รายงานวิจัยฉบับสมบูรณ์

โครงการ ผลของน้ำตาลและเกลือต่อสมบัติทางด้านกายภาพของ
เจลผสมของ xyloglucan กับแป้งมันสำปะหลัง

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

บทคัดย่อ

แป้งมันสำปะหลัง (TS) นิยมใช้ในอุตสาหกรรมอาหารเพื่อเป็นส่วนประกอบของอาหารในการเป็นสารให้ความหนืด เนื่องจากมีราคาถูก ลักษณะเจลแป้งที่ได้ใส การผสมแป้งมันสำปะหลังกับไซโลกลูแคน (XG) เป็นเทคนิคหนึ่งที่ใช้เพื่อให้อาหารมีลักษณะเนื้อสัมผัสตามต้องการ และมีความคงตัวต่อการกวน รวมทั้งคงตัวในระหว่างการเก็บรักษา ส่วนน้ำตาลและเกลือเป็นส่วนประกอบที่สำคัญในการผลิตอาหาร การศึกษาลักษณะของระบบของผสมที่มีไฮโดรคอลลอยด์ และแป้ง โดยมีน้ำตาล เกลือ เป็นส่วนประกอบจึงมีความสำคัญต่อการนำความรู้ที่ได้ไปพัฒนาผลิตภัณฑ์อาหาร งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาผลของไซโลกลูแคน น้ำตาล และ เกลือต่อสมบัติด้านกายภาพโดยเฉพาะด้านรีโอโลจีและการเปลี่ยนแปลงทางด้านความร้อนของแป้งมันสำปะหลัง

งานวิจัยในตอนที่หนึ่งเป็นการศึกษาลักษณะทางด้านรีโอโลจีและด้านความร้อนของของผสม (dispersions) ระหว่างแป้งมันสำปะหลัง (TS) กับไซโลกลูแคน (XG) โดยวิธีการรีโอเมทรีที่เป็นทั้ง dynamic และ steady shear และวิธี DSC (differential scanning calorimetry) เพื่อศึกษาผลของ XG ต่อการเจลาติไนเซชันและรีโทรกราเดชันของ TS พบว่า ความหนืดของเจล TS ที่ผสม XG (โดยมีความเข้มข้นรวมคงที่ 3.5% w/w) หลังการเจลาติไนเซชันทันทีนั้นมีค่าสูงขึ้นเมื่อความเข้มข้นของ XG เพิ่มขึ้น เจลของ TS ที่ไม่มีการเติม XG มีพฤติกรรมการไหลแบบ pseudoplastic ที่ค่า shear rate ต่ำ และมีพฤติกรรมการไหลแบบ dilatant เมื่อ shear rate สูงกว่า 1 s^{-1} โดยของผสมที่เติม XG ไม่แสดงลักษณะ dilatant เมื่อศึกษาสมบัติด้วยการวัด dynamic test พบว่า mechanical spectra ของเพสต์ (pastes) TS ผสม XG แสดงสมบัติที่เป็นของเหลวซึ่งเรียกว่า liquid-like มากกว่าเพสต์ของ TS เพียงอย่างเดียว เมื่อพิจารณาผลการเก็บรักษา พบว่า XG ให้ความคงตัวด้าน shear แก่เพสต์ของ TS ดีขึ้น และการเพิ่มขึ้นของค่า dynamic moduli ในเพสต์ TS ที่เก็บ ณ 5^{o}C ลดลงเมื่อมี XG ผสมอยู่ด้วย ในทางตรงกันข้าม เมื่อศึกษาสมบัติด้วย DSC พบว่า อัตราส่วนรีโทรกาเดชัน (retrogradation ratio) จาก DSC มีค่าเพิ่มขึ้นอย่างรวดเร็วโดยเฉพาะในช่วงแรกเมื่อมี XG แสดงให้เห็นว่า XG ทำให้เกิดเฟสต่อเนื่องที่เป็นของเหลวในของผสมซึ่งให้ความคงตัวทางกลดีขึ้นในระหว่างการเก็บ แต่จะเร่งการจัดเรียงตัวของพอลิแซคคาไรด์แป้งจากการที่ปริมาณน้ำที่แป้งจะนำไปใช้ได้ลดน้อยลง

ในขั้นต่อมาเป็นการศึกษาผลของ XG ต่อการเกิดเจลาติไนเซชันของ TS ด้วยความเข้มข้นของพอลิแซคคาไรด์ทั้งหมด (TS และ XG) 5% ศึกษาด้วย Rapid Visco-Analyzer (RVA) และรีโอมิเตอร์ทั้งแบบ steady shear และ dynamic shear พบว่า จากกราฟ RVA ความหนืดสูงสุด (peak viscosity) และ ความหนืดสุดท้าย (final viscosity) มีค่าสูงขึ้นเมื่อความเข้มข้นของ XG ในระบบเพิ่มขึ้น โดยผลจาก steady shear ค่าความหนืดของเพสต์ของผสม TS และ XG สูงกว่าของเพสต์จากแป้ง TS เพียงอย่างเดียว โดยกราฟการไหลที่ได้เป็น shear thinning เมื่อให้ความร้อนแก่แป้งที่ผ่านการให้ความร้อนแล้ว พบว่า ความหนืดปรากฏลดลงเมื่ออุณหภูมิสูงขึ้น ณ shear rate 50 s^{-1} เมื่อศึกษาผลของอุณหภูมิต่อการเปลี่ยนแปลงความหนืด ณ shear rate 50 s^{-1} ด้วยการสร้างกราฟอาร์รีเนียส พบว่า พลังงานกระตุ้น (E_a) ของระบบของผสม TS และ XG ให้ค่าต่ำกว่าของแป้งเพียงอย่างเดียว แสดงให้เห็นว่า XG ปรับปรุงคุณภาพด้านความคง

ตัวที่เกี่ยวกับความหนืดเมื่ออุณหภูมิเปลี่ยนแปลงไป ค่า loss tangent (G''/G') ที่ระบุสมบัติที่คล้ายของเหลว (liquid-like) ของของผสม TS และ XG เพิ่มขึ้นเมื่อความเข้มข้นของ XG เพิ่มขึ้น ผลที่ได้แสดงให้เห็นว่า XG ให้ความหนืดสูงขึ้น มีความคงตัวทางด้านความร้อน และให้สมบัติทางรีโอโลจีที่คล้ายของเหลวต่อของผสมที่ผ่านการเจลาติไนส์แล้ว

จากการศึกษาผลของซูโครสต่อลักษณะทางกายภาพของระบบ TS เพียงอย่างเดียวและระบบของผสม TS และ XG (สัดส่วน 9:1) เพื่อใช้เป็นแนวทางในการพัฒนาสมบัติทางกายภาพของผลิตภัณฑ์ที่ใช้แป้งเป็นส่วนประกอบ โดยการเตรียมของผสม TS ให้มีความเข้มข้นรวมของพอลิแซคคาไรด์ 25% ที่มี XG 0 และ 2.5% w/w และซูโครส 0 ถึง 20% w/w และติดตามการเกิดเจลาติไนเซชันของเพสต์ TS เพียงอย่างเดียวและเพสต์ TS และ XG ความเข้มข้นรวม 25% ด้วย DSC รวมทั้งเจลของ TS อย่างเดียวและเจลของ TS และ XG ที่มีความเข้มข้นพอลิแซคคาไรด์รวม 25% มีซูโครส 0, 10 หรือ 20% w/w และเตรียมให้อยู่ในรูปของทรงกระบอกที่มีเส้นผ่าศูนย์กลาง 22 mm วัดค่าลักษณะเนื้อสัมผัสด้วย texture profile analysis (TPA) หลังเก็บไว้ ณ 5°C 24 ชม โดยตัดทรงกระบอกให้มีความสูง 20 mm พบว่า อุณหภูมิเจลาติไนเซชัน (T_o, T_p, T_c) เพิ่มขึ้นเมื่อความเข้มข้นของซูโครสเพิ่มขึ้น ค่า T_o และ T_p เคลื่อนไปที่อุณหภูมิสูงขึ้นเล็กน้อยเมื่อมี XG ในดิสเพอร์ชัน (dispersion) โดยเอนทัลปีของเจลาติไนเซชันของเพสต์ที่มีซูโครส 20% w/w มีค่าสูงขึ้นทั้งระบบที่เป็น TS เพียงอย่างเดียวและระบบของผสม TS และ XG (สัดส่วน 9:1) ซูโครสมีผลทำให้ความแข็งทั้งค่า hardness และ stiffness มากขึ้น การใช้ XG แทนในแป้ง TS ลดความแข็งแต่เพิ่มค่า cohesiveness ของเจลแสดงให้เห็นว่า XG ลดความแข็งของโครงสร้างตาข่ายด้วยการลดการเกิดโครงสร้างของอะไมโลสใน TS และซูโครสทำให้เจลแข็งแรงขึ้นและชะลอการเจลาติไนเซชันของ TS ด้วย

ผลของเกลือ (0 ถึง 4%) ต่อสมบัติทางกายภาพของระบบ TS เพียงอย่างเดียวและระบบของผสม TS และ XG (สัดส่วน 9:1) ที่มีความเข้มข้นรวมของพอลิแซคคาไรด์ 5% พบว่า RVA pasting profiles ให้ค่า pasting temperatures เพิ่มขึ้นเมื่อความเข้มข้นเกลือ NaCl, KCl, $CaCl_2$ เพิ่มขึ้น อุณหภูมิของเจลาติไนเซชันจากการวัดด้วย dynamic แสดงค่าเพิ่มขึ้นเมื่อความเข้มข้นของเกลือเพิ่มขึ้น เช่นเดียวกับค่าที่วัดได้จาก DSC โดย G' จากการวัด dynamic test ณ 5°C ของวงจรที่ทำให้เย็นลงหลังการให้ความร้อนมีค่าใกล้เคียงกันแม้ความเข้มข้นเกลือแตกต่างกัน เอนทัลปีของการเจลาติไนเซชันจาก DSC แสดงให้เห็นว่ามีแนวโน้มเพิ่มขึ้นเมื่อมีเกลือในระบบสูงขึ้น

ผลจากการศึกษานี้ จะใช้ในการปรับปรุงระบบอาหารที่มีความคงตัวและมีเนื้อสัมผัสที่ดีขึ้นในการพัฒนาผลิตภัณฑ์และกระบวนการผลิต

ABSTRACT

Tapioca starch (TS) is used in the food industry as a thickening agent because of high viscosity and clear appearance of its gelatinized paste. Blending of TS with xyloglucan (XG) is a technique to maintain desirable texture and improve the stability to shear during storage. Sucrose and salts are major ingredients in the food formulations. Mixed systems of sucrose or salts, hydrocolloids and starch were interested to characterize for further food application. The objectives of this study are to investigate effect of XG, sucrose and salts on the rheological and thermal properties of the tapioca starch.

The first part of this study was to investigate TS/XG rheological and thermal properties. Dynamic and steady shear rheometry and differential scanning calorimetry (DSC) were used to investigate effects of xyloglucan (XG) on gelatinization and retrogradation of tapioca starch (TS). The viscosity of TS/XG pastes immediately after gelatinization increased with increasing XG content at the total polysaccharide concentration of 3.5%. Gelatinized TS alone showed pseudoplastic flow at low shear rates and dilatant behavior at higher shear rates (about >1 s^{-1}), while mixtures with XG did not show dilatancy. Mechanical spectra of TS pastes containing XG were more liquid-like than those of TS pastes without XG. XG provides shear stability to the TS during storage. Increases in dynamic moduli during storage at 5°C were suppressed in the presence of XG. In contrast, the retrogradation ratio determined based on DSC increased more rapidly in the presence of XG. These results suggest that XG forms a continuous liquid phase in a mixture to impart better mechanical stability during storage but to accelerate reordering of starch polysaccharides by effectively reducing the amount of water available for starch.

Effects of xyloglucan (XG) on heat-induced gelatinization of tapioca starch (TS) were investigated using a Rapid Visco-Analyzer (RVA) and steady and dynamic shear rheometer. RVA pasting tests were conducted at the total polysaccharide concentration of 5% (w/w) and revealed that peak and final viscosities increased with increasing XG concentration. In steady shear experiments, viscosity values of gelatinized TS/XG mixtures were generally higher than those of gelatinized individual TS pastes, while both samples showed shear thinning behavior. When gelatinized samples were reheated, the apparent viscosities at 50 s^{-1} decreased with increasing temperature. Arrhenius plotting of the apparent viscosities at 50 s^{-1} resulted in a lower activation energy (E_a) value of a TS/XG mixture compared to that of TS alone, suggesting improved heat-stability of the mixtures. The mechanical loss tangent (G''/G') of the TS/XG mixtures increased with increasing XG concentration. The present results confirmed that XG imparted more viscous, heat-stable, and liquid-like rheological properties to the gelatinized mixtures.

The effect of sucrose on the physical properties of TS and TS/XG dispersions was investigated to improve the physical property of starch-based products. TS dispersions at total polysaccharide concentration of 25% containing xyloglucan (0 and 2.5 % w/w) and sucrose (0 to 20 % w/w) and were prepared. Gelatinization behavior was monitored using a differential scanning calorimeter. Gelatinized pastes containing 25% w/w polysaccharides and 0, 10, or 20% w/w sucrose were prepared in plastic cases to form cylindrical gels with 22 mm in diameter. The gels were kept at 5 ^{o}C for 24 h and cut into 20 mm in height for texture profile analysis (TPA). Gelatinization temperatures (T_o, T_p, T_c) at both TS/XG mixing ratios (10/0 and 9/1) increased with increasing sucrose concentration. The onset

and peak temperatures slightly shifted to higher temperatures in the presence of XG. The gelatinization enthalpy of pastes containing 20 % w/w sucrose showed a higher value for both mixing ratios of TS and XG. Sucrose increased the hardness and stiffness of the gels prepared from both TS alone and TS/XG. Incorporation of XG into TS decreased the hardness and stiffness but increased the cohesiveness of the gels compared with those of TS alone, suggesting that XG can decrease network rigidity by reducing the structure formation of the amylose in TS and sucrose strengthens the gels and delays the gelatinization of TS.

The effect of salts on the physical properties of TS and TS/XG dispersions was investigated. For RVA measurement, pasting temperatures of 5% TS and TS/XG (9/1) dispersions increased with increasing salts (NaCl, KCl, or $CaCl_2$). The gelatinization temperatures determined from dynamic viscoelastic measurement also increased with increasing salt content. G' of TS and TS/XG pastes containing different concentrations of NaCl and $CaCl_2$. at 5°C showed almost identical during cooling. DSC curves gave the higher gelatinization temperatures with increasing NaCl concentration but gelatinization enthalpy of 25% TS and TS/XG dispersions showed a trend of slightly increase with increasing the NaCl concentration

The results from this study were used to improve the food system for better stability and texture in product and process development.

EXECUTIVE SUMMARY

1. โครงการ ผลของน้ำตาลและเกลือต่อสมบัติทางด้านกายภาพของเจลผสมของไซโลกลูแคนกับแป้งมันสำปะหลัง

2. ชื่อหัวหน้าโครงการ

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3. วัตถุประสงค์

1. เพื่อให้ทราบว่าผลของไซโลกลูแคน น้ำตาล และเกลือต่อสมบัติทางกายภาพของแป้งมันสำปะหลัง
2. เพื่อเป็นองค์ความรู้พื้นฐานในการนำไปประยุกต์เพื่อการพัฒนาผลิตภัณฑ์และกระบวนการ

4. วิธีดำเนินการวิจัย (research methodology/ work plan)

4.1 ศึกษาลักษณะทางด้านรีโอโลจีและด้านความร้อนของของผสม (dispersions) ระหว่างแป้งมันสำปะหลัง (TS) กับไซโลกลูแคน (XG) โดยวิธีการรีโอเมทรีที่เป็นทั้ง dynamic และ steady shear และวิธี DSC (differential scanning calorimetry)

4.2 ศึกษาผลของซูโครสต่อลักษณะทางกายภาพของระบบ TS เพียงอย่างเดียวและระบบของผสม TS และ XG โดย RVA, rheometer, TPA และ DSC

4.3 ศึกษาผลของเกลือต่อลักษณะทางกายภาพของระบบ TS เพียงอย่างเดียวและระบบของผสม TS และ XG โดย RVA, rheometer และ DSC

5. ผลที่ได้รับจากโครงการ (out put)

1. XG ทำให้เกิดเฟสต่อเนื่องที่เป็นของเหลวในของผสมซึ่งให้ความคงตัวทางกลดีขึ้นในระหว่างการเก็บรักษา โดยจะเร่งการจัดเรียงตัวของพอลิแซคคาไรด์แป้งจากการที่ปริมาณน้ำที่แป้งจะนำไปใช้ได้ลดน้อยลง XG นอกจากให้ความหนืดสูงขึ้น ยังให้ความคงตัวทางด้านความร้อน และให้สมบัติทางรีโอโลจีที่คล้ายของเหลวต่อของผสมที่ผ่านการเจลาติไนส์
2. จากการศึกษาผลของซูโครส (น้ำตาลทราย) และเกลือ ซึ่งมักใช้เป็นส่วนประกอบของอาหารต่อสมบัติทางกายภาพของระบบ TS เพียงอย่างเดียวและระบบของผสม TS และ XG (สัดส่วน 9:1) เพื่อใช้เป็นแนวทางในการพัฒนาสมบัติทางกายภาพของผลิตภัณฑ์ที่ใช้แป้งเป็นส่วนประกอบ พบว่า ซูโครสมีผลทำให้ความแข็งทั้งค่า hardness และ stiffness มากขึ้น การใช้ XG แทนในแป้ง TS ลดความแข็งแต่เพิ่มค่า cohesiveness ของเจลแสดงให้เห็นว่า XG ลดความแข็งของโครงสร้างตาข่ายด้วยการลดการจัดเรียงตัวโครงสร้างของอะไมโลสใน TS และซูโครสทำให้เจลแข็งแรงขึ้นและชะลอการเจลาติไนเซชันของ TS ด้วย โดยซูโครสและเกลือมีผลทำให้ gelatinization temperature สูงขึ้นเมื่อความเข้มข้นของซูโครสหรือเกลือเพิ่มขึ้น
3. ได้ส่ง manuscript ไปตีพิมพ์ในวารสาร Food Hydrocolloids 1 paper ซึ่งได้รับการตอบรับหลังการแก้ไขเล็กน้อยก่อน และยังได้เตรียม manuscript อีก 2 เรื่อง เพื่อส่งไปตีพิมพ์ในวารสารระดับนานาชาติ

CONTENT

I. Introduction

Tapioca starch (TS), produced from cassava roots, is a favorable thickener in food industries due to its high viscosity, clear appearance, and low production cost, compared to other starches, especially in Southeast Asia (Rapaille and Vanhemelrijck, 1997). In food production, long shelf-life stability is needed during distribution and household storage. However, starch pastes often suffer from low stability against shear or other mechanical stimuli. It is usually the case that the viscosity of a starch paste decreases when mechanically disturbed. This drives the industries to use a relatively high concentration of starch compared to other hydrocolloids (Sriroth and Piyachomkwan, 2000). Additionally, although tapioca starch itself has traditionally been used as a thickener, the slimy texture can be regarded as somewhat less than desirable. This textural instability during storage is the driving force to modify the starch for improving the shelf life of product using tapioca starch as a thickener.

Incorporation of a proper amount of hydrocolloids may improve textural properties and stability of tapioca starch in food products. Blending of starches with other biopolymers is a well-known technique to modify texture or maintain desirable texture during a long storage period (Lee *et al.,* 2002; Tester and Sommerville, 2003). When a starch/hydrocolloid mixture is used as a texture modifier, understanding of its rheological and thermal properties is important. Thus, various studies on rheological and thermal properties of mixtures between starches and hydrocolloids have been reported (Shi and BeMiller, 2002; Sudhakar *et al.,* 1995). In general, the viscosity of a mixed system is greatly higher than starch alone since most biopolymers are strongly hydrophilic and compete with starch for water (Christianson *et al.,* 1981; Sudhakar *et al.,* 1996). The extent of starch granule swelling or melting of crystalline parts during gelatinization is influenced by the presence of hydrocolloids and synergistic interactions between hydrocolloids and starch may be anticipated (Closs *et al*., 1999; Shi *et al*., 2002). 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 and 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 *et al.,* 1999).

From viewpoints of texture and stability modification, xyloglucan (XG) is an interesting hydrocolloid (Nishinari *et al.,* 2000). XG has a β-(1-4) linked D-glucan backbone that is partially substituted at the O-6 position of its glucopyranosyl residues with α-D-xylopyranose. Some of the xylose residues are further substituted at the O-2 position with β-D-galactopyranose (Nishinari *et al.*, 2000). XG exhibits a high water holding capacity and good stability to heat, acids and shear. In food industry, XG is widely used as a thickener, stabilizer, fat replacer, or starch modifier in many products for example ice cream, dressing, mayonnaise, noodles, stew, etc., to improve rheological and thermal properties of products (Nishinari *et al.*, 2000). It has been shown that an addition of XG extracted from the seeds of tamarind or *Hymenaea courbaril* into corn starch yielded high paste viscosity but it could have no influence on pasting temperature (Freitas *et al.*, 2003) or slightly lower (Prabhanjan and Ali, 1995) or increase the pasting temperature (Yoshimura *et al.*, 1999). However, gelatinization and retrogradation behavior of TS in the presence of XG has rarely been investigated.

Sugars are the most common ingredients presented in food systems. Non-ionic solutes, such as saccharides have been found to increase the gelatinization temperature of

starch depending on the sugar concentration (D'Appolonia, 1972; Lelievre, 1976). The addition of saccharides into starch generally increase the gelatinization temperature due to the retardation of the swelling of starch granules (Baek *et al.*, 2004; Chinachoti *et al.*, 1990; Eliasson, 1992; Gonera and Cornillon, 2002; Aee *et al.*, 1998; Ikeda *et al.*, 2001; Kohyama and Nishinari, 1991; Kruger *et al.*, 2003; Maaurf *et al.*, 2001; Spies and Hoseney, 1982) and changes in the structure of water phase. However, the effect of sugars on starch showing different behaviors depends on types of starch and saccharide, concentration and preparation methods. In the case of XG, at high concentration of sucrose gel formation of XG was reported (Nishinari *et al.*, 2000).

Salt is another comon ingredient used in food industry. Various types of salts give different effects on paste viscosity by entangling with starch paste or by interfereing the swelling of starch including gelatinization and retrogradation (Sudhakar *et al.*, 1995; Tomasik *et al.*, 2000). Salts have a different and rather complex effect on the gelatinization of starch. It has been reported that salts can cause an elevation or depression of gelatinization temperature and gelatinization enthalpy depending on the type of salt and their concentration (Evans and Haisman, 1982; Jane, 1993). In the presence of NaCl, onset temperature (T_o) , peak temperature (T_p) and conclusion temperature (T_c) from DSC measurements increased initially with increasing salt concentration and then decreased as the salt concentration was increased further for various types of starches (Evans and Haisman, 1982; Lii *et al.*, 2002). It seems that the monovalent cations, such as Na or K, increased swelling power of the starch while bivalent cations, such as Ca, may involve in a stronger bond, causing the decrease in water adsorption capacity (Oosten, 1982).

Effect of XG on the gelatinization and retrogradation of corn or maize starch has been reported (Yoshimura *et al.*, 1999; Freitas *et al.*, 2003). However, considering TS, the gelatinization and retrogradation behavior of TS in the presence of XG has rarely been investigated and effect of small molecules solutes such as sugars or salts on starch swelling, gelatinization and retrogradation of starch in the mixed systems with XG are not well understood.

The objectives of this study were to study the effect of XG on rheological and thermal properties of TS. The .effects of sucrose and various salts on the pasting properties, mechanical properties and thermal properties were also determined, using RVA, rheometry and DSC, respectively to obtain fundamental knowledge needed for further food applications in product and process development.

II. Materials and Methods

2.1 Materials

Tapioca starch (TS) produced in March 2002 was purchased from a manufacturer located in the area of Chonburi province, Thailand. The tapioca starch was kept under a controlled temperature (10±2°C). A proximate analysis of the starch was made according to the AOAC method (AOAC, 1995) and shown in Table 2.1. Amylose content of tapioca starch was determined using alpha-amylase and HPSEC technique (Govindasamy *et al.*, 1992).

Xyloglucan (XG) obtained from tamarind seed was a gift from Dainippon Pharmaceutical Co., Ltd. (Osaka, Japan). The moisture content of the xyloglucan was 6.4% w/w. Protein, fat and ash contents were 0.2, 0.1 and 0.25% (w/w, db), respectively. Both biopolymers were used without further purification.

Sucrose and salts (NaCl, KCl, and $CaCl_2$) used in these experiments were analytical grade.

Table 2.1 Compositions of tapioca starch.

Composition	Tapioca starch (% w/w)[a]
Moisture	12.10±0.13
Protein	0.11±0.01*
Fat	0.07±0.02*
Fiber	0.12±0.03*
Ash	0.25±0.03*
Amylose content	22.0±0.14*

[a] Mean ± standard deviation.
*dry basis.

2.2 Effect of XG on TS physical properties

The total polysaccharide concentration of 3.5 w/w with different mixing ratios (TS/XG = 10/0, 9/1, 8/2, 7/3, 6/4 or 5/5) was selected to study the effect of XG on rheological properties (pasting properties, mechanical properties) of TS system. For the thermal properties determined using DSC, the total polysaccharide concentration of 25% w/w was selected to determine the gelatinization temperature, enthalpy and retrogradation during the storage at 5 °C.

2.2.1. Dynamic viscoelasticity measurements

2.2.1.1. Pasting behavior

Changes in dynamic mechanical properties during a heating/cooling process of TS/XG mixtures were monitored using a stress-controlled rheometer (RheoStress1, Haake, Germany). Three mixing ratios (TS/XG = 7/3, 6/4 and 5/5) were chosen at the total polysaccharide concentration of 3.5% w/w in order to avoid sedimentation of starch granules during the experiments. TS and XG powders were dispersed together into distilled water at room temperature (25°C), loaded into the cup of a double gap cylinder test fixture (DG41-Ti, Haake, Germany) preset at 50°C, and immediately covered with silicone oil to prevent water loss during heating-cooling cycle. Dynamic moduli of the samples were measured during temperature ramp from 50 to 95°C at the rate of 0.5°C/min and successive cooling down to 5°C at the rate of -0.5°C/min. The storage modulus (G') and loss modulus (G'') were determined using a strain-controlled mode with a strain of 1% at a

frequency of 10 rad/s. Stress sweep measurements were performed to confirm that data were obtained within the linear viscoelastic strain region.

2.2.1.2. Evolution of mechanical spectra during storage

Weighed amounts of TS and XG were dispersed into distilled water at the total polysaccharide content of 3.5% w/w with five mixing ratios (TS/XG = 10/0, 9/1, 8/2, 7/3, and 6/4). Sodium azide (0.04% w/w) was added to prevent microbial spoilage. The mixtures were stirred using a magnetic stirrer for 1 h at room temperature (25°C), heated in a boiling-water bath, and then further stirred for 30 min while the sample temperature was maintained at 95-98°C. An aliquot was divided into 10 ml screw-cap glass tubes for storage test and the sample tubes were cooled down in an iced-water bath to 25°C immediately without further stirring and kept in refrigerated room at 5°C. After pre-specified storage periods at 5°C, measurements of frequency dependence of dynamic moduli were performed at 5°C using a Rheometric Fluids Spectrometer (RFSII, Rheometrics Co. Ltd., USA) with a parallel plate test fixture (50 mm diameter, 1.5 mm gap) in the frequency range from 0.1 to 100 rad/s. Values of strain used for all experiments were confirmed to be within the linear viscoelastic regions determined based on strain sweep experiments. The experiments were done in duplicates.

2.2.2. Steady shear viscosity measurements

TS and XG (3.5% total polysaccharide content) were weighed and mixed together at five mixing ratios (TS/XG = 10/0, 9/1, 8/2, 7/3, and 6/4) in distilled water. The total polysaccharide content of all samples was selected to be 3.5% to generate sufficient torque responses for the measuring instruments (RFSII, Rheometrics Co., Ltd., USA). Sodium azide (0.04%) was added to all samples for preventing microbial spoilage. The mixtures were first stirred using a magnetic stirrer for 1 h at room temperature (25°C), and then heated in a boiling-water bath to reach 95-98°C. Stirring was further continued for 30 min at 95-98°C and cooling immediately after an aliquot being divided into 10 ml screw-cap glass tubes for storage test. The steady shear viscosity was determined using a steady mode, transducer 1, and a parallel plate test fixture (25 mm in diameter) of RSFII. The gap between the plates was set to be 1.5 mm. The shear rate was stepwisely increased from 0.02 to 500 s^{-1} and immediately decreased from 500 to 0.02 s^{-1}. The measurements were done in duplicated and the average value was reported.

2.2.3. Differential scanning calorimetry

A differential scanning calorimeter (DSC6100, Seiko Instruments, Inc., Japan) was used to determine thermal properties of TS/XG mixtures. The total polysaccharide content of all samples was selected to be 25% due to the sensitivity of the instrument. TS and XG mixtures with the TS/XG mixing ratios of 10/0, 9.5/0.5, 9/1, 8.5/1.5, 8/2 were dispersed into distilled water and stirred for 2 h at room temperature using a magnetic stirrer, and then 40 mg of the dispersions was weighed into a 70 mg silver DSC pan. The effect of XG on gelatinization of TS was studied by heating the pans from 25°C to 130°C at the rate of 1°C/min. The onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) were determined based on first-run heating DSC curves. The gelatinization enthalpy was evaluated based on the area of the main endothermic peak. After the first-run heating, the gelatinized samples were cooled down to 25°C at –10°C/min using a cooling controller unit (Seiko Instruments, Inc., Japan) and kept at 5°C for 3, 7, 14, 21, 35, 49, and 63 days. The stored samples were heated again to study the effect of XG on retrogradation of TS.

The retrogradation ratio was calculated by dividing the re-gelatinization enthalpy in the second-run heating by the gelatinization enthalpy in the first-run heating.

2.2.4. Statistical analysis

All experiments described above were carried out using at least two freshly prepared samples. The data presented were the means of each experiment.

2.3 Determination of temperature dependency of the TS/XG mixtures

2.3.1. Sample preparation

TS and XG were prepared at five mixing ratios (TS/XG = 10/0, 9/1, 8/2, 7/3, and 6/4) of 5% total polysaccharide concentration for all measured samples in distilled water. XG dispersions were first prepared at room temperature and stirred using magnetic stirrer at least 2 h, then TS powder was added into the XG dispersion, and continuously mixing for 1 h for RVA pasting and rheological properties. The mixtures for investigation of rheological properties were then heated to 95 °C, hold at the temperature 95-98 °C for 30 min, and cooled down to 40 °C in water bath. Samples were centrifuged at 190 g for 2 min to remove air bubbles.

2.3.2 RVA Pasting properties of TS/XG mixtures

The pasting properties of mixed polysacharrides of TS and XG were determined using a Rapid Visco Analyser (RVA-4, Newport Scientific, Australia) interfaced with a personal computer. Precalculated amounts of XG (0.0 to 0.56 g) were added to preweighed deionized distilled water in a RVA canister and let XG disperse through out the sol for at least 2 h. Then, TS (0.84 to 1.4 g) was added finally to achieve a total weight of 28 g for preparing 5% w/w TS/XG mixtures. Before the measurement, each mixed suspension was stirred manually by rotating the plastic paddle of the RVA for 15 to 30 sec to disperse the sample uniformly and to remove starch lumps. The viscosity of the sample was monitored during a thermal treatment, of which results are called pasting profiles (for details, see Newport Scientific, 1995). The temperature profile consisted of equilibrating the starch slurry at 50°C for 1 min, raising the temperature to 95°C at a heating rate of 6°C/min, holding the temperature at 95°C for 5 min, lowering 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. Pasting profiles were determined in duplicate in order to confirm the reproducibility of data and evaluated parameters were averaged.

2.3.3. Steady shear viscosity of gelatinized samples

Steady shear measurements were performed using rotational mode of a stress controlled rheometer (Haake, Model RheoStress1, Germany), equipped with a 60 mm-diameter Titan cone and plate test fixture (C60/2Ti, cone angle 2°, gap 0.105 mm). Sample was loaded onto the plate of the rheometer and allowed the sample to reach equilibrium on the plate (± 0.5 °C). Apparent viscosity were collected from shear rate stepwisely increased from 0.02 to 1000 s^{-1} in 400 s. The measurements were done at temperatures of 5, 15, 25, 30 and 40°C. The temperature was controlled by a circulator (Haake, Model DC30), connected with a cooling bath (Haake, Model K10). Arrhenius equation was used to investigate the effect of temperature on viscosity dependency. The measurements were done in duplicated and the average value was reported. Steady shear measurement of 1, 1.5 and 2 %w/w xyloglucan dispersions were also determined for the comparison.

2.3.4. Dynamic viscoelasticity measurements of gelatinized samples

Measurements of frequency dependence of dynamic moduli were performed at 25° C using a Rheometric Fluids Spectrometer (RFSII, Rheometrics Co. Ltd., USA) with a parallel plate test fixture (50 mm diameter, 1.5 mm gap) in the frequency range from 0.1 to 100 rad/s. Values of strain used for all experiments were confirmed to be within the linear viscoelastic regions determined based on strain sweep experiments. The experiments were done in duplicates.

2.4 Effect of sucrose on physical properties of TS/XG mixtures

2.4.1. RVA pasting properties

Pasting properties of tapioca starch were determined using a Rapid Visco-Analyser (RVA) (RVA-4, Newport Scientific, Australia). Precalculated amounts of XG (0.0 to 0.6 g) were added to preweighed deionized distilled water in RVA canisters and let XG dispersed through out the sol for at least 2 h. The canisters were occasionally mixed using vortex mixer. Then, TS (0.8 to 1.4 g) and sucrose (0-11.2 g) were added to finally achieve a total weight of 28 g for preparing 5% TS/XG mixtures at mixing ratios of 10/0, 9/1, 8.5/1.5, 8/2, 7/3 and 6/4 containing 0, 10, 20 and 40 %w/w sucrose. The dispersions were kept at room temperature for 30 min and stirred occasionally in order to disperse the sample uniformly before measurement. The pasting profiles of the sample were monitored during a thermal treatment. The RVA temperature profile consisted of equilibrating the starch slurry at 50°C for 1 min, raising the temperature to 95°C at a heating rate of 6° C/min, holding the temperature at 95°C for 5 min, lowering 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. Pasting profiles were determined in duplicate in order to confirm the reproducibility of data and evaluated parameters were averaged.

2.4.2. Dynamic test of gelatinized mixed polysaccharides

Precisely weighed amounts of TS, XG and sucrose were dispersed into deionized distilled water at room temperature to obtain 5% w/w total polysaccharide dispersions with three mixing ratios (TS/XG = 10/0, 9/1 and 8/2) and containing 0, 10, 20 and 30 %w/w sucrose. The mixtures were stirred using a magnetic stirrer for at least 2 h at room temperature (25°C) to ensure uniform hydration of polysaccharides. The mixtures were heated in a 95°C water bath, and then further stirred for 30 min while the sample temperature was maintained at 95-98°C. After that, it was cool down to 40°C immediately without further stirring. Samples were then centrifuged at 1,000 rpm (190g) for 2 min to remove air bubbles and kept in 40°C water bath before measurements. Measurements of frequency dependence of dynamic moduli were performed at 25°C using Physica rheometer (MCR300, Physica Messtechnik GmbH, Germany) with a cone and plate test fixture (50 mm diameter, 1 degree, 0.05 mm gap) in the frequency range from 0.1 to 100 rad/s. Values of 4% strain used for all experiments were confirmed to be within the linear viscoelastic regions determined based on strain sweep experiments at 1 rad/s. The experiments were done in duplicates. Single plot of loss tangent (G''/G') was selected to represent the frequency dependence of each samples.

2.4.3. Texture profile analysis (TPA)

The 25% total polysaccharide content of TS and XG mixtures at mixing ratios of 10/0 and 9/1 containing 0 to 20% w/w sucrose was selected to determine the properties of gel by Texture Profile Analysis (TPA). TS with and without XG were dispersed into

deionized distilled water and stirred for at least 2 h at room temperature using a magnetic stirrer to ensure the complete solubilization. The precalculated amount of sucrose was added into the dispersions to obtain 0 to 20%w/w sucrose. All dispersions were stirred further at least 30 min, then heated to hold at 65°C for 2 min in a water bath for partially swelling of starch to avoid sedimentation of starch granules and removed air bubbles formation using vacuum pump. The hot dispersions were immediately transferred into a plastic case (250 x 22 mm diameter), sealed with rubber band both ends, heated in a water bath to maintain temperature at 95-98°C 30 min for completing the gelatinization. The plastic cylinder tubes were cooled in an ice/water bath for 10 min and stored overnight at 5°C before TPA measurement.

Gels were removed from the plastic cylinder cases and cut into 22 ± 0.03 mm diameter and 20 ± 0.05 mm height cylinders. The TPA measurement was carried out with texture analyzer (TA500, Lloyd Instruments Ltd., UK) equipped with a texture NEXYGEN^{TM} 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 orignial sample height) at a 0.5 mm/s using a 50-mm diameter aluminum probe with a flat end in both upward and downward direction without time allowed to elapse between the two compression cycles. Textural parameters of hardness (the maximum force of the first compression), springiness (the distance of the sample was compressed during the second compression to the peak force, divided by the initial sample height, reported as springniess index) cohesiveness (the ratio of the positive force area during the second compression to that during the first compression) and stiffness (the ratio of stress to deformation at the beginning of the first compression) were derived from the instrument software. All measurements were done at least 10 times (10 gels).

2.4.4. Differential scanning calorimetry (DSC)

The dispersions of 25% total polysaccharide content of TS and XG mixtures at mixing ratios of 10/0 and 9/1 containing 0 to 20% w/w sucrose were selected to determine the thermal properties using a differential scanning calorimeter (DSC822^{e} module, Mettler-Toledo GmbH, Switzerland). The DSC calibration was performed with indium. About 16-19 mg of the dispersions was weighed into a 40 µl aluminum DSC pan and hermetically sealed. The effect of sucrose on gelatinization of TS/XG was studied by heating the pans from 25°C to 110°C at the rate of 10°C/min. The onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) were determined based on heating DSC curves. The gelatinization enthalpy (ΔH) was evaluated based on the area of the DSC endothermic peak. Empty pan was used as reference and weight of sample pan before and after heating process was observed to confirm that there was no leak occurring during the measurements.

2.4.5. Statistical analysis

All experiments described above were carried out using at least two freshly prepared samples. The data presented were the means of each experiment.

2.5 Effect of salts on physical properties of TS/XG mixtures

2.5.1. RVA pasting properties

Three types of salts (NaCl, KCl, $CaCl_2$) were selected to investigate the effect of salt on pasting properties of tapioca starch using a Rapid Visco-Analyser (RVA) (RVA-4, Newport Scientific, Australia). Precalculated amounts of XG (0.0 to 0.6 g) were added to preweighed deionized distilled water in RVA canisters and let XG dispersed through out the sol for at least 2 h. The canisters were occasionally mixed using vortex mixer. Then,

TS (0.8 to 1.4 g) and salts (0-0.56 g) were added to finally achieve a total weight of 28 g for preparing 5% TS/XG mixtures at mixing ratios of 10/0 and 8.5/1.5, containing 0, 0.5, 1.0 and 2.0 %w/w salt. The dispersions were kept at room temperature for 30 min and stirred occasionally in order to disperse the sample uniformly before measurement. The pasting profiles of the sample were monitored during a thermal treatment. The RVA temperature profile consisted of equilibrating the starch slurry at 50°C for 1 min, raising the temperature to 95°C at a heating rate of 6°C/min, holding the temperature at 95°C for 5 min, lowering 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. Pasting profiles were determined in duplicate in order to confirm the reproducibility of data and evaluated parameters were averaged.

2.5.2. Dynamic pasting behavior

Changes in dynamic mechanical properties of mixed polysaccharides containing different salts (NaCl, KCl and $CaCl_2$) during a heating/cooling process of TS/XG mixtures were monitored using a stress-controlled rheometer (RheoStress1, Haake, Germany). A mixing ratio (TS/XG = 6/4) was chosen at the total polysaccharide concentration of 3.5% w/w in order to avoid air bubbles in the dispersion during heating. TS, XG and salt powders were dispersed into distilled water at room temperature (25°C), loaded into the cup of a double gap cylinder test fixture (DG41-Ti, Haake, Germany) preset at 50°C, and immediately covered with silicone oil to prevent water loss during heating-cooling cycle. Dynamic moduli of the samples were measured during temperature ramp from 50 to 95°C at the rate of 0.5°C/min and successive cooling down to 5°C at the rate of -0.5°C/min. The storage modulus (G') were reported using a strain-controlled mode with a strain of 1% at a frequency of 10 rad/s. Stress sweep measurements were performed to confirm that data were obtained within the linear viscoelastic strain region.

2.5.4. Differential Scanning Calorimetry (DSC)

Dispersions of 25% total polysaccharide content of TS and XG mixtures at mixing ratios of 10/0 and 9/1 containing 0, 0.5, 1 and 2% w/w NaCl were selected to determine the thermal properties using a differential scanning calorimeter (DSC822^e module, Mettler-Toledo GmbH, Switzerland). The DSC calibration was performed with indium. About 16-19 mg of the dispersions was weighed into a 40 µl aluminum DSC pan and hermetically sealed. The effect of NaCl salt on gelatinization of TS/XG was studied by heating the pans from 25°C to 110°C at the rate of 10°C/min. The onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) were determined based on heating DSC curves. The gelatinization enthalpy (ΔH) was evaluated based on the area of the DSC endothermic peak. Empty pan was used as reference and weight of sample pan before and after heating process was observed.

III. Results and Discussion

3.1 Effect of XG on gelatinization and retrogradation of TS

3.1.1 ***Pasting behavior***

Dynamic rheological properties of an aqueous dispersion of native starch granules are often difficult to be measured due to sedimentation of the granules. It is anticipated that sedimentation is sufficiently retarded by incorporating water-soluble non-starch polysaccharide that significantly increases the viscosity of the dispersing medium. Figure 3.1 shows examples of the evolution in the storage (G') and loss (G'') moduli of TS containing XG during heating from 50°C to 95°C and immediate cooling down to 5°C. In Figure 3.1d, data for an aqueous solution of XG (1.4%) solubilized at room temperature is also presented. The observed increase in the storage modulus of XG over 75°C to 95°C was not observed in previous studies (Yoshimura *et al.*, 1999) when XG was heated up to 80°C during the measurement. Indeed, we solubilized XG by heating at 95-98°C for 30 min before running the test, no increase in the storage modulus was observed during heating up to 95°C (not shown). Therefore, XG seems to be solubilized higher by heating to 95°C and leads to the increase of storage modulus. In the presence of XG (1.05 to 1.75%), sedimentation of TS granules in 3.5% total polysaccharide concentration was effectively prevented during experiments. Before heating, all samples showed liquid-like behavior (i.e. $G''>G'$) at the examined frequencies. When the mixtures were heated from 50°C at a constant heating rate of 0.5°C/min, both moduli slightly decreased as usually observed for common liquids, then both G' and G'' values started to drastically increase around 60°C. Such an increment in the moduli presumably represents the onset of gelatinization, the swelling of the starch granules that can absorb a large amount of water (Fukuoka *et al.*, 2002; Gonera and Cornillon, 2002; Rojas *et al.*, 1999).

The onset temperature of a rapid increase in moduli, defined as the pasting temperature, was almost identical for all examined samples (Table 3.1), suggesting that XG had little influence on the pasting temperature. No such an abrupt increase in G' or G'' was observed for XG solutions without TS.

Table 3.1. Gelatinization temperatures and storage modulus of 3.5%TS/XG mixtures.

TS/XG	T_o(°C)	Onset G' (Pa)	T_p (°C)	Peak G' (Pa)
5/5	60.7±0.3	0.9±0.0	76.5±2.0	5.6±0.4
6/4	60.0±0.0	0.7±0.2	76.2±1.1	4.7±0.5
7/3	60.1±0.1	0.2±0.0	75.2±1.0	5.4±1.4

Note: Onset temperature (T_o) is a temperature that the storage modulus (G') of sample begins to increase during heating
Peak temperature (T_p) is a temperature which G' shows maximum value on heating.
Values are mean ± range. (n =2).

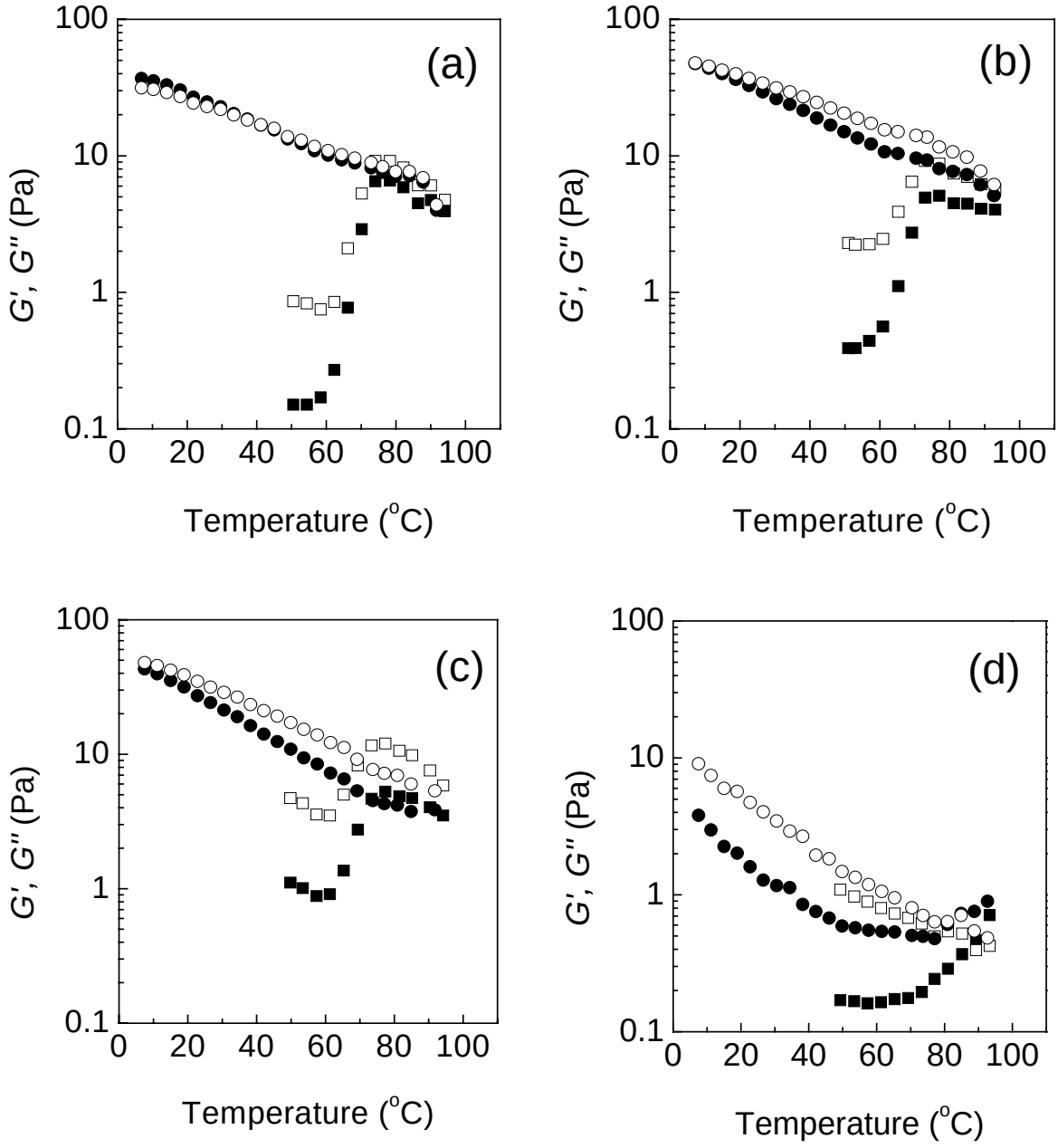


Figure 3.1. Temperature dependence of the storage (solid) and loss (open) moduli on heating (square) and cooling (circle) at frequency 10 rad/s, 1% strain of mixtures of 2.45% w/w TS and 1.05% w/w XG (a), 2.1% w/w TS and 1.4% w/w XG (b), 1.75% w/w TS and 1.75% w/w XG (c), and 1.4%XG (d).

On heating the mixed samples beyond the pasting temperature, the moduli values continuously increased until the temperature reached around 75-77°C, shown in Table 3.1 as peak temperature (T_p), and then gradually decreased (Figure 3.1). In the case that a large deformation testing method, Rapid Visco-Analysis (RVA), is employed to monitor gelatinization behavior of starch during heating, thinning after showing a peak viscosity is usually regarded as a measure of disintegration of particle structures of starch granules at

constant temperature during shearing, and is called “breakdown” (Cooke and Gidley, 1992; Pongsawatmanit *et al.*, 2002). However, in the present case, the samples were subjected to small strains in the linear viscoelastic region. Thus, the decrease in the moduli over 75°C is likely to largely represent the temperature dependence of the moduli and, to lesser extent, disintegration of granules. At the end of the heating treatment, liquid like characteristics ($G''>G'$) were still preserved (Figure 3.1).

Both G' and G'' values in the TS/XG mixtures gradually increased on cooling to 5° C (Figure 3.1), which should be attributed not only to the temperature dependence of the normal liquid samples but also re-association of starch polysaccharides, especially that of amylose that retrogrades much faster than amylopectin (Miles *et al*, 1985). The magnitude of increments in G' was larger than that of G'' and crossovers of these moduli were observed. The crossover temperature appeared to shift to a lower temperature as the XG concentration increased: the crossover temperature was ca. 43°C and 5°C at the TS/XG mixing ratios of 7/3 and 6/4, respectively, but no crossover was observed at the mixing ratio of 5/5 for the studied temperature range. These results suggest that XG tends to lower the gelation temperature of mixed systems. Substituting TS with XG at the total polysaccharide concentration of 3.5% w/w causes a reduction in the content of the gelling component (starch), but the viscosity of the continuous aqueous phase is likely to be increased. Another factor anticipated to contribute to interfere with the formation of percolated networks of starch polysaccharides is possible immiscibility between TS polysaccharides and XG. It is often the case that different species of polysaccharides are thermodynamically incompatible, which tends to cause phase separation and weaken the mechanical strength of a mixed system (Williams and Phillips, 1995).

3.1.2. Steady shear viscosity

Figure 3.2 shows the shear rate dependence of the steady shear viscosity of gelatinized TS in the absence and presence of XG at 5°C. The shear rate was first increased from 0.02 s^{-1} to 500 s^{-1} and then decreased from 500 s^{-1} to 0.02 s^{-1}. The 3.5% w/w TS immediately after gelatinization (Figure 3.2a) showed shear-thinning at low shear rates and shear-thickening at shear rates higher than about 1 s^{-1}. Similar behavior has been reported in the cases of 2 to 3% tuber and waxy cereal starch pastes (Carriere and Loffredo, 1998; Dintzis *et al*, 1996; Kim *et al*, 2002; Rao and Tattiyakul, 1999). A higher viscosity at a higher shear rate may indicate an increased probability of contacts among swollen TS granules under faster flow. Granules may be more packed in a paste that has exposed to a high shear rate. The gelatinized 3.5% w/w TS exhibited a rheopectic (time-dependent thickening) hysteresis loop (Figure 3.2a), suggesting an involvement of time-dependent structure building under steady shear flow.

The 3.15% w/w TS and 0.35% w/w XG paste showed a thixotropic (time-dependent thinning) hysteresis loop, while no hysteresis was observed for the 2.1% w/w TS and 1.4% w/w XG paste (Figure 3.2b). In the presence of XG, swelling of TS granules during gelatinization may be suppressed, leading to more pronounced contribution to flow properties from the continuous phase. Substituting a part of TS with XG tended to increase the viscosity at a certain shear rate (Figure 3.2c). These results suggest that steady flow properties of TS/XG mixtures are dominated by those of XG at the examined solid content level.

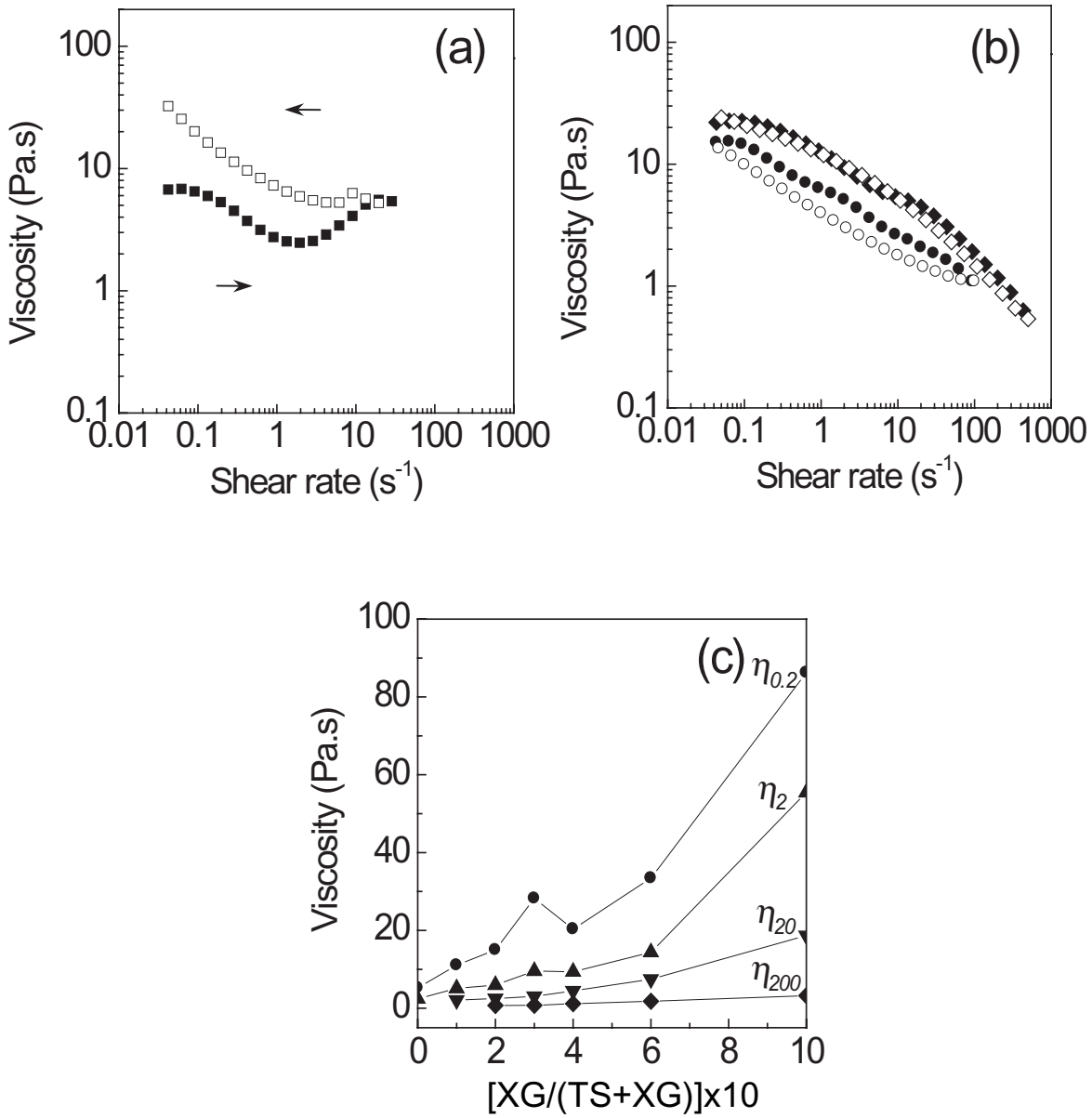


Figure 3.2. Shear rate dependence of the steady shear viscosity at 5 °C of 3.5% w/w TS (a) and mixtures of 3.15% w/w TS and 0.35% w/w XG (circles in b) and 2.1% w/w TS and 1.4% w/w XG (diamonds in b) immediately after gelatinization. The shear rate was first increased from 0.02 s^{-1} (solid) and then decreased (open). (c) The steady shear viscosity at shear rates of 0.2 s^{-1} (circle), 2 s^{-1} (upper triangle), 20 s^{-1} (lower triangle), and 200 s^{-1} (diamond) of 3.5% w/w TS/XG mixtures plotted as a function of the weight fraction of XG in the total polysaccharide content.

After the gelatinized TS/XG paste mixtures were kept for 35 days at 5°C, steady shear flow properties of rate dependence of the viscosity of TS/XG pastes were evaluated again by increasing shear rate from 0.02 s^{-1} to 500 s^{-1} and then decreasing from 500 s^{-1} to 0.02 s^{-1}. The 3.5% w/w TS (Figure 3.3a) showed shear-thinning and thixotropic behavior. Shear-thickening at shear rates higher than about 1 s^{-1} obtained from freshly gelatinized paste disappeared after storage for 35 days. The amount of amylose leached from the heated starch granules is sufficiently high enough to form initial inter-connected amylose network between the swollen granules or amylopectin clusters after heating (Ring *et al.*, 1987). Since amylopectin undergoes retrogradation process at a much lower rate than amylose does (Ikeda *et al*, 2001), the retrogradation of amylopectin molecules in 3.5% w/w TS forming a complicated structure gave more pronounced contribution in the main network of starch gels after storage. As the main molecular forces which stabilized the network of starch gel are believed to be secondary bonds such as hydrogen bond. This leads to the weak structure network of starch pastes which formed over a certain period of time compared with that formed by amylose immediately after gelatinized when the sample is at rest. This indicates by the change of flow behavior of TS paste to time-dependent thinning after longer storage.

In the presence of XG, the 3.15% w/w TS and 0.35% w/w XG paste still showed a thixotropic (time-dependent thinning) hysteresis loop, while no hysteresis was observed for the 2.1% w/w TS and 1.4% w/w XG paste (Figure 3.3b) after keeping gelatinized pastes for 35 days. These results suggest that XG molecules dissolved in the continuous phase have dominant effect in flow behavior of the samples and mask rheological deterioration caused by retrogradation of starch during storage.

Viscosity of various TS/XG mixing ratios as a function of storage time at shear rate 0.1 s^{-1} is shown in Figure 3.3c. After the first week, 3.5% w/w TS showed the most pronounced increase in viscosity. A higher XG concentration in the mixture pastes appeared to result in a lower change in viscosity during storage. Incorporation of XG into TS is thus considered to be advantageous to maintain desirable textural properties during storage.

3.1.3. Dynamic viscoelasticity

Oscillatory testing is one of the most common dynamic methods for studying the viscoelastic behavior of food because the results are very sensitive to chemical composition and physical structure (Steffe, 1996). Figure 3.4 shows the mechanical spectra of 3.5% w/w TS/XG with different mixing ratios immediately after gelatinization and after keeping gelatinized pastes for 35 days at 5°C. For the pastes immediately after gelatinization, the storage shear modulus G' (Figure 3.4a) and loss shear modulus G'' (Figure 3.4b) of all TS/XG mixing ratios increased with increasing frequency. These behaviors of 3.5% w/w of TS/XG pastes may be classified as a concentrated solution (Clark and Ross-Murphy, 1987). At any frequency, both G' and G'' moduli for all 3.5% w/w mixed TS/XG dispersions were larger than those of TS alone. In addition, both moduli for all mixed TS/XG pastes increased with increasing XG concentration. The increments of G' indicate more pronounced entanglements among XG molecules present in the system.

Mechanical spectra of the dispersions of TS and XG after 35 days of storage at 5°C are shown in Figure 3.4c and 3.4d. The storage shear modulus (G') of 3.5% w/w TS dispersion showed larger values than that of the freshly prepared pastes at low frequencies and remained almost constant within the frequency range studied, while the loss shear modulus (G'') of TS paste increased slightly with increasing frequency above 0.1 rad/s. These are typical behavior of a biopolymer gel. The increase of storage shear modulus (G') during storage was believed to be mainly due to an increase in the stiffness of swollen

molecules and association of amylopectin molecules. In the presence of XG, G' values at low frequencies (<1 rad/s) increased with increasing TS content. It appears that XG tends to form a continuous liquid phase in a mixture and inhibits the formation of continuous network structure of TS. When tan δ (= G''/G') values are plotted against the frequency (Figure 3.5), tan δ of freshly prepared TS pastes showed almost constant values at around 0.8-0.9 at frequencies lower than 1 rad/s (Figure 3.5a). In contrast, tan δ of freshly prepared TS/XG mixtures increased with increasing frequency. The frequency at which the tan δ value equals to unity ($G'' = G'$) shifts to a lower frequency with increasing XG content, confirming that the XG fraction dominates liquid-like behavior of the mixtures.

Tan δ of TS paste after storage at 5°C for 35 days was lower than 0.2 and almost independent of frequency (Figure 3.5b) suggesting that the retrograded paste is predominantly high solid-like behavior. In addition, tan δ of TS/XG mixtures increased with increasing XG content, confirms the higher liquid like behavior of the XG in the systems.

Figure 3.6 shows the evolution of G' and G'' at 1 rad/s of 3.5% w/w mixed TS/XG pastes (10/0, 9/1, 8/2, 7/3, 6/4) during storage at 5°C. The storage modulus values of the 3.5% w/w TS paste was highest compared with those of other TS/XG mixed pastes after 1 week of storage, and slightly increased during storage up to 35 days. The loss modulus values increased with increasing in the XG in the 3.5% w/w TS/XG mixed pastes and the 2.1% w/w TS and 1.4% w/w XG paste gave an almost constant G''. The results confirm the good stability of XG in maintaining the liquid-like characteristics in food product during storage.

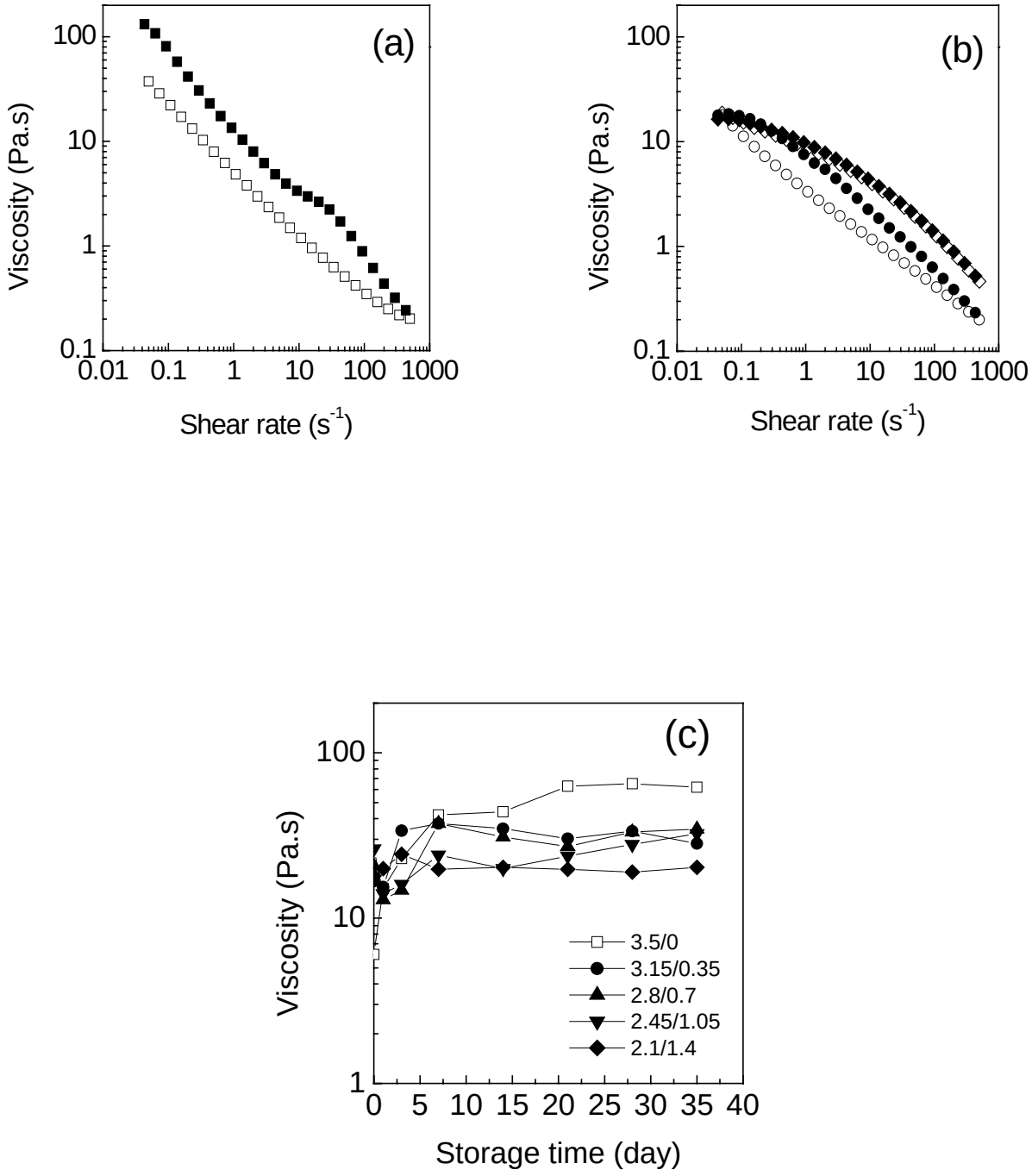


Figure 3.3. Shear rate dependence of the steady shear viscosity of 3.5% w/w TS (a) and mixtures of 3.15% w/w TS and 0.35% w/w XG (circles in b) and 2.1% w/w TS and 1.4% w/w XG (diamonds in b) stored for 35 days at 5 °C. The shear rate was first increased from 0.02 s^{-1} (solid) and then decreased (open). (c) Developments in the steady shear viscosity at 0.1 s^{-1} during storage at 5 °C. TS (% w/w)/XG (% w/w): 3.5/0 (square); 3.15/0.35 (circle); 2.8/0.7 (upper triangle); 2.45/1.05 (lower triangle); 2.1/1.4 (diamond).

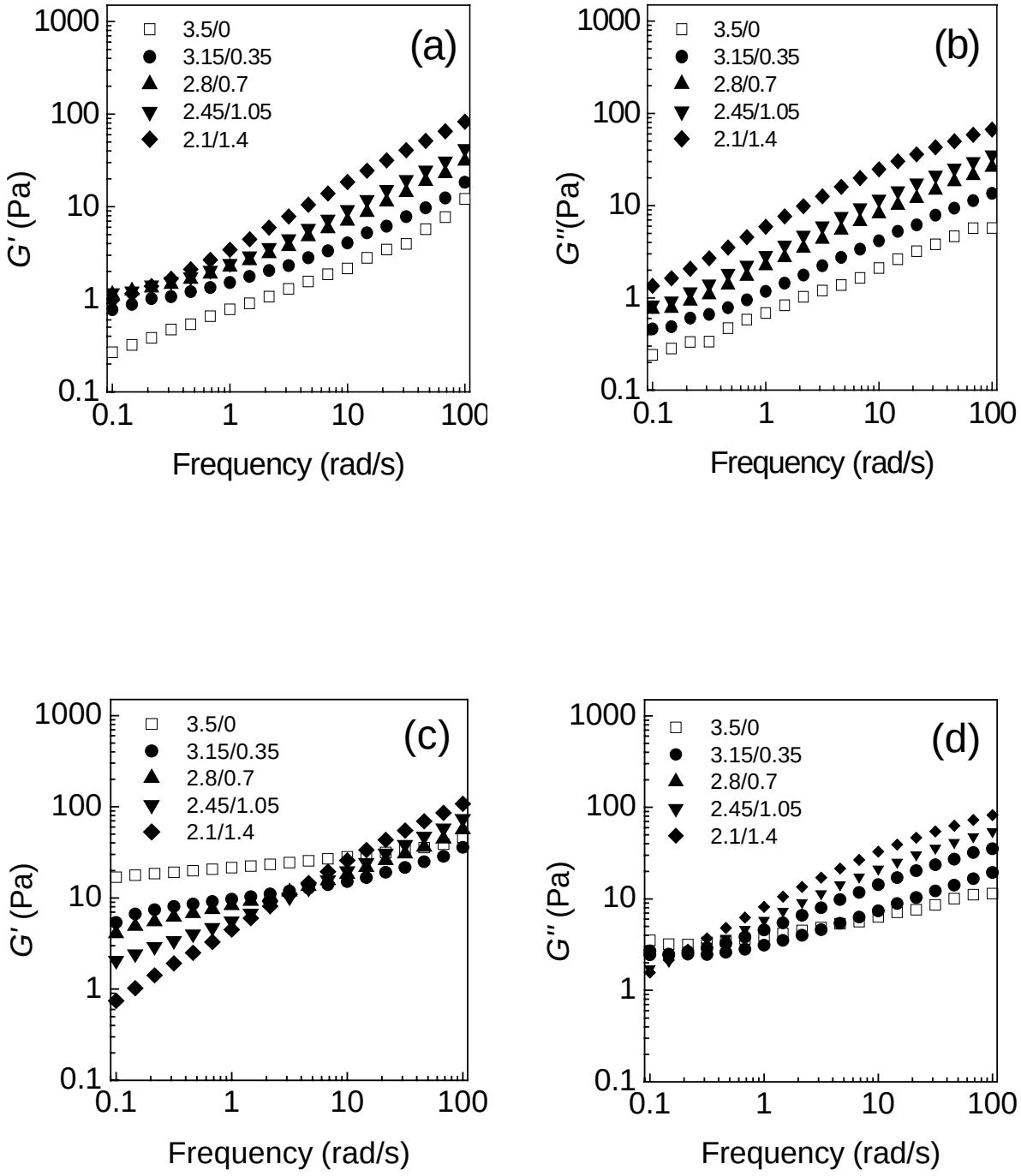


Figure 3.4. Frequency dependence of the storage (a and c) and loss (b and d) moduli of 3.5% w/w TS (square) and mixtures of 3.15% w/w TS and 0.35% w/w XG (circle), 2.8% w/w TS and 0.7% w/w XG (upper triangle), 2.45% w/w TS and 1.05% w/w XG (lower triangle), and 2.1% w/w TS and 1.4% w/w (diamond) immediately after gelatinization (a and b) and 35 days after storage at 5 °C (c and d).

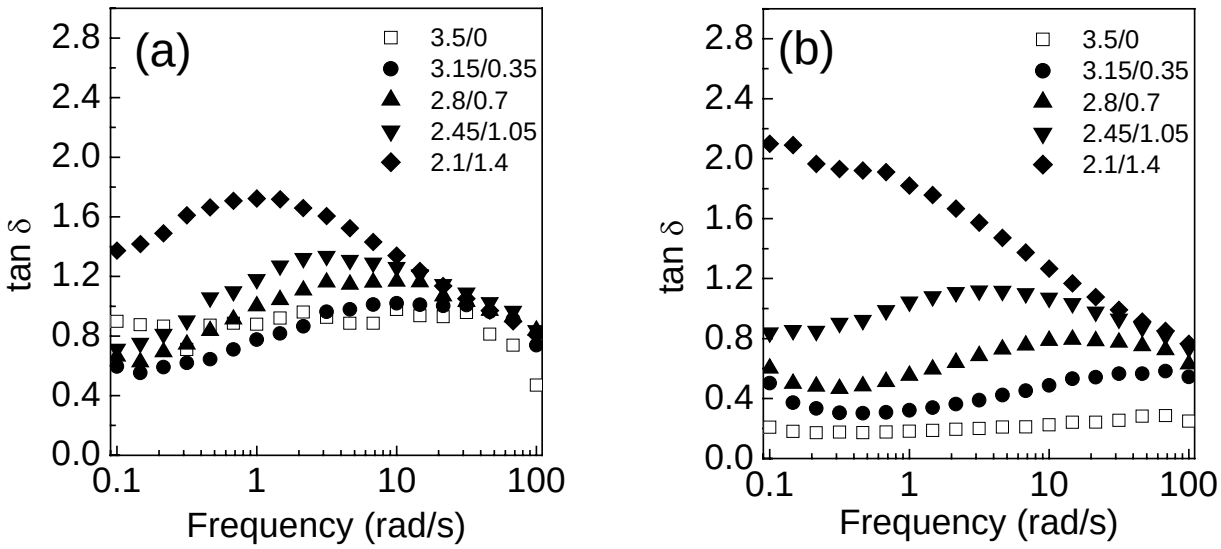


Figure 3.5. Frequency dependence of the loss tangent (tan δ) of 3.5% w/w TS (square) and mixtures of 3.15% w/w TS and 0.35% w/w XG (circle), 2.8% w/w TS and 0.7% w/w XG (upper triangle), 2.45% w/w TS and 1.05% w/w XG (lower triangle), and 2.1% w/w TS and 1.4% w/w (diamond) immediately after gelatinization (a) and 35 days after storage at 5°C (b).

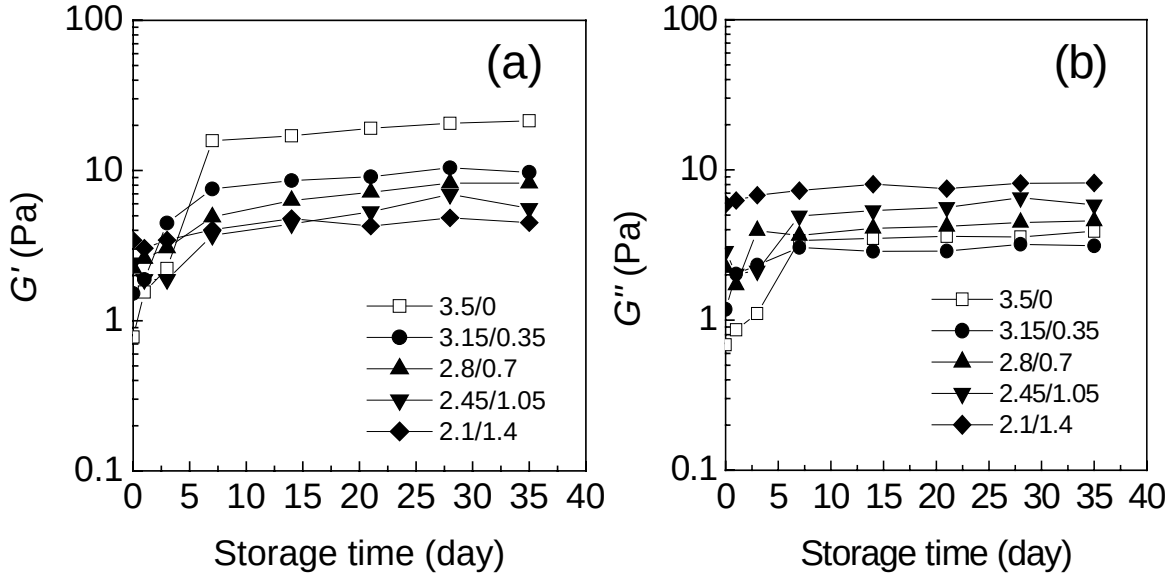


Figure 3.6 Developments in the storage (a) and loss moduli (b) at 1 rad/s during storage at 5 °C of gelatinized 3.5%TS (square), 3.15% w/w TS and 0.35% w/w XG (circle), 2.8% w/w TS and 0.7% w/w XG (upper triangle), 2.45% w/w TS and 1.05% w/w XG (lower triangle), and 2.1% w/w TS and 1.4% w/w (diamond).

3.1.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to investigate the gelatinization and retrogradation of starch. The endothermic DSC peaks are indicative of melting of native starch structure (Cooke *et al.,* 1992; Zobel and Stephen, 1995). In the present DSC measurements, total polysaccharide concentration at 25% w/w was used and this concentration was much higher than those in rheological measurements (3.5% w/w) because the retrogradation process can not be observed with such lower concentration when evaluated with the used DSC equipment. During the first-run heating of TS in the absence or presence of XG, single large endothermic peaks were observed (Figure 3.7). All dispersions showed peak temperature (T_p) around 70-71°C. These peak temperatures shifted slightly to higher temperature with increasing XG content (Table 3.2). The onset temperature (T_o) and conclusion temperature (T_c) of TS and TS/XG dispersions were about 55-57°C and 80°C, respectively for all examined samples. The gelatinization enthalpy was evaluated from the area under endothermic curve observed during the first-run heating (ΔH_1) and summarized in Table 3.2. Dispersions of individual XG did not show any exothermic or endothermic peak (not shown). The ΔH_1 values of TS/XG mixtures were similar to that of tapioca starch dispersion. These results suggest that XG does not associate synergistically with TS. Similar results have been reported in the case of corn starch mixed with xyloglucan (Yoshimura *et al*., 1999).

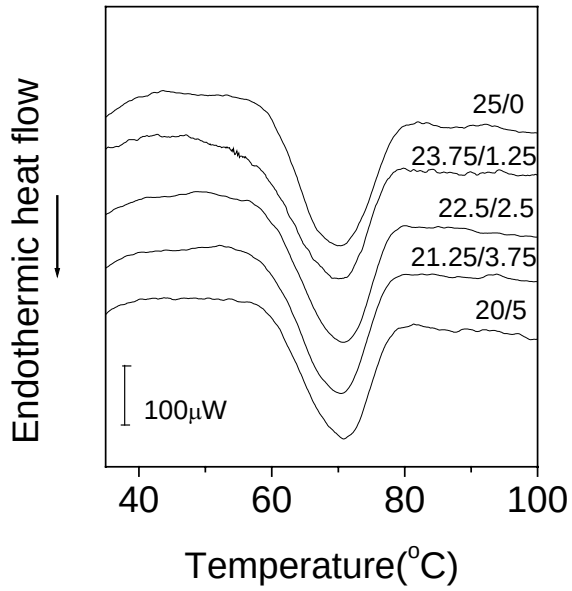


Figure 3.7. First-run heating DSC thermograms of 25% w/w TS and mixtures of 23.75% w/w TS and 1.25% w/w XG, 22.5% w/w TS and 2.5% w/w XG, 21.25% w/w and 3.75% w/w XG, and 20% w/w TS and 5% w/w XG. Heating rate was 1 °C/min.

After gelatinization, the samples were cooled down to 25°C at -10°C/min and kept at 5°C for 3, 7, 14, 21, 35, 49 and 63 days to investigate the retrogradation. The retrogradation ratio was defined as the ratio of enthalpy determined from the second-run heating (ΔH_2) to that of the first-run (ΔH_1) (Kohyama and Nishinari, 1991) and the results

are shown in Figure 3.8. The retrogradation ratio of TS pastes increased for the first 3 weeks of storage and levelled off after that. In the presence of XG, the retrogradation ratio determined based on DSC continued to increase during the entire period of investigation (63 days). These results suggest that the observed rheological stability of TS/XG mixtures is not because XG retards or prevents retrogradation of TS. In the case of corn starch (CS), the DSC-determined retrogradation ratio has been shown to increase by substituting a small portion of starch with either konjac glucomannan or xyloglucan as long as the storage period is less than two weeks. During longer storage, both konjac glucomannan and XG were shown to retard the increase in retrogradation ratio of the starch (Yoshimura *et al.*, 1996; Yoshimura *et al.*, 1999). The effectiveness of XG to retard the increase in retrogradation ratio of TS is lower than that of CS due to the difference between TS and CS.

Table 3.2. Gelatinization temperatures and enthalpy of the 25% TS/XG mixtures at various ratios.

TS/XG	T_o (°C)	T_p (°C)	T_c(°C)	Enthalpy (J/g dry starch)
10/0	55.1±1.9	70.2±0.3	80.1±0.9	16.3±0.7
9.5/0.5	54.8±1.9	70.3±0.3	79.7±0.5	16.1±0.4
9/1	56.1±0.8	70.6±0.2	79.9±0.5	15.9±0.8
8.5/1.5	56.5±1.2	70.7±0.6	80.2±0.4	16.6±0.6
8/2	56.8±1.1	71.1±0.5	80.2±1.1	16.6±0.8

Values are mean ± SD (n = 10).
T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature.

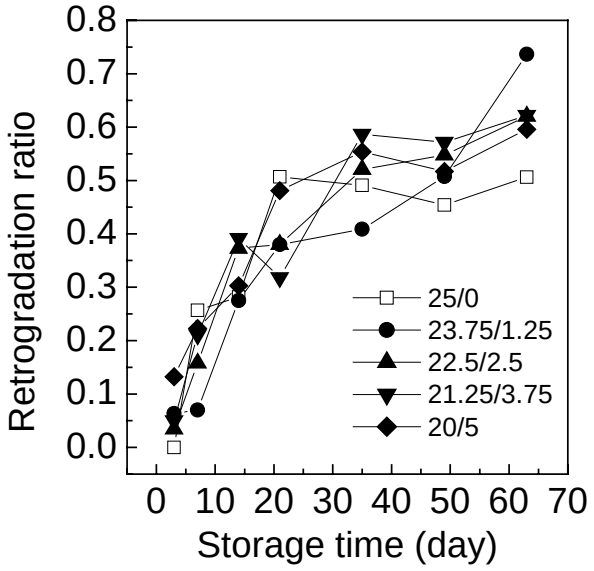


Figure 3.8. Retrogradation ratio ($\Delta H_2/\Delta H_1$) of 25% w/w TS (square) and mixtures of 23.75% w/w TS and 1.25% w/w XG (circle), 22.5% w/w TS and 2.5% w/w XG (upper triangle), 21.25% w/w and 3.75% w/w XG (lower triangle), and 20% w/w TS and 5% w/w XG (diamond) as a function of storage time at 5 °C.

3.2 Temperature dependency of the TS/XG mixtures

3.2.1 RVA pasting properties

The typical RVA pasting curves of total polysaccharide concentration of 5% w/w TS/XG mixtures with different mixing ratios (TS/XG = 10/0, 8/2, and 6/4) are selected to show in Figure 3.9. The peak viscosity (Figure 3.9) is considered to represent the equilibrium point between swelling and rupture of starch granules. As the sample is subsequently cooled down to 50°C after holding at 95 °C, the viscosity increases to a final viscosity, which is attributed to the retrogradation or reassociation of amylose molecules. RVA viscosity profiles were affected by adding xyloglucan into tapioca starch-water systems. Both the peak viscosity and the final viscosity of total polysaccharide concentration of 5% w/w TS/XG mixtures increased with increasing xyloglucan content (Figure 3.10). These results gave the same tendency as those obtained from steady shear experiments.

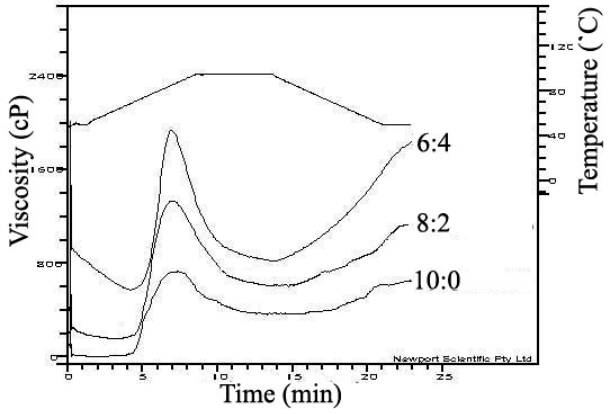


Figure 3.9 Typical RVA profiles of selected tapioca starch/xyloglucan mixtures (5% w/w). TS/XG mixing ratios 10/0, 8/2 and 6/4.

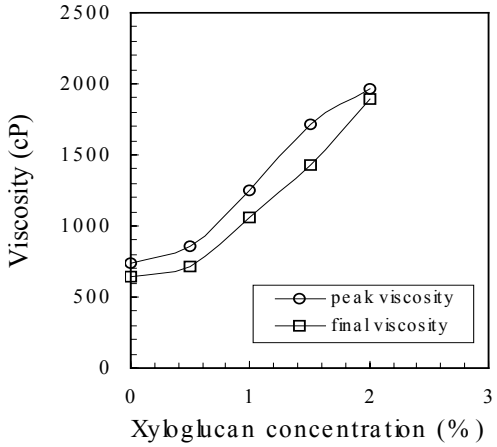


Figure 3.10 Peak viscosity and final viscosity from RVA pasting profiles as a function of xyloglucan concentration in the total polysaccharide concentration (5% w/w) of tapioca starch and xyloglucan at diffierent mixing ratios (10/0, 9/1, 8/2, 7/3, 6/4).

3.2.2 steady shear viscosity and dynamic viscoelasticity properties

The viscosity values of 5% gelatinized TS/XG mixtures with different mixing ratios were generally higher than those of gelatinized individual TS pastes (Figure 3.11) at 25 °C, while all mixtures and starch alone showed shear thining behavior. Considering the effect of temperature on the apparent viscosity of 5% total polysaccharide concentration for both gelatinized TS alone and mixed TS/XG, the results showed that apparent viscosities at 50 s^{-1} decreased with increasing temperature for all samples while the magnitude of decrement in apparent viscosity of gelatinized TS alone was larger than those of gelatinized mixed TS/XG (Figure 3.12).

When the temperature dependency of apparent viscosity was investigated by the Arrhenius plot of the apparent viscosities at 50 s^{-1} (Figure 3.13), the results showed that apparent viscosities at 50 s^{-1} decreased with increasing temperature for all samples while the magnitude of decrement in apparent viscosity of gelatinized TS alone was larger than those of gelatinized mixed TS/XG (Figure 3.13). This indicated that TS/XG mixtures gave lower temperature dependency as shown by investigating the lower values of activation energy (E_a) of the mixtures compared with that of TS alone (Table 3.3). The apparent viscosity values of only XG dispersions (1, 1.5 and 2% w/w) without starch showed the lower viscosity than those of 5% w/w TS/XG mixtures but less temperature dependent (Table 3.3). This results suggest that xyloglucan improved the heat-stability of the TS/XG mixtures

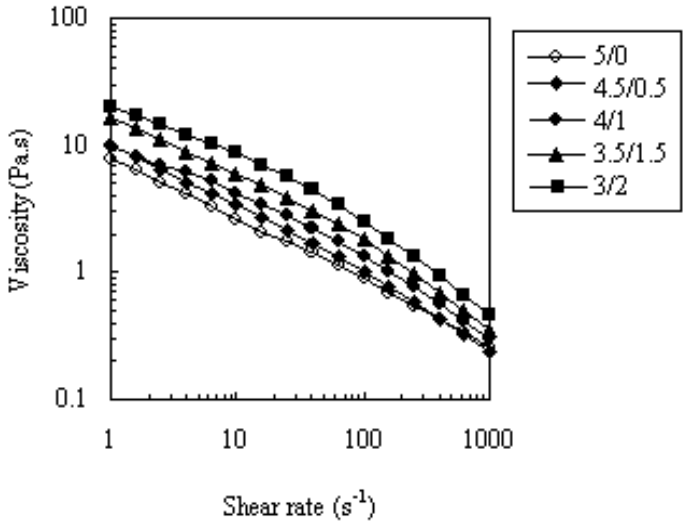


Figure 3.11 Viscosity of 5% (w/w) TS/XG mixtures at different mixing ratios (10/0, 9/1, 8/2, 7/3, 6/4) as a function of shear rate at 25 °C.

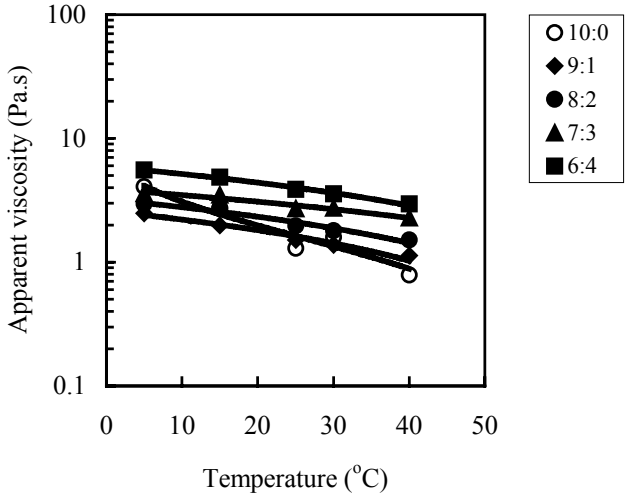


Figure 3.12 Apparent viscosity of 5% w/w TS/XG mixtures at different mixing ratios (10/0, 9/1, 8/2, 7/3, 6/4) as a function of temperature. Shear rate at 50 s^{-1}.

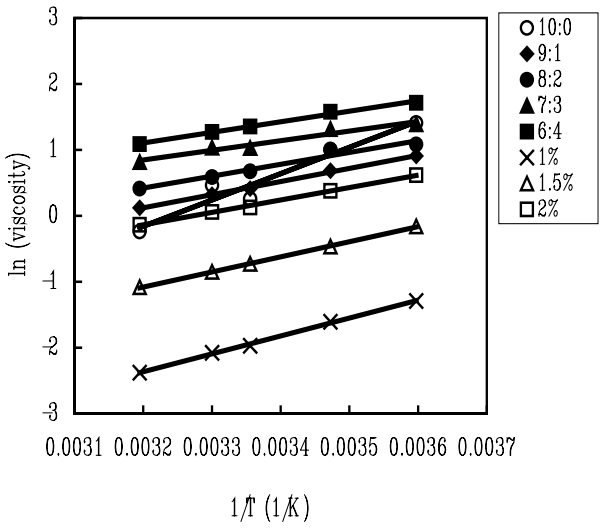


Figure 3.13. Arrhenius plots of apparent viscosity of 5% (w/w) TS/XG dispersions of at different mixing ratios (10/0, 9/1, 8/2, 7/3, 6/4) and only XG dispersions (1, 1.5, and 2%) at shear rate 50 s^{-1}.

Table 3.3 Activation energy of dispersions of 5% (w/w) mixtures of TS/XG (10/0, 9/1, 8/2, 7/3, 6/4) and dispersions of xyloglucan (1, 1.5, and 2%) from Arrhenius model for temperature dependency of apparent viscosity at 50 s^{-1}.

Dispersions	E_a (kJ/mole)
5% TS	33.67 ± 0.9
5% TS/XG 9/1	16.76 ± 2.7
5% TS/XG 8/2	14.97 ± 2.4
5% TS/XG 7/3	12.24 ± 1.7
5% TS/XG 6/4	13.35 ± 0.7
1% XG	22.62 ± 0.9
1.5% XG	19.02 ± 0.1
2% XG	15.67 ± 0.9

When the dynamic viscoelastic measurement was performed to determine the storage modulus (*G′*) and loss modulus (*G″*) of total polysaccharide concentration of 5% w/w TS/XG mixtures at different mixing ratios (TS/XG = 10/0, 9/1, 8/2, 7/3 and 6/4), the mechanical loss tangent (*G″/G′*) of the TS/XG mixtures increased with increasing XG concentration (Figure 3.14). The present results confirmed that XG imparted more viscous, provided heat-stable, and liquid-like rheological properties to the gelatinized TS/XG mixtures.

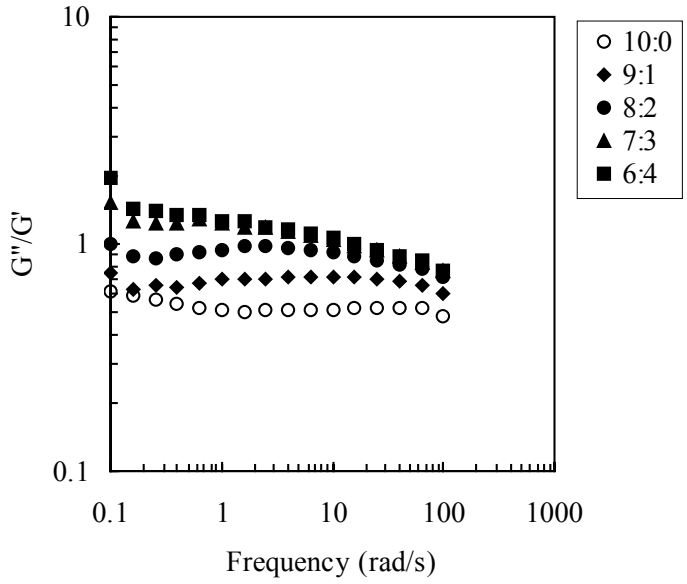


Figure 3.14. The loss tangent (*G″/G′*) of 5% w/w TS/XG mixtures at different mixing ratios (10/0, 9/1, 8/2, 7/3, 6/4). The measurements were done at 25 °C.

3.3 Effect of sucrose on physical properties of TS and XG mixtures

*3.3.1 RVA **Pasting behavior***

The RVA viscosity profiles of TS and TS/XG dispersions containing sucrose at various concentrations were shown in Figure 3.15. At the beginning of RVA testing before the gelatinization occurred, the viscosity of starch dispersions remained low. During dispersions were heated to 95 °C, the starch granules swelled to the higher extent. As a result, the viscosity of the dispersions rapidly increased to the peak viscosity. Pasting temperature of TS was increased with increasing sucrose concentration (Table 3.4). This indicated that sucrose delayed the gelatinization temperature of the TS alone and TS/XG mixtures. The dispersions containing XG also gave a trend of higher pasting temperatures. This maybe XG imparted more viscous of continuous phase in the dispersions and gave a higher pasting temperature. After the pasting temperature, the swelling of starch granule increased and reflected in the steepness of the initial rise in viscosity in the pasting curve while the granules ruptured and some amylose leached out with some slower rate amylopectin. The peak viscosity occurred at the equillibrium point between swelling causing an increase in viscosity, and rupture and alignment causing its decrease. The peak viscosity values increased with increasing XG and sucrose concentrations as shown in Figure 3.16a.

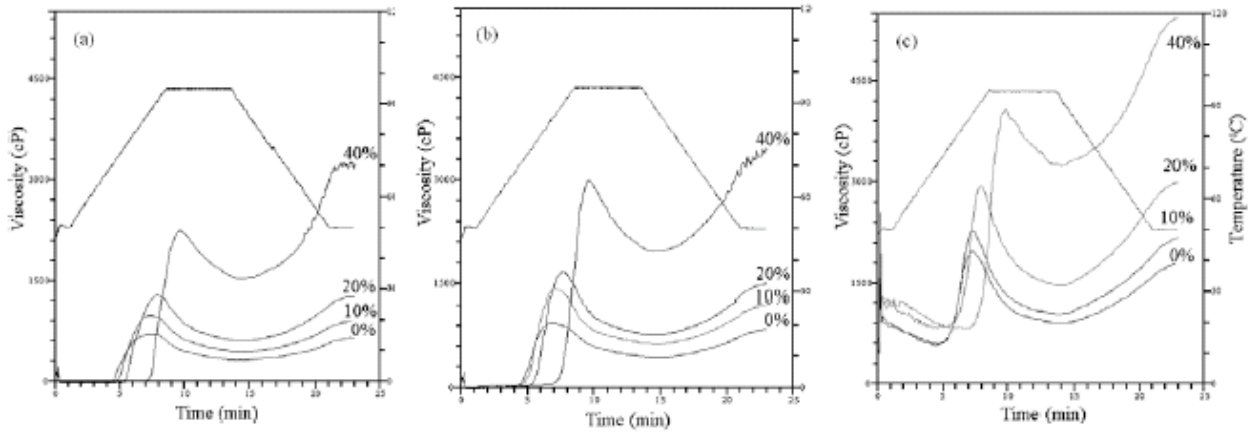


Figure 3.15 Typical RVA viscosity profiles of 5% TS/XG showing some mixing ratios of 10/0 (a), 8.5/1.5 (b) and 6/4 (c) containing 0, 10, 20, and 40% sucrose.

Table 3.4. Effect of sucrose on RVA pasting temperatures of 5%TS alone and 5% TS/XG mixtures at various mixing ratios (9/1, 8.5/1.5, 8/2, 7/3 and 6/4).

Dispersions	Sucrose concentration (%w/w)			
	0	10	20	40
5%TS	72.3 ± 1.2	74.2 ± 1.0	75.4 ± 3.5	88.3 ± 1.7
4.5%TS and 0.5%XG	73.3 ± 0.3	75.1 ± 0.6	78.4 ± 0.2	89.5 ± 1.1
4.25%TS and 0.75%XG	73.1 ± 1.7	73.7 ± 1.3	76.5 ± 0.8	86.7 ± 1.1
4.0%TS and 1.0%XG	72.2 ± 0.2	74.5 ± 0.3	78.3 ± 0.1	89.1 ± 0.6
3.5%TS and 1.5%XG	72.3 ± 1.2	74.7 ± 0.7	76.1 ± 1.9	91.8 ± 0.6
3%TS and 2%XG	75.4 ± 0.3	74.5 ± 0.9	78.5 ± 2.6	89.4 ± 2.9

Values are mean ± SD of duplicate analyses

During the hold period of the test, the pastes were subjected to a period of constant high tmperature (95°C) and mechanical shear stress. More amylose molecules leached out into the pastes, which were alligned in the direction of shear. As the dispersions were subsequently cooled down to 50°C, the amylose re-association occurred which resulted in the increase of viscosity to a final viscosity. Final viscosity increased with increasing XG and sucrose contents (Figure 3.16b). This may be explained by decreasing water available for the starch due to the XG and sucrose dissolving in the systems. In addition, sucrose may stabilize TS gel structure through out the formation of sugar bridges between melted crystalline regions and amorphous regions as reported in the case of rice starch gels (Katsuta *et al.*, 1992).

3.3.2. Dynamic viscoelasticity

Dynamic mechanical data showed the loss tangent (G''/G') of 5% w/w TS alone and TS/XG dispersions (mixing ratios 9/1 and 8/2) containing sucrose (0, 10, 20 and 30%) immediately after gelatinization (Figure 3.17). Loss tangent of the TS (Figure 3.17a) decreased with increasing sucrose concentration indicating the increase of solid-like properties of TS granules. In the presence of XG (Figure 3.17b and 3.17c), at frequency higher than 1 s^{-1}, loss tangent was higher than those of TS alone, indicating XG provided liquid-like property to the TS. However, when the mixed TS/XG containing higher sucrose content (40%) especially for the mixture TS/XG ratio at 8:2, the results showed a significant decrease in loss tangent values, suggesting that solid-like properties were enhanced explained by the gel formation between the XG and sucrose (Nishinari *et al*., 2000).

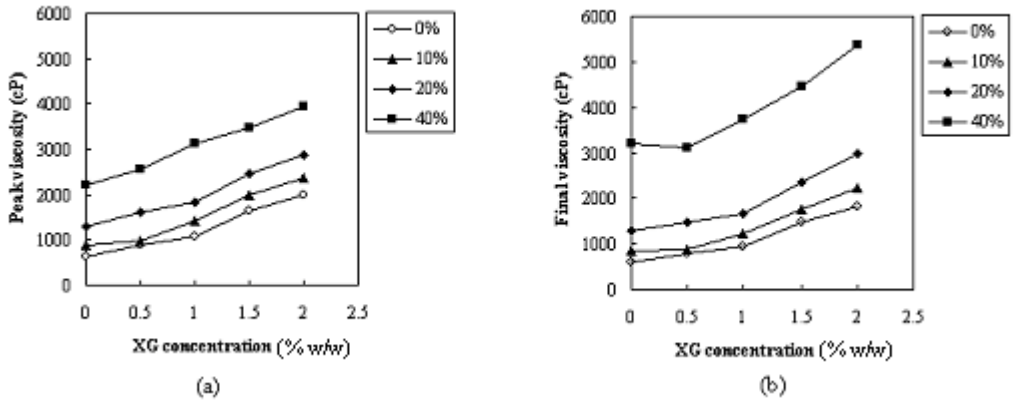


Figure 3.16 Peak viscosity (a), and final viscosity (b) of the 5% TS/XG mixtures with 0 (circle), 10 (triangle), 20 (diamond) and 40% (square) sucrose.

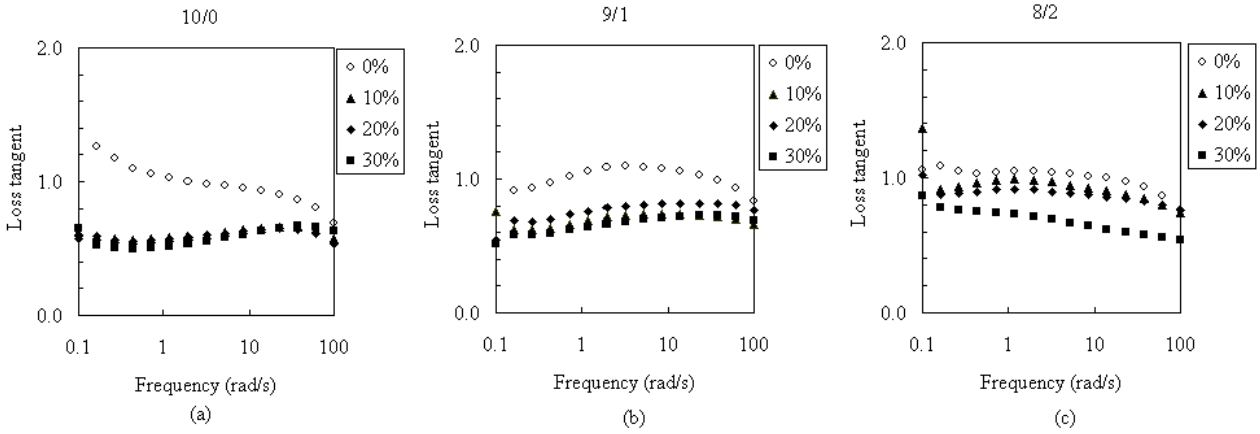


Figure 3.17 Frequency dependence of loss tangent of 5%TS/XG mixtures at different mixing ratios of 10/0 (a), 9/1(b) and 8/2 (c) containing 0 (circle), 10 (triangle), 20 (diamond) and 30% (square) sucrose.

3.3.3. Texture Profile analysis

Texture profile analysis (TPA) is a method used for measurement of food textural properties (Bourne, 1982) and evaluate changes in mechanical properties of starch gels (Devesa and Martinez-Anaya, 2003). TPA profiles of 25%TS and TS/XG (9/1) with and without 20% w/w sucrose after 24 h storage at 5°C are shown in Figure 3.18. TPA parameters can be obtained from TPA curves as shown in Figure 3.18a. Hardness is defined as the peak force during the first compression cycle; Springiness is defined as the distance the sample was compressed during the second compression to the peak force, divided by the initial sample height; Cohesiveness is defined as the ratio of the area under the first and second compression (A_2/A_1); Stiffness is defined as the ratio between stress and strain. Sucrose increased the hardness of the both gels prepared from TS alone (10/0) and TS/XG (9/1) (Figure 3.19a). Hardness values increased with increaseing sucrose content (Figure 3.19a). Adding XG in the TS gel impart the lower hardness of the TS gel which showed the same trend of the stiffness values for both TS alone and mixed TS/XG (Figure 3.19d). An increase of stiffness of the gels could be due to the formation of clusters of ordered chains along the amylopectin molecules or crosslinks between amylopectin molecules (Keetels et al., 1996a). This indicated that XG decreased network rigidity by reducing the structure formation of the amylose in TS. In addition, the substitution a part of TS with XG decreased amylose content in the system compared to TS alone.

Springiness of TS gel alone without sucrose was higher than that of TS/XG gel (Figure 3.19b). However, the springiness of the mixed TS/XG gels increased with increasing sucrose content. This indicates that elasticity of mixed TS/XG gels increased with increasing sucrose content. Cohesiveness is a measure of the degree of difficulty in breaking down the gel's internal structure (Sanderson, 1990). Cohesiveness of TS gel alone with and without sucrose was lower than that of TS/XG mixed gel, indicating that internal structure of mixed gels may be more difficult to break down during the first compression than that of TS gel alone. Mixed TS/XG gels gave a lower cohesiveness with increasing the sucrose up to 20% (Figure 3.18c) indicating that sucrose content (up to 20%) could be affected the internal structure of mixed gel to be broken down easier.

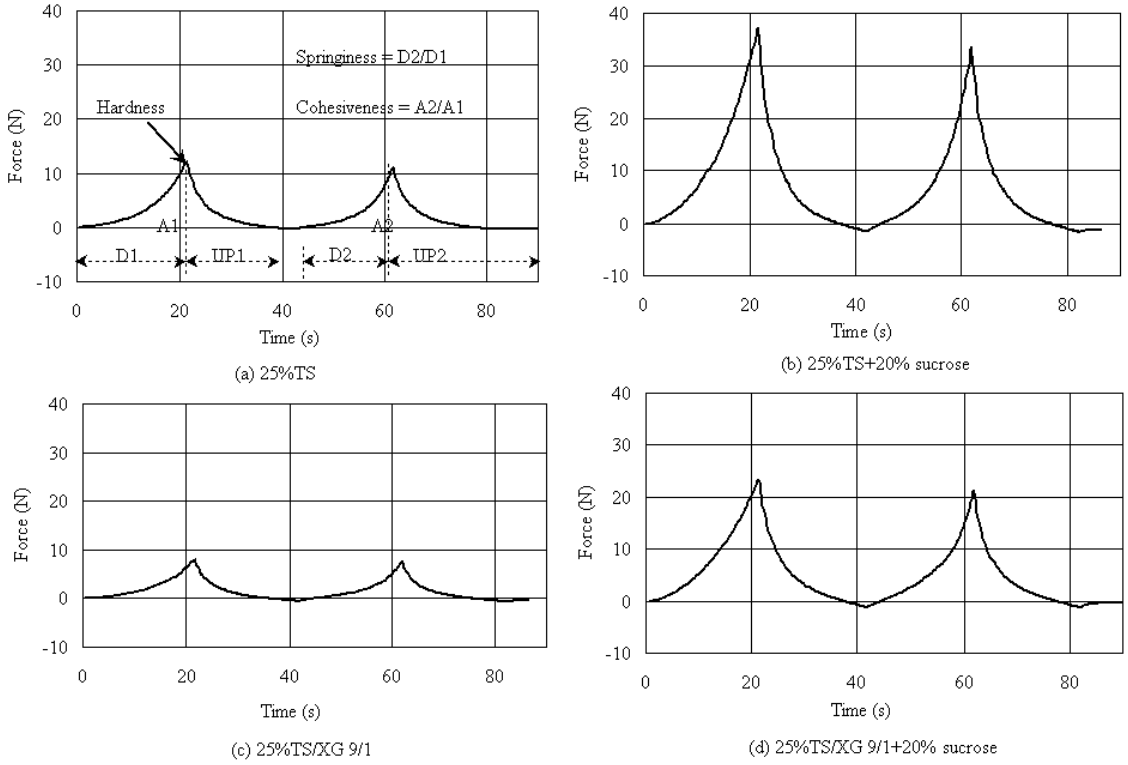


Figure 3.18 TPA profiles of 25% w/w TS gels without sucrose (a) and with 20% sucrose (b), and the profiles of mixed gels of 22.5% w/w TS and 2.5%w/w XG without sucose (c) and with 20% w/w sucrose (d). In Figure 3.18a, D1 and D2 mean the downward movement of the test fixture during the first and the second compressions, UP1 and UP2 means the upward movement of the first compression and second compression, respectively.

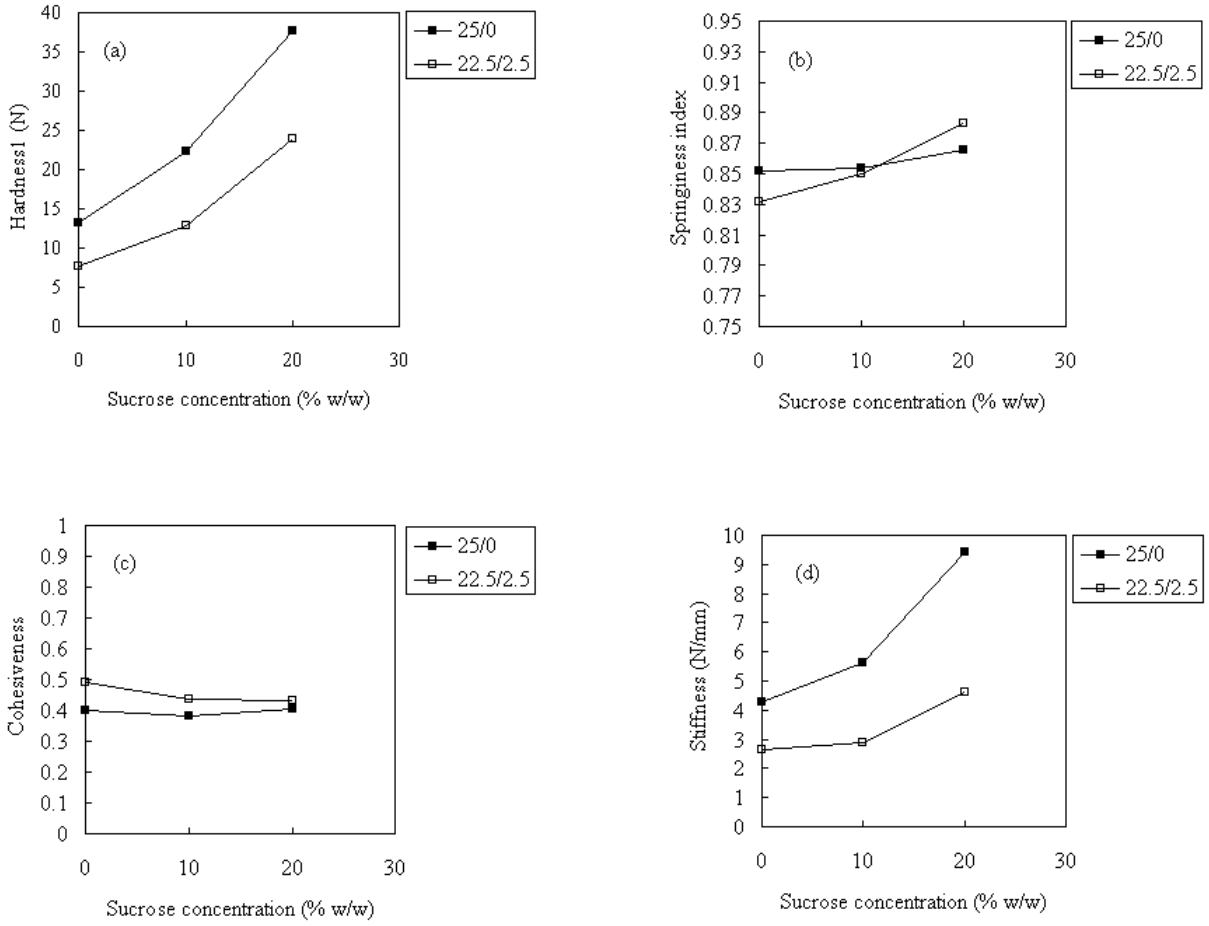


Figure 3.19 Effect of sucrose on TPA parameters, hardness (a), springiness index (b), cohesiveness (c) and stiffness (d) of 25% w/w TS (10/0) and mixtures of 22.5%TS and 2.5%XG (9/1).

3.3.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to investigate the gelatinization of starch. Figure 3.20 showed DSC thermograms of TS and TS/XG (mixing ratio 9/1) dispersions containing 0, 5, 10, 15 and 20% w/w sucrose contents. Total polysaccharide concentration at 25% w/w was used to observe gelatinization. Single large endothermic peaks were observed for all dispersions without any significant change in the peak shape caused by the sugar or XG addition. The gelatinization temperatures (T_o, T_p, T_c) of dispersions were shifted to the higher temperatures with increasing sucrose content for both TS alone and TS/XG dispersions (Figure 3.21). The slightly delayed onset (T_o) and peak temperatures (T_p) of the mixed TS/XG were shown compared with those of TS alone. Gelatinization enthalpy values of 25%TS/XG containing 0 to 15% sucrose of the mixing ratios at 10/0 and 9/1 ranged between 15.7-16.4 J/g dry TS (Table 3.5). XG in the system seemed to be no influence on gelatinization enthalpy of TS at low sucrose concentration (up to 15%). However, gelatinization enthalpy of TS/XG mixtures at 20% sucrose (17.5 J/g dry TS) was higher than that of TS without XG (16.9 J/g dry TS). The gelatinization

temperatures were shifted to higher temperature and enthalpies were slightly increased with increasing sucrose content due to the antiplasticizing effect of sucrose (Pongsawatmanit *et al*., 2002) with lower water activity and mobility of the water in the system (Chinachoti *et al*., 1991; Chinachoti *et al*., 1990) because sucrose decreased free volume of available water for gelatinization especially at higher sucrose concentration. Spies and Hoseney (1982) suggested that sucrose limited the swelling of starch granules and leaded to higher gelatinization enthalpy and gelatinization temperatures.

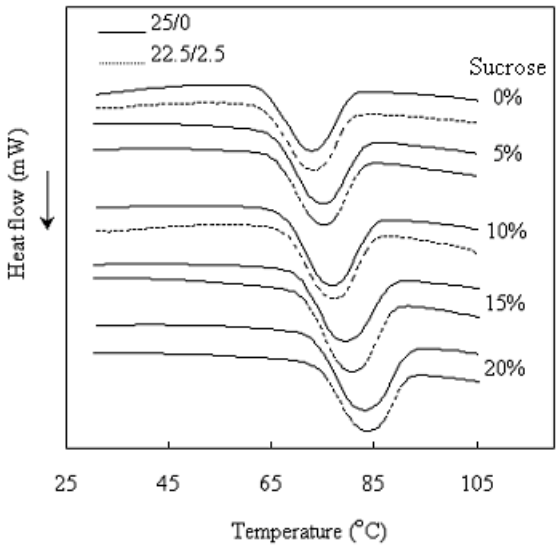


Figure 3.20 DSC thermograms of TS and TS/XG (mixing ratio 9/1) dispersions containing 0, 5, 10, 15 and 20% w/w sucrose contents.

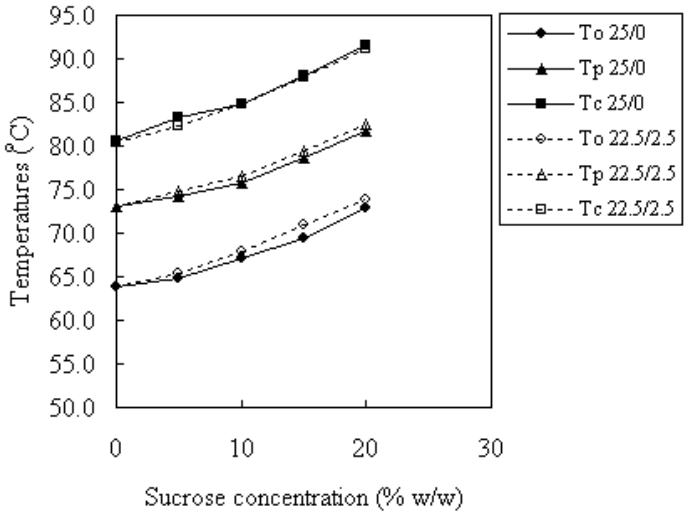


Figure 3.21 Effect of sucrose on onset temperature (circle), peak temperature (triangle) and conclusion temperature (square) of 25% w/w TS (solid) and mixtures of 22.5%TS and 2.5%XG (open).

Table 3.5 Effect of sucrose on gelatinization enthalpy of 25% TS (10/0) and TS/XG at mixing ratio of 9/1.

Sucrose (%w/w)	Enthalpy (J/g dry TS)	
	10/0	9/1
0	16.2 ± 0.3	15.9 ± 0.4
5	15.7 ± 0.0	16.0 ± 0.1
10	15.8 ± 0.7	15.7 ± 0.3
15	16.4 ± 0.8	16.3 ± 0.9
20	16.9 ± 1.1	17.5 ± 0.4

Values are mean ± SD

3.4 Effects of salts on pasting properties of TS/XG mixtures

3.4.1 Pasing behavior

The parameters of RVA pasting profiles obtained from TS alone and TS/XG dispersions containing 0 to 2.0% w/w salt of NaCl, KCl and $CaCl_2$ as shown in Table 3.6, 3.7 and 3.8, respectively. NaCl, KCl and $CaCl_2$ showed the tendency to delay gelatinization process of both TS and mixed TS/XG dispersions by increasing pasting temperature. This suggested that there was starch-salt interactions by electrolytes (Jane, 1993). However, all types of salts showed a trend of no influence on peak and final viscosity values both of TS alone and TS/XG mixtures. The final viscosity of starch in the presence of XG at the mixing ratio of 6/4 increased with increasing salt concentration for NaCl, KCl and $CaCl_2$. This observation agrees with the previous report that the gel strength of TS was insensitive to the low concentration of salts (up to 10mM) (Muhrbeck and Eliasson, 1987). As the salt concentration increased, the final viscosity of TS/XG mixtures at a high mixing ratio of 6/4 slightly increased. This may be the limitation of available water for TS to gelatinize during heating process.

Table 3.6. Effect of NaCl concentration on RVA pasting temperature, peak viscosity and final viscosity of 5%TS, 4.25%TS and 0.75%XG, and 3%TS and 2%XG.

Dispersion (%w/w)	NaCl (% w/w)	Pasting temperature (^oC)	Peak viscosity (cP)	Final viscosity (cP)
5%TS	0	72.32	678	647
5%TS	0.5	76.12	698	722
5%TS	1.0	77.32	680	720
5%TS	2.0	78.65	708	758
4.25%TS and 0.75%XG	0	72.42	988	874
4.25%TS and 0.75%XG	0.5	74.70	901	877
4.25%TS and 0.75%XG	1.0	76.30	989	921
4.25%TS and 0.75%XG	2.0	78.25	839	870
3%TS and 2%XG	0	75.36	1952	1800
3%TS and 2%XG	0.5	76.81	1888	1850
3%TS and 2%XG	1.0	78.55	1975	1951
3%TS and 2%XG	2.0	78.62	2060	2059

Values are mean of duplicate analyses.

Table 3.7. Effect of KCl concentration on RVA pasting temperature, peak viscosity and final viscosity of 5%TS, 4.25%TS and 0.75%XG, and 3%TS and 2%XG.

Dispersion (%w/w)	KCl (% w/w)	Pasting temperature (^oC)	Peak viscosity (cP)	Final viscosity (cP)
5%TS	0	72.32	678	647
5%TS	0.5	75.38	675	694
5%TS	1.0	75.50	684	698
5%TS	2.0	77.87	710	729
4.25%TS and 0.75%XG	0	72.42	988	874
4.25%TS and 0.75%XG	0.5	74.75	994	887
4.25%TS and 0.75%XG	1.0	75.55	827	814
4.25%TS and 0.75%XG	2.0	76.30	899	878
3%TS and 2%XG	0	75.36	1952	1800
3%TS and 2%XG	0.5	76.63	1990	1928
3%TS and 2%XG	1.0	78.45	1971	1950
3%TS and 2%XG	2.0	79.72	1987	1970

Values are mean of duplicate analyses.

Table 3.8. Effect of $CaCl_2$ concentration on RVA pasting temperature, peak viscosity and final viscosity of 5%TS, 4.25%TS and 0.75%XG, and 3%TS and 2%XG.

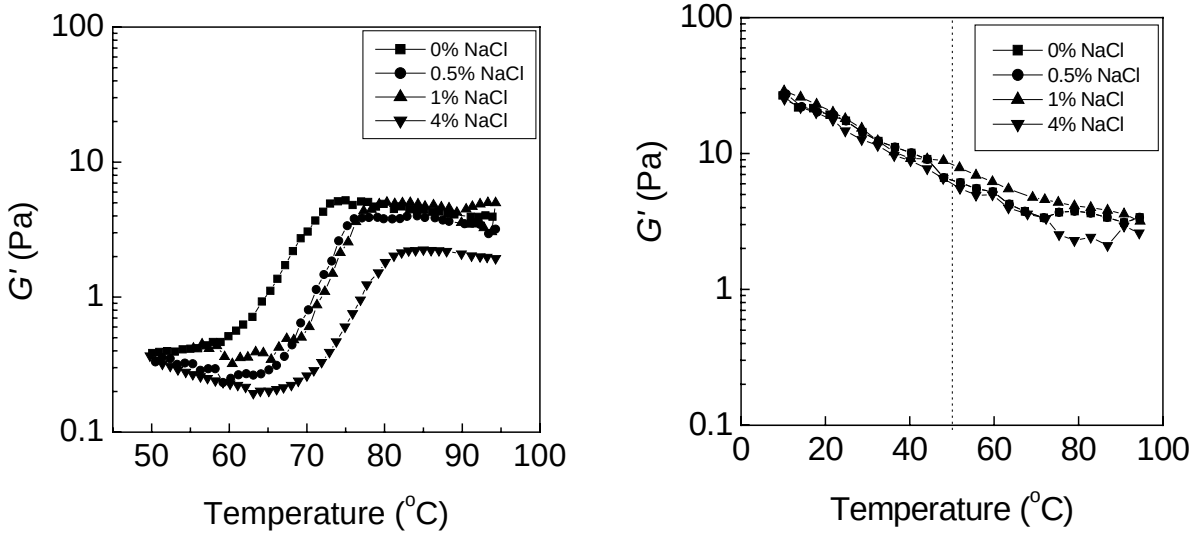
Dispersion (%w/w)	$CaCl_2$ (% w/w)	Pasting temperature (^oC)	Peak viscosity (cP)	Final viscosity (cP)
5%TS	0	72.32	678	647
5%TS	0.5	75.50	661	643
5%TS	1.0	76.35	677	648
5%TS	2.0	77.12	704	660
4.25%TS and 0.75%XG	0	72.42	988	874
4.25%TS and 0.75%XG	0.5	74.80	944	859
4.25%TS and 0.75%XG	1.0	75.95	1006	890
4.25%TS and 0.75%XG	2.0	77.05	1000	881
3%TS and 2%XG	0	75.36	1952	1800
3%TS and 2%XG	0.5	76.72	2015	1928
3%TS and 2%XG	1.0	77.42	2059	1954
3%TS and 2%XG	2.0	79.30	1974	1954

Values are mean of duplicate analyses.

The pasting behaviour of 2.1%TS and 1.4%XG in the presence of salts (0 to 4%w/w) of NaCl, KCl and $CaCl_2$ were also observed by dynamic mechanical measurement. The concentration of total concentration of TS/XG mixtures used in this study was less than those of RVA measurements because it was hard to remove air bubbles from the 5%TS/XG dispersions at a mixing raio of 6/4 containing high concentration of XG. In this case, the pasting behaviour was undertaken under the small starin deformation.

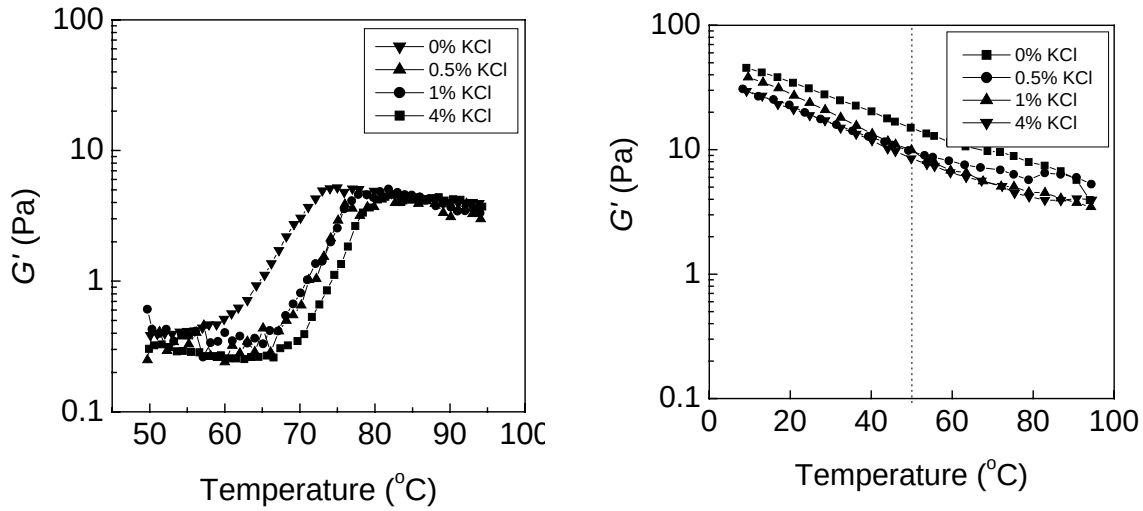
Figure 3.22 shows examples of the evolution in the storage modulus (*G′*) of 2.1%TS and 1.4%XG dispersions in the presence and absence of NaCl during heating from 50°C to 95°C (Figure 3.22a) and immediate cooling down to 5°C (Figure 3.22b). Gelatinization temperature increased with increasing NaCl content especially at 4%. Similar behaviours were also observed in the case of KCl and $CaCl_2$ as shown in Figure 3.23a and Figure 3.24a. For dynamic test, heating of TS dispersion corresponded for pasting of TS without shear. An increase in volume fraction of the progressive swollen granules may be responsible for the increase of storage modulus (*G′*) during heating (Chiotelli *et al.*, 2002).

On cooling, *G′* increased which is attributed to the gelation of leached amylose (Chiotelli *et al.*, 2002). Figure 3.22b 3.23b and 3.24b showed the storage modulus (*G′*) of 2.1%TS with 1.4% in the presence of NaCl, KCl, and $CaCl_2$, respectively, during the cooling of the gelatinized mixtures. *G′* of TS and TS/XG pastes during cooling at 5°C showed almost identical for various concentrations of NaCl and $CaCl_2$.



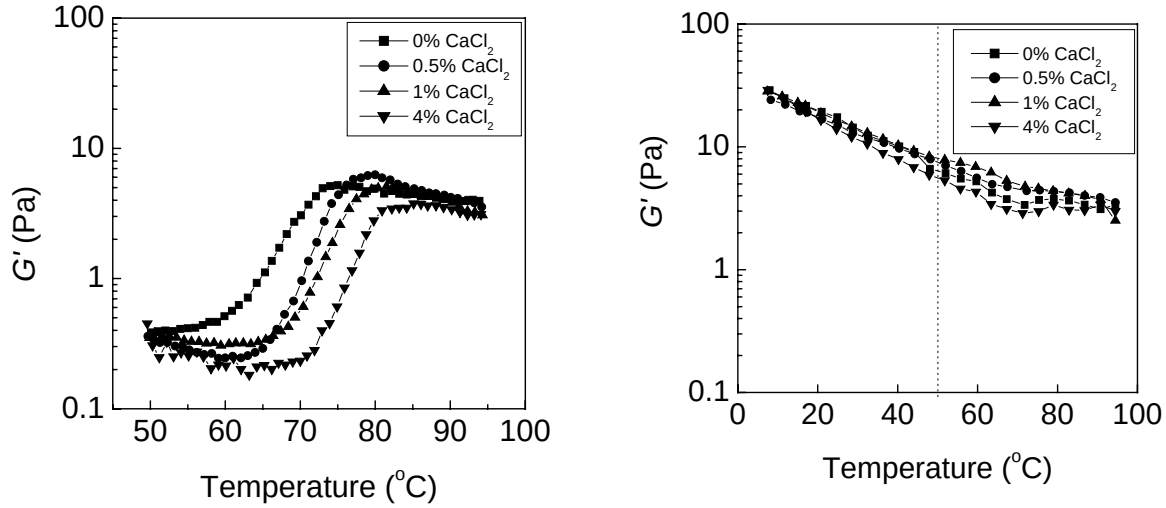
(a) (b)

Figure 3.22 Storage modulus (*G′*) during heating (a) and cooling (b) of the mixtures of 2.1%TS and 1.4%XG in the presence of 0, 0.5, 1, and 4 wt% NaCl.



(a) (b)

Figure 3.23 Storage modulus (*G′*) during heating (a) and cooling (b) of the mixtures of 2.1%TS and 1.4%XG in the presence of 0, 0.5, 1, and 4 wt% KCl.



(a) (b)

Figure 3.24 Storage modulus (*G′*) during heating (a) and cooling (b) of the mixtures of 2.1%TS and 1.4%XG in the presence of 0, 0.5, 1, and 4 wt% $CaCl_2$.

3.4.2 DSC measurement

The gelatinization temperature of 25% TS and TS/XG (mixing ratio 9/1) dispersions showed the higher values (T_o, T_p, T_c) with increasing NaCl concentrations (Figure 3.25). The XG substition (10% of TS) showed no significant effect on changes of gelatinization temperatures. The gelatinization enthalpy of 25% TS and TS/XG showed a trend of slightly increase with increasing the NaCl concentration (Table 3.9).

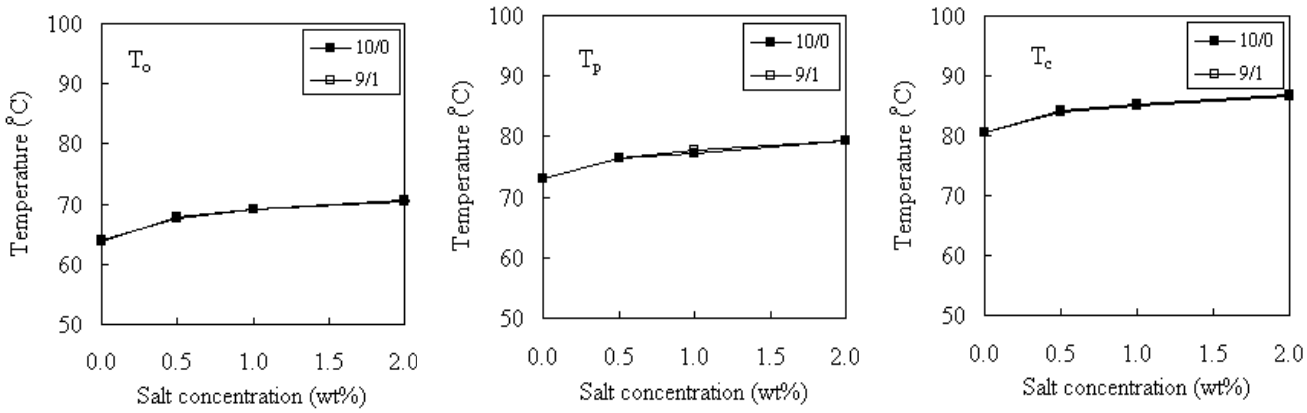


Figure 3.25. Onset (T_o), peak (T_p), and conclusion temperatures (T_c) of the 25%TS (10/0) and 22.5%TS and 2.5%XG (9/1) containing NaCl 0 to 2 wt%.

Table 3.9 Effect of NaCl on gelatinization enthalpy of 25% TS and 22.5%TS and 2.5% containing NaCl 0 to 2 wt%.

NaCl (%w/w)	Enthalpy (J/g dry TS)	
	10/0	9/1
0	16.2 ± 0.3	15.9 ± 0.3
0.5	16.6 ± 0.1	16.4 ± 0.1
1	16.8 ± 0.5	16.3 ± 0.1
2	16.6 ± 0.2	16.7 ± 0.0

Values are mean ± SD

IV CONCLUSION

Partial substitution of TS with XG yielded highly viscous and pseudoplastic liquids. XG appears to form a continuous phase in a TS/XG mixture and confine starch polysaccharides into discontinuously dispersed phases. As a result, the rheological stability of TS paste against shear deformation and that during storage were improved by partially substitution TS with XG. In addition, XG imparted more viscous, heat-stable, and liquid-like rheological properties to the gelatinized mixtures. Incorporation of XG into TS is thus considered to be advantageous to maintain desirable textural properties during storage. In addtion, XG can decrease network rigidity by reducing the structure formation of the amylose in TS. Sucrose and NaCl increased the gelatinization temperatures of TS and TS/XG dispersions with slightly influence on the values of peak and final viscosity, including gelatinization enthalpy.

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Output ที่ได้จากโครงการ

1. Temsiripong, T., R. Pongsawatmanit, S. Ikeda and K. Nishinari. Influence of xyloglucan on gelatinization and retrogradation of tapioca starch. Food Hydrocolloids (manuscript is revising according to reviewer comments).

2. Temsiripong, T., R. Pongsawatmanit, T. Suwonsichon, S. Ikeda and K. Nishinari. Effect of sucrose on gelatinization and rheological properties of tapioca starch and xyloglucan mixtures (preparation).

3. Pongsawatmanit, R., T. Temsiripong, S. Ikeda and K. Nishinari. Effects of xyloglucan on the thermal and rheological properties of tapioca starch (preparation).

บทความเผยแพร่

โครงการ ผลของน้ำตาลและเกลือต่อสมบัติทางด้านกายภาพของเจลผสมของ ไซโลกลูแคน กับแป้งมันสำปะหลัง

แป้งมันสำปะหลังเป็นแป้งที่มีการผลิตมากในประเทศมักนิยมใช้เป็นสารให้ความหนืดในอุตสาหกรรมอาหารเนื่องจากมีราคาถูก ลักษณะเจลแป้งที่ได้ใส แต่มีข้อจำกัดในการนำไปใช้คือ แป้งมันสำปะหลังไม่ทนต่อแรงกวนที่เรียกว่า shear ทำให้ความหนืดลดลง ดังนั้นในทางปฏิบัติอุตสาหกรรมอาหารซึ่งต้องการลักษณะอาหารที่มีความคงตัวดี อายุการเก็บนาน จึงมีการใช้ไบโอพอลิเมอร์หรือที่เรียกว่าไฮโดรคอลลอยด์เติมเข้าไปในแป้ง เพื่อให้อาหารมีลักษณะความคงตัวตามต้องการ โดยทำให้เกิดการเปลี่ยนแปลงในด้านรีโอโลจี (สมบัติที่ว่าด้วยการเสียรูปหรือการไหลที่เกิดขึ้นเมื่อได้รับแรงกระทำ) นอกจากนี้ยังทำให้กระบวนการเปลี่ยนแปลงต่างๆ ของแป้งจากการได้รับความร้อนเปลี่ยนไป โดยมักทำให้ความหนืดของแป้งที่ผ่านการเจลาติไนเซชันสูงขึ้นเนื่องจากไบโอพอลิเมอร์ส่วนใหญ่มีความสามารถในการดูดน้ำได้ดี นอกจากนี้ยังทำให้ลักษณะการคืนตัวของแป้งที่เรียกว่ารีโทรกราเดชัน (retrogradation) ของแป้งเปลี่ยนไป ในการทดลองนี้เลือกใช้ไซโลกลูแคน (xyloglucan) ซึ่งเป็นไบโอพอลิเมอร์ที่สกัดได้จากเม็ดมะขามมาทดแทนแป้งมันสำปะหลังบางส่วนโดยเลือกทำการทดลองที่ช่วงความเข้มข้นต่ำ (3.5-5% โดยน้ำหนัก) และความเข้มข้นสูง (25% โดยน้ำหนัก) เพื่อให้สามารถนำไปประยุกต์ใช้ในผลิตภัณฑ์อาหารต่างๆ เช่น ซุปหรือ ซอส และอาหารที่เป็นเจล เช่น ขนมชั้น ลอดช่องสิงคโปร์ เป็นต้น

งานวิจัยในตอนที่หนึ่งเป็นการศึกษาลักษณะทางด้านรีโอโลจีและด้านความร้อนของของผสม (dispersions) ระหว่างแป้งมันสำปะหลัง (TS) กับไซโลกลูแคน (XG) โดยวิธีการรีโอเมทรีที่เป็นทั้ง dynamic และ steady shear และวิธี DSC (differential scanning calorimetry) เพื่อศึกษาผลของ XG ต่อการเจลาติไนเซชันและรีโทรกราเดชันของ TS พบว่า ความหนืดของเจล TS ที่ผสม XG (โดยมีความเข้มข้นรวมคงที่ 3.5% w/w) หลังการเจลาติไนเซชันทันทีนั้นมีค่าสูงขึ้นเมื่อความเข้มข้นของ XG เพิ่มขึ้น เมื่อศึกษาสมบัติด้วยการวัด dynamic test พบว่า mechanical spectra ของเพสต์ (pastes) TS ผสม XG แสดงสมบัติที่เป็นของเหลวซึ่งเรียกว่า liquid-like มากกว่าเพสต์ของ TS เพียงอย่างเดียว เมื่อพิจารณาผลการเก็บรักษา พบว่า XG ให้ความคงตัวด้าน shear แก่เพสต์ของ TS ดีขึ้น และการเพิ่มขึ้นของค่า dynamic moduli ในเพสต์ TS ที่เก็บ ณ 5°C ลดลงเมื่อมี XG ผสมอยู่ด้วย ในทางตรงกันข้ามเมื่อศึกษาสมบัติด้วย DSC พบว่า อัตราส่วนรีโทรกาเดชัน (retrogradation ratio) จาก DSC มีค่าเพิ่มขึ้นอย่างรวดเร็วโดยเฉพาะในช่วงแรกเมื่อมี XG แสดงให้เห็นว่า XG ทำให้เกิดเฟสต่อเนื่องที่เป็นของเหลวในของผสมซึ่งให้ความคงตัวทางกลดีขึ้นในระหว่างการเก็บ แต่จะเร่งการจัดเรียงตัวของพอลิแซคคาไรด์แป้งจากการที่ปริมาณน้ำที่แป้งจะนำไปใช้ได้ลดน้อยลง นอกจากนี้เมื่อศึกษาผลของอุณหภูมิต่อการเปลี่ยนแปลงความหนืด ณ shear rate 50 s^{-1} ด้วยการสร้างกราฟอาร์รีเนียส พบว่า พลังงานกระตุ้น (E_a) ของระบบของผสม TS และ XG ให้ค่าต่ำกว่าของแป้งเพียงอย่างเดียวกัน นั่นคือ XG ปรับปรุงคุณ

ภาพด้านความคงตัวที่เกี่ยวกับความหนืดเมื่ออุณหภูมิเปลี่ยนแปลงไป ผลที่ได้แสดงให้เห็นว่า XG ให้ความหนืดสูงขึ้น ให้ความคงตัวทางด้านความร้อน และให้สมบัติทางรีโอโลจีที่คล้ายของเหลวต่อของผสมที่ผ่านการเจลาติไนส์แล้ว

จากการศึกษาผลของซูโครส (น้ำตาลทราย) และเกลือ ซึ่งมักใช้เป็นส่วนประกอบของอาหารต่อสมบัติทางกายภาพของระบบ TS เพียงอย่างเดียวและระบบของผสม TS และ XG (สัดส่วน 9:1) เพื่อใช้เป็นแนวทางในการพัฒนาสมบัติทางกายภาพของผลิตภัณฑ์ที่ใช้แป้งเป็นส่วนประกอบ โดยการเตรียมของผสม TS ให้มีความเข้มข้นรวมของพอลิแซคคาไรด์ 25% ที่มีซูโครส 0 ถึง 20% w/w และ XG 0 และ 2.5% w/w และติดตามการเกิดเจลาติไนเซชันของเพสต์ด้วย DSC และเตรียมให้อยู่ในรูปของทรงกระบอกที่มีเส้นผ่าศูนย์กลาง 22 mm วัดค่าลักษณะเนื้อสัมผัสด้วย texture profile analysis (TPA) หลังเก็บไว้ ณ 5°C 24 ชม โดยตัดทรงกระบอกให้มีความสูง 20 mm พบว่า อุณหภูมิเจลาติไนเซชัน (T_o, T_p, T_c) เพิ่มขึ้นเมื่อความเข้มข้นของซูโครสเพิ่มขึ้น ค่า T_o และ T_p เคลื่อนไปที่อุณหภูมิสูงขึ้นเล็กน้อยเมื่อมี XG ในดิสเพอร์ชัน (dispersion) โดยเอนทัลปีของเจลาติไนเซชันของเพสต์ที่มีซูโครส 20% w/w มีค่าสูงขึ้นทั้งระบบที่เป็น TS เพียงอย่างเดียวและระบบของผสม TS และ XG (สัดส่วน 9:1) ซูโครสมีผลทำให้ความแข็งทั้งค่า hardness และ stiffness มากขึ้น การใช้ XG แทนในแป้ง TS ลดความแข็งแต่เพิ่มค่า cohesiveness ของเจลแสดงให้เห็นว่า XG ลดความแข็งของโครงสร้างตาข่ายด้วยการลดการเกิดโครงสร้างของอะไมโลสใน TS และซูโครสทำให้เจลแข็งแรงขึ้นและชะลอการเจลาติไนเซชันของ TS ด้วย

เกลือ (0 ถึง 4%) ก็ให้ผลการเปลี่ยนแปลงสมบัติทางกายภาพของระบบ TS เพียงอย่างเดียวและระบบของผสม TS และ XG (สัดส่วน 9:1) ที่มีความเข้มข้นรวมของพอลิแซคคาไรด์ 5% พบว่า RVA pasting profiles ให้ค่า pasting temperatures เพิ่มขึ้นเมื่อความเข้มข้นเกลือ NaCl, KCl, $CaCl_2$ เพิ่มขึ้น อุณหภูมิของเจลาติไนเซชันจากการวัดด้วย dynamic แสดงค่าเพิ่มขึ้นเมื่อความเข้มข้นของเกลือเพิ่มขึ้น เช่นเดียวกับค่าที่วัดได้จาก DSC โดยเอนทัลปีของการเจลาติไนเซชันจาก DSC มีแนวโน้มเพิ่มขึ้นเมื่อมีเกลือในระบบสูงขึ้น

ผลจากการศึกษาที่เป็นความรู้พื้นฐานนี้ สามารถนำไปเป็นแนวทางเพื่อใช้ในการปรับปรุงระบบอาหารที่มีความคงตัวและมีเนื้อสัมผัสที่ดีขึ้นในการพัฒนาผลิตภัณฑ์และกระบวนการผลิตในอุตสาหกรรมอาหารต่อไป