b	1677 ± 14a	529 ± 11a	0.32 ± 0.01c	1367 ± 12a	219±7c	0.16 ± 0.01d

Mean ± standard deviation values followed by a different lower-case letter within the same column are significantly different ($p < 0.05$) by Duncan's multiple range test.
[a] PT = pasting temperature, PV = peak viscosity, BD = breakdown, FV = final viscosity, SB = setback.

When the starches are subsequently cooled, re-association between macromolecules constituting starch especially amylose molecules occurs and viscosity increases to a final viscosity (FV) which is a parameter indicating the ability of the material to form a viscous paste or gel on cooling. The addition of Xan increased significantly the FV of the TS paste (882 mPa s to 1367 mPa s) as well as an increase in PV. The difference between the FV and the minimum viscosity after PV is called as setback (SB) which can be correlated with texture of products. Therefore, Xan enhanced PT, PV, FV and BD. However, Xan could reduce SB significantly (419 mPa s to 219 mPa s). When the terms of BD/PV and SB/FV were calculated (Table 4), it was found that relative BD (BD/PV) decreased with increasing Xan. A reduction of relative BD in a mixed system could hint at a protection of the swollen granules by Xan (Tsutsui et al., 2006) and it could be caused by the higher viscosity of the continuous phase, thereby leading to less importance in the BD of the starch phase in a relative term. In a similar way, the decreased SB at increasing Xan concentration does not necessarily point to reduce retrogradation, but may also be caused by a smaller relative contribution of starch retrogradation to the viscosity of the system as a whole.

Hot paste viscosity at the end of hold at 95 °C (HPV), FV at 50 °C and FV/HPV is shown in Table 5, because those parameters are most closely related to those of steady shear viscosity results to be discussed in the following Sections 3.5 and 3.6. HPV values were 486, 729, 1013 and 1168 mPa s for TS/Xan mixing ratios of 10/0, 9.5/0.5, 9/1 and 8.5/1.5, respectively, suggesting that blend rheology is dominated by Xan, with moderate breakdown of the starch granules. FV/HPV (=retrogradation effect) is diminished by adding Xan. This is likely due to a relatively smaller contribution of the TS phase to the blend rheology.

3.5. Temperature dependence of steady shear viscosity for TS/Xan mixtures

The thermal scanning measurement of steady shear viscosity of 5% w/w TS/Xan dispersions (9.95/0.05, 9.5/0.5, 9/1 and 8.5/1.5) on heating from 10 to 95 °C, cooling from 95 to 10 °C, and reheating from 10 to 95 °C were performed using the Physica rheometer with a shear rate of 10 s^{-1} and scan rate of 1 °C/min. The presence of 0.025% Xan in the TS/Xan (=9.95/0.05) mixture effectively retarded the sedimentation of TS granules during experiments. Fig. 6 shows the temperature dependence of steady shear viscosity at four mixing ratios (9.95/0.05, 9.5/0.5, 9/1 and 8.5/1.5). The steady shear viscosity of Xan dispersions alone (0.5% and 0.75%) was also measured at the same measurement condition of TS/Xan mixtures. Trends in viscosity after gelatinization at 95 °C, 50 °C and viscosity ratio of η(50 °C)/η(95 °C) (Table 6) revealed a similar trend to that in HPV, FV and FV/HPV of RVA measurement (Table 5), respectively. This suggests that shear conditions in sample preparation and testing in RVA and steady shear measurements are comparable.

Table 5
Viscosity of TS/Xan mixtures at hot paste viscosity at the end of holding at 95 °C (HPV), final viscosity at 50 °C (FV) and FV/HPV from RVA measurement.

Sample (TS/Xan)	HPV (Pa s)	FV (Pa s)	FV/HPV
10/0	0.486 ± 0.003	0.882 ± 0.014	1.82 ± 0.03
9.5/0.5	0.729 ± 0.014	0.972 ± 0.013	1.33 ± 0.01
9/1	1.013 ± 0.016	1.250 ± 0.011	1.23 ± 0.02
8.5/1.5	1.168 ± 0.006	1.367 ± 0.002	1.17 ± 0.01

Mean ± standard deviation values.

Before the gelatinization process (temperature <60 °C), the viscosity of TS/Xan dispersions increased with increasing Xan content from 0.025 to 0.75% due to the thickening ability of Xan. Viscosity values of TS/Xan at the mixing ratios = 9.95/0.05 and 9.5/0.5 decreased slightly in the temperature range from 10 to 60 °C (Fig. 6a and b) whereas that at mixing ratios = 9/1 and 8.5/1.5 started to slightly increase at the temperature approximately 35 °C (Fig. 6c and d). This is consistent with findings in dynamic viscoelastic measurements shown in Fig. 1. The viscosity of Xan dispersions (0.5 and 0.75%) shown in Fig. 6(e) and (f) was similar with that of dispersions of TS/Xan before gelatinization took place. Initial dispersion viscosity (before starch gelatinization) depends largely on Xan concentration. Paste viscosity after gelatinization onset is due to contributions of swollen granules accompanied by a concentration increase of gum and solubilized starch in the continuous phase (Christianson et al., 1981).

The viscosity of TS/Xan dispersions was dramatically increased by the gelatinization of TS after heating the dispersion to 62–63 °C (Fig. 6a–d). Viscosity at peak of TS/Xan mixtures increased with increasing Xan content which is in a good agreement with the RVA pasting profile (Fig. 5). In addition, the temperature at which the blend viscosity showed the maximum shifted to higher temperatures with increasing Xan concentration up to 0.25% Xan (mixing ratio = 9.5/0.5) and then the peak temperature increased only slightly above 0.25% Xan.

After the TS/Xan mixtures were gelatinized and heated to 95 °C, TS/Xan pastes formed were cooled down from 95 to 10 °C, immediately. The viscosity of TS/Xan increased with decreasing temperature due to the re-association of amylose molecules. The increase in viscosity of TS (using representative with TS/Xan = 9.95/0.05) on cooling to 10 °C (5.7 Pa s) (Table 6) suggests starch retrogradation even at a shear rate of 10 s^{-1}. The extensive irreversible degradation of the TS phase during the sample preparation for small deformation in Fig. 2, which has led to a very low G' of TS/Xan = 10/0, may play an important role in this case. The increase in viscosity of TS/Xan on lowering temperature (first cooling in Fig. 6(b)–(d)) was far smaller than that of moduli shown in Fig. 2(b)–(d), and this increase was decreased with increasing Xan content in the large deformation measurement. This is due to the pronounced shear thinning characteristics of Xan and also the inhibition of structure formation by the large deformation. Then the cooled pastes were reheated again from 10 to 95 °C, the viscosity of TS/Xan paste decreased with increasing temperature, as expected. The viscosity of TS/Xan on cooling from 95 to 10 °C and reheating from 10 to 95 °C did not coincide, and the values during cooling were higher than those during reheating (Fig. 6a–d).

Steady shear viscosity of TS/Xan pastes at a shear rate of 10 s^{-1} on cooling (from 95 to 10 °C) and reheating (from 10 to 95 °C) became less temperature dependent with increasing Xan concentration

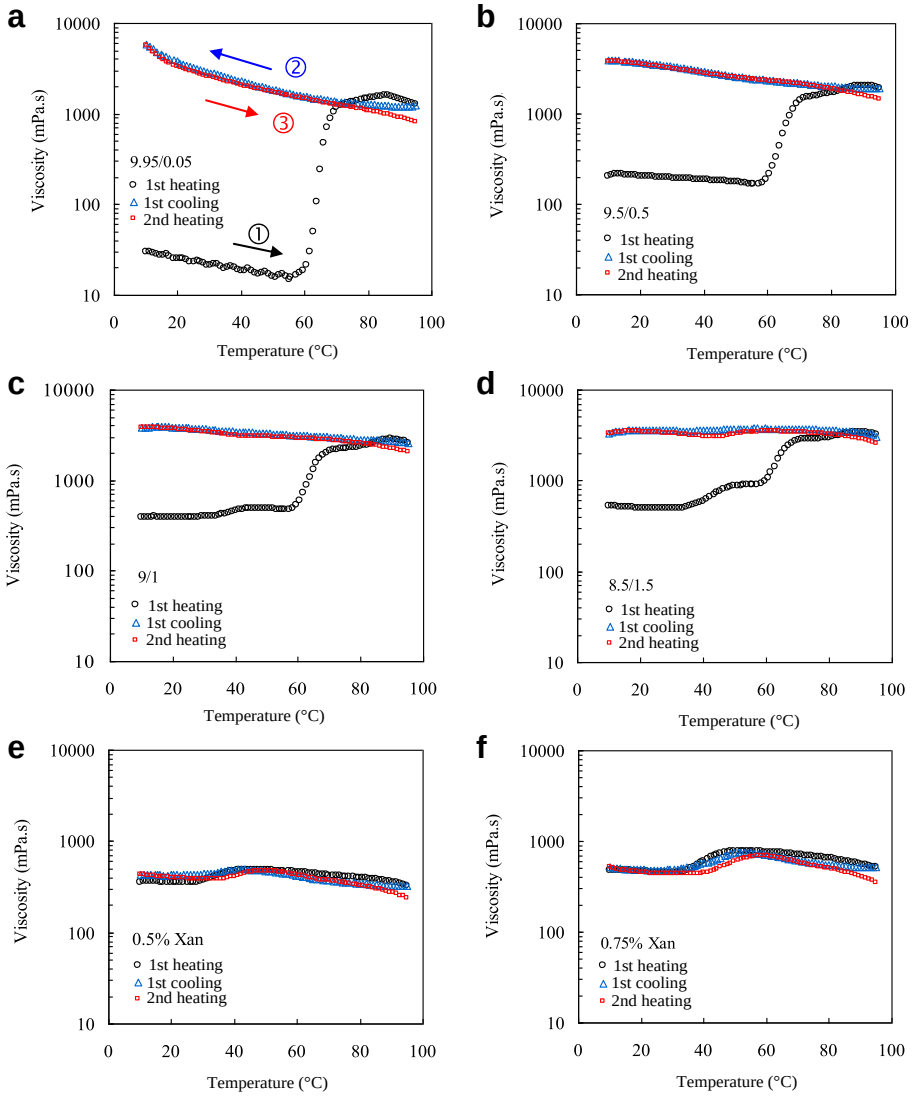

Fig. 6. Temperature dependence of steady shear viscosity of 5% w/w TS/Xan mixtures: 9.95/0.05 (a), 9.5/0.5 (b), 9/1 (c) and 8.5/1.5 (d), and 0.5% Xan (e) 0.75% Xan (f). Shear rate: 10 s^{-1}. Heating–cooling condition: ① heating from 10 to 95 °C ② cooling from 95 to 10 °C, ③ and finally reheating from 10 to 95 °C at the rate of 1 °C/min.

(Fig. 6) due to the thermal stability of the viscosity of Xan. In agreement with RVA results (Fig. 5 and Table 5), Xan reduces the short term retrogradation due to the lower setback of the pastes containing Xan on cooling (Section 3.4). The changes in steady shear viscosity of TS/Xan pastes at low temperatures in Fig. 6 decreased with increasing Xan content, confirming that Xan reduces the short term retrogradation. The consistency in the results between the RVA (Fig. 5) and steady shear viscosity (Fig. 6) was expected because both were observed at large deformations. Table 6 shows the viscosity at the shear rate 10 s^{-1} at three different temperatures (95, 50 and 10 °C). The trend in viscosity ratio of η(10 °C)/η(95 °C) in Table 6 is opposite to that in G'(10 °C)/G'(90 °C) in Table 2. This is explained by the suppression of starch retrogradation triggered by the gelation of amylose under shear.

Fig. 7 shows the viscosity at various shear rates of 5% w/w TS/Xan paste (8.5/1.5) after being kept for 5 h at 10 °C on cooling from 95 °C at 1 °C/min. The viscosity increased with decreasing shear rate indicating the non-equilibrium nature of the viscosity value at

Table 6
Viscosity (η) of TS/Xan pastes (shear rate 10 s^{-1}) at three different temperatures (95, 50 and 10 °C) (prepared by magnetic stirring at room temperature for 30 min) with heating to 95 °C and subsequently cooling to 10 °C at 1 °C/min.

Sample (TS/Xan)	η (95 °C) (Pa s)	η (50 °C) (Pa s)	η (10 °C) (Pa s)	η(50 °C)/η(95 °C)	η(10 °C)/η(95 °C)
9.95/0.05	1.27 ± 0.03	1.86 ± 0.05	5.69 ± 0.14	1.46 ± 0.01	4.48 ± 0.01
9.5/0.5	1.94 ± 0.02	2.58 ± 0.06	3.84 ± 0.05	1.33 ± 0.05	1.98 ± 0.00
9/1	2.62 ± 0.01	3.31 ± 0.03	3.79 ± 0.11	1.26 ± 0.01	1.45 ± 0.04
8.5/1.5	3.18 ± 0.10	3.72 ± 0.02	3.33 ± 0.04	1.17 ± 0.04	1.05 ± 0.02
0.5% Xan	0.33 ± 0.00	0.47 ± 0.00	0.43 ± 0.00	1.42 ± 0.01	1.30 ± 0.00
0.75% Xan	0.52 ± 0.01	0.74 ± 0.02	0.51 ± 0.00	1.42 ± 0.06	0.98 ± 0.00

Mean ± standard deviation values.

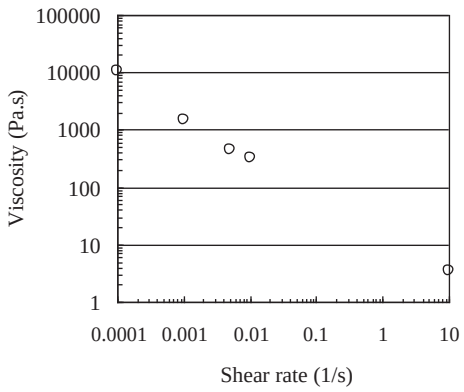

Fig. 7. Viscosity at various shear rates of 5% w/w TS/Xan paste (8.5/1.5) kept for 5 h at 10 °C after cooling from 95 °C at 1 °C/min.

10 °C in Fig. 6. When the temperature was lowered from 95 °C, the steady shear viscosity observed at 10 s^{-1} increased but the structure being formed was partially destroyed. This destruction became less serious with decreasing shear rate. A similar situation was reported in the gelation of HPMC (hydroxypropylmethyl cellulose) (Silva et al., 2008). Since HPMC forms a gel on heating, it was found that the viscosity first decreased as in normal liquid, and then the viscosity showed a steep increase at a gelation temperature. This steep increase in the viscosity was hindered with increasing shear rate. The increase of the viscosity of TS/Xan on cooling in Fig. 6 should be compared with the increase in G' and G'' shown before in Fig. 2. Gelling process for both heat-set and cold-set gelling materials has been studied by small amplitude oscillational measurement rather than by large deformation viscosity measurement which destroys the structure being formed during gelation (Nishinari, 1997, 2000).

3.6. Steady shear viscosity measurement of TS/Xan pastes

To confirm shear thinning behavior of TS/Xan pastes at selected temperatures, steady shear viscosity of 5% w/w TS/Xan (10/0, 9.5/0.5, 9/1 and 8.5/1.5) from RVA experiment was determined as a function of shear rate at 25 and 50 °C. All gelatinized TS pastes with and without Xan exhibited shear thinning behavior (Fig. 8). As expected, viscosity of all TS/Xan pastes at lower temperature (25 °C) was higher than that at higher temperature (50 °C). At 25 °C, viscosities of TS/Xan pastes were lower than those of TS paste at shear rates >0.5 s^{-1} (Fig. 8a). However, when the measurement was performed at 50 °C, the viscosities of pastes of TS alone were lower than those of pastes containing Xan in the studied shear rate range (Fig. 8c) indicating the contribution of thermal stability of Xan to TS pastes. It should be pointed out that all the TS pastes with and without Xan showed a Newtonian plateau at lower shear rates indicating that all systems are viscoelastic liquids rather than solids at 50 and 25 °C: they have no yield stress and no permanent network structure at these temperatures. It may take a long time for TS paste to show a detectable yield stress at these temperatures. Moreover, the increase in the viscosity at lower shear rates was observed with increasing Xan content. This phenomenon could be explained by higher degree of shear thinning of Xan and the structure formation, but the details should be studied further.

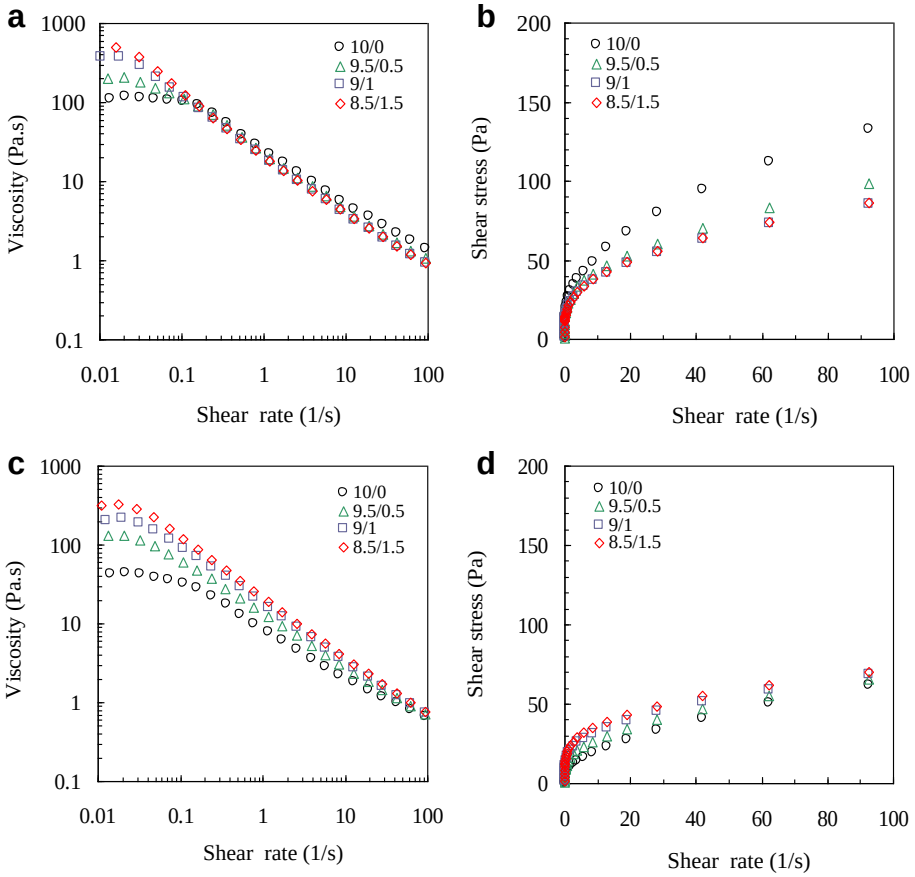

Fig. 8. Shear rate dependence of the steady shear viscosity (25 °C (a), 50 °C(c)) and of shear stress (25 °C (b), 50 °C (d)) for 5% w/w gelatinized TS/Xan pastes (mixing ratios = 10/0, 9.5/0.5, 9/1 and 8.5/1.5). The pastes (50 °C) from RVA measurement kept in controlled temperature chamber at 50 °C and measurement within 1 h.

Table 7
Power law parameters (K = consistency coefficient, n = flow behavior index) of 5% w/w TS/Xan pastes with different mixing ratios (10/0, 9.5/0.5, 9/1 and 8.5/1.5) determined from the shear rate range 0.01–100 s^{-1} at 25 and 50 °C.

Temperature (°C)	TS/Xan	K (Pa s^n)	n (−)	r^2
25	10/0	16.4 ± 2.6cd	0.437 ± 0.008b	0.941
	9.5/0.5	19.5 ± 1.7abc	0.367 ± 0.016c	0.969
	9/1	20.8 ± 2.2 ab	0.319 ± 0.010d	0.970
	8.5/1.5	21.9 ± 0.2a	0.308 ± 0.001de	0.963
50	10/0	6.2 ± 1.4f	0.478 ± 0.016a	0.987
	9.5/0.5	12.3 ± 0.7e	0.380 ± 0.011c	0.982
	9/1	15.6 ± 2.4d	0.324 ± 0.007d	0.972
	8.5/1.5	18.4 ± 2.0bcd	0.295 ± 0.012e	0.947

Mean ± standard deviation values followed by a different lower-case letter within the same column are significantly different ($p < 0.05$) by Duncan's multiple range test.

Flow curves of TS/Xan pastes are plotted at 25 and 50 °C as shown in Fig. 8b and d. All pastes exhibited pseudoplastic behavior. The power law (Equation (1)) was found to model all TS/Xan pastes with different mixing ratios with $r^2 = 0.95–0.99$ at both 25 and 50 °C. The consistency coefficient (K) of all TS pastes increased with increasing Xan substitution (0–0.75%) especially at 50 °C from 6.2 to 18.4 Pa s^n, respectively. We observed that addition of 0.75% Xan in TS pastes (mixing ratio = 8.5/1.5) decreased the flow behavior index of the pastes from 0.44 to 0.31 and 0.48 to 0.30 for 25 and 50 °C, respectively. The results suggest that substitution of Xan in TS pastes enhanced the shear thinning behavior showing the deviation of n from the Newtonian value (one) (Table 7). The temperature dependence of K (Table 7) is strongest for 10/0, which is in agreement with Fig. 6 and the value of FV/HPV of RVA experiment (Table 5) including viscosity ratios of η(50 °C)/η(95 °C) or η(10 °C)/η(95 °C) in Table 6.

4. Conclusion

The influence of Xan on pasting and rheological properties of TS was observed by increasing gelatinization temperature, peak and final viscosity, and breakdown but decreasing setback values. G' and G'' of TS dispersions and pastes depended on Xan concentration. Thermal stability of TS paste in terms of steady shear viscosity was obtained by adding Xan. Freshly prepared TS pastes containing Xan showed larger G' compared with TS pastes and G' increased with increasing Xan for both on cooling and heating. Holding TS/Xan pastes for 10 h after cooling to 10 °C enhanced the network structure formation leading to much larger G' on reheating from 10 to 90 °C than those without holding time. Partial substitution of TS with Xan could improve pasting and rheological properties of TS dispersion and paste.

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Quality of Batter and Sponge Cake Prepared from Wheat-Tapioca Flour Blends

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ABSTRACT

The type of flour used in a sponge cake plays an important role in improving product quality. The possibility of cake preparation using tapioca starch (TS) as partial substitution for wheat flour (WF) for further application in the food industry was investigated. Sponge cake batter formulations containing flour blends of WF (10–20%) and TS (0–10%) at three mixing ratios (100:0, 75:25 and 50:50) were studied. Apparent viscosity of batters was determined from steady shear measurement and decreased with increasing TS substitution for WF. The batter density decreased with increasing TS content, indicating a higher amount of air incorporated into the cake batter during mixing. The specific volume of cakes after baking at 175 °C for 20 min increased with increasing TS substitution. The texture profile analysis hardness values of baked cakes containing 50% TS substitution were significantly ($P < 0.05$) lower than those prepared from only WF. Softness and overall liking scores of cakes prepared from WF and TS (mixing ratio = 50:50) were significantly ($P < 0.05$) higher than those prepared from only WF. The results suggest that partial replacement of WF by TS (up to 50%) decreased batter viscosity and density leading to higher specific volume and lower hardness in sponge cakes after baking. Therefore, TS could be used in sponge cake preparation for modifying textures in the baking industry.

Keywords: viscosity, power law model, specific volume, texture, sensory evaluation

INTRODUCTION

The quality of the ingredients and the nature of their interactions influence the quality of a final food product. In the bakery industry, cake is one type of air-leavened product. The quality of cakes depends on many factors such as the ingredients used for batter preparation, aeration of batters and process conditions. There are many reports investigating the quality of cake batter determining the final quality of cake products (Sakiyan *et al.*, 2004; Yang and Foegeding, 2010). Batters are obtained by aerating the liquid mixture via mechanical mixing to form a foam structure in order to obtain cakes as the final product; therefore, these batters are complex emulsion systems whose density and rheological properties play an essential role in determining the characteristics of the resulting cakes. High quality cakes can be characterized as having various attributes, including high volume, uniform crumb structure, softness and a long shelf life with tolerance to staling (Gelinas *et al.*, 1999). The expansion of cake products comes from the volume of air bubbles entrapped in the cake batter and the liquid part in the system. The cake

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expansion increases with increasing temperature of the batter according to the gas laws and with increasing water vapor pressure from the liquid in the mixture (Matz, 1992). As the ingredients play an important functional role in the structure and eating quality of the product (Conforti, 2006), cake batters prepared from whole eggs containing egg yolk lipids exhibit very fine bubbles in the crumb (internal structure) of baked products leading to a silky and tender texture. In addition, a formula based on egg yolks containing added shortening further changed the structural qualities of both the batter and the baked cake (Matz, 1992). Baking powder is also used in sponge cake and has been suggested to be added at the final stage of ingredient mixing (Matz, 1992).

Not only wheat flour but also other flour types have been investigated for developing cakes of lower cost and better quality in terms of consumer acceptance (Turabi *et al.,* 2008). The cakes studied were prepared from various types of flour such as wheat-chickpea flour blends (Gomez *et al.,* 2008), rice flour (Turabi *et al.,* 2008) and flour obtained from wheat, rye, and barley (Gomez *et al.,* 2010). Tapioca starch (TS), produced from cassava roots, is a thickener used in the food industry due to its high viscosity, clear appearance and low production cost compared to other starches, especially in Thailand. However, the effect of partial substitution of wheat flour (WF) with TS on the quality of the batter and the sponge cake has rarely been investigated. Therefore, the objective of the present study was to establish the influence of partial substitution of WF with different levels of TS in the cake formulation on the rheological properties, density and microscopic analysis of cake batters. In addition, the influence of the partial substitution of WF with TS on cake volume, texture and the sensory properties of baked cake was also determined. The results of the present study could be used to design cake emulsions with improved properties needed for further applications in product and process development.

MATERIALS AND METHODS

Materials

Tapioca starch (TS) was purchased from Siam Modified Starch Co., Ltd. (Pathum Thani, Thailand) with 11.1% moisture, 1.0% protein and 0.2% ash contents on a wet basis and was determined using a hot air oven at 105 °C, by the Kjeldahl method, and by dry ashing in a furnace at 550 °C, respectively, according to the methods of AOAC (2000). Wheat flour (WF) for cake preparation containing 11.6% moisture, 7.9% protein and 0.4% ash contents on a wet basis (AOAC, 2000) was used in the study. Fresh whole eggs, whole milk powder, baking powder with double-action, emulsifier (SP®), sugar and butter containing 1.5% salt (Orchid®) were purchased from a supermarket and used without any further purification.

Cake preparation

The experiments used sponge cake batter formulations containing WF (10–20%) and TS (0–10%) to obtain flour blends at three mixing ratios (WF:TS = 100:0, 75:25 and 50:50), 28.0% liquid whole eggs, 2.0% whole milk powder, 0.4% baking powder, 1.6% emulsifier, 24.0% sugar, 16.0% butter and 8.0% water (Table 1). In the cake batter preparation (500 g), the liquid whole eggs, water, sugar and emulsifier were mixed in a Kitchen-Aid mixer (5K5SS, St. Joseph, MI, US with machine speeds from 1 to 10) at speed 3 for 1 min and further mixed at speed 6 for 9 min. Then, dry ingredients (the flour blend of WF and TS, whole milk powder and baking powder) were added simultaneously to the mixture at speed 1 for 1 min and further mixed at speed 3 for 2 min. The melted butter was added finally and mixed at speed 1 for 20 s. Each batter formulation (125 g) was placed in an aluminum pan ($8.5 \times 16 \times 5$ cm) and baked in an electric oven (Teba™, TFL10-

Table 1 Percentage of ingredients in sponge cake formulations (100 g) containing different mixing ratios of wheat flour (WF) and tapioca starch (TS).

Ingredients	Flour blend (WF:TS) (%)		
	100:0	75:25	50:50
Wheat flour (for cake)	20.0	15.0	10.0
Tapioca starch	0	5.0	10.0
Liquid whole egg	28.0	28.0	28.0
Whole milk powder	2.0	2.0	2.0
Baking powder	0.4	0.4	0.4
Water	8.0	8.0	8.0
Emulsifier (SP®)	1.6	1.6	1.6
Sugar	24.0	24.0	24.0
Butter (1.5% salt)	16.0	16.0	16.0
Total	100.00	100.00	100.00

31) at 175 °C for 20 min. After baking, the cakes were removed from the pans, cooled upside down on a wire rack for 30 min at room temperature and kept in plastic bags to prevent drying before being measured for physical properties and sensory evaluation within 12 h.

Batter quality measurement

Apparent viscosity

The shear stress and apparent viscosity of the prepared batters were recorded as a function of a shear rate range between 2.5 and 62.5 s^{-1} controlled at 25 °C using a rotational viscometer (DV-III, Brookfield-RVT) with the coaxial cylinder geometry of the small sample adapter and the SC4- 29 spindle according to the method of Ketjarut *et al.* (2010). Sample temperatures were kept constant for at least 5 min before starting measurements. The flow behavior of each batter formulation was evaluated using a power law model as shown in Equation 1 by plotting *ln* (shear stress) and *ln* (shear rate) to obtain the consistency coefficient (*K*) and flow behavior index (n):

$$\tau = K\dot{\gamma}^n \quad (1)$$

where: τ = shear stress (Pa)

$\dot{\gamma}$ = shear rate (s^{-1})

K = consistency coefficient ($Pa.s^n$)

n = flow behavior index.

The coefficient of determination (R^2) was also calculated. All measurements were carried out at a controlled temperature (25 ± 2 °C). At least three replications were completed.

Batter density

The batter was filled into an aluminum cup immediately after removal from the mixer, leveled off using a rubber spatula and weighed. The batter density was calculated as the ratio of the batter weight (W_1) to the distilled water weight (W_2) filled in the same cup (modified from Gomez *et al.*, 2007). The density of the water was 1 g/cm^3.

Microscopic analysis

For each cake batter sample with and without TS substitution, a thin layer of freshly prepared samples was prepared immediately by placing a drop of the batter on a microscope slide and covering with a cover slip. The samples were observed under an optical microscope (Model CH30RF200, Olympus®, Tokyo, Japan) with a 10× magnification. A digital camera was mounted on the microscope for taking photographs.

Cake quality determination

Specific volume

The final cake volume was obtained using the rapeseed displacement method. The cake

was cut into 25 × 25 × 25 mm cubes. Then, one piece of cake was weighed (W_o), placed in a container and the rest of the container volume was filled with rapeseed (V_2). The volume of the empty container (V_1) was calculated by filling with rapeseed. Both V_1 and V_2 were later determined by a graduated cylinder and the difference between V_1 and V_2 was defined as the cake volume (V_o). The specific volume was then calculated as the ratio of the volume to weight (V_o/W_o).

Crumb texture

Texture profile analysis (TPA) was performed to evaluate the texture of the cakes using a Texture Analyzer (TA-500, Lloyd Instruments Ltd., UK) equipped with the texture NEXYGEN™ software program (Ametek, Inc., UK). The cake samples were cut into 25 × 25 × 25 mm cubes before TPA measurement. A standard double-cycle program was used to compress the samples at a speed of 50 mm/min with 50% deformation using a 50 mm diameter probe (modified from Pongsawatmanit *et al.,* 2007) without the waiting time before starting the second compression. Hardness (N), cohesiveness (no unit), springiness (mm) chewiness (Nm) and gumminess (N) were calculated by the software program. At least 5 samples were measured to obtain an average value of all texture parameters for each formulation.

Sensory evaluation

An affective test for sensory evaluation of sponge cake containing different TS levels was performed using 30 untrained panelists (the students and staff of the Department of Product Development, Kasetsart University). Each panelist was presented with individual cake samples (about 3 × 3 × 1.5 cm) with and without TS that had been baked within the previous 12 h and were placed on a tray in a plastic bag coded with a three-digit random number and served in a randomized order. During the panel session, water was provided to panelists to minimize any residual effect before testing a new sample. Each panelist was asked to rate the liking of quality attributes according to appearance, color, odor, softness and overall liking of each sample using a 9-point hedonic scale (1 = dislike extremely, 5 = neither dislike nor like, and 9 = like extremely).

Statistic analysis

All measurements were performed using three replications. The results were reported as the mean value with standard deviation. The data were subjected to analysis of variance (ANOVA) using the SPSS V.12 statistical software package (SPSS (Thailand) Co., Ltd.). Duncan's multiple range test (DMRT) was also applied to determine significant differences at the 5% level of significance ($P < 0.05$) between the treatment parameters associated with the properties of the batter and baked cake.

RESULTS AND DISCUSSION

Quality of cake batter with and without tapioca starch

The flow curves of the cake batters containing different mixing ratios of WF and TS (100:0, 75:25, 50:50) were determined from steady shear measurements at 25 °C. All batters with and without TS exhibited a pseudoplastic behavior. The apparent viscosity of the batters decreased with increasing shear rate and TS substitution for WF (Figure 1a). The results obtained were in good agreement with the results obtained from batters containing WF and TS mixtures for fried products (Ketjarut *et al.,* 2010). Therefore, the WF content in the cake batter played a predominant role in increasing the batter viscosity due to the wheat protein being the main cause of batter viscosity development during mixing (Loewe, 1993).

Since the shear-thinning behavior was exhibited in the middle region, the apparent viscosity decreased with increasing shear rate for the shear thinning fluid. Thus, the power law equation (Equation 1) described the flow behaviors

of all cake batter formulations with different mixing ratios of WF and TS (R^2 = 0.998–1.000; Table 2; Figure 1b). The consistency index (*K*) of all batters decreased with increasing TS substitution from 15.4 to 8.0 for batters without TS and with 50% TS substitution for WF (Table 2), respectively. The addition of TS in the batters significantly altered the flow behavior index of the batters from 0.64 to 0.71 for the samples without and with TS, respectively (Table 2) suggesting that the batters containing TS had more pronounced Newtonian behavior due to the value of *n* approaching close to one.

In general, the methods used to characterize cake batters are mainly based on the measurement of the viscosity and the density. Density is a key measurement used in the industry to characterize aeration. It is generally measured by weighing a known volume of batter (Fox *et al.*, 2004). Then, the batter density can be related to the amount of air incorporated in the batter during the mixing process and applied to determine the expected quality of the final baked cake. The present study found that the batter density decreased with increasing TS substitution (Table 2), indicating there was a higher amount of air incorporated into the batter. The lower viscosity was expected to have lower resistance to the applied shear during the mixing process leading to a higher amount of air being incorporated. The batter without TS (100% WF) showed the highest batter density values (0.488 g/cm^3) but was not significantly different to the batter containing 25% TS substitution for WF (0.467 g/cm^3), whereas the

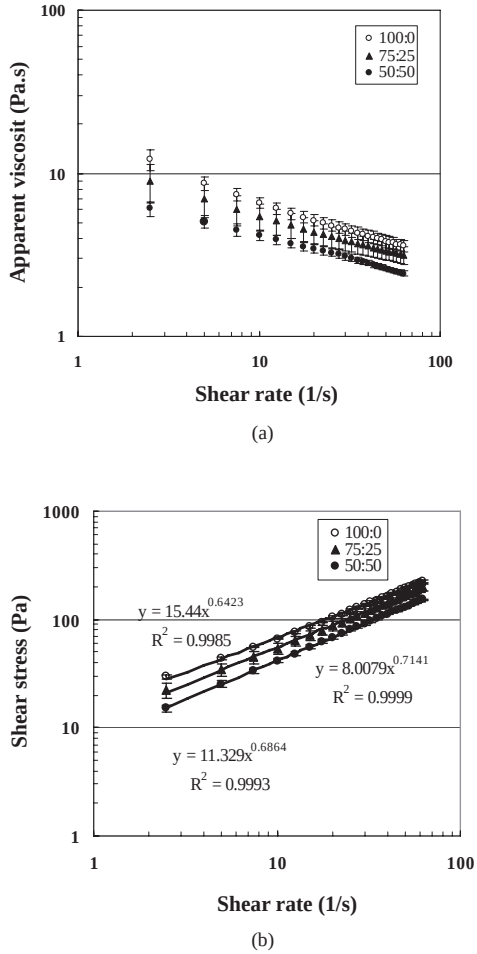

Figure 1 Apparent viscosity shown as mean ± standard deviation bars (a) and rheogram with power law model (b) of cake batters prepared from flour blends with different mixing ratios of WF and TS (100:0, 75:25 and 50:50) determined at 25 °C. The equations in the plot follow Equation 1: $\tau = K\dot{\gamma}^n$.

Table 2 Power law constants and density of batters prepared from flour blends of wheat flour (WF) and tapioca starch (TS) with different mixing ratios.

Flour blend (WF:TS)	*K* (Pa.s^n)	*n*	R^2	Batter density (g/cm^3)
100 : 0	15.4±0.4^a	0.64±0.01^b	0.998	0.488±0.015^a
75 : 25	11.4±2.1^b	0.70±0.02^a	0.999	0.467±0.009^{ab}
50 : 50	8.0±0.9^c	0.71±0.03^a	1.000	0.459±0.037^b

Mean ± standard deviation values (n = 9) followed by a different lower-case letter within the same column are significantly different ($P < 0.05$) by Duncan's multiple range test.

batter density was significantly different to that containing 50%TS substitution (0.459 g/cm^3) as shown in Table 2. To confirm the explanation of the relationship between the batter density and bubble size and distribution, images of the cake batters are shown in Figures 2a–2c. The bubble size distribution was dependent on the batter density as well as on the level of TS substitution for WF. The smaller bubble size with more uniform appearance was observed in the batter samples prepared from WF only, due to the higher batter viscosity with higher WF content (Table 2). The bubbles in the batters containing TS with lower batter density (0.467–0.459 g/cm^3) exhibited a wide variation in bubble size distribution due to the low viscosity of the batter containing TS having lower gluten content which affected the larger number of air cells initially incorporated during mixing (Sahi and Alava, 2003). A higher number of larger air bubbles was observed in the photomicrographs of cake batters containing higher TS contents. The larger air bubble sizes that existed in the batters containing TS with lower viscosity were expected to reveal evidence of coalescence where two or more bubbles had merged to form a larger bubble (Irene *et al.*, 2006) during the aeration stage before baking.

Quality of cakes containing tapioca starch

The specific volume of baked cake indicates the amount of air that can remain in the final product. A higher gas retention and higher expansion of the product (Gomez *et al.*, 2008) leads to a higher specific volume. After baking at 175 °C for 20 min, the specific volumes of cake with and without TS were determined and showed a significantly higher value with increasing TS content indicating a higher amount of air remained in the cake. When the specific volume of baked

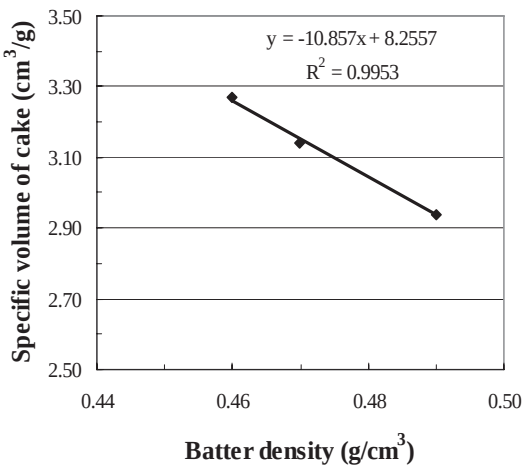

Figure 3 Specific volume of cake as a function of batter density prepared from flour blends with different mixing ratios of WF and TS (100:0, 75:25 and 50:50).

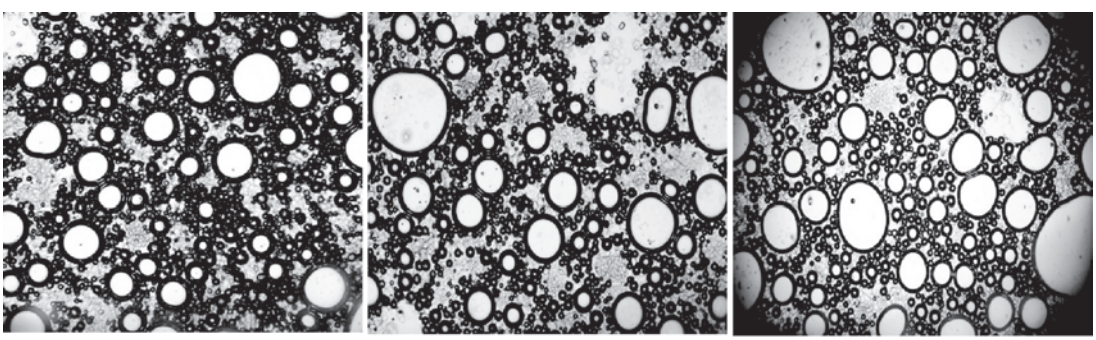

Figure 2 Images of aerated cake batters (a-c) (10× magnification) prepared from different mixing ratios of WF and TS. (a) 100:0; (b) 75:25; (c) 50:50.

cake as a function of batter density was plotted (Figure 3), a linear relationship was observed. Cake batters containing TS with lower batter density exhibited higher gas retention resulting in a higher specific volume, due to the expansion of gas retained in the batter. The air entrapped in the system that related to final cake volume could be explained by the changes in batter viscosity during baking.

According to a preliminary rapid visco analyzer (RVA) experiment for monitoring the heating profile of the cake batter (data not shown), the viscosity of the batters increased after being subjected to the pasting temperature due to the starch gelatinization and protein denaturation (Wilderjans *et al*., 2008). The cake batter viscosity increased earlier in the samples containing higher TS contents. Peak viscosity increased with increasing TS content along with the earlier increase in viscosity, leading to air bubbles created during whipping being retained in the cake crumb. Thus the changes of batter viscosity during baking with different mixing ratios of WF and TS were expected to modify the cake structure (data not shown). However, the baked cakes prepared from 100% TS had a very low volume with a dense, gummy layer at the bottom. Therefore, the relationship between specific volume and batter density as shown in Figure 3 could explain the batters prepared from the WF and TS within the studied mixing ratios.

Texture profile analysis is a very useful technique for investigating food products. In the present study, the TPA parameters of cake with and without TS substitution were determined from the texture analyzer using double compression tests and are shown in Table 3. Hardness was defined as the maximum force of the first compression of the product at the point of 50% compression (12.5 mm) of the original sample height. The hardness values of baked cakes decreased significantly with increasing TS substitution up to 50% (Table 3) from about 4.5 to 3.4 N in the cakes containing only WF and 50% TS substitution, respectively. However, cohesiveness determined from the area of work during the second compression divided by the area of work during the first compression (Borne, 2002) ranged between about 0.52 and 0.56 with no significant difference between any samples with and without TS. Springiness was defined as the distance to which the sample recovered in height during the time that elapsed between the end of the first compression cycle and the start of the second compression cycle. The springiness of baked cakes with and without TS exhibited no significant difference (Table 3). Gumminess was calculated by the product of (that is by multiplying) hardness and cohesiveness, whereas chewiness, defined as the energy required to masticate solid food to a state of readiness for swallowing (Karaoglu and Kotancilar, 2009) was obtained from the product of hardness, cohesiveness and springiness. Chewiness and gumminess values in cakes with and without TS exhibited a similar trend with the hardness values, as shown in Table 3. Significantly lower chewiness and gumminess were found in the cake samples containing 50%

Table 3 TPA parameters of sponge cakes prepared from different mixing ratios of WF and TS.

Flour blend (WF:TS)	Hardness (N)	Cohesiveness (-)	Springiness (mm)	Gumminess (N)	Chewiness (Nm)
100 : 0	4.49±0.70^{a}	0.523±0.053^{a}	10.8±1.0^{a}	2.366±0.551^{a}	0.026±0.008^{a}
75 : 25	4.69±0.31^{a}	0.559±0.112^{a}	10.5±0.8^{a}	2.604±0.387^{a}	0.027±0.003^{a}
50 : 50	3.39±0.37^{b}	0.529±0.046^{a}	10.9±0.9^{a}	1.797±0.273^{b}	0.020±0.003^{b}

Mean ± standard deviation values (n = 30) followed by a different lower-case letter within the same column are significantly different ($P < 0.05$) by Duncan's multiple range test.

Table 4 Sensory scores of sponge cakes prepared from different ratios of WF and TS*.

Flour blend (WF:TS)	Appearance	Color	Odor	Softness	Overall liking
100 : 0	6.7±1.3^{a}	6.7±1.4^{a}	6.7±1.4^{a}	6.4±1.6^{b}	6.3±1.3^{b}
75 : 25	6.5±1.2^{a}	6.7±1.5^{a}	6.6±1.5^{a}	6.8±1.6^{ab}	6.6±1.3^{ab}
50 : 50	6.2±1.5^{a}	6.6±1.6^{a}	6.5±1.4^{a}	7.4±1.2^{a}	7.0±1.3^{a}

Mean ± standard deviation values (n = 30) followed by a different lower-case letter within the same column are significantly different ($P < 0.05$) by Duncan's multiple range test.

* = Sensory scores are based on a 9-point hedonic scale ranging from 1 = dislike extremely to 9 = like extremely.

TS substitution (Table 3). The results suggest that partial (50%) TS substitution for WF in cakes increased the cake volume and softened the texture (as shown by lower values of hardness, chewiness and gumminess).

The sensory evaluation was carried out by rating the liking of the sensory attributes of cakes with and without TS substitution for appearance, color, odor, softness and overall liking using a 9-point hedonic scale. There was no significant difference among the samples with and without TS substitution for the liking scores of appearance, color and odor exhibited (Table 4). However, the mean scores of cakes evaluated in terms of softness and overall liking were higher with higher TS content in the cake and significantly different (Table 4). The overall liking score of the cake with 50% TS substitution was about 7.0 (like moderately) and was significantly different from the cake prepared from 100% WF (Table 4). It was observed that the higher softness scores with higher TS substitution resulted in an increase in the overall liking values.

CONCLUSION

Substitution of WF by TS decreased batter viscosity with the decrease in batter density indicating more air was incorporated into the cake batter during mixing. The higher specific volume in baked cakes containing TS was expected from the retention of air bubbles during baking leading to lower hardness of the cake after baking. The results suggested that TS substitution up to 50% for WF could be used in cake preparation for modifying textures in the bakery industry. As a result, in the food industry, the quality of cake in terms of softness, leading to higher overall liking, can be improved by partial substitution of WF with TS.

ACKNOWLEDGEMENTS

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Effect of Xanthan Gum on the Quality of Syrup Thickened by Modified Starch during Heating and Storage

Rungnaphar Pongsawatmanit*, Natee Yakard and Thongchai Suwonsichon

ABSTRACT

In heating during production and in storage, the reduction in the viscosity of fruit syrup stabilized by starch is a problem in the food industry due to starch degradation, especially in low pH systems. The influence of xanthan gum (Xan) on the rheological properties of syrups with different heating times and during storage was investigated. Blueberry syrups were prepared using 4% total concentration of polysaccharides with different mixing ratios of modified tapioca starch (MTS) and Xan (MTS/Xan = 4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3). The syrups were heated to 90°C and further heated for 20, 40, 60 and 80 min. All formulations with different heating times exhibited lower viscosity with shear rate. Viscosities of the syrups containing Xan were higher than those without Xan. The syrup containing 0.2%Xan (MTS/Xan = 3.8/0.2) obtained from heating at 90°C for 40 min was selected to evaluate the quality change during storage according to the highest sensory scores of thickness and overall liking. The syrup with 0.2% Xan substitution for MTS exhibited higher viscosity and a lower rate of viscosity reduction than that without Xan. Zero-order equations were used for shelf life evaluation of the syrups. Overall liking scores of the syrup with 0.2% Xan before and after storage for 16 wk were not significantly ($p>0.05$) different and exhibited higher scores than those without Xan. The results suggested that Xan could be used in fruit syrup to enhance quality and stability in terms of viscosity during heating and storage.

Keywords: shelf life, hydrocolloid, storage test, viscosity, zero-order reaction

INTRODUCTION

Fruit syrup is one of the important ingredients that can be created to have different flavor, taste, color and texture properties using different sugars, acids, fruit flavors, fruit purée and colorants including polysaccharides. In the food industry, many types of polysaccharides are used in syrup as a thickening agent to modify the rheological properties of the products (Bedi *et al.*, 2005) and hence increase the stability. Starch is one of the polysaccharides widely used for enhancing the viscosity. However, starch-based syrup is subjected to both shear stress and thermal treatment during processing, resulting in the breakdown of starch molecules. The viscosity of the syrup is one of the important quality parameters to be considered in food applications and is observed to decrease after the heat and shear treatments leading to instability of viscosity during storage (Temsiripong *et al.*, 2005; Biliaderis, 2009).

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Hydrocolloids are one of the ingredients used in starch-based products to enhance quality and stability, including the shelf life, in terms of viscosity stability. The incorporation of hydrocolloids is a well-known technique used to improve or maintain desirable textural properties and the stability of most starch-based products during long storage periods, by controlling rheological properties in the continuous phase and the textural properties of product (Yoshimura *et al.*, 1998; Mandala *et al.*, 2002; Temsiripong *et al.*, 2005; Pongsawatmanit and Srijunthongsiri, 2008). Xanthan gum is used in the food industry for improving the stability of many food products. It is a unique hydrocolloid, providing an excellent stability in thermal and acid systems (Morris, 1995). There are many foods that use a mixture of starch and xanthan gum to improve the product quality (Chantaro and Pongsawatmanit, 2010). For example, the structure of strawberry dessert sauces thickened with potato starch and xanthan gum provided stable sensory and textural properties after a 3-month storage period (Sikora *et al.*, 2001).

Therefore, blueberry syrup stabilized by modified tapioca starch (MTS) was used as a food model for investigation. The objective of this study was to determine the effect of heating time on the viscosity of blueberry syrup containing different combinations of MTS and xanthan gum (Xan). The quality of selected syrups during storage was also determined. The modified starch used as a stabilizer and/or thickener in this study was hydroxypropyl distarch phosphate (HDP; E1442).

MATERIALS AND METHODS

Materials

MTS (Siam Modified Starch, Thailand) as hydroxypropyl distarch phosphate (HDP; E1442) and commercial Xan (Dessen Biochemical, China) were used in this study. Commercial sucrose, 42% dextrose equivalent (DE) glucose syrup, citric acid monohydrated, blueberry flavor and food colorants were purchased from local suppliers. Frozen blueberry purée (total soluble solids (TSS) = 10.6°Brix, pH = 3.46) prepared by the individual quick frozen (IQF) process was used. Oriented polyamide (OPA) film (360 ± 5 mm length, 240 ± 5 mm width, 100 ± 10 μm thickness) was used for packing the syrup during the storage test.

Effect of heating time on quality of blueberry syrup

Blueberry syrup preparation for various heating times

Blueberry syrup samples containing 4% total concentration of polysaccharides were prepared with different mixing ratios of MTS and Xan (MTS/Xan = 4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3). Each formulation consisted of other ingredients with fixed percentages: 54% sugars (glucose syrup and sucrose), 10% blueberry purée, 31.2% water and 0.8% citric acid, sorbic acid, color and flavor.

A batch of blueberry syrup (2 kg) was prepared for each formulation. MTS was added into water for preparing the MTS dispersion. For MTS/Xan mixtures, Xan was mixed with a part of the sucrose from the formulation, dispersed in the water and stirred continuously for 1 h, before adding the MTS. Then, fruit purée, sugar, glucose syrup and color were added and mixed using a stirrer for a further 1 h at room temperature to hydrate the starch and hydrocolloid.

Each mixture was heated using a water bath and stirred until the temperature of the syrup reached 90°C. The citric acid and sorbic acid were added when the syrup temperature reached about 70°C. Finally, the flavor was added at 90°C. Each syrup formulation was heated further for 80 min and sampled for quality evaluation at 20, 40, 60 and 80 min of heating time.

Quality measurement of blueberry syrup

The apparent viscosity of a sample of the

prepared blueberry syrup (16 mL) from each heating time at 90°C was measured as a function of shear rate and ranged from 2.5 to 62.5 s^{-1} at 25 ± 0.1°C using a rotational viscometer (DV-III, Brookfield-RVT) with coaxial cylinder geometry on a small sample adapter and an SC4-29 spindle. Sample temperatures were kept constant for at least 5 min before starting measurement. The flow characteristics of the syrups were evaluated.

Blueberry syrups with and without Xan with selected heating times at 90°C were analyzed for total soluble solids using a refractometer (Atago, Japan), pH with a pH meter and water activity using a dew point hygrometer, Aqualab Series 3B (Decagon Devices, Pullman, Washington, USA) at 25°C. The sensory evaluation of the products with and without Xan was performed using 30 untrained panelists for acceptance testing. Each syrup sample (20 g) with and without Xan was served in a cup with pieces of bread. The panel members were asked to rate the liking of quality attributes according to appearance, color, odor, thickness and overall liking using a 9-point hedonic scale, with 1 = dislike extremely to 9 = like extremely.

Quality change of blueberry syrup during storage

The blueberry syrup formulation containing Xan that had a good quality in terms of viscosity and a sensory evaluation score was selected for appraisal of quality change during storage. Twenty kilograms of each syrup preparation with and without Xan (as control) were prepared by heating the syrups for 40 min at 90°C, hot filling into an OPA bag (500 g), hermetically sealing, cooling and keeping at ambient temperature (average 30±3°C) for 16 wk. The syrups were sampled for quality measurement after certain periods of storage time. The viscosity, total soluble solids and pH values were determined using the methods mentioned above.

Sensory evaluation of the product with and without Xan before and after storage for 16 wk was performed using 30 untrained panelists for acceptance testing, using the procedure described above.

Statistical analysis

All measurements were performed with at least two replications. Mean values ± standard deviation were reported. Analysis of variance (ANOVA) was used to determine any significant differences among treatment parameters with regard to the quality properties. Duncan's multiple range test was also applied to determine the difference of means from the ANOVA, using a significance test level of ($p<0.05$).

RESULTS AND DISCUSSION

Quality of blueberry syrup with different heating times

The apparent viscosity as a function of the shear rate of the blueberry syrups with different mixing ratios of MTS and Xan (4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3) after heating for 20 to 80 min at 90°C was investigated at 25°C (Figure 1). The viscosity values of the syrups increased significantly ($p<0.05$) with increasing Xan content at the same shear rate, and values were higher than those of the syrup without Xan (MTS/Xan = 4.0/0.0). The syrup without Xan had a lower viscosity value with longer heating time. All syrups with and without Xan exhibited shear thinning fluid properties, as the apparent viscosity decreased with increasing shear rate.

The condition of heating at 90°C for 40 min was selected for further investigation of the effect of Xan on syrup quality due to its similarity to the conditions of the hot-fill process used by food manufacturers. Data on the shear stress and shear rate of syrups (MTS/Xan = 4/0, 3.9/0.1, 3.8/0.2 and 3.7/0.3) were plotted to describe the behavior of non-Newtonian fluids using the Herschel-Bulkley, power law and Bingham models

(data not shown). Coefficients of determination (r^2) indicated that the power law equation (r^2 = 0.996-0.999) provided the best model of the experimental data (Steffe, 1996). Subsequently, the power law model was used to calculate the power law parameters, as shown in Equation (1):

$$\tau = K\dot{\gamma}^n \quad (1)$$

where τ = shear stress (Pa), $\dot{\gamma}$ = shear rate (s^{-1}), K = consistency coefficient ($Pa.s^n$), and n = flow behavior index.

For all syrup formulations with different mixing ratios of MTS and Xan, the consistency coefficient value (K) of syrup thickened by only MTS (15.6 $Pa.s^n$) was lower than the syrups containing Xan (25-52 $Pa.s^n$) (Table 1) and increased with Xan substitution. The flow behavior index (n) of all syrups was below 1, as expected for shear thinning liquids (Steffe, 1996). The substitution of Xan for MTS in the syrups also altered the flow behavior index (n) of the syrups from 0.7 to 0.61, 0.54 and 0.48 for 0.1, 0.2 and 0.3% Xan subsitution (Table 1), respectively. The n values decreased with increasing Xan substitution. The results suggested that the syrups containing Xan enhanced the viscosity of the products and exhibited more pronounced non-Newtonian behavior due to the flow behavior index deviating from the n value of 1 for a Newtonian fluid.

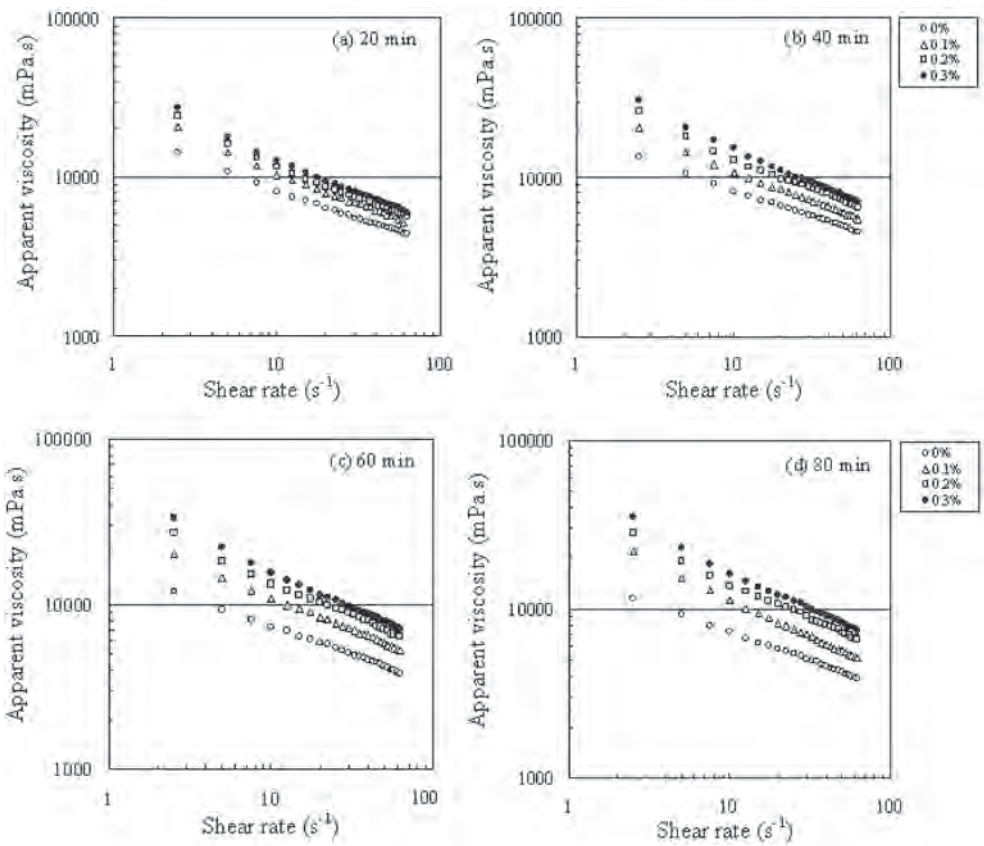

Figure 1 Apparent viscosity of blueberry syrups stabilized by MTS and Xan mixtures with different mixing ratios prepared from heating at 90°C for (a) 20 min; (b) 40 min; (c) 60 min; and (d) 80 min. Measurements were performed at 25°C.

Total soluble solids (TSS), pH values and water activity of the syrups with and without Xan were not significantly ($p>0.05$) different. The TSS and pH values of syrups were about 55.6-56.0° Brix and 2.45-2.48, respectively, whereas the water activity of all syrups was about 0.92.

The quality of the syrups was assessed by sensory evaluation using a 9-point hedonic scale. The results showed that the overall liking scores of the blueberry syrup containing 0.2%Xan were the highest among samples in terms of thickness and overall liking ($p<0.05$, Table 2). Therefore, the blueberry syrup containing 0.2%Xan (MTS/Xan = 3.8/0.2) was selected for storage studies and compared to syrup without Xan (4%MTS) as a control sample.

Quality change of blueberry syrup during storage

Batches (20 kg) of blueberry syrup containing 4% MTS and 4% MTS/Xan (mixing ratio = 3.8/0.2) were prepared for the storage stability test. The syrups with and without Xan were heated to 90°C, with further heating for 40 min, before being hot filled into OPA bags (500 g), hermetically sealed and cooled, and then kept at ambient temperature (average temperature 30±3°C). The product samples were tested for viscosity and other quality measurements over a 16-week storage period. The viscosity at shear rate 10 s^{-1} of blueberry syrups with and without Xan decreased with storage time (Figure 2). The rate of viscosity reduction of syrup containing 0.2% Xan was lower than that of syrup without Xan addition, as shown by the slope values of both syrups with and without Xan of about 19 and 41 mPa.s/d, respectively. The results indicated that Xan addition enhanced the viscosity stability of the syrup during storage at ambient temperature. The changes in the syrup viscosity during storage (Figure 2) were found to follow zero-order kinetics at ambient temperature (30±3°C) with $r^2 > 0.98$. Therefore, for both syrups, the viscosity (mPa.s) at a shear rate of 10 s^{1}, as a function of storage time could be determined using Equations (2) and (3):

Table 1 Power law constants (K = consistency coefficient, n = flow behavior index) of syrups with and without Xan determined from the shear rate range of 2.5-62.5 s^{-1} at 25°C prepared from further heating for 40 min at 90°C.

Xan substitution (%)	K ($Pa.s^n$)	n (-)	r^2
0	15.9±0.1d	0.695±0.001a	0.996
0.1	25.6±0.5c	0.607±0.001b	0.999
0.2	36.7±0.2b	0.545±0.000c	0.999
0.3	52.3±0.3a	0.481±0.001d	0.996

Mean ± standard deviation values followed by different lower case letters within the same column are significantly ($p<0.05$) different by Duncan's multiple range test.

Table 2 Mean sensory scores of blueberry syrups with and without Xan prepared from heating 40 min at 90°C.

Xan substitution (%)	Appearance	Color	Odor	Thickness	Overall liking
0.0	6.6±0.7a	6.5±0.8a	6.2±1.0a	6.5±1.0b	6.1±1.0c
0.1	6.6±0.7a	6.4±0.7a	6.0±1.0a	6.8±1.1ab	6.6±0.9b
0.2	6.7±0.7a	6.5±0.7a	6.2±0.7a	7.4±0.6a	7.1±0.9a
0.3	5.5±0.9b	6.3±0.6a	5.9±1.0a	5.8±1.4c	5.9±0.9c

Mean ± standard deviation values followed by different lower case letters within the same column are significantly ($p<0.05$) different by Duncan's multiple range test.

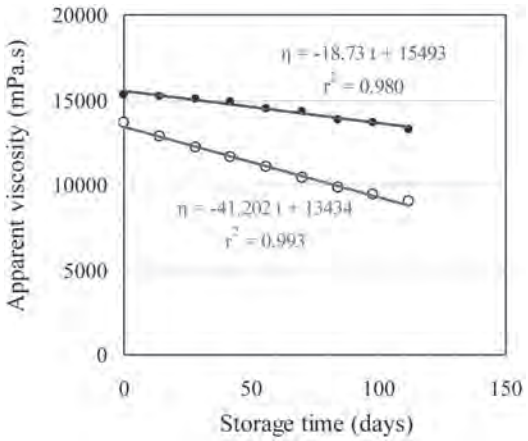

Figure 2 Apparent viscosity at shear rate 10 s^{-1} of blueberry syrups thickened by a combination of 4% MTS (○) and 4% MTS/Xan (3.8/0.2) (●) and heated for 40 min at 90°C during 16 wk storage at ambient temperature.

For syrup with 4% MTS;

$$\eta = -18.73\ t + 15493 \quad (2)$$

For syrup with 4% MTS/Xan;

$$\eta = -41.202t + 13434 \quad (3)$$

where: η = apparent viscosity (mPa.s) and t = storage time (d).

The shelf life can be defined as the length of time that a product may be stored under specified conditions without becoming unsuitable for use or consumption. Thus, for syrup, viscosity plays an important role in determining the end-of-shelf-life quality of the product. Using Equations (2) and (3), it was possible to estimate the shelf life of blueberry syrup kept at ambient temperature, if the criteria specifying the end of the shelf life are provided. For example, if the viscosity of syrup below 9,000 mPa.s is used as the end point of acceptable quality, the shelf life values of syrups with and without Xan were 346 and 107 d based on Equations (2) and (3), respectively. The results suggested that the addition of 0.2% Xan in the blueberry syrup could enhance the shelf life of the product in terms of viscosity.

Shear stress and shear rate data of fresh and stored blueberry syrups containing 4% MTS and 4% MTS/Xan were predicted using a power law model with the values of the coefficient of determination (r^2) about 0.997-0.999 (Table 3). The consistency coefficient value (*K*) of stored syrup thickened by MTS only (12 $Pa.s^n$) was significantly ($p<0.05$) lower than that of fresh samples (17 $Pa.s^n$) during storage, due to the degradation or hydrolysis of MTS with the low pH in the system. However, the addition of Xan in the syrup produced no significant ($p>0.05$) difference (Table 3) in the *K* values for fresh (33 $Pa.s^n$) and stored (32 $Pa.s^n$) products. The flow behavior index (*n*) of the syrups without Xan altered the *n* value of fresh sample from 0.591 to 0.622 (Table 3) after storage for 16 wk, whereas the *n* value of syrup containing 0.2% Xan changed from 0.514 to 0.496 with no significant ($p>0.05$) difference (Table 3). The difference in the power law constants of syrups with and without 0.2%Xan in Tables 3 and 1 was considered to be an effect of the production scale.

The TSS and pH values of both syrup formulations were about 55.4-56.0 °Brix and 2.42-2.48, respectively, over 16 wk of storage and showed no significant ($p>0.05$) differences. In the present study, the syrup was prepared as hot-filled product, with the addition of 1,000 mg/kg sorbic acid as an antimicrobial agent. Total plate count (TPC) and yeast/mold counts of syrups with and without Xan sampled before and after storage (16 wk) were found to be < 10 cfu/g.

The sensory evaluation of fresh blueberry syrups containing 0.2% Xan (MTS/Xan = 3.8/0.2) before storage exhibited a higher overall liking score than syrup without Xan addition (Table 4). After storage for 16 wk, there was no significant ($p>0.05$) difference in overall liking of the syrup with 0.2% Xan (MTS/Xan = 3.8/0.2) between the fresh and stored samples. The results suggested

Table 3 Power law constants of blueberry syrups with and without Xan packed in OPA film for 0 and 16 wk of storage.

Xan substitution (%)	Storage (wk)	K (Pa.s^n)	n (-)	r^2
0	0	17.1±1.4b	0.591±0.028b	0.998
0	16	12.1±0.3c	0.622±0.006a	0.999
0.2	0	33.2±0.2a	0.514±0.001c	0.999
0.2	16	31.9±0.3a	0.496±0.003c	0.997

Mean ± standard deviation values followed by different lower case letters within the same column are significanty ($p<0.05$) different by Duncan's multiple range test.

Table 4 Mean sensory scores of blueberry syrups with and without Xan packed in OPA film for 0 and 16 wk of storage.

Xan substitution (%)	Storage (wk)	Appearance	Color	Odor	Thickness	Overall liking
0	0	7.0±0.65b	6.8±0.62a	6.7±0.74a	7.0±0.47bc	7.0±0.59b
0	16	6.7±0.52c	6.5±0.57a	6.6±0.67a	6.7±0.81d	6.7±0.55c
0.2	0	7.5±0.57a	6.8±0.55a	6.7±0.48a	7.4±0.50a	7.6±0.50a
0.2	16	7.3±0.59a	6.7±0.48a	6.6±0.50a	7.3±0.44ab	7.4±0.50a

Mean ± standard deviation values followed by different lower case letters within the same column are significantly ($p<0.05$) different by Duncan's multiple range test.

that blueberry syrup obtained from a combination of 3.8%MTS and 0.2%Xan was more stable than syrups without Xan, in terms of viscosity and overall liking after storage for 16 wk.

CONCLUSION

The apparent viscosities of the blueberry syrups containing Xan were higher than those without Xan (MTS/Xan = 4/0) for all heating times at 90°C, whereas the TSS, pH and water activity values of syrups were not significantly ($p>0.05$) different among all samples. The syrup containing 0.2%Xan (MTS/Xan = 3.8/0.2) prepared by heating at 90°C for 40 min produced the highest overall liking score. The viscosity of syrups with and without 0.2%Xan decreased with storage time and followed zero-order kinetics. A lower rate of viscosity reduction was found in the syrup containing 0.2%Xan. Overall liking scores of the syrup with 0.2% Xan for both fresh and stored samples were not significantly ($p>0.05$) different and exhibited higher values than those without Xan. Therefore, Xan could be used in the food industry in fruit syrup to enhance the quality and stability during heating and storage.

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Effect of Heating Time on the Quality of Tapioca Starch and Xanthan Gum Mixture

Prawta Chantaro and Rungnaphar Pongsawatmanit*

ABSTRACT

Heating is an important step for preparing starch-based products, as heating affects the quality of the products due to gelatinization and degradation of the starch. The effect of thermal treatment on the pasting properties of tapioca starch (TS) with and without xanthan gum (Xan) under constant shear was investigated using a rapid visco-analyzer (RVA). The freeze-thaw stability of the TS and TS/Xan pastes was also determined. Two mixtures of 5% (w/w) TS and TS/Xan (mixing ratio = 9/1) at pH 7 were assessed. Final viscosities decreased with heating time at 95°C. A longer heating time increased the breakdown of the gelatinized TS and TS/Xan mixtures ($p<0.05$). Substitution of Xan for TS depressed the setback of the TS pastes ($p<0.05$). Changes in viscosity values of both the TS and TS/Xan mixtures during heating at 95°C with a constant shear rate in the RVA profile exhibited a pseudo-first-order reaction with respect to heating time. From the repeated freeze-thaw treatments, the TS pastes containing Xan exhibited lower water separation compared with those of the TS pastes alone for the same heating time. The results may have important implications for industrial applications by improving the pasting properties and freeze-thaw stability of TS-based products.

Keywords: first- order reaction, freeze–thaw stability, pasting properties, RVA, setback

INTRODUCTION

Starch is a major polysaccharide composed of amylose and amylopectin molecules. When starch granules in excess water are heated and then gelatinized, structural and rheological changes take place. In the food industry, during production, starch-based products are subjected to both shear stress and thermal treatment that result in the breakdown of starch molecules. The decrease in the molecular weight due to shorter polymer chains affects many properties of starch-based products, such as cold paste viscosity, water solubility and absorption, the degree of retrogradation and gelling properties (Mua and Jackson, 1997; Pongsawatmanit and Srijunthongsiri, 2008).

Tapioca starch (TS) is used as a thickener and stabilizer in many products, such as soups, sauces, fruit pies, puddings, soy and meat products. The required functional properties of tapioca starch-based products play an important role in product and process development for improving product quality during storage. However, the viscosity of the tapioca starch paste decreases after heat and shear treatments during production leading to textural instability during storage (Temsiripong *et al.*, 2005; Biliaderis, 2009). Incorporation of hydrocolloids is one method used

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to improve or maintain desirable textural properties and stability in most starch-based products during a long storage period, by controlling the rheological properties in the continuous phase and the textural properties of the product (Yoshimura *et al.*, 1998; Mandala *et al.*, 2002; Pongsawatmanit and Srijunthongsiri, 2008). Many investigations have reported on the properties of starch/hydrocolloid mixtures. The pasting properties of potato starch were affected using carboxymethyl cellulose (CMC), carrageenans, alginate and xanthan gum (Shi and BeMiller, 2002). The RVA peak and final viscosities of tapioca starch increased with increasing xyloglucan content (Temsiripong *et al.*, 2005; Pongsawatmanit *et al.*, 2006). The peak viscosity (13%) of a wheat starch system during gelatinization increased with the addition of 0.5-1.0% hydrocolloids (guar gum, tara gum, locust bean gum and konjac glucomannan) (Funami *et al.*, 2005). Pongsawatmanit and Srijunthongsiri (2008) reported on the rheological properties and freeze–thaw stability in a system of partial substitution of starch with xanthan gum at a fixed total polysaccharide level for improving the quality of TS-based products. Van den Einde *et al.* (2004) considered the effect of heating on starch breakdown and the quality of starch-based products, such as waxy corn, in a starch-water system under heating-shearing conditions. Xanthan gum is used in the food industry for improving the stability of many food products. It is a unique hydrocolloid providing excellent stability in thermal and acid systems and is produced by the fermentation of *Xanthomonas campestris* (Morris, 1995). Therefore, the objectives of the current study were to investigate the influence of heating time on the pasting properties of a tapioca starch/xanthan gum mixture at pH 7 using a rapid visco-analyzer (RVA) and to investigate the quality of the starch during frozen storage using repeated freeze-thaw treatments. A pH of 7 was selected to gain more understanding on applications with some neutral food products, such as coconut milk, soy milk or some vegetable soups that can be stabilized by tapioca starch during product development.

MATERIALS AND METHODS

Materials

Tapioca starch (TS) (Siam Modified Starch, Pathumthani, Thailand) and xanthan gum (Xan) (CP Kelco, San Diego) were used without any further purification. The moisture content of the TS and Xan was 11.1 and 8.6%, respectively determined by the hot air oven method at 105°C (AOAC, 2000). Analytical grade NaOH was used to adjust the pH of the TS and TS/Xan mixtures.

Preparation of the TS/Xan mixtures

TS/Xan dispersions with and without Xan were prepared at two mixing ratios (TS/Xan = 10/0 and 9/1) with 5% total polysaccharide concentration. Precalculated TS was added into the RVA canisters containing deionized distilled water to achieve a total weight of 28 g for the RVA measurement. In the case of the 5% TS/Xan mixture, Xan was dispersed in the deionized distilled water in the RVA canisters and allowed to disperse for at least 6 h before adding the TS. All dispersions were kept at room temperature for a further 30 min to hydrate the starch. Then, 0.1 N NaOH was used to adjust the pH of the mixture to 7, which was followed by mixing for 2 min to disperse the sample uniformly before RVA measurement. The pH values of the dispersions before and after RVA measurements were 7.02 - 7.08. To prevent microbial spoilage, sodium azide (0.04%) was added into all TS/Xan mixtures.

Rapid visco-analyser (RVA) measurement with different heating time at 95°C

The pasting properties of 5% w/w tapioca starch was determined using a rapid visco-analyser (RVA) (RVA-4, Newport Scientific, Narrabeen,

Australia). The TS/Xan dispersions were stirred manually to mix the sample uniformly before measurement. The RVA pasting profile was monitored during thermal treatment, according to the method of Pongsawatmanit *et al.* (2006), with the modification of a holding time at 95°C by: equilibrating the starch slurry at 50°C for 1 min; increasing the temperature to 95°C at a heating rate of 6°C/min; holding the temperature at 95°C for either 5, 10 or 15 min; decreasing the temperature to 50°C at 6°C/min; and holding at 50°C for the remainder of the run. The total run times were 23, 28 and 33 min for heating times of 5, 10 and 15 min, respectively. The agitation speed of the paddle commenced at 960 rpm for the first 10 s and was kept constant at 160 rpm until the end of the experiment. The pasting profiles were evaluated in triplicate and the average values of evaluated pasting parameters were reported.

Freeze-thaw stability measurement

The freeze-thaw stability evaluation used the gelatinized TS and TS/Xan pastes with pH 7 obtained from different holding times (5, 10 and 15 min) at 95°C from the RVA measurements. Each mixture was poured into 10-mL plastic tubes, centrifuged to remove entrapped air bubbles and cooled at 5°C overnight, before being kept in a freezer (-25°C) for 22 h. Each paste was thawed at 40°C for 2 h repeatedly up to seven cycles. Five-mL plastic syringes without the tip and plunger were used for water separation in the thawed TS and TS/Xan pastes, by placing a single piece of filter paper on the bottom of each syringe, topping up with 0.02–0.03 g cotton, and then adding deionized distilled water to moisten the cotton (Pongsawatmanit *et al.*, 2006). The cotton layer was pressed with a glass rod to ensure a complete seal at the bottom of the syringe. The syringes were centrifuged at 2100 g for 10 min to remove excess water from the cotton and then weighed. Thawed paste samples (W_s) (about 2.5 g ±0.1 mg) of the TS and TS/Xan pastes from the selected freeze-thaw cycles were added into each syringe and centrifuged at 2100 g for 10 min. The weight before (W_b) and after (W_a) centrifugation was recorded. The percentage of water separation was calculated based on the weight of the thawed TS or TS/Xan pastes using Equation 1:

$$\text{Water separation (\%)} = (W_b - W_a) \times 100 / W_s. \quad (1)$$

At least three measurements were carried out to ensure the reproducibility of the data.

Statistical analysis

Each measurement was carried out using at least three freshly prepared samples. The results were reported as the mean ± standard deviation. Statistical analysis was performed using SPSS V.12 statistical software (SPSS (Thailand) Co., Ltd.).

RESULTS AND DISCUSSION

Pasting properties from rapid visco-analyser measurement

The rapid visco-analyser was used to investigate the effect of thermal treatment under constant shear on the pasting properties of the TS and TS/Xan (mixing ratio = 9/1) mixtures heated at 95°C for 5-15 min. The pasting profiles of the 5% w/w TS and TS/Xan mixtures at pH 7 are shown in Figure 1 and indicate that the viscosities of the mixtures from the initial pasting to the peak (the highest apparent viscosity obtained) were almost identical among the different holding times. Pasting temperatures of the TS and TS/Xan mixtures with different heating times (5, 10 and 15 min) at 95°C were 68.6-69.3°C and 72.4-73° C, respectively, whereas peak viscosities from these three heating times were about 851-861 mPa.s and 1476-1495 mPa.s for the TS and TS/Xan mixtures, respectively. Pasting temperatures and peak viscosities for the TS and TS/Xan mixtures compared within different heating times at 95°C were not significantly ($p>0.05$) different,

as expected, due to the same heating profile for the first 13.5 min of each total RVA sequence. However, the pasting temperatures and peak viscosities of the TS/Xan mixtures were higher than those of TS alone, due to the contribution of the Xan in the continuous phase of the mixtures (Temsiripong *et al.*, 2005). When the system was maintained at 95°C, the mixtures were subjected to both thermal and shear stresses, leading to further disruption of the starch granules and leaching out of starch molecules. A greater decrease in viscosity was observed in the systems with higher holding times at 95°C. The breakdown values of the TS and TS/Xan mixtures increased with heating time (Figure 2a, $p<0.05$). The greater increase in the breakdown of the TS/Xan suspensions under the shear forces indicated that the aggregates of xanthan molecules in the pastes (formed through hydrogen bonding and polymer entanglement) were disrupted with increasing heating time (Sworn, 2000; Pongsawatmanit and Srijunthongsiri, 2008).

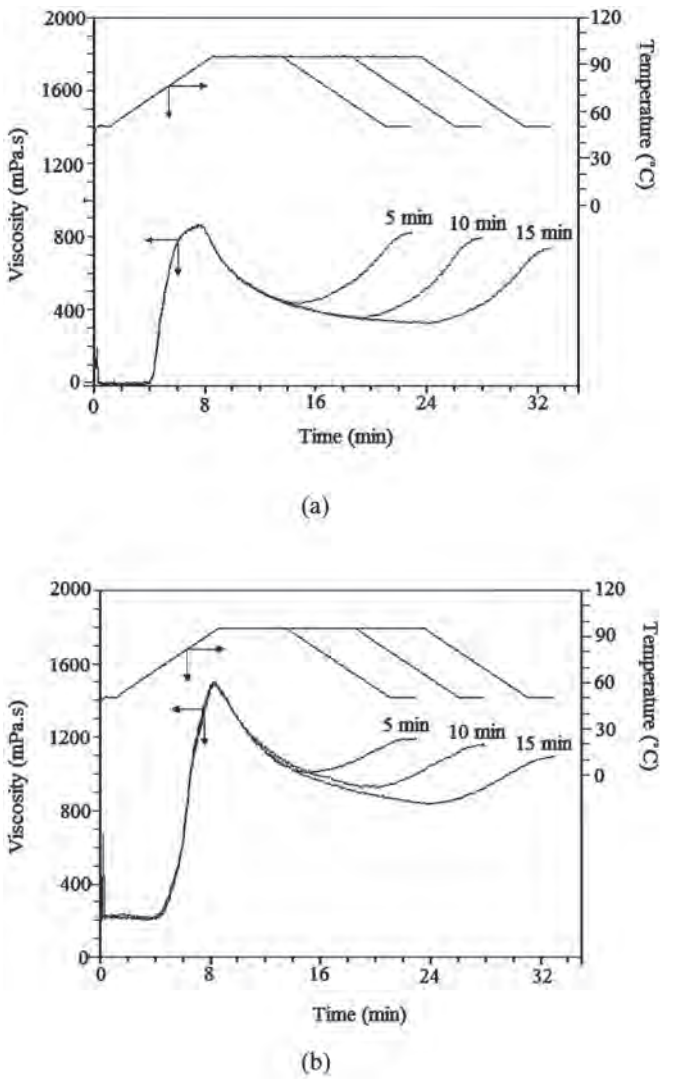

Figure 1 RVA pasting profiles of 5% w/w with pH 7 at different holding times at 95°C (5, 10 and 15 min) for: (a) TS; and (b) TS/Xan = 9/1; .

The final viscosities (the viscosity values at the end of RVA measurement) of the TS/Xan pastes were higher than those of the TS pastes (Figure 2b, $p<0.05$). The final viscosities of both the TS and TS/Xan pastes decreased as the heating time increased from 5 to 10 or to 15 min ($p < 0.05$). The setback value of the TS and TS/Xan pastes increased as the holding time at 95°C increased from 5 to 10 or to 15 min (Figure 2c, $p<0.05$), but the addition of the Xan resulted in a significant decrease in the setback of the TS/Xan pastes ($p<0.05$) compared with pastes containing only TS at the same holding time at 95°C. Usually, a high setback is associated with syneresis during the freeze–thaw cycles and is used to indicate the extent of short-term retrogradation (Pongsawatmanit and Srijunthongsiri, 2008). These results suggested that the short-term retrogradation of the TS/Xan mixtures under thermal stress could be depressed by Xan.

To analyze the gelatinized TS or TS/Xan mixtures, the pastes were subjected to both thermal and shear stresses at holding temperature (95°C) for 5, 10 and 15 min, according to the RVA time at 13.5, 18.5 and 23.5 min, respectively. The RVA profiles (Figure 1) exhibited lower viscosity with increasing heating time, which indicated there was higher breakdown of the starch molecules. The rate of starch breakdown at the initial heating time at 95°C was observed to be much higher than those heated after 3.5 min (Figure 1). After plotting the viscosity of the TS and TS/Xan pastes from all three heating-time treatments (Figure 3a), the viscosity values of both the TS and TS/Xan mixtures during heating at 95°C from 3.5 min to 15 min were used to calculate the reaction rate of starch degradation under thermal and shear stresses. The kinetics of degradation exhibited a pseudo-first- order reaction with respect to heating time. The plot indicated that the pastes containing only TS were more dependent on the heating time than the TS/Xan pastes, as evidenced by the reaction rate of the TS and TS/Xan being 0.035 and 0.023, respectively (Figure 3b). The results

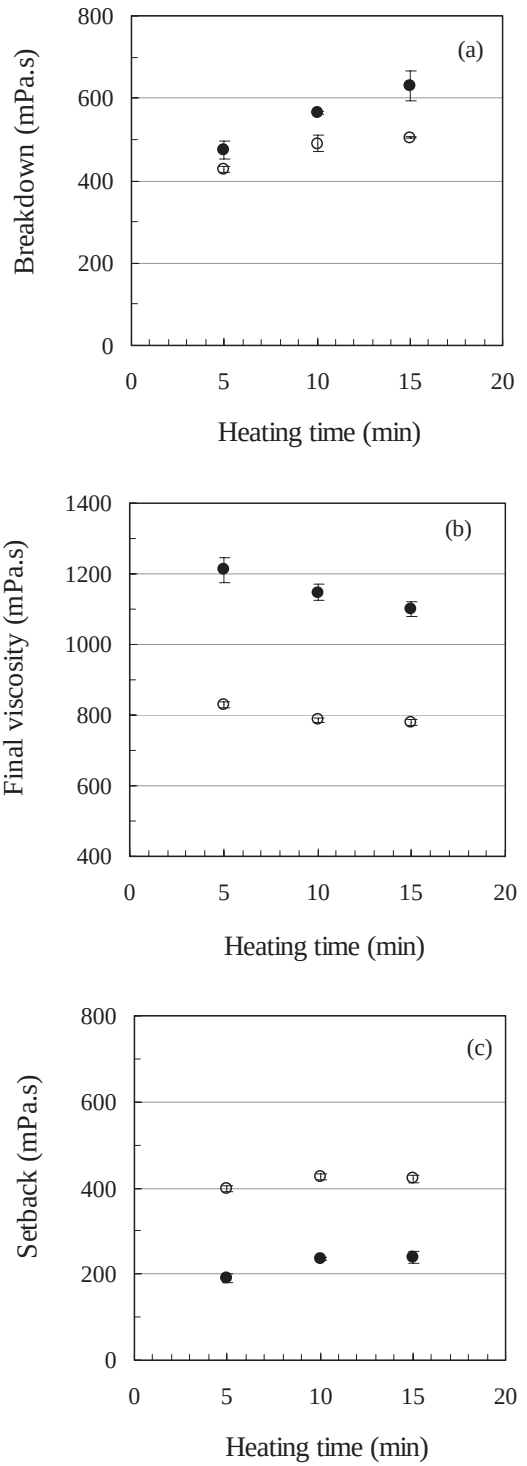

Figure 2 Plots as a function of RVA heating time at 95°C for TS (○) and TS/Xan (●): (a) breakdown; (b) final viscosity; and (c) setback.

confirmed the contribution by the Xan to better thermal stability than in the TS pastes alone.

Freeze-thaw stability measurement

Freeze-thaw stability is important in the frozen food industry, as it represents the ability of a product to maintain its composition and integrity after repeated cycles of freezing and thawing. The thawed liquid within the product causes larger ice crystals after refreezing leading to the breakdown of the structure in a product. Water separation of the TS and TS/Xan pastes increased with the number of freeze-thaw cycles and the heating time (Figure 4), confirming the higher breakdown of starch molecules (Figure 2) in the systems. However, the TS pastes containing Xan exhibited lower water separation ($p<0.05$) compared with those made of TS paste alone. The increase in

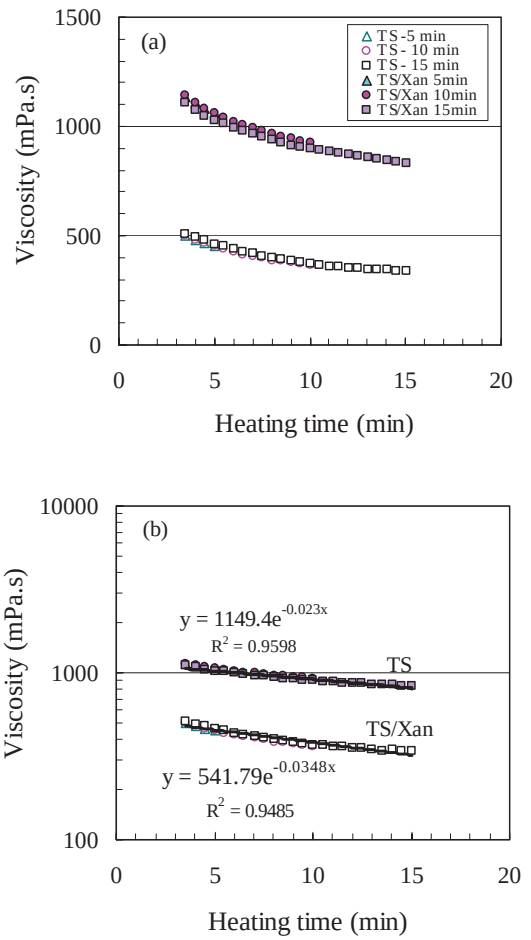

Figure 3 Plots of 5% TS (open symbol) and TS/Xan (filled symbol) pastes as a function of RVA heating time at 95°C: (a) viscosity; and (b) first order plot of viscosity.

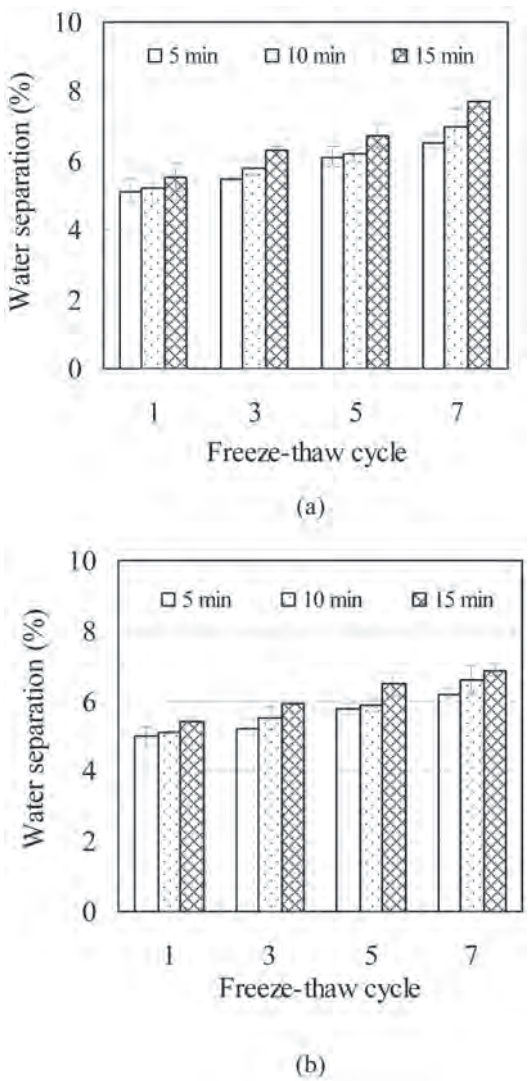

Figure 4 Water separation of 5% w/w gelatinized pastes with pH 7 at different holding times at 95°C (5, 10 and 15 min) of: (a) TS; and (b) TS/Xan = 9/1. The vertical bars represent the mean ± standard deviation).

water separation as a function of heating time from the TS and TS/Xan pastes was characterized in terms of the different values of water separation (%) from the thawed pastes after repeated freeze–thaw cycle 7 and cycle 1 as (W_7-W_1). The water separation at cycle 7 compared to cycle 1 (W_7-W_1) of the TS pastes was much higher than that of the TS/Xan pastes with increasing RVA heating time at 95°C (Figure 5). The change in (W_7-W_1) of the TS pastes (approximately 0.076) as a function of heating time was higher than that of TS/Xan pastes (approximately 0.0265). The results confirmed again the contribution by the Xan of better freeze–thaw stability than in the TS pastes alone.

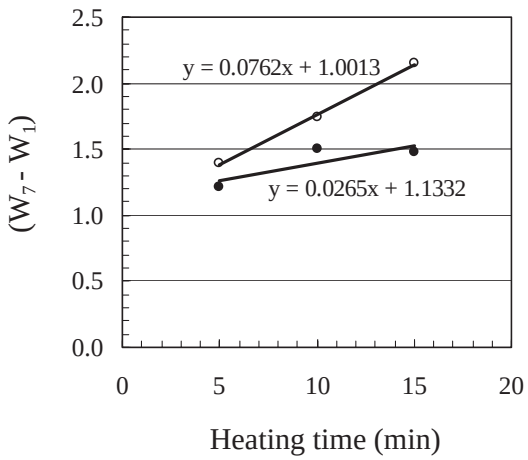

Figure 5 Difference of water separation obtained from freeze-thaw cycle 7 and 1 of 5% TS (○) and TS/Xan (●) pastes as a function of RVA heating time.

CONCLUSION

At a total polysaccharide concentration of 5% w/w for the TS and TS/Xan mixtures, the longer heating time at 95°C under a constant shear stress increased the breakdown but decreased the final viscosity of the system. The TS pastes containing Xan exhibited better thermal stability with lower setback of starch molecules leading to better freeze-thaw stability than in the pastes made from the TS only. The current study provided information that may help improve the understanding of the role that Xan plays in determining the stability of the TS paste at pH 7 during heating and a repeated freeze-thaw process.

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Influence of sucrose on thermal and pasting properties of tapioca starch and xanthan gum mixtures

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ABSTRACT

Sugars and hydrocolloids are used in starch-based product formulations during processing for improving the final quality of foods. Effect of sucrose (0–30%) on thermal and pasting properties of 5% w/w tapioca starch (TS) – xanthan gum (Xan) mixtures was investigated using differential scanning calorimeter (DSC), rapid visco-analyser (RVA) and rheometer. Sucrose increased gelatinization temperatures and enthalpies of TS and TS/Xan dispersions. RVA pasting temperatures, peak viscosity, final viscosity, breakdown and setback values of TS/Xan mixtures increased with increasing sucrose concentration ($p < 0.05$). Addition of sucrose in all TS/Xan pastes increased the rate of viscosity breakdown during RVA heating under constant shear and temperature. Setback values of TS/Xan pastes increased with sucrose addition but decreased significantly with increasing Xan content. Xan enhanced thermal stability of steady shear viscosities to TS pastes with and without sucrose. Linear regression from pasting profile revealed a good relationship for predicting final viscosity. These results could facilitate the development of TS-based products with improved thermal and pasting properties.

1. Introduction

In food industry, many ingredients are used to develop desired functional properties of final products. Starch is one of the most important polysaccharides used in food systems. The characteristics of starch granular swelling, gelatinization and retrogradation during processing and storage are important for controlling the rheological properties of foods (Nishinari et al., 2000). To enhance the quality and shelf life of the foods, non-starch polysaccharides have been widely used to improve stability and maintain overall qualities during storage and distribution by controlling rheological and textural properties (Pongsawatmanit and Srijunthongsiri, 2008). Since rheological and thermal properties of starch/hydrocolloid mixtures play an important role in texture modification, various studies on the properties of starch and hydrocolloid mixtures have been reported (Christianson et al., 1981; Sudhakar et al., 1996; Temsiripong et al., 2005; Yoshimura et al., 1999). In general, the viscosity of starch and hydrocolloid mixtures is much higher than that of starch alone due to the synergistic effect and the competition for water between hydrophilic biopolymers and starch (Christianson et al., 1981; Funami et al., 2005; Temsiripong et al., 2005).

Sugars are low molecular weight components compared with polysaccharides and are used in food formulations for taste and stability modification. Sugars can alter thermal and physical properties of starch-based foods (Pongsawatmanit et al., 2007). The effect of sugar on gelatinization and retrogradation of starches such as increasing gelatinization temperatures of starches or decreasing the swelling of starch granules has been studied (Baek et al., 2004; Chungcharoen and Lund, 1987; Ikeda et al., 2001; Kruger et al., 2003; Pongsawatmanit et al., 2002). Most of sugars exhibit on anti-plasticizing effect leading to a lower amount of amylose leaching and higher gelatinization temperatures and enthalpy (Ahmad and Williams, 1999; Kohyama and Nishinari, 1991).

The influence of sucrose on ingredient interactions affecting gelatinization and retrogradation during heating and cooling plays an important role in determining the final qualities of starch-based foods. Therefore, understanding the thermal and pasting properties of starch/hydrocolloid/sucrose systems is necessary for process and product development in terms of process design, quality and shelf life extension. Tapioca starch (TS), a thickener used in many food products, was selected for investigation. Xanthan gum (Xan) is a heteropolysaccharide produced by the fermentation of *Xanthomonas campestris*. It is used in the food industry for improving the stability of emulsions, foams and particulate suspensions in, for example, dairy, bakery, meat and fish, condiment, and beverage products (Morris, 1995; Urlacher and Dalbe, 1992). Xanthan gum is a unique hydrocolloid providing excellent stability in thermal and acid systems. Sucrose is an important sweetener used in food products. Therefore, the objectives of this study were to evaluate the effect of sucrose on the thermal and pasting properties of TS

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and Xan mixtures. Gelatinization and pasting profiles of the mixtures with and without sucrose were characterized using differential scanning calorimetry (DSC), rapid visco-analysis (RVA) and steady shear rheometry. The regression analysis from RVA pasting profile was also established to determine the final viscosity. The results of this study are expected to improve the understanding of how sucrose and xanthan gum affect thermal and rheological properties of tapioca starch-based products for further application in product development.

2. Materials and methods

2.1. Materials

Tapioca starch (TS) was supplied by Chorchaiwat Industry Co., Ltd. (Cholburi, Thailand). The moisture and amylose contents of the starch were 11.52% and 19.4% determined by the hot air oven method at 105 °C (AOAC, 1995) and high performance size exclusion chromatography (HPSEC) (modified method of Govindasamy et al., 1992), respectively. Xanthan gum (Xan) (CP Kelco, San Diego) containing 12.73% w/w moisture content was also determined using hot air oven at 105 °C (AOAC, 1995). Both polysaccharides were mixed on a dry basis and used without any further purification. Sucrose (Merck, Germany) was used as provided.

2.2. Differential scanning calorimetry measurement

Thermal properties of TS and Xan mixtures with and without sucrose were performed using a differential scanning calorimeter (DSC822e, Mettler-Toledo GmbH, Switzerland). The total polysaccharide content of 5% w/w TS/Xan mixtures with mixing ratios of 10/0, 9.5/0.5 and 9/1 was selected to study the effect of sucrose (0–30% w/w). Precalculated amounts of Xan were added to preweighed deionized distilled water and allowed to disperse throughout the sol for at least 6 h at room temperature (25 °C) using a magnetic stirrer to ensure fully hydration of the polysaccharide. TS or TS mixed with sucrose were added into the dispersions with continued stirring for a further 30 min. About 15 mg of the dispersions were weighed directly into a 40-μl aluminum DSC pan and the pans were hermetically sealed. The gelatinization behaviors of TS and Xan mixtures containing sucrose were investigated by heating the pans from 25 °C to 110 °C at the rate of 5 °C/min. A sealed empty pan was used as a reference. Onset temperature (T_o) peak temperature (T_p) and conclusion temperature (T_c) were determined based on heating DSC thermograms. Gelatinized enthalpy expressed as J/g dry starch was evaluated based on the area of the main endothermic peak. The sample pan was weighed before and after measurements to ensure that no weight was lost during the measurement. Three freshly prepared samples were measured and each average value was reported.

2.3. Rapid visco-analyser (RVA) measurement

Pasting properties of 5% w/w TS and Xan mixtures at different mixing ratios (TS/Xan = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) containing sucrose (0–30%) were determined using a rapid visco-analyser (RVA) (RVA-4, Newport Scientific, Narrabeen, Australia). For each mixture of TS/Xan/sucrose, precalculated amounts of Xan were added to preweighed deionized distilled water in RVA canisters and allowed to disperse throughout the sol for at least 6 h. TS with and without sucrose was then added to achieve a total weight of 28 g for preparing 5% w/w TS/Xan pastes containing 0–30% sucrose. The dispersions were kept at room temperature for a further 30 min to hydrate the starch. Each suspension was stirred manually to disperse the sample uniformly before measurement. The pasting profile of the sample and agitation speeds of the paddle were monitored during a thermal treatment according to the method of Pongsawatmanit et al. (2006) as follows: equilibrating the starch slurry at 50 °C for 1 min, increasing the temperature to 95 °C at a heating rate of 6 °C/min, holding the temperature at 95 °C for 5 min, decreasing the temperature to 50 °C at 6 °C/min, and holding at 50 °C for the remainder of the run. The total run time was 23 min. Agitation speed of paddle was started at 960 rpm for the first 10 s and kept constant at 160 rpm until the end of the experiment. Pasting profiles were evaluated in triplicate and the average values of evaluated pasting parameters were reported.

2.4. Steady shear viscosity measurement

Selected gelatinized TS/Xan/Sucrose mixtures obtained from the RVA experiments were used for steady shear viscosity measurement using a rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany). All pastes were centrifuged at 190*g* for 2 min to remove air bubbles and then a portion of each paste was placed onto the measuring plate using cone and plate geometry (50 mm diameter, 1°cone angle and 0.05 mm gap) which was equilibrated to the measured temperatures (25 and 50 °C) beforehand. Sample temperature was kept constant at 25 °C or 50 °C for at least 2 min before starting the measurement. Apparent viscosity was recorded by increasing the shear rate from 0.01 to 100 s^{-1}.

2.5. Data and statistical analysis

Each of the measurements was carried out using at least three freshly prepared samples. The results were reported as the mean and standard deviation. Statistical analysis was performed by SPSS V.12 statistical software (SPSS (Thailand) Co., Ltd.). Linear regression was conducted to relate the RVA final viscosity with the xanthan and sucrose contents to predict a set of response/dependent variables.

3. Results and discussion

3.1. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used as a thermal analysis technique and applied to determine the effect of sucrose on the gelatinization of starch in this study. Total polysaccharide concentration at 5% w/w of TS and Xan dispersions (at mixing ratios = 10/0, 9.5/0.5 and 9/1) containing 0–30% sucrose was prepared to investigate the changes in gelatinization process of the mixtures. The concentrations of Xan used in the study were ranged from 0 to 0.5% due to the common concentration range applied in food products (Sharma et al., 2006). Sucrose concentrations (0–30%) in TS/Xan mixtures were investigated for further application in real products such as chilli dipping sauces or plum sauces containing up to 30% sucrose. A single endothermic peak was observed (Fig. 1) due to the disintegration of the native starch structure at high water content (more than 60% w/w) (Biliaderis, 1990; Aee et al., 1998). Glass transition of the amorphous regions of starch granule that surround the crystalline zones to a mobile rubbery state, at a glass transition temperature (T_g), precedes gelatinization during heating have been reported (Biliaderis et al., 1986; Jacobs and Delcour, 1998). However, no change in heat capacity could be observed in the region that preceded the gelatinization endotherm from this study. The result is in agreement with the report of Ferrero and Zaritzky (2000).

The onset, peak and conclusion temperatures (T_o, T_p and T_c) of all TS/Xan dispersions without sucrose were about 64 °C, 69 °C and 74 °C, respectively. The gelatinization temperatures (T_o, T_p

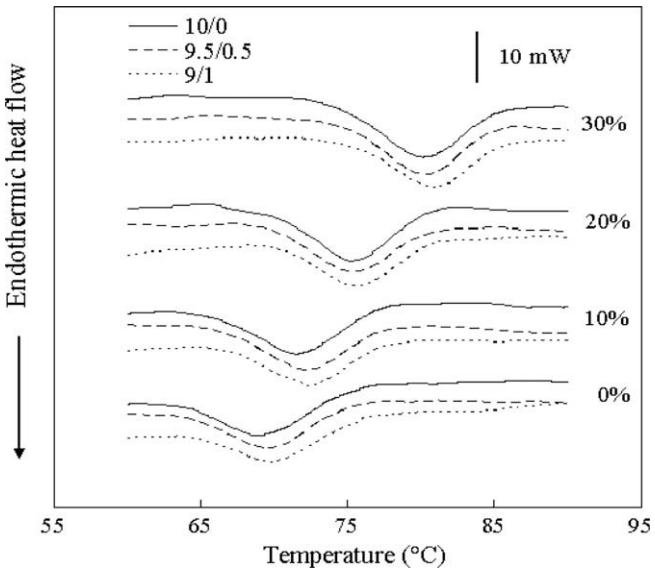

Fig. 1. DSC thermograms of 5% w/w TS and TS/Xan mixtures at various mixing ratios (10/0, 9.5/0.5 and 9/1) containing sucrose (0–30%).

and T_c) shifted significantly to higher temperatures with increasing sucrose concentration for all mixing ratios of TS and Xan ($p < 0.05$, Table 1) due to the anti-plasticizing effect because the presence of sucrose dissolving in the continuous phase enhances higher viscosity accompanied with the lower water mobility in the dispersion (Pongsawatmanit et al., 2002, 2007; Kohyama and Nishinari, 1991). However, at the same sucrose concentration, Xan did not affect each gelatinization temperature (T_o, T_p, T_c) of the TS/Xan dispersions ($p > 0.05$, Table 1). These results are in agreement with those reported from previous studies of TS-xyloglucan mixtures (Pongsawatmanit et al., 2007) and maize starch – 0.5% guar gum (Tester and Sommerville, 2003).

Endothermic enthalpy (ΔH) values for the gelatinization of TS/Xan/sucrose mixtures were evaluated from the areas under the single endothermic curves during heating. The transition enthalpy of TS dispersion indicated that the quantity of energy required to gelatinize the starch was 13.6 J/g dry starch; gelatinization enthalpies of TS reported in the literature are 12.4 J/g (Hung and Morita, 2005) and 16.0 J/g (Pongsawatmanit et al., 2007). Difference in gelatinization enthalpy is expected from differences in cassava cultivar and harvesting time which lead to the difference in physicochemical properties of TS (Sriroth et al., 1999). The gelatinization enthalpy values of TS alone increased from 13.6 to 16.9 J/g dry starch for the dispersions containing sucrose from 0% to 30% ($p < 0.05$, Table 1), respectively. No exothermic or endothermic peak of Xan dispersions with and without sucrose was observed (data not shown). The enthalpy of 5% w/w TS/Xan increased with increasing sucrose concentration for each mixing ratio. At the same sucrose concentration, the enthalpy of TS showed a significant decrease with partial substitutions of TS with Xan ($p < 0.05$, Table 1).

3.2. RVA pasting properties

RVA is used to observe the changes in pasting properties of starch during heating and cooling processes affecting the quality of final starch-based products. An addition of hydrocolloids and sugars can alter the pasting properties of starch. Pasting profiles of 5% w/w TS/Xan mixtures (mixing ratios = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) containing sucrose (0–30%) were investigated during RVA experiment. A strong influence of sucrose on pasting properties for each TS/Xan mixing ratio was observed as shown in the selected typical RVA pasting profiles of 5% w/w TS and TS/Xan (mixing ratio = 9/1) (Fig. 2). RVA pasting properties are related to the gelatinization and short-term retrogradation of starch-based samples during heating and cooling since no peak was observed in the mixture of 1% Xan containing 30% sucrose. Pearson's correlation coefficients (r) were analyzed to quantify the relationship between sucrose and RVA parameters. The r values revealed significant positive correlations ($p < 0.05$, Table 2). Pasting temperatures of TS/Xan pastes increased significantly with sucrose concentration ($p < 0.05$, Table 3). These results are in agreement with the DSC gelatinization temperatures (T_o, T_p and T_c) and suggest that sucrose reduces the available water in the system. The anti-plasticizing effect of sucrose leads to a lower amount of amylose leaching and causes a retardation in gelatinization of TS and TS/Xan mixtures (Ahmad and Williams, 1999; Kohyama and Nishinari, 1991) leading to higher pasting temperatures (Table 3) (Hirashima et al., 2005). Sucrose may play an important role in the inhibition of hydration for starch granules or the non-starch polysaccharide fraction (Yoshimura et al., 1996). Therefore, in systems containing higher concentrations of sugar, the competition between sucrose and Xan to be hydrated by water in the 5% w/w of total polysaccharides may lead to an increase in pasting temperatures of TS/Xan mixtures from 72–78 °C to 82–90 °C with increasing sucrose concentration from 0% to 30%, respectively (Table 3).

The viscosity at the peak of the RVA profile (peak viscosity) is considered as the equilibrium point between swelling and rupture of starch granules during heating, while final viscosity is the viscosity after cooling at the end of RVA experiment (23 min for this

Table 1
Effect of sucrose on gelatinization temperatures and enthalpy of 5% w/w TS and TS/Xan mixtures.

DSC gelatinization parameters	TS/Xan mixtures	Sucrose concentration (%)			
		0	10	20	30
T_o (°C)	10/0	63.7 ± 0.1^{Ad}	66.3 ± 0.1^{Ac}	69.7 ± 0.4^{Ab}	74.5 ± 0.8^{Aa}
	9.5/0.5	63.9 ± 0.1^{Ad}	66.6 ± 0.2^{Ac}	69.7 ± 0.2^{Ab}	74.8 ± 0.6^{Aa}
	9/1	64.0 ± 0.4^{Ad}	66.6 ± 0.3^{Ac}	70.2 ± 0.4^{Ab}	75.1 ± 0.3^{Aa}
T_p (°C)	10/0	69.2 ± 0.2^{Ad}	71.8 ± 0.1^{Ac}	75.3 ± 0.5^{Ab}	80.2 ± 0.4^{Aa}
	9.5/0.5	69.4 ± 0.2^{Ad}	71.8 ± 0.2^{Ac}	75.5 ± 0.3^{Ab}	80.3 ± 0.3^{Aa}
	9/1	69.5 ± 0.2^{Ad}	72.0 ± 0.1^{Ac}	75.8 ± 0.2^{Ab}	80.6 ± 0.1^{Aa}
T_c (°C)	10/0	74.6 ± 0.4^{Ad}	76.8 ± 0.3^{Ac}	80.3 ± 0.3^{Ab}	85.0 ± 0.1^{Aa}
	9.5/0.5	74.4 ± 0.2^{Ad}	76.6 ± 0.1^{Ac}	80.2 ± 0.4^{Ab}	84.8 ± 0.2^{Aa}
	9/1	74.0 ± 0.7^{Ad}	76.8 ± 0.3^{Ac}	80.4 ± 0.3^{Ab}	85.0 ± 0.4^{Aa}
ΔH (J/g dry starch)	10/0	13.6 ± 0.6^{Ac}	15.1 ± 0.1^{Ab}	16.2 ± 0.4^{Aa}	16.9 ± 0.5^{Aa}
	9.5/0.5	12.6 ± 0.2^{Bc}	13.8 ± 0.3^{Bb}	15.7 ± 0.8^{Aa}	15.9 ± 0.5^{Ba}
	9/1	12.5 ± 0.3^{Bb}	13.0 ± 0.9^{Bb}	15.0 ± 0.5^{Ba}	15.8 ± 0.2^{Ba}

Mean ± standard deviation values followed by different small and capital letters are significantly different ($p < 0.05$) by Duncan's multiple range test within the same row (sucrose effect) and column (TS/Xan effect for each DSC parameter), respectively.

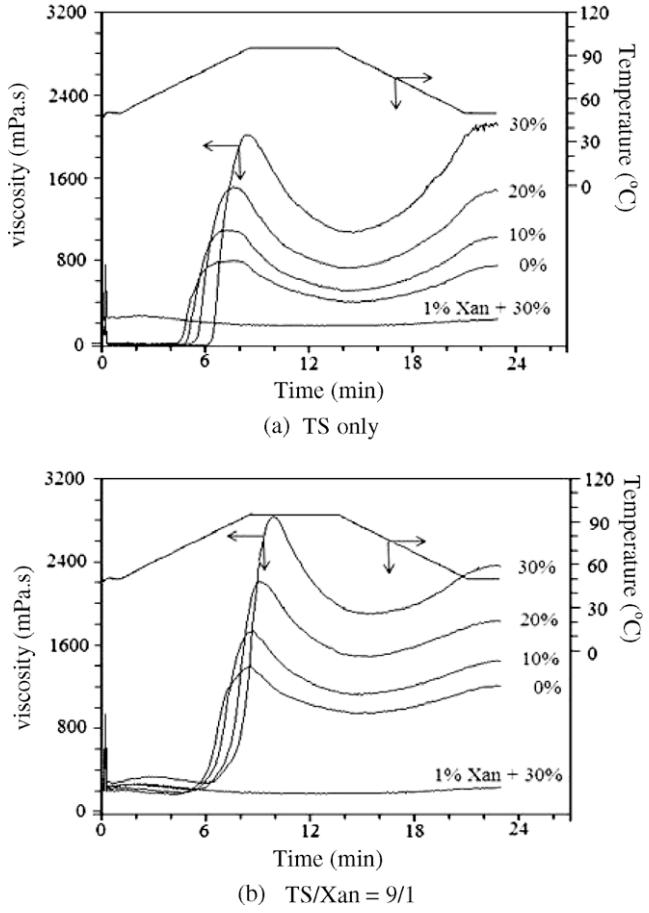

Fig. 2. Typical RVA pasting profiles of 5% w/w TS (a) and 5% w/w TS/Xan mixtures (mixing ratio = 9/1) and (b) with sucrose addition (0–30%). RVA profile of 1% xanthan gum containing 30% sucrose also included.

study). The addition of sucrose enhanced both the peak and final viscosities of the gum-starch pastes ($p < 0.05$) and had a much greater influence than Xan substitution (Fig. 3a and b), indicating that the synergistic effect of sucrose and TS or TS/Xan systems is dominant.

After TS or TS/Xan dispersions were gelatinized, the pastes were subjected to both thermal and shear stresses at the holding temperature (95 °C). Further disruption of starch granules and leaching out of starch molecules caused a decrease in viscosity. The resultant drop in viscosity from peak to a holding strength (minimum viscosity after the peak, occurring around the beginning of RVA cooling stage) was determined and defined as breakdown. Therefore, the breakdown measures the susceptibility of gelatinized starch to disintegration due to the loss of starch granule integrity and subsequent disruption, leading to a reduction of the paste viscosity (Christianson et al., 1981; Pongsawatmanit et al., 2007). The breakdown of TS/Xan pastes revealed almost constant values with increasing Xan substitution ($p > 0.05$) at the same sucrose concentration. However, breakdown values of TS or TS/Xan pastes increased significantly with sucrose addition ($p < 0.05$, Table 2, Fig. 3c) under the influence of applied shear to the mixtures. The results indicate that formed aggregates among polysaccharides and sucrose molecules in the pastes through hydrogen bonding and polymer entanglement are more sensitive to disruption under isothermal shear with increasing sucrose concentration.

The RVA setback obtained from the measurement occurs not only due to the degree of reassociation of gelatinized starch (particularly amylose) molecules during cooling, but also due to the simple kinetic effect of cooling on viscosity. The setback value indicates short-term retrogradation of starch (Pongsawatmanit et al., 2006). It was determined from the increase in viscosities of TS and TS/Xan pastes from holding strength value to final viscosity after cooling down to 50 °C at 6 °C/min. Setback increased with increasing sucrose concentration and decreased with increasing Xan substitution ($p < 0.05$) (Fig. 3d). The effect of Xan on the extent of the decrease in setback values of TS/Xan pastes with and without sucrose was also observed. Setback values of 5% w/w TS and TS/Xan pastes (mixing ratio = 9/1) decreased from 1050 mPa s to 440 mPa s and from 360 mPa s to 260 mPa s for the pastes containing 30% and 0% sucrose, respectively. These results imply that for the TS-based formulation containing sucrose, Xan addition could reduce the setback of the TS pastes leading to lower syneresis (Pongsawatmanit and Srijunthongsiri, 2008).

Table 2
Pearson's correlation coefficients between selected RVA parameters of 5% TS/Xan mixtures and sucrose.

RVA parameters	Pearson's correlation coefficient
Pasting temperature	0.850*
Peak viscosity	0.903*
Breakdown	0.985*
Final viscosity	0.954*
Setback	0.723*

* $p < 0.05$ (two-tailed).

3.3. Analysis of viscosity breakdown under RVA isothermal shear stress

During RVA heating at 95 °C, viscosities of each TS/Xan mixture with and without sucrose from a RVA running time range (600–780 s) under isothermal shear were used to calculate the rate of viscosity breakdown from the slope of each curve. Rates of viscosity breakdown for each sucrose concentration were plotted against Xan concentration (Fig. 4). The rates of viscosity breakdown for TS/Xan mixtures (0% sucrose) increased only slightly with increasing Xan substitution (slope = 0.434) whereas relatively large increase in the value (slope = 3.168) was observed from TS/Xan mixtures

Table 3
Pasting temperatures (°C) of 5% TS/Xan mixtures as affected by Xan and sucrose concentrations.

Xan concentration (%)	Sucrose concentration (%)			
	0	10	20	30
0.0	71.8 ± 0.22^{Ed}	73.5 ± 0.38^{Dc}	76.7 ± 0.03^{Db}	81.8 ± 0.29^{Ea}
0.125	72.7 ± 0.43^{Dd}	75.4 ± 0.31^{Cc}	78.8 ± 0.20^{Cb}	83.2 ± 0.42^{Da}
0.25	74.4 ± 0.52^{Cd}	77.2 ± 0.42^{Bc}	80.7 ± 0.43^{Bb}	85.0 ± 0.95^{Ca}
0.375	76.4 ± 0.52^{Bd}	78.8 ± 0.45^{Ac}	81.8 ± 0.80^{Ab}	87.7 ± 0.25^{Ba}
0.5	78.1 ± 0.59^{Ac}	79.3 ± 1.19^{Ac}	82.7 ± 0.68^{Ab}	90.5 ± 1.14^{Aa}

Mean ± standard deviation values followed by different small and capital letters are significantly different ($p < 0.05$) by Duncan's multiple range test within the same row and

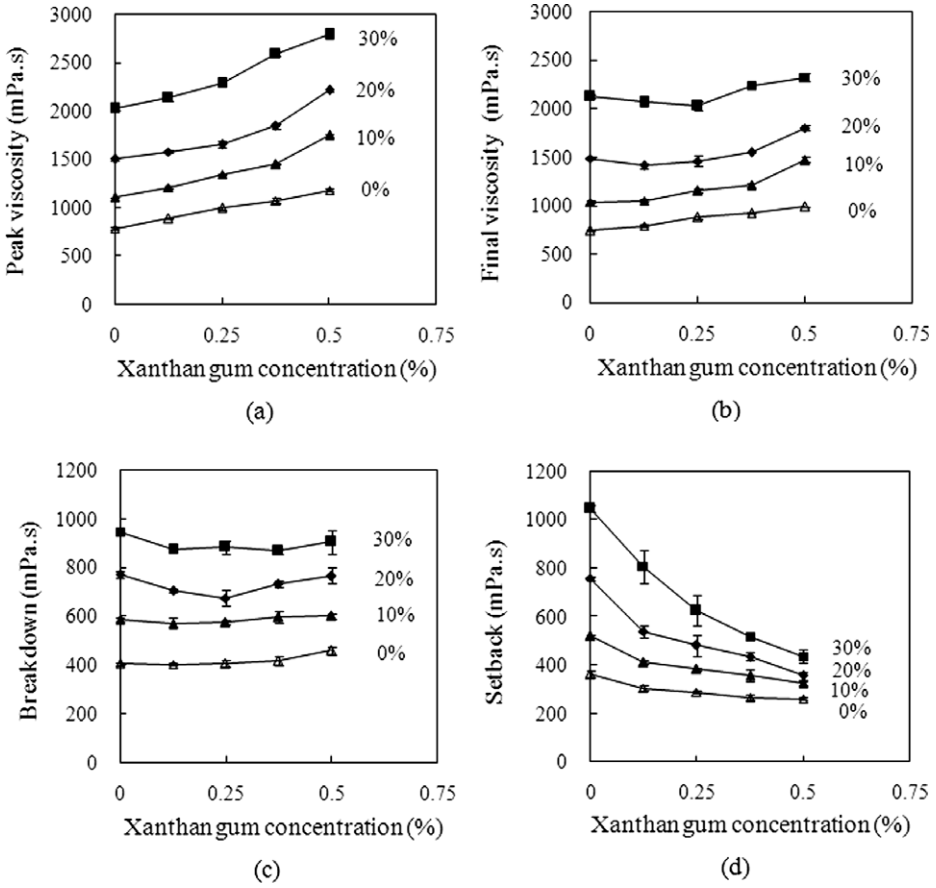

Fig. 3. Influence of sucrose on peak viscosity (a), final viscosity (b), breakdown (c) and setback (d) of 5% w/w TS/Xan mixtures at mixing ratios of 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75, and 9/1.

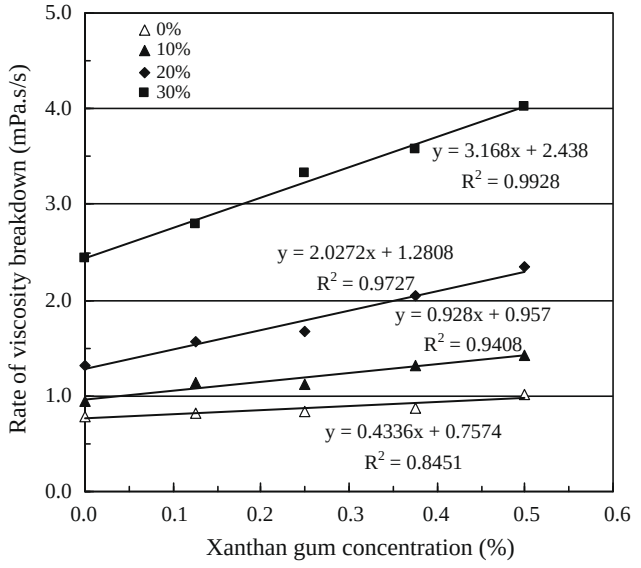

Fig. 4. Rate of viscosity breakdown calculated from RVA pasting profiles of 5% w/w TS/Xan mixtures (mixing ratios = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75, and 9/1) containing different sucrose contents under heating at 95 °C with RVA paddle speed at 160 rpm and running time from 600 to 780 s.

containing 30% sucrose. The slopes obtained from each linear curve increased with increasing sucrose concentration, confirming that hydrogen bonding and polymer entanglement among polysaccharides and sucrose molecules in the pastes are more susceptible to disruption under isothermal shear with increasing sucrose content.

3.4. Steady shear viscosity of TS/Xan pastes

Steady shear viscosity measurement was applied to characterize the properties of TS/Xan pastes with and without sucrose at 25 °C and 50 °C. Selected gelatinized TS and TS/Xan pastes at three mixing ratios (10/0, 9.75/0.25, 9.5/0.5) with and without sucrose (0% and 30%) from RVA experiments were used to evaluate the shear rate dependence of the steady shear viscosity after starch gelatinization. Since the TS/Xan mixture was agitated by the RVA paddle at the speed of 160 rpm during heating and cooling profiles, a homogeneous gelatinized TS/Xan mixture was obtained. In addition, air bubbles formed and trapped in TS/Xan pastes during heating and cooling were removed by centrifuging before shear viscosity measurement. The pasting properties imitating RVA analysis using the rheometer plate (cone and plate geometry) from this study were not appropriate for further investigating the shear viscosity due to the lack of mixing and air bubbles retained in the pastes. This seems to be supported by the observation of higher steady shear viscosities of TS/Xan pastes with and without sucrose compared with those prepared from RVA experiment (data not shown).

All gelatinized TS and TS/Xan pastes exhibited shear thinning behavior (Fig. 5). At 25 °C, TS/Xan pastes showed lower viscosities than those of TS pastes at shear rates higher than 1 s^{-1} (Fig. 5a). The viscosity values of all TS and TS/Xan pastes containing sucrose (30%) (Fig. 5b) were higher than those without sucrose significantly at any given shear rate. Sucrose may have a greater access to the hydration layer of the starch chains and create a localized environment of increased viscosity producing a strong anti-plasticizing effect compared to water alone (Kruger et al., 2003).

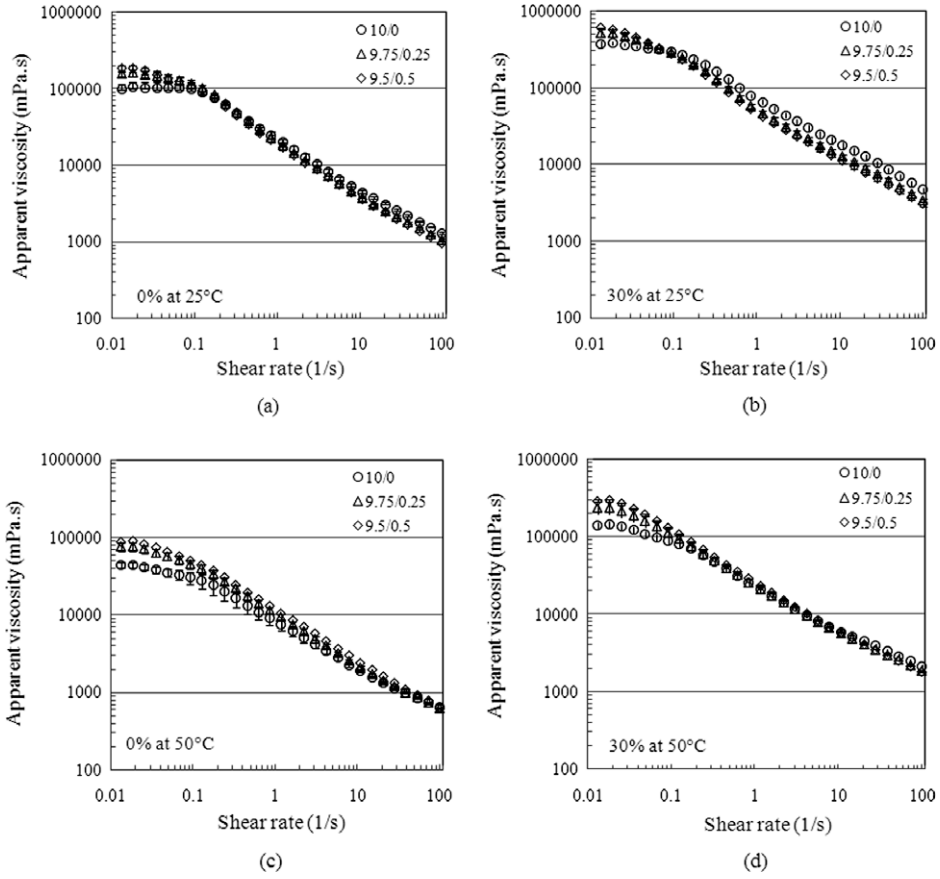

Fig. 5. Shear rate dependence of the steady shear viscosity for 5% w/w gelatinized TS/Xan mixtures (mixing ratios = 10/0, 9.75/0.25, 9.5/0.5) at 25 °C without sucrose (a), 25 °C with 30% sucrose (b), 50 °C without sucrose (c) and 50 °C with 30% sucrose (d). The vertical bar represents the standard deviation.

When the viscosity measurement of TS and TS/Xan pastes was carried out at higher temperature (50 °C), shear thinning behaviors were also observed. However, the viscosities of only TS pastes were lower than those of pastes containing Xan in the studied shear rate range (Fig. 5c). Steady shear viscosities of all TS and TS/Xan pastes containing 30% sucrose were higher than those without sucrose (Fig. 5d). In these mixtures containing 30% sucrose, viscosities of TS/Xan pastes at shear rates less than 1 s^{-1} were also higher than those of TS pastes significantly at higher temperature, indicating the contribution of thermal stability of Xan to TS pastes.

3.5. Regression model and model validation of final viscosity

Final viscosity plays an important role in colloidal system stabilization and product handling in the food industry. The final viscosity of TS paste depends on both Xan and sucrose concentrations in the system as discussed in the previous sections. Therefore, the experimental RVA final viscosity from TS and TS/Xan pastes was plotted as a function of Xan and sucrose concentrations (data not shown). Since the mechanism for explaining the final viscosity depends on the amount of hydrocolloid and sucrose in the TS/Xan/sucrose mixtures, linear regression was conducted to relate the RVA final viscosity with Xan and sucrose to predict response/dependent variable (*Y: final viscosity*) from a set of explanatory/independent variables (*X: xanthan gum and sucrose*). The linear regression analysis yielded Eq. (1) for predicting final viscosity (mPa s):

$$\text{Final viscosity} = 712.417 + 355.267(\text{Xan}) + 42.303(\text{Sucrose}) \quad (1)$$

where Xan = xanthan gum concentration (0–0.5%) and Sucrose = sucrose concentration (0–30%).

To test the model performance from Eq. (1), another group of RVA experiments was performed with newly prepared different TS/Xan/Sucrose pastes (TS/Xan = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1, sucrose content = 0–30%) to determine the final viscosity. Final viscosity values were plotted against those calculated from Eq. (1) using the different Xan and sucrose concentrations. A

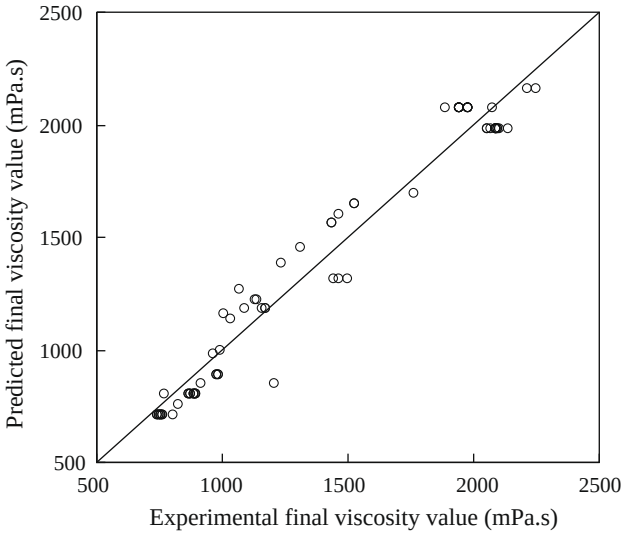

Fig. 6. Predicted final viscosity value using Eq. (1) against experimental RVA final viscosity from 5% w/w TS/Xan pastes at different mixing ratios (10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) containing sucrose concentrations (0–30%) (r = 0.980, RMSE = 84.4).

good predictability of the viscosity at various sucrose and Xan concentrations between the modeling dataset and testing dataset was achieved, indicated by the corresponding correlation coefficient ($r = 0.980$) and small value of the root mean square error (RMSE = 84.4) between them as shown in the Fig. 6.

4. Conclusion

The strong influence of sucrose on the thermal and pasting properties of 5%w/w TS and TS/Xan mixtures was observed by increasing gelatinization temperatures and enthalpy, peak and final viscosities, breakdown and setback values. Partial substitution of TS with Xan imparted more stability to the gelatinized TS pastes in terms of setback reduction and viscosity change due to temperature, especially in the case of pastes containing sucrose. The rate of viscosity breakdown in TS pastes was more prominent with increasing concentrations of both sucrose and Xan under shear and isothermal conditions. The regression model performance from RVA measurements in predicting the final viscosity revealed good agreement with the experimental dataset. Therefore, sucrose and Xan can be used to create TS-based products with better thermal and pasting properties. This finding will assist product development efforts in the food industry.

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