รายงานวิจัยฉบับสมบูรณ์

โครงการ

“ผลของไฮโดรคอลลอยด์ต่อสมบัติทางกายภาพและความคงตัวของระบบที่มีแป้งมันสำปะหลังเป็นส่วนประกอบ”

โดย

รศ. ดร. รุ่งนภา พงศ์สวัสดิ์มานิต

27 มกราคม 2552

สัญญาเลขที่ RMU4880027

รายงานวิจัยฉบับสมบูรณ์

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ส่วนประกอบต่างๆ ที่เติมในอาหารเพื่อกำหนดสมบัติทางหน้าที่ของผลิตภัณฑ์ แป้งมันสำปะหลังเป็นสารให้ความหนืดที่นิยมใช้ในผลิตภัณฑ์อาหารหลายชนิด อันตรกิริยาของส่วนประกอบต่างๆ ระหว่างแป้งมันสำปะหลังและพอลิแซคคาไรด์ที่ไม่ใช่แป้งที่เกี่ยวข้องกับเจลาติไนเซชันและรีโทรกราเดชันระหว่างการให้ความร้อนและทำให้เย็น ล้วนมีผลต่อคุณภาพสุดท้ายของผลิตภัณฑ์ที่มีแป้งเป็นส่วนประกอบ ดังนั้น ความเข้าใจในเรื่องผลของไฮโดรคอลลอยด์ต่อสมบัติทางกายภาพและความคงตัวของระบบที่ใช้แป้งมันสำปะหลัง จึงสำคัญต่อการพัฒนาผลิตภัณฑ์และกระบวนการในเทอมของการเพิ่มคุณภาพและการยืดอายุการเก็บ แซนแทนกัม (Xan) และอัลจีเนต (Alg) เป็นไฮโดรคอลอลยด์ที่ศึกษาที่มีผลต่อสมบัติทางกายภาพและความคงตัวของแป้งมันสำปะหลัง (TS) ด้วยวิธีการต่างๆ เช่น RVA, steady shear measurement, DSC, การละลายและแช่แข็งหลายรอบ ผลที่ได้คือ ไฮโดรคอลลอยด์ทั้งสองชนิดเพิ่มสมบัติทางเพสติง การแทนที่แป้งมันสำปะหลังบางส่วนด้วยแซนแทนกัม สามารถปรับปรุงให้สมบัติเพสติงและความคงตัวทางด้านการแช่แข็งและละลายของแป้งมันสำปะหลังได้ดีขึ้นภายใต้สภาวะที่เป็นกรด (pH 3 ถึง 7) เมื่อศึกษาสหสัมพันธ์ระหว่างค่า setback และการแยกตัวของน้ำจากของผสม TS/Xan พบว่า สามารถใช้เพื่อทำนายการแยกตัวของน้ำที่เกิดขึ้น ณ วงจรการแช่แข็งและละลายใดๆ จากค่า RVA setback นอกจากนี้ การเติมน้ำตาลยังมีผลต่อการเพิ่มอุณหภูมิเพสติง ความหนืดของพีค ความหนืดสูงสุด ค่า breakdown และ setback ของของผสม TS/Xan (p<0.05) ส่วนอัลจีเนตสามารถปรับปรุงความคงตัวทางด้านการแช่แข็งและละลายของแป้งมันสำปะหลังได้ดีขึ้นเมื่อมี pH 5 ถึง 7 การเติมอัลจีเนตมีผลให้ส่วนผสม TS/Alg มีความคงตัวทางด้านความร้อนดีกว่าของเพสต์แป้งมันสำปะหลังเท่านั้นเนื่องจากมีค่าพลังงานกระตุ้นต่ำกว่า อัตราส่วนรีโทรกราเดชันของส่วนผสม TS/Alg ที่หาจาก DSC ดำเนินไปเร็วกว่าที่ได้จาก TS เท่านั้นเมื่อเก็บไว้ที่ 5°C แสดงว่า Alg เร่งการจัดเรียงตัวของแป้ง การเก็บเจลแป้งที่อุณหภูมิต่ำ 5°C เพิ่มความแข็งแรงของโครงสร้างเจลแป้งเนื่องจากรีโทรกราเดชัน แต่อัลจีเนตลดสภาพแข็งเกร็งจากการยับยั้งการเกิดโครงสร้างของอะไมโลสในแป้งมันสำปะหลังระหว่างการเก็บ

คำหลัก : รีโทรกราเดชัน สมบัติเพสติง ความคงตัวด้านแช่แข็งและละลาย แซนแทนกัม อัลจีเนต

Abstract

Project Code: RMU4880027

Project Title: Influence of hydrocolloids on physical properties and stability of tapioca starch-based system

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Many ingredients are added into foods to determine the functional properties of products. Tapioca starch (TS) is a favorable thickener used in many food products. The ingredient interactions between TS and non-starch polysaccharide related to gelatinization and retrogradation during heating and cooling, respectively, play an important role to determine final qualities of starch-based products. Therefore, understanding the influence of hydrocolloids on physical properties and stability of TS-based system is important for product and process development in terms of quality enhancement and shelf life extension. Xanthan gum (Xan) and alginate (Alg) were selected to study the ingredient interactions with TS affecting physical properties and stability using various methods such as RVA, steady shear measurement, DSC, repeated freeze-thaw treatment. The results revealed that addition of both hydrocolloids increased the RVA pasting properties. The substitution of a part of TS with Xan can improve pasting properties and the freeze–thaw stability of TS under acidic systems (pH 3 to 7). The investigated correlation between setback and water separation of TS/Xan mixtures was proven to be a useful approach for predicting water separation from RVA setback value at any given freeze-thaw cycles. In addition, RVA pasting temperatures, peak viscosity, final viscosity, breakdown and setback values of 5% w/w TS/Xan mixtures increased with increasing sucrose contents ($p<0.05$). Alginate can be used for improving the freeze-thaw stability at in TS-based products containing pH 5 to 7. Added alginate in TS represented the heat stability of TS/Alg mixtures compared with TS alone due to the lower activation energy values. The retrogradation ratios of TS/Alg mixtures determined from DSC proceeded faster than those of TS alone after keeping at 5°C, suggesting that Alg accelerates re-ordering of the starch. Keeping the starch gels at 5°C enhanced the strength of gel structure due to the retrogradation of starch but Alg can decrease network rigidity by reducing the structure formation of the amylose in TS during the storage

Keywords : Retrogradation, Pasting properties, Freeze-thaw stability, Xanthan gum, Alginate

Executive summary

In food industry, many ingredients are added for determining the functional properties of products. Starch is one of the most important polysaccharides used in food systems. The characteristics of starch granular swelling, gelatinization and retrogradation during processing are important for controlling rheological properties of foods (Nishinari, Zhang & Ikeda, 2000). 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.

Tapioca starch (TS), produced from cassava roots especially in Thailand, 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. Tapioca starch 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. Therefore, the influence of selected hydrocolloids on on rheological properties and thermal stability of tapioca starch (TS) using a Rapid Visco-Analyzer (RVA), steady and dynamic shear rheometers was investigated. The influence of temperature, pH and sucrose on the rheological properties, thermal properties and freeze-thaw stability of TS pastes with and without hydrocolloids was also investigated using RVA, DSC, and repeated freeze-thawing treatments for discussion of storage stability and shelf life extension.

Effect of xanthan gum on the viscosity and thermal stability of tapioca starch (TS) at different mixing ratios of TS and xanthan gum containing different pH values was investigated using a Rapid Visco-Analyzer (RVA) and repeated freeze-thaw treatment. At a total polysaccharide concentration of 5% (w/w) tapioca starch (TS) and TS/xanthan gum mixtures, the RVA peak and final viscosities increased with xanthan gum concentration. Final viscosity of gelatinized TS alone under pH 3 exhibited the lowest value compared with those of TS at pH 5 and 7 but the extent of difference between those of pH 3 and pH 5 or 7 was lower with increasing gum content. Freeze-thaw stability of TS pastes containing xanthan gum exhibited lower water separation (<10%) compared with that of TS pastes alone (>10%) after 3 cycles of repeated freeze-thaw treatment. The study shows that the substitution of a part of tapioca starch with xanthan gum can improve pasting properties and the freeze–thaw stability of tapioca starch under acidic systems which could be applied to food industry.

Freeze-thaw stability of tapioca starch (TS) can be modified using hydrocolloids. Alginate (Alg) was investigated in this study using a repeated freeze-thaw treatment. The gelatinized 5% TS/Alg dispersions (10/0, 9/1, 8/2) at different pH values (5 to 7) were prepared. The results showed that water separation of TS paste alone after 7 freeze–thaw cycles at pH 5 was the highest value compared with those of TS pastes at pH 6 and 7. The water separations of gelatinized TS/Alg (9/1 and 8/2) were lower than those of TS pastes alone after seven freeze-thaw cycles for all studied pH whereas water separation was lower with higher pH. The results suggest that alginate can be used for improving the freeze-thaw stability at the studied pH (5 to 7) in TS-based products.

Hydrocolloids have been widely used for improving textural properties and stability of starch during the storage. The effect of temperatures (5 to 55°C) on viscosity of tapioca starch (TS) and sodium alginate (Alg) at different mixing ratios was investigated to gain more understanding for applications in tapioca starch based - products. Gelatinized TS/Alg mixtures were evaluated using a rheometer. Apparent viscosity and consistency index (*K*) values of TS and TS/Alg pastes were decreased with increasing temperatures. The viscosities of mixed TS/Alg pastes were higher than that of TS at temperature >25°C but lower at 5°C. The activation energy values of TS/Alg mixtures were lower than that of TS alone according to the Arrhenius plot, indicating the heat stability of TS/Alg mixtures. The results suggested that sodium alginate could be applied to modify the viscosity and temperature stability of tapioca starch based food product

Physical properties and storage stability of tapioca starch (TS) can be modified using hydrocolloids. Xanthan gum (Xan) was investigated in this study for further application in TS-based products. The TS and TS/Xan mixtures at a total polysaccharide concentration of 5% w/w (db) were prepared. From RVA pasting profiles, pasting temperature, peak and final viscosities of TS pastes increased with increasing Xan concentration ($p<0.05$) whereas the setback values indicating the short-term retrogradation were lower ($p<0.05$). Flow curves of all TS and TS/Xan pastes from steady shear measurement exhibited shear thinning behavior. Water separation values of TS/Xan pastes were also lower than those of TS pastes alone from repeated freeze-thaw experiment, indicating Xan preventing the reassociation of starch molecules. The correlation between setback and water separation was investigated and proven to be a useful approach for predicting water separation from RVA setback value at any given freeze-thaw cycles. These results have important implications for the formulation of TS-based products with improved rheological properties and freeze-thaw stability

Sugars and hydrocolloids are added into starch-based products during processing for improving the final qualities of food. Effect of xanthan gum (Xan) (0 to 0.5%) and sucrose (0 to 30%) on the pasting properties of tapioca starch (TS) was investigated using a Rapid Visco-Analyzer (RVA). RVA pasting temperatures, peak viscosity, final viscosity, breakdown and setback values of 5% w/w TS/Xan mixtures increased with increasing sucrose contents ($p<0.05$) according to the Pearson's correlation analysis. Setback values of TS/Xan pastes decreased significantly with increasing xanthan concentration during cooling ($p<0.05$) from 95 to 50°C. The rate of viscosity breakdown was increased in TS and TS/Xan mixtures with the addition of sucrose. Steady shear viscosities of TS/Xan pastes exhibited thermal stability of xanthan gum contributing to TS pastes for the systems with and without added sucrose. Specific viscosity of TS/Xan pastes containing sucrose up to 20% exhibited a single master curve. The linear regression analysis from RVA pasting profile was derived for predicting final viscosity with a good relationship and can be applied to predict the viscosities of TS/Xan/Sucrose mixtures below 2000 mPa.s from steady shear measurement. These results have essential implications for the formulation of TS-based products containing sucrose and xanthan gum in food industry.

Effects of sodium alginate (Alg) on the thermal and rheological properties of tapioca starch (TS) at different mixing ratios were investigated using swelling power, RVA, DSC, steady shear viscosity and freeze-thaw stability measurements. Pasting temperatures of 5 wt% of TS/Alg dispersions at five mixing ratios (TS/Alg = 10/0, 9.5/0.5, 9/1, 8.5/1.5 and 8/2) slightly increased with increasing Alg content. Addition of Alg increased peak and final viscosities of TS evaluated from RVA profiles, indicating that Alg enhances the gelatinization temperature and thickening properties of TS dispersion. Gelatinization temperatures (T_o, T_p, T_c) of 25 wt% TS/Alg at mixing ratios of 10/0, 9.5/0.5 and 9/1 shifted to higher temperatures whereas the gelatinization enthalpy of TS pastes slightly increased in the presence of Alg without significant difference ($p>0.05$). The retrogradation ratios of TS/Alg mixtures determined from DSC proceeded faster than those of TS alone after keeping at 5°C, suggesting that Alg accelerates re-ordering of the starch. The viscosity values of TS paste was lower than those of TS/Alg pastes especially at low shear rates. Alg was effective in stabilizing the starch gel against repeated freeze-thaw treatments. The results from the study suggest that Alg could be used for enhancing quality of TS based food product in terms of rheological properties.

The hardness and stiffness values of each 25% TS/Alg gel increased with increasing storage time but these two values were lower with increasing Alg content at the same storage time. However, cohesiveness of the TS/Alg gels exhibited the lower values with increasing storage time but increased with increasing Alg substitution. The results suggest that keeping the starch gels at 5°C enhanced the strength of gel structure due to the retrogradation but Alg can decrease network rigidity by reducing the structure formation of the amylose in TS during the storage.

Project title: Influence of hydrocolloids on physical properties and stability of tapioca starch-based system

1. Objectives

1. To know the effect of interactions of tapioca starch/hydrocolloid/water system on physical properties of tapioca starch
2. To understand the effect of hydrocolloids on the physical properties of tapioca starch at various temperature and pH
3. To publish at least two international papers and one mini-patent
4. To gain collaborative research among the researchers at both national and international levels
5. To apply the knowledge gained from the research for tapioca starch-based products.

2. Materials and methods

2.1 Materials

For the experiment of effect of xanthan gum and pH on pasting properties and freeze-thaw stability of tapioca starch (2.2), Tapioca starch was purchased from a manufacturer located in the area of Chonburi province, Thailand. The moisture contents of TS and commercial xanthan gum (Thai food and chemical Co., Ltd, Thailand) were 12.1 and 11.9% w/w determined by the hot air oven method at 105°C (AOAC, 1995) for 6 h. Amylose content of TS was 22.0% determined by HPSEC (modified method of Govindasamy, Oates and Wong, 1992). The samples were used without any further purification. HCl was analytical grade for adjusting required pH of the mixture suspensions.

The materials in other experiments of this research were used as shown below.

Tapioca starch was supplied by Chorchaiwat Industry Co., Ltd. (Cholburi, Thailand). The moisture and amylose contents of the starch were 11.9% and 19.4% determined by the hot air oven method at 105°C (AOAC, 1995) and HPSEC (modified method of Govindasamy, Oates & Wong, 1992), respectively. Particle size distribution of TS (Mastersizer 2000, Malvern) was shown in Fig. 2.1.1 and d_{32} value was about 7.3 μm. Xanthan gum (CP Kelco, San Diego) was donated by Winner Group Enterprise Ltd. (Bangkok, Thailand) containing 12.8% w/w moisture content determined by the hot air oven method at 105°C (AOAC, 1995). Food grade sodium alginate (Alg) was kindly donated by TIC gums (TIC Pretested® Colloid 488T). The supplier reported that this product had an M:G ratio of about 55:45, was of “medium” viscosity, and had a molecular mass of 216 kDa. The moisture content of Alg was 12.2 wt%. Sucrose (Merck) was used as obtained. Potato amylose (Sigma- Aldrich, St Louis, MO, USA) was used as the standard curve of amylose. All samples were mixed on a dry basis and used without any further purification.

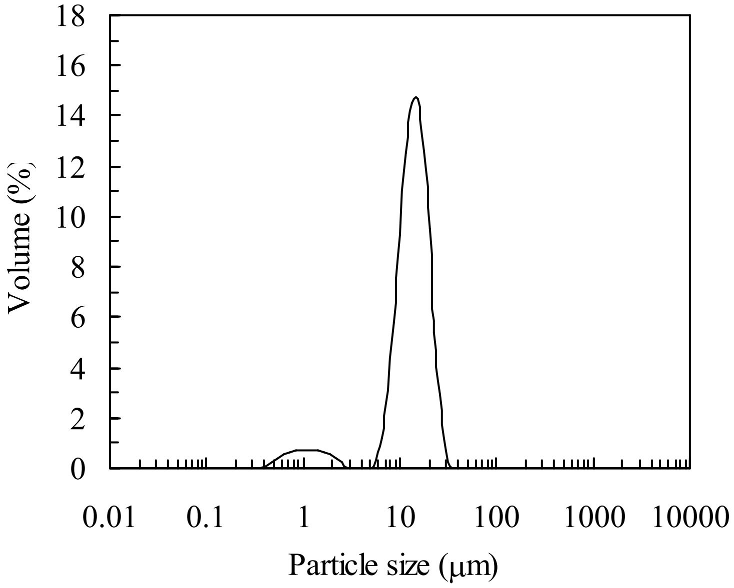


Fig. 2.1.1. Particle size distribution of tapioca starch using Malvern

2.2. Effect of xanthan gum and pH on pasting properties and freeze-thaw stability of tapioca starch

2.2.1 Sample preparations

TS and Xan were prepared at different mixing ratios (TS/Xan = 10/0, 9.5/0.5 and 9/1) of 5% total polysaccharide concentration for all measured samples in distilled water adjusted to be at various pH values (3, 5 and 7) using 0.1 N HCl. Xanthan gum dispersions were first prepared at room temperature, stirred using magnetic stirrer at least 2 h and kept at 5^{O}C at least 6 h to ensure completely hydration. Then TS powder was added into the gum dispersion, and continuously mixed for 1 h before RVA measurement and freeze-thaw stability test.

2.2.2 Determination of RVA pasting properties and freeze-thaw stability

Pasting properties of TS/Xan mixtures were determined using a Rapid Visco-Analyser (RVA-4, Newport Scientific, Narrabeen, Australia), interfaced with a personal computer equipped with Thermocline software (Newport Scientific) according to the method and temperature profile of Pongsawatmanit et al. (2006). Pasting profiles were determined in triplicate and the evaluated parameters were averaged.

For the determination of freeze–thaw stability, dispersions of TS or TS/Xan were heated to 95^{O}C, held at the temperature 95-98^{O}C for 30 min, and cooled down to 40^{O}C in ice-water bath. The gelatinized TS/Xan pastes (5% w/w total polysaccharide concentration) with three mixing ratios (10/0, 9.5/0.5 and 9/1) and different pH values (3, 5 and 7) were investigated by storing the pastes in the freezer (-25°C) for 20 h, and then thawing at 40°C for 2 h repeatedly from 1 to 3 cycles according to the method of Pongsawatmanit et al. (2006). Sodium azide (0.04% w/w) was added to prevent microbial spoilage. The percentage of water separation using centrifugation at 2100 g for 10 min was calculated from the following equation:

$$\text{Water separation (\%)} = (W_1 - W_2) \times 100 / [(W_1 - W_t)] \qquad (1)$$

When : W_t = weight of syringes without paste samples after centrifugation at 2100 g for 10 min

W_1 = weight of syringes with paste samples before centrifugation

W_2 = weight of syringes with paste samples after centrifugation

2.2.3 Statistical analysis

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

2.3 Freeze-thaw stability of tapioca starch and alginate mixtures at different pH

Tapioca starch (TS) and sodium alginate (Alg) were prepared at three mixing ratios (TS/Alg = 10/0, 9/1 and 8/2). The 5 % total polysaccharide concentrations of all mixtures were prepared for the freeze-thaw stability measurement. Alginate dispersions were first prepared at room temperature, stirred using magnetic stirrer at least 2 h to ensure complete hydration. Then TS powder was added into the gum dispersion, and continuously mixed for 30 min. Then, all TS/Alg mixture were adjusted to various pH values (5, 6 and 7) using 0.1 N HCl or NaOH. The dispersions of TS or TS/Alg were heated to 95C, held at the temperature 95-98°C for 30 min, and cooled down in ice-water bath. All samples were prepared in the closed system for preventing moisture loss during preparation. The gelatinized TS/Alg pastes were investigated by storing the pastes in the freezer (-25°C) for 20 h, and then thawing at 40C for 2 h repeatedly from 1 to 7 cycles. Water separation from the TS/Alg pastes at defined freeze-thaw cycles was carried out according to the method of Pongsawatmanit et al. (2006) in section 2.2.2.

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

2.4 **Influence of temperature on viscosity of tapioca starch containing sodium alginate**

Weighed amounts of TS and Alg were dispersed into deionized distilled water at the total polysaccharide content of 5 wt% with various mixing ratios (TS/Alg = 10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2). Sodium alginate solution was first prepared and stirred using a magnetic stirrer for 2 h prior mixing with TS to ensure fully hydration of polysaccharide. The mixtures were stirred using a magnetic stirrer for 1 h at room temperature, heated in a boiling-water bath, and then further stirred for 30 min while the sample temperature was maintained at 95 – 98°C and cooling immediately. The mixtures were centrifuged at 190 g for 2 min to remove air bubbles.

Gelatinized TS/Alg pastes with different mixing ratios of 10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2 (5 wt% total polysaccharide concentration) were studied. Steady shear viscosity of gelatinized TS and Alg mixtures was measured using a rheometer (Physica MCR300, Anton Paar GmbH, Stuttgart, Germany), equipped with a cone-plate test fixture (50 mm diameter, 1° cone angle and 0.05 mm gap). Sample was loaded onto the plate of the rheometer and allowed to reach equilibrium on the plate. Apparent viscosity was recorded by increasing the shear rate from 0.1 to 1000 s^{-1}. Measurements were done at 5, 15, 25, 35, 45, and 55°C. The Arrhenius equation was also used to investigate the temperature dependency of the apparent viscosity of all mixtures.

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 Influence of xanthan gum on rheological properties and freeze-thaw stability of tapioca starch

2.5.1 Rapid Visco Analyser (RVA) measurement

Pasting properties of 5% w/w TS and xanthan gum (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) were determined using a Rapid Visco Analyser (RVA) (RVA-4, Newport Scientific, Narrabeen, Australia). 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. Then, TS was added finally to achieve a total weight of 28 g for preparing pastes of 5% w/w TS/Xan mixtures. The dispersions were kept at room temperature for further 30 min to hydrate the starch. Before the measurement, each 28 g TS/Xan suspension was stirred manually to disperse the sample uniformly. The pasting profile of the sample was monitored during a thermal treatment 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 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 during the measurement was started at 960 rpm for the first 10 s and kept constant at 160 rpm until the end of experiment. Pasting profiles were determined in triplicate in order to confirm the reproducibility of the data and the average values of evaluated pasting parameters were reported.

2.5.2 Steady shear viscosity measurement

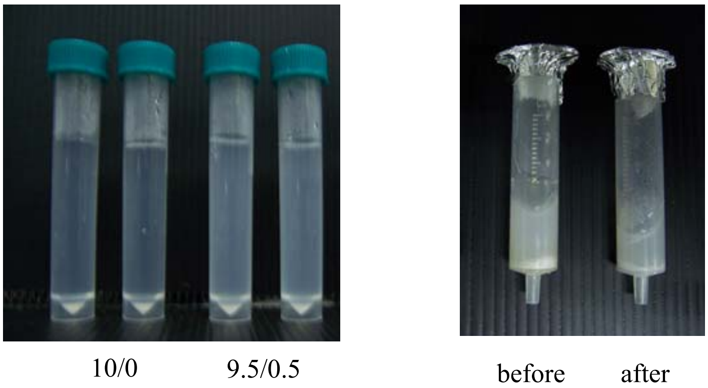
Gelatinized TS and TS/Xan mixtures (5% w/w total polysaccharide concentration) at five mixing ratios obtained from RVA experiment were used for steady shear viscosity measurement using a rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany). All pastes were centrifuged at 190 x g for 2 min 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 or 50 °C for at least 30 s before starting the measurement. Apparent viscosity was recorded by increasing the shear rate from 0.1 to 100 s^{-1}. The measurements were done using at least three freshly prepared samples and each average value was reported.

2.5.3 Freeze-thaw stability measurement

TS and Xan were prepared at different mixing ratios (TS/Xan = 10/0, 9.5/0.5 and 9/1) with 5% w/w total polysaccharide concentration in deionized distilled water. In the case of TS/Xan dispersions, Xan dispersion was first prepared at room temperature and stirred using a magnetic stirrer for at least 6 h, and then TS was added into the Xan dispersion and mixed for at least 30 min. The dispersions of TS or TS/Xan were heated to 95°C, held at the temperature of 95-98°C for 30 min, and cooled down in an ice-water bath. Each mixture was poured into the freeze-thaw plastic tubes (Fig. 2.5.1a). All samples were centrifuged at 190 x g for 2 min to remove air bubbles. Sodium azide (0.04 %) was also added to prevent microbial spoilage.

The freeze-thaw stability of TS/Xan pastes was determined by storing the gelatinized pastes in the freezer (-25°C) for 20 h, and then thawing at 40°C for 2 h repeatedly up to seven cycles. To measure water separation from the TS/Xan pastes at defined freeze-thaw cycles, 5-ml plastic syringes without the tip and plunger of the syringe were used (Fig. 2.5.1b) according to the methods of Pongsawatmanit et al. (2006) and Zheng and Solsuski (1998). The syringes were centrifuged at about 2100 x g for 10 min to remove excess water from the cotton and then weight (W_t). Paste samples (2.5 g) after thawing at selected freeze-thaw cycles were added into each syringe. The syringe was weighed before and after centrifugation at 2100 x g for 10 min and the weights were recorded as W_1 and W_2, respectively (Pongsawatmanit et al., 2006). The percentage of water separation was calculated as shown in equation (1) (section 2.2.2) Water separation (%) = $(W_1\text{-}W_2) \times 100/ (W_1\text{-}W_t)$

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



(a) (b)

Fig. 2.5.1 Freeze-thaw plastic tubes containing TS/Xan pastes (10/0, 9.5/0.5) (a) plastic syringes containing thawed pastes (TS/Xan = 9.5/0.5) before and after centrifugation for water separation determination (b).

2.5.4 Data and statistical analysis

Each of the mentioned measurements was carried out using at least three freshly prepared samples. Statistical analysis was performed by SPSS V.12 statistical software (SPSS (Thailand) Co., Ltd.). The results are reported as the mean and standard deviation. The RVA parameters and water separation values at different freeze-thaw cycles were related by Pearson's correlation. The linear regression was also conducted to relate the RVA parameters and water separation to predict a set of response/dependent variables.

2.6 Influence of xanthan gum and sucrose on the pasting properties of tapioca starch

2.6.1 Rapid Visco Analyser (RVA) measurement

Pasting properties of 5% w/w TS and xanthan gum (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, 10, 20 and 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 finally 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 further 30 min to hydrate the starch. Each TS/Xan/Sucrose suspension was stirred manually to disperse the sample uniformly before measurement. The pasting profile of the sample and agitation speeds of paddle were monitored during a thermal treatment according to Pongsawatmanit and Srijunthongsiri (2008) as following: 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 for the first 10 s was started at 960 rpm and kept constant at 160 rpm until the end of experiment. Pasting profiles were evaluated in triplicate to confirm the data reproducibility and the average values of evaluated pasting parameters were reported.

2.6.2 Steady shear viscosity measurement

Selected gelatinized TS/Xan/Sucrose mixtures obtained from RVA experiment were used for steady shear viscosity measurement using a rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany). All pastes were centrifuged at 190g 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 or 50 °C for at least 2 min before starting the measurement. Apparent viscosity was recorded by increasing the shear rate from 0.1 to 1000 s^{-1}. The measurements were done using at least three freshly prepared samples and each average value was reported.

2.6.3 Data and statistical analysis

Pasting profiles were determined in triplicate in order to confirm the reproducibility of the data. 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.). The linear regression was conducted to relate the RVA final viscosity with the xanthan and sucrose contents to predict a set of response/dependent variables.

2.7 Thermal properties and storage stability of tapioca starch containing alginate

2.7.1 Sample preparation of gelatinized TS and TS/Alg pastes

TS and Alg were prepared at different mixing ratios (TS/Alg = 10/0, 9/1, 8/2, 7/3, and 6/4) with 5% total polysaccharide concentration for all measured samples in distilled water. In the case of TS/Alg dispersions, Alg dispersions were first prepared at room temperature and stirred using a magnetic stirrer for at least 2 h, then TS powder was added into the Alg dispersion, and continuously further mixed for at least 30 min. The dispersions of TS or TS/Alg were heated to 95°C, held at the temperature 95-98°C for 30 min, and cooled down in an ice-water bath immediately. Samples were centrifuged at 190 g for 2 min to remove air bubbles before the measurements of rheological properties and freeze-thaw stability

2.7.2 Swelling power and water soluble index

Swelling power (SP) and water soluble index (WSI) of TS and TS/Alg mixtures were determined using modified methods of Leach, McCowen and Schoch (1959) and Mandala & Bayas (2004). The total polysaccharide content of 1 wt% with the mixing ratios of TS/Alg = 10/0, 9.5/0.5, 9/1, 8.5/1.5 and 8/2 was selected to study. The TS or TS/Alg mixtures were prepared in centrifuge tubes (10 g) with screw caps and heated in a shaking water bath at 95°C for 30 min. After heating, the samples were immediately cooled by immersing in ice-water bath and centrifuged at 12000 g for 15 min. Precipitated paste was separated from supernatant and weighed (W_p). The supernatant was dried to constant weight (W_{dss}) in a hot air oven at 105°C for 6 h. The SP was calculated as the ratio of the wet weight of the precipitated paste (hydrated granule) to its dry weight (W_{dp}). WSI was the percentage of dried solubilized starch in supernatant to the total starch weight (db) (W_s). The calculation was based on the assumption that the total amount of gum remained in the supernatant (Li & Yeh, 2001) and the amount of alginate was substracted for calculating WSI as following equations:

$$SP = W_p / [W_{dp}] \text{ (g/g)} \quad (2)$$

$$WSI = [W_{dss} / W_s] \times 100\% \quad (3)$$

2.7.3 Amylose leaching determination

Leached amylose in the dissolved material was determined following the colorimetric method (Chrasil, 1987). The supernatant (1.0 ml) was pipetted into a 20 ml test-tube. After addition of 1.0 N NaOH (2 ml) and water (4 ml), the sample was capped, mixed and heated at 95°C for 30 min with occasional mixing, and then immediately cooled in an ice-water bath. The sample solution (0.1 ml) was added to 5 ml of 0.5% tricholoroacetic acid (TCA) in the other test-tube. The solutions were mixed, and freshly prepared 0.05 ml of 0.01 N I_2 – KI solution (1.27 g of I_2 per liter + 3 g of KI per liter) was added, mixed immediately and kept in dark at room temperature for 30 min. The blue color was read at 630 nm using UV- Vis spectrophotometer (Helios Alpha, Thermo Spectronic, UK). The absorbance of the reaction blanks with water was zero. Leached amylose contents of TS and TS/Alg were reported as mg of amylose leached per 100 mg of dry matter starch. Amylose from potato (Sigma- Aldrich, St Louis, MO, USA) was used for the stardard curve.

2.7.4 Rapid Visco Analyzer (RVA) measurement

Pasting properties of 5% TS and Alg mixtures at the mixing ratios of 10/0, 9.5/0.5, 9/1, 8.5/1.5 and 8/2 were determined using a Rapid Visco Analyzer (RVA) (RVA-4, Newport Scientific, Narrabeen, Australia). Precalculated amounts of Alg were added to preweighed deionized distilled water in RVA canisters and allowed to disperse throughout the sol for at least 2 h. Then, TS was added finally to achieve a total weight of 28 g for preparing pastes of 5% TS/Alg mixtures. The dispersions were kept at room temperature for further 30 min to hydrate the starch. Before the measurement, each 28 g TS/Alg suspension was stirred manually by rotating the plastic paddle of the RVA for 15 to 30 s to disperse the sample uniformly. The pasting profile of the sample was monitored during a thermal treatment 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 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 during the measurement was started at 960 rpm for the first 10 s and kept constant at 160 rpm until the end of experiment. Pasting profiles were determined in triplicate in order to confirm the reproducibility of the data and the evaluated pasting parameters were averaged.

2.7.5 Steady shear viscosity measurements

TS and Alg (5% total polysaccharide concentration) were weighed and mixed together at five mixing ratios (TS/Alg = 10/0, 9/1, 8/2, 7/3, and 6/4) in distilled water. Alg was first stirred using a magnetic stirrer for 2 h and TS was added. The mixtures were stirred for 1 h at room temperature, 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. Steady shear viscosity of gelatinized TS and Alg mixtures was measured using a rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany). Samples were placed into the rheometer measuring system (cone and plate geometry, 50 mm diameter, 1°cone angle and 0.05 mm gap) which was equilibrated to 25°C. Apparent viscosity was recorded by increasing the shear rate from 0.1 to 1000 s^{-1}. The measurements were done using at least two freshly prepared samples and the average value was reported.

2.7.6 Dynamic viscoelasticity measurement

TS and Alg were weighed and mixed together at five mixing ratios (TG/Alg = 10/0, 9.5/0.5 and 9/1) in distilled water for preparing 5% total polysaccharide concentration. Alg was first stirred using a magnetic stirrer for 2 h and TS was added. The mixtures were stirred for 1 h at room temperature, 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. The mixtures were centrifuged at 190g for 2 min to remove air bubbles. The frequency dependence of the dynamic moduli (storage shear modulus and loss shear modulus) was evaluated at 25°C with a cone and plate geometry (50 mm diameter, 1 degree of cone angle, 0.05 mm gap) in the frequency range from 0.1 to 100 rad/s using a rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany). A constant strain (1%) determined based on strain sweep experiments, which fell within the linear viscoelastic regions of each TS/Alg mixture was used to determine the mechanical spectra. The experiments were done in triplicate.

2.8 Freeze-thaw stability measurement

TS and Alg were prepared at different mixing ratios (TS/Alg = 10/0, 9/1 and 8/2) with 5 wt% total polysaccharide concentration in deionized distilled water. Alg dispersions were first prepared at room temperature and stirred using a magnetic stirrer for at least 2 h, and then powdered TS was added into the Alg dispersion and continuous mixed for at least 30 min. The dispersions of TS or TS/Alg were heated to 95°C, held at the temperature of 95-98°C for 30 min, and cooled down to 40°C in an ice-water bath. Samples were centrifuged at 190 g for 2 min to remove air bubbles. The freeze-thaw stability of gelatinized TS/Alg pastes (mixing ratios of TS/Alg = 10/0, 9/1 and 8/2) with 5 wt% total polysaccharide concentration was investigated by storing the gelatinized pastes in the freezer (-25°C) for 20 h, and then thawing at 40°C for 2 h repeatedly up to four cycles. Sodium azide (0.04 wt%) was added to prevent microbial spoilage. Water separation from the TS/Alg pastes at defined freeze-thaw cycles was carried out according to the method of Pongsawatmanit et al. (2006) in section 2.2.2. At least three measurements were carried out to ensure the reproductivity of the data.

2.9 Differential scanning calorimetry (DSC)

A differential scanning calorimeter (DSC822^{e}, Mettler-Toledo GmbH, Switzerland) was used to determine thermal properties of TS and Alg mixtures. The total polysaccharide content of 25% w/w with the mixing ratios of 10/0, 9.5/0.5 and 9/1 was selected to study. Each TS and Alg mixture was dispersed into deionized distilled water and stirred for 2 h at room temperature (25°C) using a magnetic stirrer to ensure fully hydration of polysaccharides. Fifteen to 19 mg of each dispersion were weighed directly into a 40 μL aluminium DSC pan and the pans were hermetically sealed. The gelatinization behavior of TS and TS/Alg mixtures was investigated by heating the pans from 25°C to 110°C at the rate of 10°C/min. Another empty pan was sealed and used as a reference. The 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. After the first run heating, the gelatinized samples were cooled down to 25°C at -5°C/min and kept at 5°C for 24 days. The stored samples were heated again to study the effect of Alg on retrogradation of TS. The retrogradation ratio was calculated by dividing the re-gelatinization enthalpy of the second-run heating by the gelatinization enthalpy of the first-run. The sample was weighed before and after measurements to confirm that no weight was lost.

2.10. Statistical analysis

Each of the measurements described above was carried out using at least three freshly prepared samples, and the results are reported as the mean and standard deviation. SPSS (SPSS Inc., Chicago, IL) for windows version 11.0 program was used for analyzing the results was used to find the significnt. ANOVA and Tukey's est were used to compared difference among the mean values at 0.05 level of confidence.

2.8 **Changes in TPA parameters of tapioca starch gels containing alginate during storage**

In the texture measurements, two compression cycles were used. TS dispersions containing alginate (Alg) (0 to 1.25 wt%) were prepared at the mixing ratios of 10/0, 9.75/0.25 and 9.5/0.5 and evaluated using Texture Analyzer (TA-500, Lloyd Instruments Ltd., UK). Precisely weighed amounts of TS and XG were dispersed into deionized distilled water at the 25% w/w total polysaccharide content and stirred for 2 h at room temperature (25°C) using a magnetic stirrer to ensure fully hydration of polysaccharides. The mixtures were then degassed under vacuum for 15-30 min before partially heated to less than 65°C in a controlled temperature water bath (95°C). According to our preliminary test, to achieve partially swelling of starch by heating TS/Alg dispersions (200 g) to less than 65°C in a controlled temperature water bath (95°C) by holding at this temperature for about 2-3 min with stirring can avoid sedimentation of starch granules before subsequent full gelatinization. The hot dispersions were immediately transferred into a plastic tube (250 x 22 mm 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 95-98°C for 30 min. The gelatinized mixtures were cooled in an iced-water bath for 10 min and stored at 5°C.

The kept gels were cut into 20 mm. in height for texture profile analysis (TPA) after storage for 1, 4, 7 and 10 days. The gel sample was compressed for a distance of 6 mm (30% compression) at a speed of 0.5 mm/s with a 50 mm-diameter probe using flat plate of the Texture Analyzer (TA.XT.plus, UK.) 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. Force-deformation curves were obtained with a 5 kN load cell. The attributes reported are: hardness (N), springiness (dimensionless), cohesiveness (dimensionless).

3. Results and discussion

3.1 Effect of xanthan gum and pH on pasting properties and freeze-thaw stability of tapioca starch

3.1.1 Influence of xanthan gum and pH on RVA pasting properties of TS

The Rapid Visco-Analyser (RVA) was used to investigate the pasting properties of TS and TS/Xan mixtures during heating and cooling processes. Typical RVA pasting profiles of selected TS/Xan mixtures at pH 7 were shown in Fig. 3.1.1.

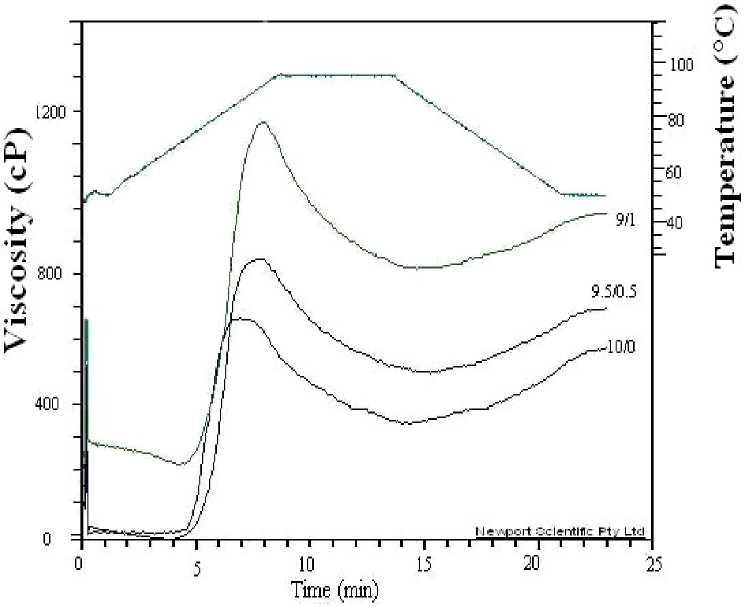


Fig. 3.1.1 Typical RVA pasting profiles of tapioca starch/xanthan gum mixtures at pH 7 with mixing ratios of 10/0, 9.5/0.5 and 9/1 (a total polysaccharide concentration of 5%).

When starch granules are heated above the gelatinization temperature in a sufficient amount of water, the granules absorb a large amount of water and swell to many times their original size and the viscosity increases. When most of the tapioca starch granules became swollen, a rapid increase in viscosity occurred. As the temperature increased further, the starch granules began to rupture and the amylose molecules leached out into the continuous phase until reaching a viscosity called the peak viscosity. The peak viscosity is considered to represent the equilibrium point between swelling and rupture of starch granules (Newport Scientific, 1995). Swelling of granules, accompanied by leaching of starch biopolymers, increased the viscosity and during further heating, granules would rupture further which resulted in a decrease in the viscosity. When the system was at the holding temperature (95 °C), the sample was subjected to mechanical shear stress, which led to further disruption of the starch granules and amylose leaching, followed at a slower rate by leaching of the amylopectin fraction. The leached-out polymer molecules were more or less aligned in the direction of flow, which contributes to a breakdown in viscosity at a constant temperature. Therefore, the reduction in the viscosity after appearance of the peak was likely to be caused by mechanical rupture of starch granules. As the sample was subsequently cooled down to 50 °C, the viscosity increased to a final viscosity at the end of RVA experiments, which was attributed to reassociation of amylose molecules or short-term retrogradation. Peak viscosity increased with xanthan gum concentration and showed no difference in the mixtures containing different pH (Fig. 3.1.2a). However, final viscosity of gelanized TS under higher acidic conditions (pH = 3) exhibited a lowest final viscosity (Fig. 3.1.2b) probably related to a more damaged granule structure at low pH. The final viscosity values of TS pastes at pH 3 increased with gum concentration and showed a lower extent of difference from those at pH 5 and 7 with increasing gum concentration. The results suggest that xanthan gum provide a good stability of TS in acid systems

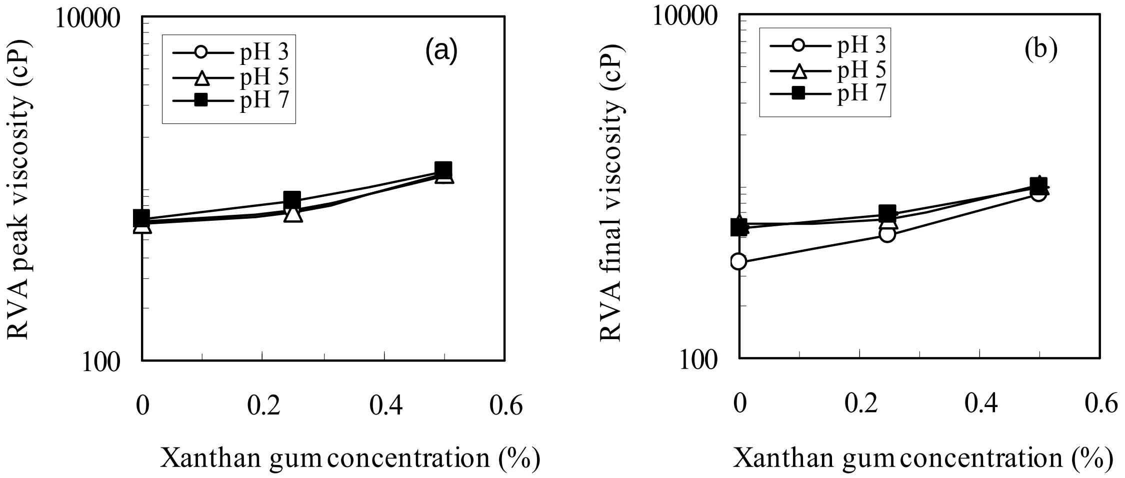


Fig. 3.1.2 RVA peak (a) and final (b) viscosities of 5%w/w tapioca starch/xanthan gum mixtures as a function of gum concentration for various pH values.

3.1.2 Influence of xanthan gum and pH on freeze–thaw stability of gelatinized TS

Freeze–thaw stability is important in the food industry. In cold chain storage, thermal fluctuations and consequent phase changes of water are the main causes of deterioration in frozen food especially in the gel matrix of starch (Pongsawatmanit et al., 2006). During cold storage, the reorganization of starch molecules may result in the release of water (or syneresis) and this may affect the functional properties in terms of viscosity or gel behavior. Repeated freeze– thaw treatment for one cycle of TS paste at pH 3 showed the highest water separation (17%) compared with those at pH 5 and 7 (10 to 11%) as shown in Fig. 3a due to the damaged granule structure during heating and starch hydrolysis promoted by acidic heat treatment (Rogols, 1986). The damage of starch network resulted in higher water separation after thawing. However, the water separations of gelatinized TS containing xanthan gum (for mixing ratios at 9.5/0.5 and 9/1) were lower than 10% for all pH studies (Fig 3.1.3b, 3c)

The thermal stability of gelatinized TS and TS/Xan pastes was investigated further with higher number of freeze–thaw cycles. After the third cycle of repeated freeze–thaw treatment, again the percentages of water separation of TS (pH 3, 5 and 7) containing xanthan gum were almost lower than 10% (Fig. 3.1.4). Percentages of water separation from TS pastes alone at pH 3 gave the highest value. This results also confirm that the substitution of a part of tapioca starch with xanthan gum improve the freeze–thaw stability of tapioca starch system under acidic condition.

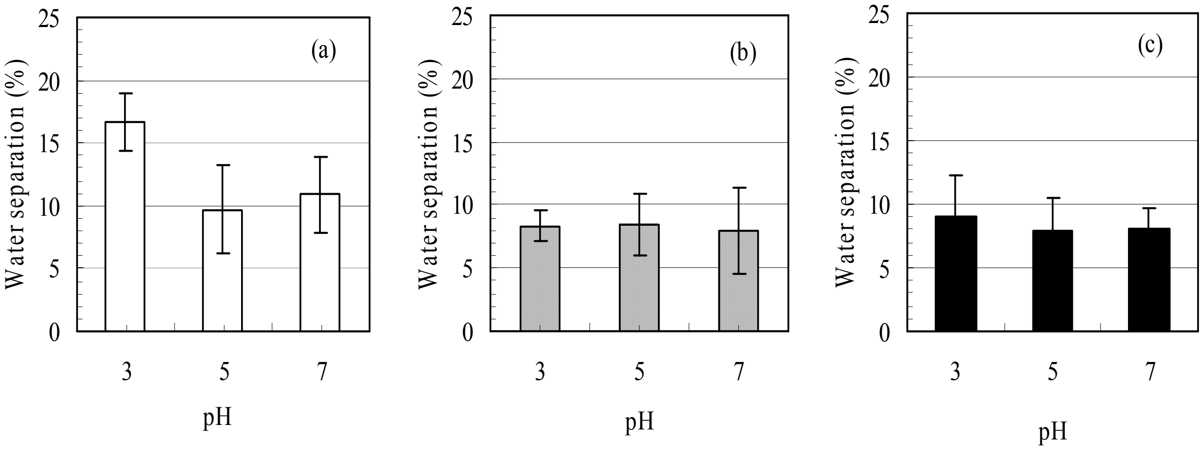


Fig. 3.1.3 Water separation of 5% w/w gelatinized tapioca starch/xanthan gum mixtures at mixing ratios of 10/0 (a), 9.5/0.5 (b) and 9/1 (c) for different pH values after freezing and thawing.

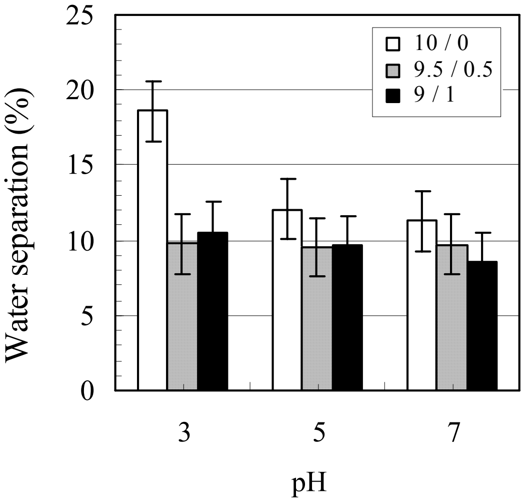
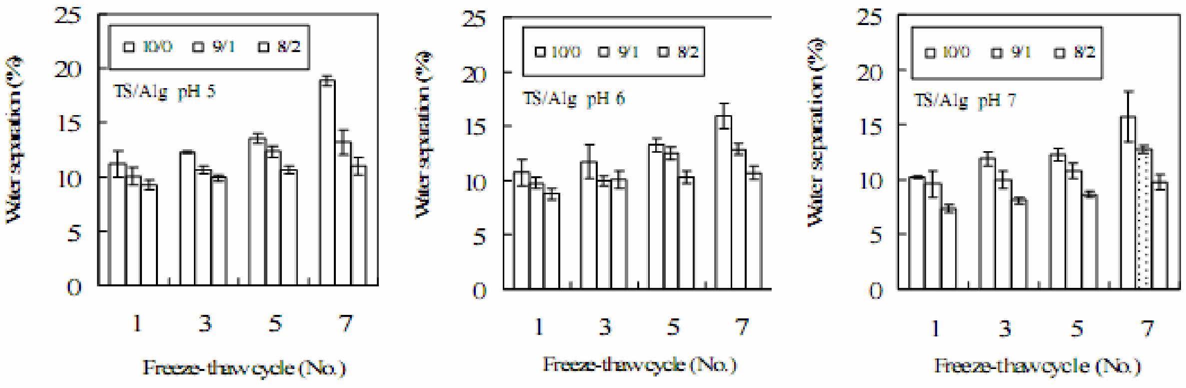


Fig. 3.1.4 Water separation of 5% w/w gelatinized tapioca starch/xanthan gum mixtures at mixing ratios of 10/0, 9.5/0.5 and 9/1 for different pH values after three cycles of repeated freeze–thaw treatment.

3.2 Freeze-thaw stability of tapioca starch and alginate mixtures at different pH

Freeze–thaw stability is important in the food industry. During cold storage, the reorganization of starch molecules may result in the release of water (or syneresis) and this may affect the functional properties in terms of viscosity or gel behavior. Water separation of TS paste alone after the seventh cycle at pH 5 showed the highest value (19%) compared with those of TS pastes at pH 6 and 7 (about 16%) (Fig. 3.2.1) suggest that the retrograded starch network or structure was easily disrupted by ice crystal formation which resulted in higher water separation on thawing (Pongsawatmanit et al., 2006; Yuan & Thompson, 1998]. The water separations of gelatinized TS containing Alg (for mixing ratios at 9/1 and 8/2) were lower than 13% after the seventh cycle for all studied pH values. Water separation values of 5% TS and TS/Alg pastes at pH 5 were higher than those at pH 6 and 7, indicating the degraded starch network occurring at the low pH resulting in larger ice crystal formation evidenced by higher water separation. These results suggest that partial substitution of TS with alginate formed a paste with improving freeze-thaw stability for pH range from 5 to 7.

Therefore, alginate can be used to formulate TS-based products containing different pH (5 to 7) with better freeze-thaw stability during product development in food industry.



(a) (b) (c)

Fig. 3.2.1 Water separation of 5% w/w gelatinized tapioca starch/alginate mixtures at mixing ratios of 10/0, 9/1 and 8/2 for different pH values pH 5 (a), pH 6 (b) and pH 7 (c) values after freezing and thawing

3.3 **Influence of temperature on viscosity of tapioca starch containing sodium alginate**

The shear viscosity of gelatinized TS/Alg was measured using a rheometer. Sample temperature was kept constant at 25 ± 0.1°C for at least 30 s before starting the measurement. At a constant temperature (25°C), the shear rate dependence of the steady shear viscosity of 5 wt% gelatinized TS/Alg mixtures at different mixing ratios (10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) and dispersion of 1 wt% Alg is shown in Fig. 3.3.1. The shear rate was increased from 0.1 to 1000 s^{-1}. All 5 wt% TS/Alg mixing ratios (10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) showed shear-thinning flow behavior in this studied range: the higher the shear rate the lower the apparent viscosity. The viscosity of the TS pastes was lower than those of the TS/Alg pastes. The TS/Alg pastes gave higher apparent viscosity with increasing Alg concentration; indicate that the steady flow behavior of TS/Alg pastes was dominated by those of Alg dissolving in the continuous phase as shown in the previous study of tapioca starch and xyloglucan mixtures (Pongsawatmanit *et al*., 2006).

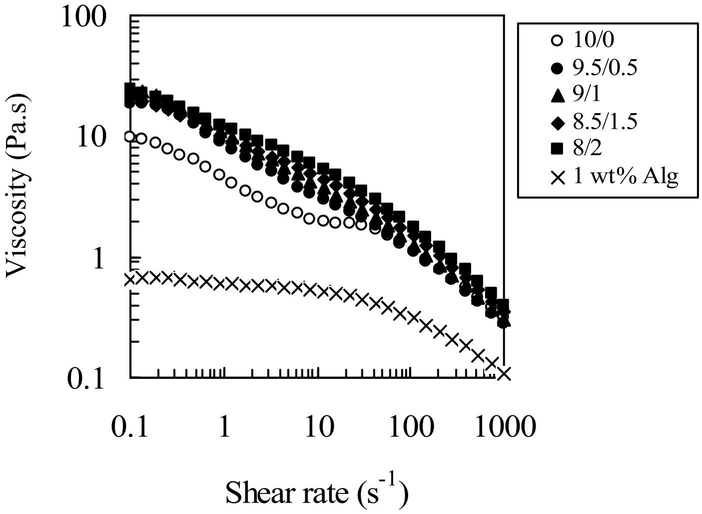


Fig. 3.3.1 Shear rate dependence of the steady shear viscosity of 5 wt% gelatinized TS/Alg mixtures at different mixing ratios of 10/0, 9.5/0.5, 9/1, 8.5/1.5, 8/2 and dispersion of 1 wt% Alg at constant temperature 25°C.

Since a wide range of temperatures are usually encountered during processing and storage of fluid foods, therefore, the influence of temperature on the apparent viscosity was studied (Fig. 3.3.2). The sample temperatures were studied at 5, 15, 25, 35, 45, and 55°C. Apparent viscosity was plotted at a shear rate of 50 s^{-1} because it has been reported as an effective oral shear rate (Morris, 1983; Marcotte *et al.*, 2001). We found that the apparent shear viscosity was decreased with increasing temperature as expected. The change in the apparent viscosity with temperature of the TS paste alone showed a higher change than those of the TS/Alg pastes.

The relationship between the steady shear stress and shear rate for all mixing ratios of TS/Alg pastes at different temperatures was analyzed by using a power law model as shown in the following equation (4):

$$\tau = K \dot{\gamma}^{n} \tag{4}$$

where τ is shear stress (Pa or N/m^2), $\dot{\gamma}$ is steady shear rate (s^{-1}), *K* is consistency index (Pa.s^n), and *n* is flow behavior index (-). The consistency index *K* is defined as the shear stress at a shear rate of 1.0 s^{-1} and the exponent *n*, the flow behavior index, is dimensionless that reflects the closeness to Newtonian flow (Rao, 1999). The *n* value is sometimes called the power law index where *n* = 1 corresponds to Newtonian fluid and the lower *n* value reflects a higher degree of pseudoplastic properties of the fluid. The power law parameters (*K* and *n*) were calculated by linear regression from a plot of log τ and log $\dot{\gamma}$ and values of *K* and *n* for all mixing ratios of 5 wt% TS/Alg are summarized in Table 3.3.1.

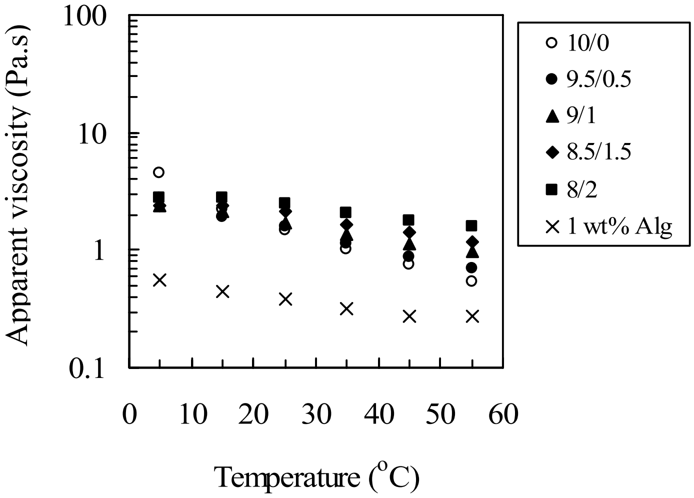


Fig. 3.3.2 Temperature dependence of apparent viscosity of 5 wt% gelatinized TS/Alg mixtures (10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) and dispersion of 1 wt% Alg for a fixed shear rate of 50 s^{-1}.

The correlation coefficients for all determinations were higher than 0.9. Considering only 1 wt% Alg dispersion, *K* values of Alg dispersion were mostly much lower than those of the 5 wt% TS and TS/Alg pastes. The *K* values of all TS and TS/Alg pastes and Alg dispersion decreased with increasing temperature. The change of *K* as a function of temperature of the gelatinized TS sample was higher than those of all gelatinized TS/Alg pastes (Fig. 3.3.3), suggest that Alg increased the thermal stability of TS/Alg pastes in terms of viscosity change with temperature.

Table 3.3.1 Power law parameters (n = power index; K = consistency index) for 5 wt% total polysaccharide content of TS/Alg at different mixing ratios and temperature determined from the shear rate range from 0.5 to 100 s^{-1}.

Dispersions	Temperature (°C)	K (Pa s^n)	n (-)	R^2
5% TS/Alg (10/0)	5	35.17 ± 0.88	0.60 ± 0.11	0.94
	15	8.22 ± 1.74	0.68 ± 0.05	0.99
	25	4.46 ± 0.88	0.72 ± 0.04	0.99
	35	3.75 ± 1.04	0.69 ± 0.05	0.99
	45	2.96 ± 0.68	0.66 ± 0.05	0.99
	55	1.98 ± 0.37	0.67 ± 0.03	0.99
5% TS/Alg (9.5/0.5)	5	28.11 ± 2.19	0.50 ± 0.05	0.93
	15	14.03 ± 0.27	0.53 ± 0.03	0.99
	25	8.70 ± 0.37	0.57 ± 0.01	0.99
	35	6.69 ± 0.09	0.58 ± 0.04	0.99
	45	4.47 ± 0.79	0.59 ± 0.04	0.99
	55	3.43 ± 0.64	0.60 ± 0.04	0.99
5% TS/Alg (9/1)	5	23.27 ± 1.09	0.48 ± 0.03	0.97
	15	14.60 ± 0.05	0.53 ± 0.01	0.99
	25	10.88 ± 1.17	0.58 ± 0.04	0.99
	35	6.79 ± 0.75	0.60 ± 0.02	0.99
	45	5.28 ± 0.50	0.61 ± 0.02	0.99
	55	4.24 ± 0.35	0.63 ± 0.01	0.99
5% TS/Alg (8.5/1.5)	5	20.45 ± 1.28	0.49 ± 0.01	0.98
	15	15.81 ± 0.51	0.55 ± 0.00	0.99
	25	10.48 ± 0.87	0.61 ± 0.00	0.99
	35	7.60 ± 0.49	0.63 ± 0.00	0.99
	45	5.76 ± 0.31	0.65 ± 0.01	0.99
	55	4.41 ± 0.18	0.67 ± 0.01	0.99
5% TS/Alg (8/2)	5	21.94 ± 1.52	0.49 ± 0.03	0.99
	15	18.45 ± 1.11	0.55 ± 0.02	0.99
	25	12.68 ± 1.04	0.61 ± 0.02	0.99
	35	9.40 ± 0.98	0.63 ± 0.02	0.99
	45	6.95 ± 0.71	0.66 ± 0.02	0.99
	55	5.63 ± 0.56	0.68 ± 0.02	0.99
1 % Alg	5	1.28 ± 0.02	0.81 ± 0.00	0.99
	15	1.15 ± 0.04	0.85 ± 0.00	0.99
	25	1.57 ± 0.08	0.88 ± 0.00	0.99
	35	2.04 ± 0.20	0.90 ± 0.02	0.99
	45	2.73 ± 0.09	0.93 ± 0.01	0.99
	55	3.12 ± 0.08	0.97 ± 0.01	0.99

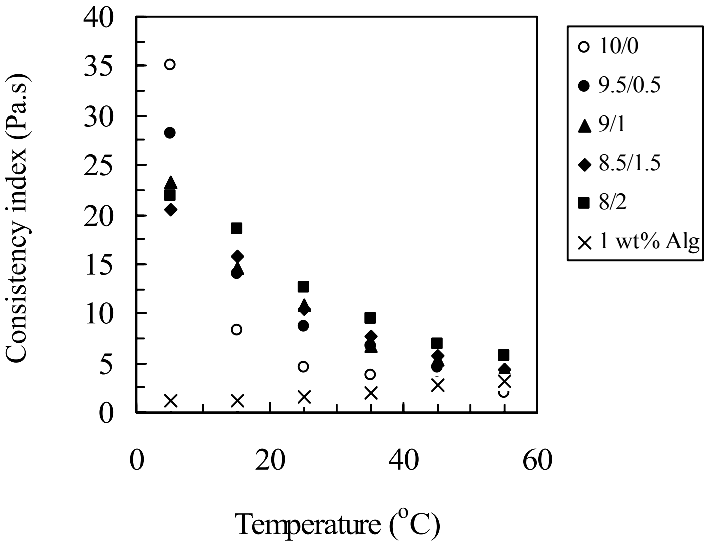


Fig. 3.3.3 Dependence of the consistency index (*K* value) on the temperature of 5 wt% gelatinized TS/Alg mixtures (10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) and dispersion of 1 wt% Alg.

For the flow behavior index, *n* values of the Alg dispersion (1 wt%) were about 0.81 - 0.97, while the magnitude of the *n* values of TS and TS/Alg pastes were lower ranging from 0.48 - 0.72, indicating that only Alg had a flow behavior which was close to Newtonian. However, this result is limited to the intermediate shear rate range because the power law model does not describe the low shear and high shear rate constant – viscosity data of shear thinning foods (Rao, 1999).

The temperature dependency of the apparent viscosity at specified shear rates of liquid or semi-solid foods can be described by the Arrhenius relationship as shown in equation (5)

$$\eta_a = \eta_{\infty A} \exp(E_a/RT) \qquad (5)$$

where η_a is the apparent viscosity at a specific shear rate, $\eta_{\infty A}$ is the frequency factor, E_a is the activation energy (J/mol), R is the gas constant (J/mol K), and T is the absolute temperature (K) (Rao, 1999). Activation energies (E_a) and correlation coefficients for the determination are shown in Table 3.3.2 using the temperature range from 15 to 55 °C. Since E_a is a parameter reflecting the sensitivity of the viscosity change due to the temperature change, gelatinized TS/Alg mixtures had a smaller temperature dependence indicated by lower E_a compared to that of TS alone. These results again suggest that Alg improved the heat stability of the TS/Alg mixtures and the viscosity of TS showed a higher sensitivity to a change in temperature compared to that of TS/Alg mixtures. Activation energies of Alg dispersion (1 wt%) were also determined at shear rate 50 s^{-1} and they were lower than that of the TS paste alone. However, we can observe that the apparent viscosity values for Alg dispersion without TS were lower than those of the 5 wt% TS/Alg mixtures.

Table 3.3.2 Activation energy for 5 wt% TS/Alg mixtures at different mixing ratios (10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) and for dispersions of Alg (1 wt%) derived from the Arrhenius relationship and evaluated at shear rates 50 s^{-1}.

Dispersions	Total concentration (wt%)	E_a (kJ/mol)	R^2
TS 10/0	5	27.43 ± 1.21	0.96
TS/Alg 9.5/0.5	5	20.72 ± 0.60	0.99
TS/Alg 9/1	5	15.96 ± 1.04	0.99
TS/Alg 8.5/1.5	5	14.24 ± 0.46	0.99
TS/Alg 8/2	5	11.67 ± 1.10	0.99
Alg	1	10.31 ± 0.34	0.95

3.4 Influence of xanthan gum on rheological properties and freeze-thaw stability of tapioca starch

3.4.1 RVA pasting properties

The pasting properties of 5% w/w TS/Xan mixtures (TS/Xan = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) were investigated during heating and cooling processes using RVA. Typical RVA pasting profiles of TS/Xan mixtures were affected by the addition of Xan (Fig. 3.4.1). Xan dispersions showed no peak or viscosity change in the RVA experiment indicating that pasting properties are related to the gelatinization of starch-based samples during the temperature change of RVA profiles. Pasting temperatures of TS/Xan were increased significantly compared with those of TS alone (about 71°C) ($p<0.05$, Table 3.4.1). The pasting temperatures of TS increased with increasing xanthan gum substitutions. The results suggest that xanthan gum alters the gelatinization temperature of TS, indicating that there are some interactions between xanthan gum and TS. In addtion, available water for gelatinization is reduced due to the increase in hydration of xanthan gum assumed to be located in the continuous phase leading to the higher pasting temperatures (Hirashima, Takahashi, & Nishinari, 2005).

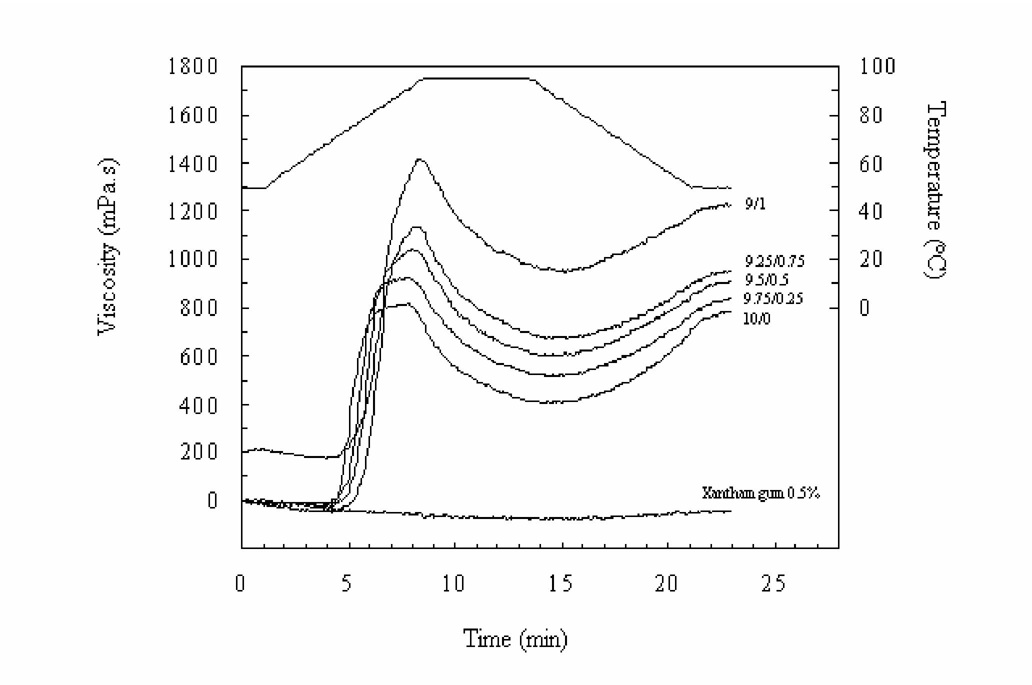


Fig. 3.4.1 Typical RVA pasting profiles of TS/Xan mixtures at different mixing ratios of 5% w/w total polysaccharide concentration.

Table 3.4.1 Pasting characteristics of TS/Xan (5% w/w total polysaccharide content) at different mixing ratios determined by Rapid Visco Analyser (RVA).

TS/Xan mixture ratop	Pasting temperature (°C)	Peak viscosity (mPa.s)	Breakdown (mPa.s)	Final viscosity (mPa.s)	Setback (mPa.s)
10/0	71.3±0.5d	818±2.3e	425±10.0c	784±16.2e	391±15.1a
9.75/0.25	72.8±0.9c	924±21.0d	413± 7.0 c	833±16.2d	323±3.9 b
9.5/0.5	74.2±0.3b	1036±17.5c	444±10.4b	905± 8.4 c	313±3.2 b
9.25/0.75	76.1±0.5a	1132±9.8 b	476±9.0 a	951±17.7b	289±6.4 c
9/1	76.7±1.0a	1429±16.0a	482±15.7a	1219±24.0a	272±3.0 d

Mean ± standard deviation values (n = 3) followed by different letters within the same column are significantly ($p<0.05$) different by Duncan's multiple range test.

The synergistic effect of TS/Xan systems resulted in higher RVA peak viscosities (Table 3.4.1). During heating of gelatinization process, the increase in starch granule swelling led to the lower volume of water to interact with xanthan gum assumed to be in the continuous phase resulted in a pronounced increase in the mixture viscosity (Alloncle, Lefebvre, Llamas, & Doublier, 1989) from about 820 to 1430 mPa·s for TS alone and TS containing 0.5% Xan, respectively. The increase in viscosity was about 74% in comparison with that of TS paste. When the system was maintained at 95°C, the mixtures were subjected to both thermal and shear stress, which led to both further disruption of the starch granules and leaching out of starch molecules causing a greater 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) defined as breakdown, increased from 425 to 480 mPa·s for TS alone and TS containing 0.5% Xan, respectively (Table 3.4.1). The increase in viscosity of TS/Xan suspensions creates the shear forces exerted on the swollen starch granules in the shear field greater than that encountered in TS-water system. This results in the loss of starch granule integrity and subsequent disruption leading to a reduction of the paste viscosity (Christianson et al. 1981). The viscosity reduction of TS pastes containing Xan under the influence of applied shear to TS/Xan mixtures, indicating the formed aggregates of xanthan molecules in the pastes through hydrogen bonding and polymer entanglement were disrupted under the shear with increasing gum content (Sworn, 2000).

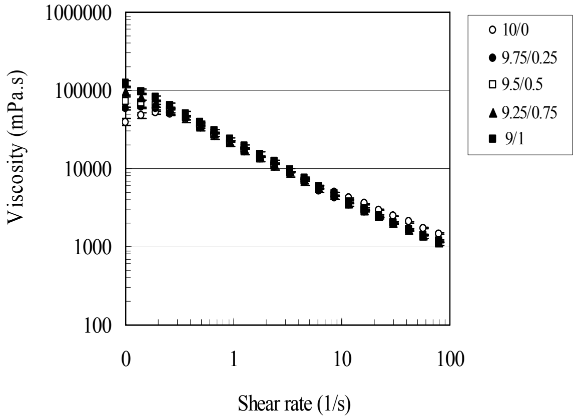
When the sample was subsequently cooled down to 50°C at 6°C/min, the viscosity of the pastes increased to a final viscosity at the end of RVA experiments. Final viscosities of TS/Xan increased with increasing Xan content ($p<0.05$). The increase in viscosities of TS and TS/Xan pastes from holding strength values to final viscosity called setback occurs not only due to the simple kinetic effect of cooling on viscosity, but also due to the reassociation of starch (particularly amylose) molecules. Addition of xanthan gum resulted in significant decrease in setback of TS/Xan pastes ($p<0.05$, Table 3.4.1). Usually, high setback is associated with syneresis during freeze-thaw cycles and is used to indicate the extent of short-term retrogradation. These results suggest that short term retrogradation of TS/Xan mixtures can be depressed by xanthan gum even at low concentration.

3.4.2 Steady shear viscosity of TS/Xan pastes

At a constant temperature (25°C), the shear rate dependence (0.1 to 100 s^{-1}) of the steady shear viscosity of gelatinized TS with and without Xan exhibited shear thinning behavior (Fig. 3.4.2a). The viscosities of TS were lower than those containing Xan at very low shear rates but revealed the higher values at higher shear rates due to the strong pseudoplastic behavior of the xanthan gum contributing to the TS pastes.

When viscosity measurement of 5% w/w TS and TS/Xan pastes was performed at higher temperature (50°C), the shear thinning behaviors were also obtained (Fig. 3.4.2b). However, the viscosities of TS were lower than those containing Xan in the studied shear rate range (0.1 to 100 s^{-1}). The TS/Xan pastes showed a smaller viscosity reduction with an increase in the Xan content, indicating the thermal stability of xanthan gum contributing to TS pastes.

(a)



(b)

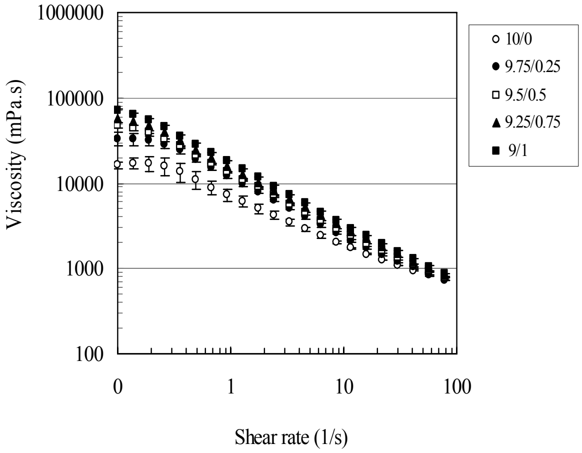


Fig. 3.4.2 Shear rate dependence of the steady shear viscosity of 5% w/w gelatinized TS/Xan mixtures at different mixing ratios of 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1 for 25°C (a) and 50°C (b). The vertical bar represents the standard deviation

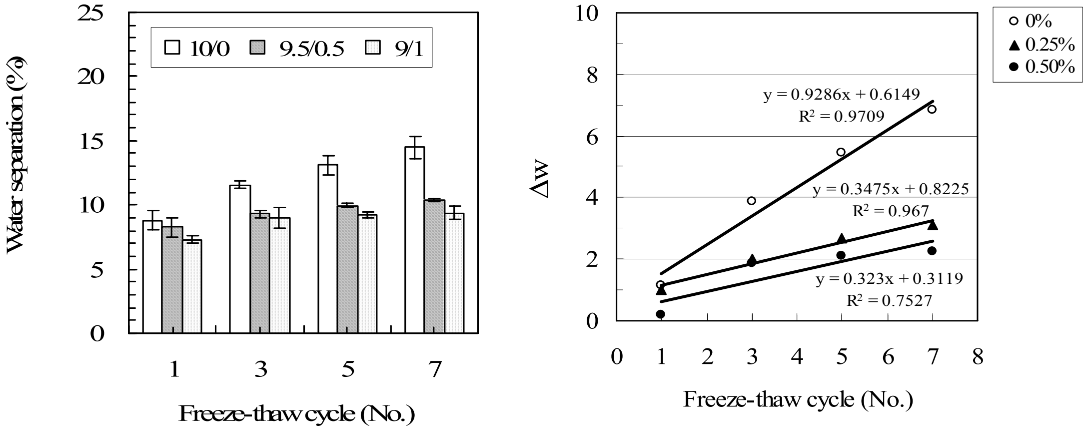
3.4.3 Freeze-thaw stability

Freeze–thaw stability is important in food industry. In cold chain storage, thermal fluctuations and consequent phase changes of water are the main causes of deterioration in frozen food especially in the gel matrix of starch (Pongsawatmanit et al., 2006). During cold storage, the reorganization of starch molecules may result in the release of water (or syneresis) and this may affect the functional properties in terms of viscosity or gel behavior. The water separation from the gelatinized TS pastes increased with increasing numbers of freeze-thaw cycles (Fig. 3.4.3a). The results suggest that the retrograded starch network or structure was easily disrupted by ice crystal formation which resulted in higher water separation on thawing (Pongsawatmanit et al., 2006; Yuan & Thompson, 1998). In this study, water separation from the gelatinized TS paste increased from 8.8 to 14.5% after 1 to 7 freeze-thaw cycles, respectively but our previous studied reported the water separation from TS pastes increased from 8 to about 20%. This difference in the water separation is expected from the difference of cassava cultivar, time and conditions at harvest leading to the difference in physicochemical properties of tapioca starch (Sriroth, Santisopasri, Petchalanuwat, Kurotjanawong, Piyachomkwan, & Oates, 1999).

For the 5% TS/Xan pastes at mixing ratios of 9.5/0.5 and 9/1 (containing 0.25% and 0.5% Xan, respectively), water separation was lower than that of the 5% TS paste after the first freeze-thaw cycle. In addition, the degree of water separation from gelatinized TS/Xan mixtures compared with that of TS paste decreased with an increase in the gum content, indicating that Xan dissolved in the continuous phase reduced the reassociation of starch molecules and this reduction in the damage to the network led to less syneresis. The results suggest that xanthan gum minimized freeze-thaw damage by reducing the available water to form ice crystals. This confirms that partial substitution of TS with xanthan gum formed a paste with improving freeze-thaw stability.

The increase in water separation as a function of repeated freeze-thaw cycles from TS and TS/Xan pastes is characterized in terms of the change in water separation: $\Delta w = w_i - w_o$ where w_i and w_o are the water separation values from thawed pastes after repeated freeze-thaw cycle i and zero (before freezing), respectively. The w_o values of TS/Xan pastes before freezing were 7.66, 7.24 and 7.11% for pastes containing 0, 0.25 and 0.5% Xan, respectively.

The change in water separation (Δw) from TS pastes alone was the highest compared with those containing Xan at any given freeze-thaw cycle. The Δw of TS pastes alone was more dependent on the number of freeze-thaw cycles than those containing Xan about 3 times evidenced by the slopes of TS (~0.93) and TS/Xan pastes (~ 0.32-0.35) as shown in Fig. 3.4.3b. The results again confirm the better freeze-thaw stability of xanthan gum contributing to TS pastes.



(a) (b)

Fig. 3.4.3 Water separation (a) and the change of water separation (Δw) (b) of 5% w/w gelatinized TS/Xan mixtures at selected mixing ratios of 10/0, 9.5/0.5 and 9/1 as a function of number of freeze-thaw cycles. The vertical bar represents the standard deviation

3.4.4 Correlation analysis and regression model

All correlations among RVA parameters and water separation from different freeze-thaw cycles for the TS/Xan mixtures (TS/Xan = 10/0, 9.5/0.5 and 9/1) are listed in Table 3.4.2. All values are significant correlation at $p<0.05$. Xanthan gum, pasting temperature, peak viscosity, final viscosity and breakdown have a significant positive correlation to each other and a significant negative correlation to setback and the water separation values after 1, 3, 5 and 7 freeze-thaw cycles.

Table 3.4.2 Correlation matrix between RVA parameters and water separation at different freeze-thaw cycles.

	Xanthan gum	Peak viscosity	Final viscosity	Setback	Pasting temperature	Trough	Breakdown	Cycle 1	Cycle 3	Cycle 5	Cycle 7
Xanthan gum	1.000										
Peak viscosity	0.986*	1.000									
Final viscosity	0.966*	0.994*	1.000								
Setback	-0.973*	-0.929*	-0.889*	1.000							
Pasting temperature	0.971*	0.954*	0.921*	-0.965*	1.000						
Trough	0.986*	0.999*	0.995*	-0.930*	0.948*	1.000					
Breakdown	0.906*	0.927*	0.905*	-0.849*	0.922*	0.910*	1.000				
Cycle 1	-0.763*	-0.739*	-0.701*	0.822*	-0.830*	-0.740*	-0.666*	1.000			
Cycle 3	-0.859*	-0.779*	-0.714*	0.932*	-0.852*	-0.775*	-0.747*	0.697*	1.000		
Cycle 5	-0.922*	-0.850*	-0.800*	0.959*	-0.895*	-0.850*	-0.781*	0.700*	0.931*	1.000	
Cycle 7	-0.887*	-0.821*	-0.758*	0.963*	-0.918*	-0.817*	-0.787*	0.865*	0.942*	0.935*	1.000

* Correlation is significant at the 0.05 level (2-tailed), $p<0.05$.

Setback and water separation at the specified freeze-thaw cycles have a positive correlation each other. Therefore, we plotted the experimental water separation values from TS and TS/Xan pastes as a function of setback and specified freeze-thaw cycles (Fig. 3.4.4). Since the mechanism for explaining the setback and water separation from freeze-thawed pastes is the retrogradation or starch reassociation of starch biopolymers in the TS or TS/Xan mixtures, the linear regression was conducted to relate the RVA setback and water separation to predict response/dependent variable (*Y: water separation*) from a set of explanatory/independent variables (*X: RVA setback and number of freeze-thaw cycles*). The linear regression analysis yielded an equation (6) for predicting water separation as shown below:

$$\text{Water separation (\%)} = -2.269 + 0.522\,(\text{cycle}) + 0.032\,(\text{setback}) \qquad (6)$$

To test the model performance, another groups of experiment data were carried out with newly prepared TS/Xan pastes (TS/Xan = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) for determining the water separation of the pastes after repeating freeze-thaw treatment for one to eight cycles. The experimental water separation values were plotted against those calculated from equation (2) using the RVA setback (Table 3.4.1) and specified freeze-thaw cycles (Fig. 3.4.5). A good predictability of the property at various freeze-thaw cycles between the modeling dataset and testing dataset was achieved, indicated by the corresponding correlation coefficient (R = 0.925) and small mean square error (MSE = 0.274) values between them. We did not present the quadratic regression equation due to a low correlation coefficient of the model testing.

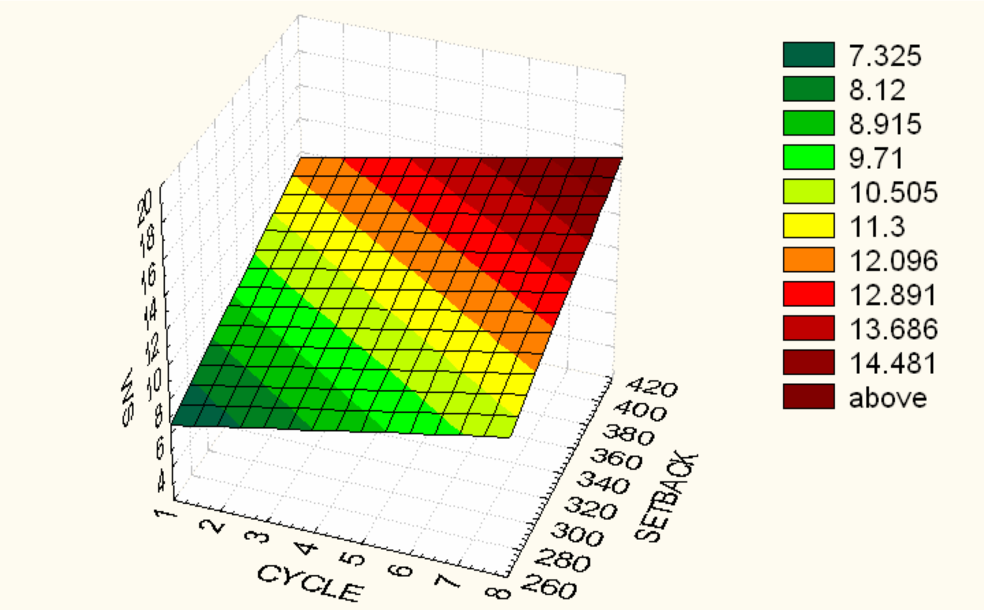


Fig. 3.4.4 Surface plot of experimental water separation as a function of freeze-thaw cycles and setback values of gelatinized TS/Xan pastes at different mixing ratios of 10/0, 9.5/0.5 and 9/1

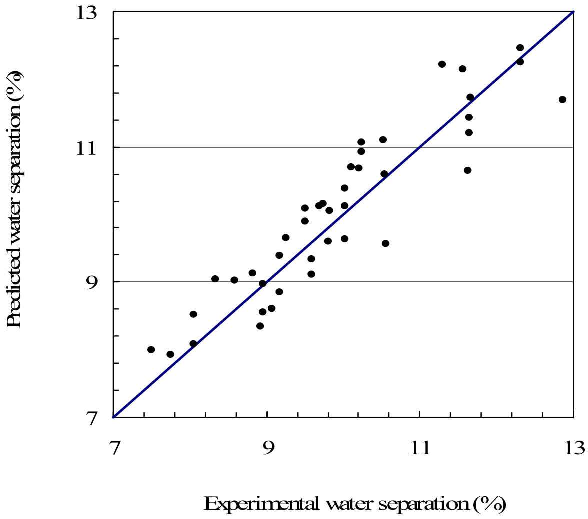
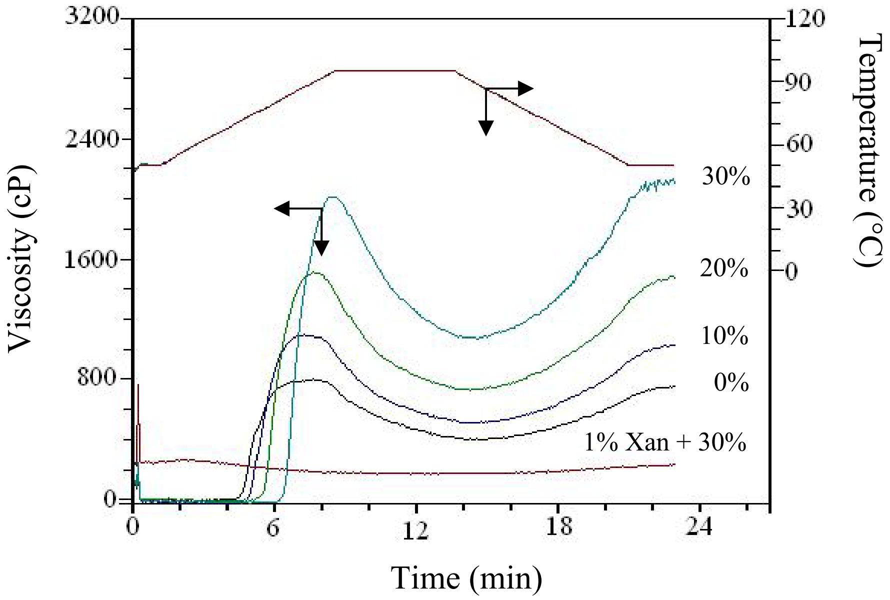


Fig. 3.4.5 Predicted water separation using equation (2) versus experimental water separation from gelatinized TS/Xan pastes at different mixing ratios (10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) (R= 0.925, MSE = 0.274).

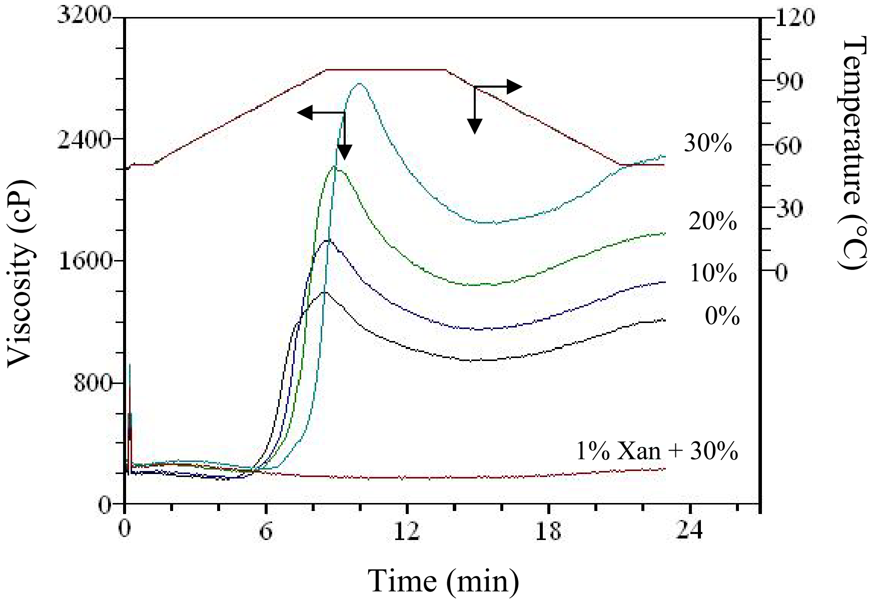
3.5 Influence of xanthan gum and sucrose on the pasting properties of tapioca starch

3.5.1 RVA pasting properties

Changes in the pasting properties of starch during heating and cooling processes can alter the qualities of final starch-based products by addition of hydrocolloids and sugars. The pasting properties of 5% w/w TS/Xan mixtures (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 investigated during RVA experiment. The concentrations of xanthan gum used in the study are ranged from 0-0.5% due to the common concentration range applied in food products (Sharma, Naresh, Dhuldhoya, Merchant & Merchant, 2006). 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. 3.5.1). RVA pasting properties are related to the gelatinization and short-term retrogradation of starch-based samples during heating and cooling since no peak of curve was observed in the mixture of 1%Xan containing 30% sucrose. The correlations among sucrose and RVA parameters were analysed and revealed significant positive correlations ($p<0.05$) (Table 3.5.1). Pasting temperatures of TS/Xan pastes increased significantly with sucrose content ($p<0.05$, Table 3.5.2). The results suggest that sucrose reduces the available water in the system and exhibits as an anti-plasticising agent leading to the lower amount of amylose leaching and causing the retardation in gelatinization of TS and TS/Xan mixtures (Ahmad & Williams, 1999; Kohyama & Nishinari, 1991). In addition, a decrease in water content in TS/Xan mixtures containing higher sucrose contents requires higher energy to gelatinization due to such anti-plasticising effect of sucrose (Pongsawatmanit et al., 2007) and leading to higher pasting temperatures (Table 3.5.2) (Hirashima, Takahashi & Nishinari, 2005), Sucrose may play an important role in the inhibition of hydration for starch granules or non-starch polysaccharide fraction (Yoshimura, Takaya & Nishinari, 1996). Therefore, in the systems containing higher concentration of sugar, the competition between sucrose and xanthan gum to be hydrated by water in the 5% w/w of total polysaccharides may be critical and leading to increase the pasting temperatures of TS/Xan mixtures from 72 - 78 to 82 - 90 °C with increasing sucrose concentration from 0 to 30%, respectively (Table 3.5.2).



(a) TS only



(b) TS/Xan = 9/1

Fig. 3.5.1 Typical RVA pasting profiles of 5% w/w TS (a) and 5% w/w TS/Xan mixtures (mixing ratio = 9/1) (b) with added sucrose (0 to 30%). RVA profile of 1% xanthan gum containing 30% sucrose also included

Table 3.5.1 Pearson's correlation between selected RVA parameters and 5% TS/Xan mixtures containing different sucrose contents (0 to 30%).

RVA parameters	Sucrose
Pasting temperature	0.850*
Peak viscosity	0.903*
Breakdown	0.985*
Final viscosity	0.954*
Setback	0.723*

* Correlation is significant at the 0.05 level (2-tailed), *p<0.05*.

Table 3.5.2 Effect of sucrose on pasting temperatures of 5% w/w TS alone and 5% w/w TS/Xan mixtures at various mixing ratios from RVA analysis

Xanthan gum concentration (%)	Pasting temperature (°C)*			
	0%	10%	20%	30%
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.

The viscosity at the peak of RVA profile called 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 peak and final viscosities of the gum-starch pastes (p<0.05*)* much higher than the influence of xanthan gum substitutions (Figs. 3.5.2a and 2b), indicating that the synergistic effect of sucrose and TS or TS/Xan systems is dominant.

After TS or TS/Xan mixtures 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) is determined and defined as breakdown due to the loss of starch granule integrity and subsequent disruption leading to a reduction of the paste viscosity (Christianson et al. 1981). The breakdown of TS/Xan pastes revealed almost constant with increasing Xan substitution ($p>0.05$). However, breakdown values of TS or TS/Xan pastes increased significantly with sucrose content ($p<0.05$, Fig. 3.5.2c, Table 1) 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 were more prone to be disrupted under isothermal shear with increasing sucrose content.

When the sample was subsequently cooled down to 50°C at 6°C/min, the viscosity of the pastes increased to a final viscosity at the end of RVA experiments. The increase in viscosities of TS and TS/Xan pastes from holding strength values to final viscosity called setback occurs not only due to the simple kinetic effect of cooling on viscosity, but also due to the reassociation of starch (particularly amylose) molecules. Setback values indicating short-term retrogradation increased with increasing sucrose and decreased with xanthan gum contents ($p<0.05$) (Fig. 3.5.2d). The effect of xanthan gum on the extent of decrease in setback values of TS/Xan pastes with and without added sucrose was also observed. Setback values for TS and TS/Xan (4.5% TS, 0.5% Xan) pastes without added sucrose were about 360 mPa.s, and 260 mPa.s, respectively while setback values of those pastes containing sucrose (30%) were 1050 mPa.s and 440 mPa.s, respectively. The results imply that for the TS-based formulation containing sucrose, the xanthan gum addition could reduce the setback of the TS pastes leading to lower syneresis especially in the case of frozen food (Pongsawatmanit & Srijunthongsiri, 2008).

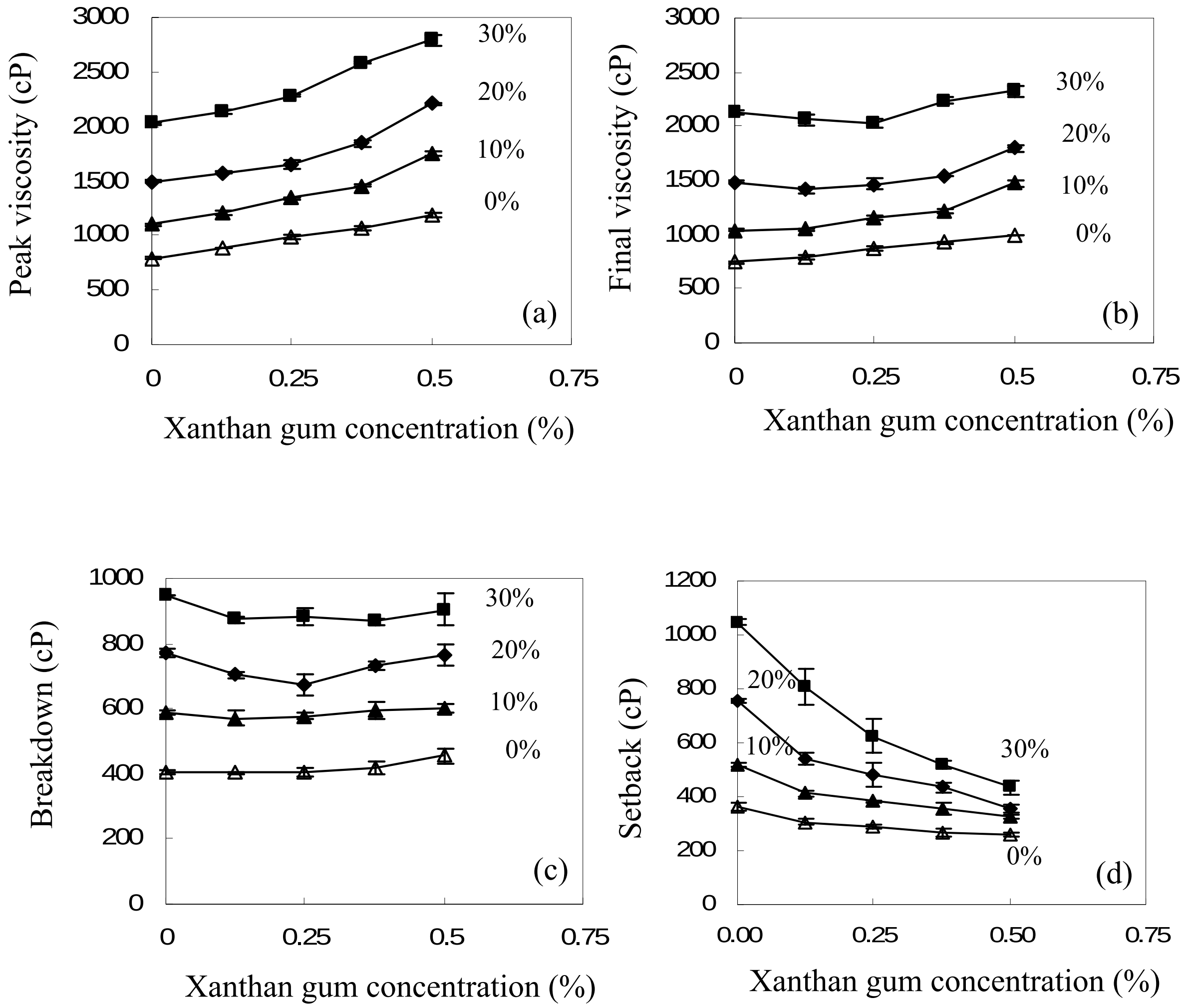


Fig. 3.5.2 Influence of sucrose on peak viscosity (a), final viscosity (b), breakdown (c) and setback (d) of 5% w/w TS/Xan mixtures at mixing ratios of 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75, and 9/1

3.5.2 Analysis of viscosity breakdown under RVA isothermal shear stress

Pasting viscosities of each TS/Xan paste with and without added sucrose were selected from RVA running time at 600 to 780 s during heating at 95°C for calculating the rate of viscosity breakdown from slope of the curve. The slope of each TS/Xan mixture was assumed to be linear relationship and plotted as a function of xanthan gum concentration (Fig. 3.5.3). The rates of viscosity breakdown for TS/Xan mixtures (0% sucrose) only slightly increased with xanthan gum concentration whereas relatively large increase of the values was observed from TS/Xan mixtures containing sucrose, especially from higher sucrose content. The slopes of the plots in Fig. 3.5.3 were noticeably increased with sucrose content. We have observed that the breakdown values of various TS/Xan mixtures containing the same sucrose content were almost constant (Fig. 3.5.2c). However, the effect of sucrose on the rate of viscosity breakdown of the system was more pronounced with increasing both concentrations of sucrose and xanthan gum.

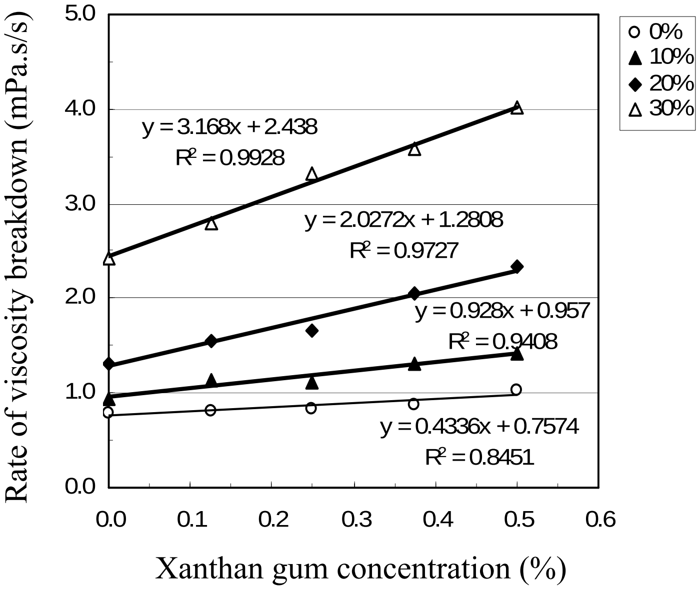
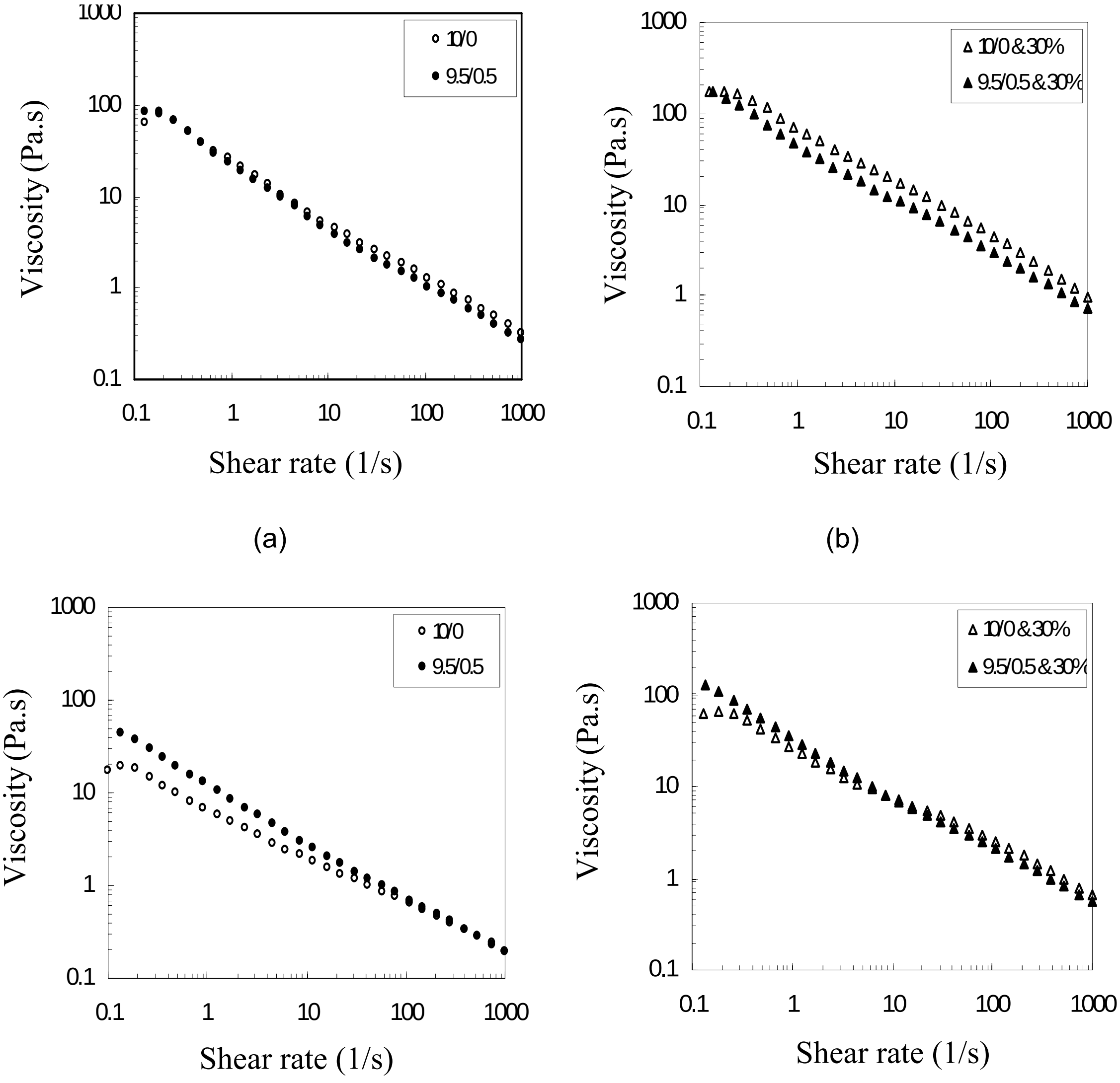


Fig. 3.5.3 Rate of viscosity breakdown calculated from RVA pasting profiles of 5% w/w TS/Xan mixtures at mixing ratios of 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75, and 9/1 containing different sucrose contents during heating at 95 °C with RVA paddle speed at 160 rpm

3.5.3 Steady shear viscosity of TS/Xan pastes

Gelatinized TS and TS/Xan pastes at various mixing ratios containing sucrose (0 to 30%) from RVA experiments was used to evaluate shear rate dependence of the steady shear viscosity. At a constant temperature (25°C), the shear rate dependence (0.1 to 1000 s^{-1}) of the steady shear viscosity of gelatinized TS and TS/Xan exhibited shear thinning behavior (Fig. 3.5.4). Selected TS/Xan paste (mixing ratio = 9.5/0.3) revealed the stronger pseudoplastic behavior than that of TS paste (Fig. 3.5.4a) due to the contribution of xanthan gum to the TS pastes (Pongsawatmanit & Srijunthongsiri, 2008). Adding sucrose (30%) enhanced the viscosity values of both TS and TS/Xan pastes. In addition, the viscosities of TS paste were higher than those of TS/Xan paste at all studied shear rates (Fig. 3.5.4b).

When the viscosity measurement of 5% w/w TS and TS/Xan pastes was performed at higher temperature (50°C), the shear thinning behaviors were also obtained. However, the viscosities of only TS pates were lower than those of pastes containing xanthan gum in the studied shear rate range (0.1 to 1000 s^{-1}) (Fig. 3.5.4c). The addition of sucrose (30%) enhanced steady shear viscosity of both TS and TS/Xan pastes (Fig. 3.5.4d). However, at higher temperature, viscosities of TS/Xan were also higher than those of TS pastes at low shear rates due to higher pseudoplastic behavior of xanthan gum in TS/Xan mixtures. The results also represent the thermal stability of xanthan gum contributing to TS pastes.



(a) (b)

(c) (b)

Fig. 3.5.4 Shear rate dependence of the steady shear viscosity of 5% w/w gelatinized TS/Xan mixtures (mixing ratios = 10/0, 9.5/0.5) with and without sucrose at 25 and 50°C: Measurement at 25°C without sucrose (a), at 25°C with 30% sucrose (b), at 50°C without sucrose (c) and at 50°C with 30% sucrose (d). The vertical bar represents the standard deviation

3.5.4 Specific viscosity of TS/Xan/sucrose

Specific viscosity represents the increase in viscosity that may be contributed by the polymeric solute. For polymer dispersions, the specific viscosity (η_{sp}) is equal to the relative viscosity of the same solution minus one and can be rearranged and calculated from the following equation (7):

$$\eta_{sp} = (\eta - \eta_s) / \eta_s \qquad (7)$$

where η = viscosity of the TS/Xan/Sucrose system, η_s = viscosity of the solvent (sucrose and water). Values of the specific viscosity are considered to be the contribution of the polymer to viscosity (Pongsawatmanit, Ikeda & Miyawaki, 1999), reflecting the effective volume occupied by polymers in the system. In TS/Xan/Sucrose/water systems, the contribution of TS and Xan to solution viscosity can be determined using viscosity values of the sucrose solution as η_s. The specific viscosities of TS/Xan pastes containing different sucrose contents (0 to 20%) at 50 °C calculated from both RVA final viscosity (Fig. 3.5.5a) and steady shear viscosity at shear rate 57.4 s^{-1} (Fig. 3.5.5b) were plotted as a function of xanthan gum concentration in total polysaccharide concentration at 5%. An average shear rate of the RVA experiment was estimated from the value of 21.5 multiplied by the angular velocity given in revolutions per second (modified from Lai, Steffe & Ng, 2000). In this study, steady shear viscosities at 57.4 s^{-1} was used to compare with the RVA final viscosity because this shear rate is approximately corresponding to the shear rate obtained from RVA at 160 rpm. The results from both types of measurement methods exhibited a single master curve (Fig. 3.5.5), indicating the effect of sucrose (0 to 20%) on the specific viscosity values was relatively small.

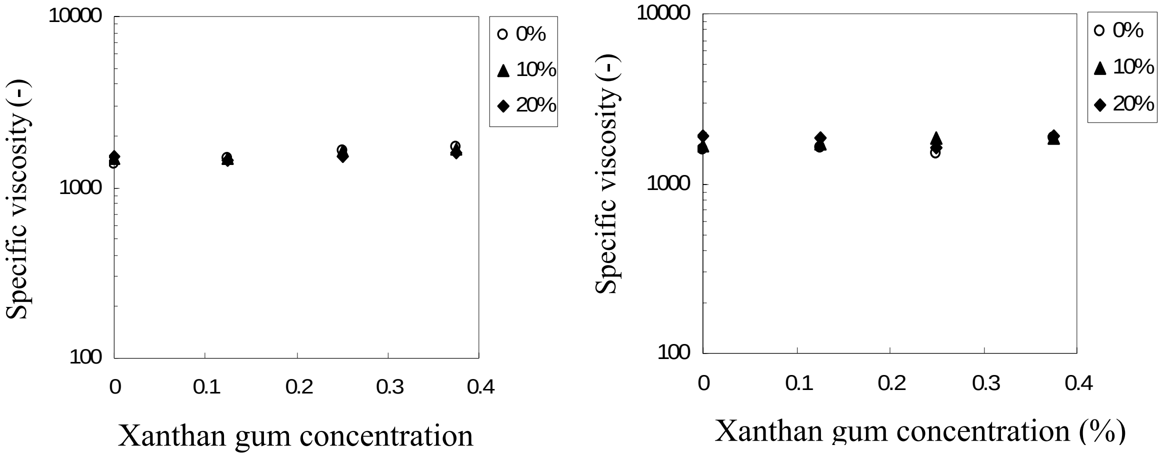


Fig. 3.5.5 Specific viscosity of 5% w/w TS/Xan pastes containing different sucrose contents measured at 50 °C from RVA (a) and steady shear (b) measurement. The viscosity of solvent used to calucate specific viscosity obtained from the viscosity of sucrose solution (0 to 30%) at 50 °C

3.5.5 Regression model and model validation of final viscosity

Final viscosity plays an important role in the colloidal system stabilization and product handling in food industry. The final viscosity of TS paste depends on both xanthan and sucrose contents in the system as discussed in the previous sections. Therefore, we plotted the experimental RVA final viscosity from TS and TS/Xan pastes as a function of xanthan gum and sucrose concentrations (Fig. 3.5.6). Since the mechanism for explaining the final viscosity depending on the amount of hydrocolloids and sucrose in the TS/Xan/Sucrose mixtures, the linear regression was conducted to relate the RVA final viscosity with xanthan gum 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 an equation (8) for predicting final viscosity as shown below:

$$\text{Final viscosity (cP)} = 712.417 + 355.267\,(\text{Xan}) + 42.303\,(\text{Sucrose}) \qquad (8)$$

Where Xan = xanthan gum concentration ranged from 0 to 0.5% and
Sucrose = sucrose concentration ranged from 0 to 30%

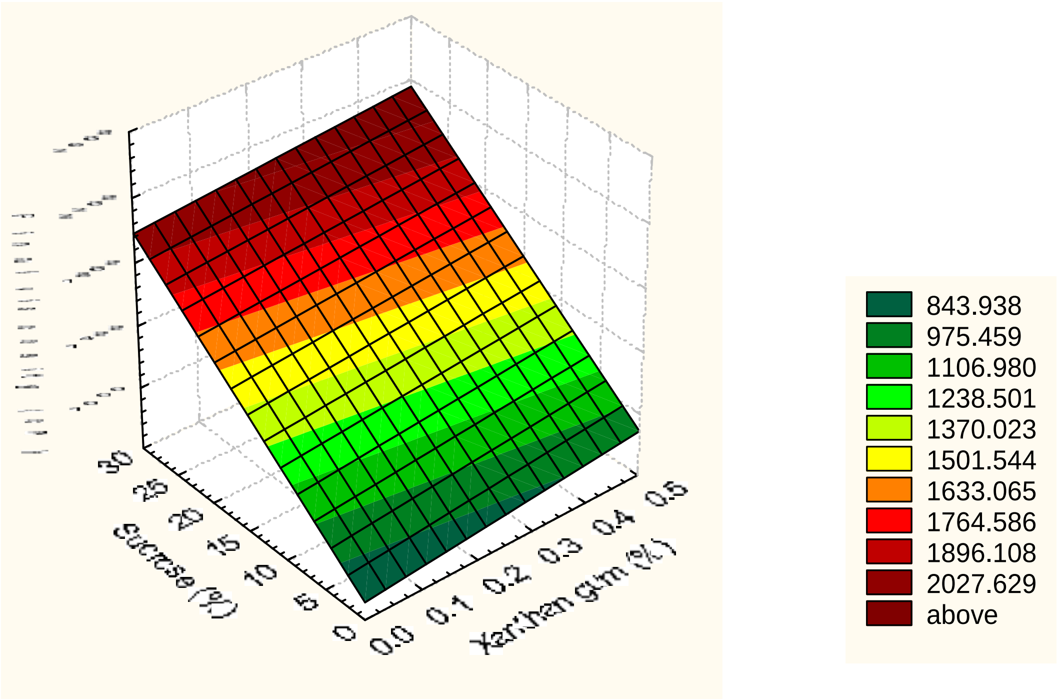


Fig. 3.5.6 Surface plot of experimental final viscosity of 5% TS/Xan pastes at different mixing ratios (10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) as a function of xanthan gum (0 to 0.5%) and sucrose (0 to 30%) concentrations.

To test the model performance, another group of RVA experiment data was carried out 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%) for determining the final viscosity. Experimental final viscosity values were plotted against those calculated from Eq. (2) using the different xanthan gum and sucrose contents. A good predictability of the viscosity at various sucrose and xanthan gum concentrations between the modeling dataset and testing dataset was achieved, indicated by the corresponding correlation coefficient (R = 0.980) and small root mean square error (RMSE = 84.4) values between them as shown in the Fig. 3.5.7a.

We also tested the model from Eq. (8) for predicting the steady shear viscosity of TS/Xan/Sucrose/water system, the result revealed that model from Eq. (2) predict the steady shear viscosity values of TS/Xan pastes containing sucrose 0 to 20% (lower than 2000 mPa.s) slightly lower than those from the experimental data with the R = 0.9039 and RMSE = 170.9 (Fig. 3.5.7b).

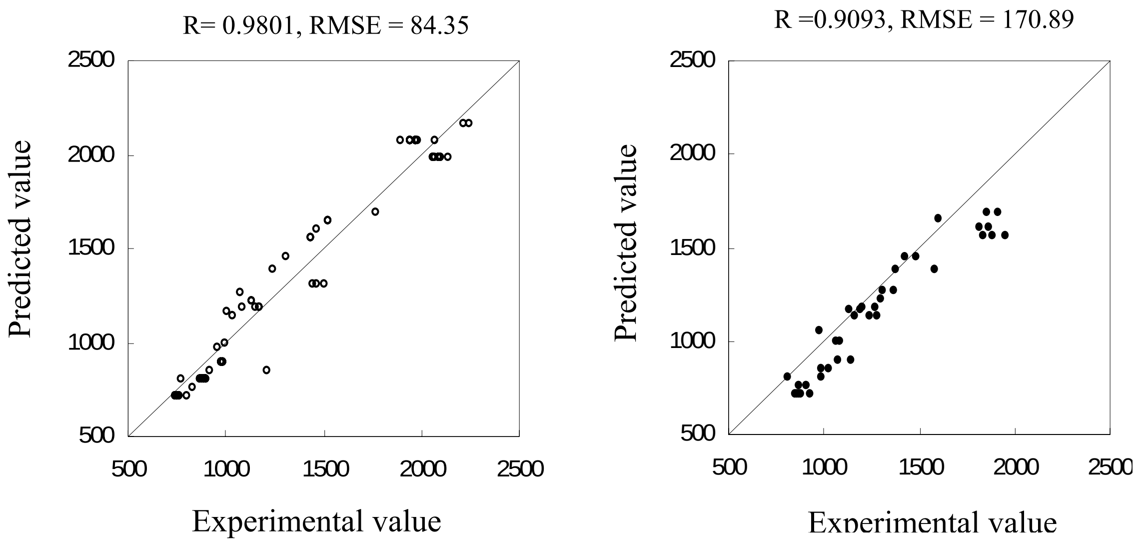


Fig. 3.5.7 Predicted final viscosity using Eq. (8) against experimental RVA final viscosity (a) and steady shear viscosity (b) from 5% w/w gelatinized TS/Xan pastes at different mixing ratios (10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) containing various sucrose concentrations.

3.6 Thermal properties and storage stability of tapioca starch containing alginate

3.6.1 Swelling power, water soluble index and amylose leaching

When starch is heated in excess water, the crystalline structure is disrupted due to the breakage of hydrogen bonds, and water molecules are linked by hydrogen bonding to the exposed hydroxyl group of amylose and amylopectin This causes an increase in granule swelling and solubility. Swelling power and solubility give the information of the magnitude of interaction between starch chains within the amorphous and crystalline areas. The extent of this interaction is influenced by the many factors such as amylose content of sample, amylose and amylopectin structure, degree of granulation.

Swelling power after heating 1 % TS or TS/Alg dispersions in excess water (TS/Alg = 10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) to 95°C for 30 min, is defined as the ratio of the wet weight of the sedimented gel formed to its dry weight. The SP (45%) from this study was a higher degree of swelling for cassava starch (tapioca starch) (swelling power was 23%) heated to 95 °C for 3% tapioca starch reported by Moore, Amante & Soldi (2005). The result indicated that the concentration of starch affect starch-water interaction. The swelling power (SP) of the tapioca starch containing different concentrations of alginate, measured at 95C was lower than TS alone (Fig. 3.6.1).

Water soluble index was lower with increasing alginate content (Fig. 3.6.1b). The results can be explained by the restrict of gum on the leaching out of soluble solid from starch. When, the well-known deep blue complex formed with idoine involves amylose in a helical conformation was carried out, the amylose leaching of TS/Alg was lower with increased gum concentration (Fig. 3.6.2). The influence of alginate on amylose leaching was corresponding to the water soluble index, indicationg that alginate restricted the leaching out of soluble solid from starch granule and limited amylose leaching.

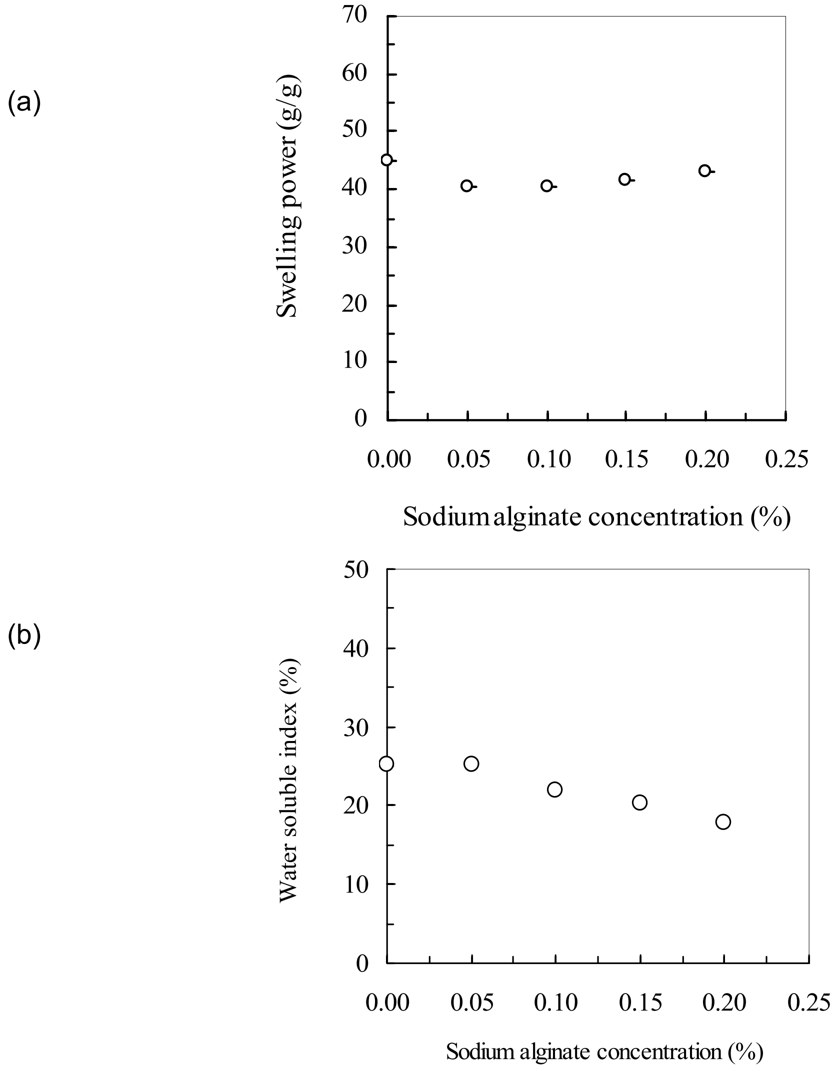


Fig. 3.6.1 Swelling power (a) and water soluble index (b) of TS and TS/Alg mixtures (1 wt% total polysaccharide content) at different mixing ratios (TS/Alg = 10/0, 9.5/0.5, 9/1, 8.5/1.5 and 8/2).

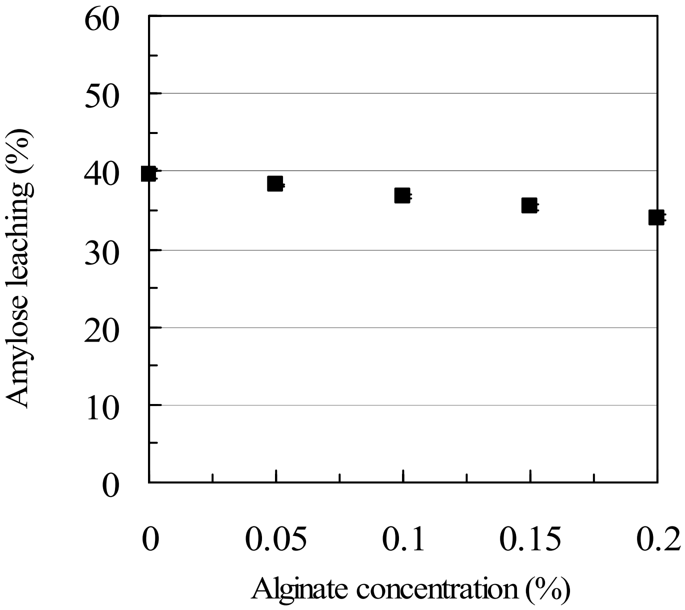


Fig. 3.6.2 Amylose leaching of TS and TS/Alg mixtures (1 wt% total polysaccharide content) at different mixing ratios (TS/Alg = 10/0, 9.5/0.5, 9/1, 8.5/1.5 and 8/2).

3.6.2 Pasting properties

The pasting properties of 5 wt% TS/Alg mixtures (TS/Alg = 10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) were investigated during heating and cooling processes using the Rapid Visco-Analyser (RVA). Typical RVA pasting profiles of selected TS/Alg mixtures were affected by the addition of Alg (Fig. 3.6.3 and Table 3.6.1). Since Alg dispersions showed no peak or viscosity change in the RVA experiment (data not shown), this indicated that pasting properties are related to the gelatinization of starch-based samples because of the change in gelatinization and retrogradation during the temperature change of RVA profiles. The TS dispersion gave a pasting temperature of about 71°C, which is within the range of 68-71°C reported in the literature by other workers (Chaisawang et al., 2006; Pongsawatmanit et al., 2006). Pasting temperatures were slightly increased with increasing Alg content and exhitbited an increase in pasting temperature at high alginate concentration (74°C) ($P \leq 0.05$) (Table 3.6.1). Addition of Alg resulted in a significant increase ($P \leq 0.05$) in peak viscosity, final viscosities, breakdown and setback of TS obtained from RVA profiles, indicating that Alg enhancing the gelatinization temperature and thickening properties of TS dispersion. This thickening properties was expected from previous studies on the influence of polysaccharides or interactions between polysaccharide and swollen starch particles or leached starch biopolymers (Funami, Kataoka, Omoto, Goto, Asai & Nishinari, 2005; Pongsawatmanit et al., 2006). Additions of alginate resulted in significant ($P \leq 0.05$) increases in peak, breakdown, setback, peak and final viscosities (Table 3.6.1).

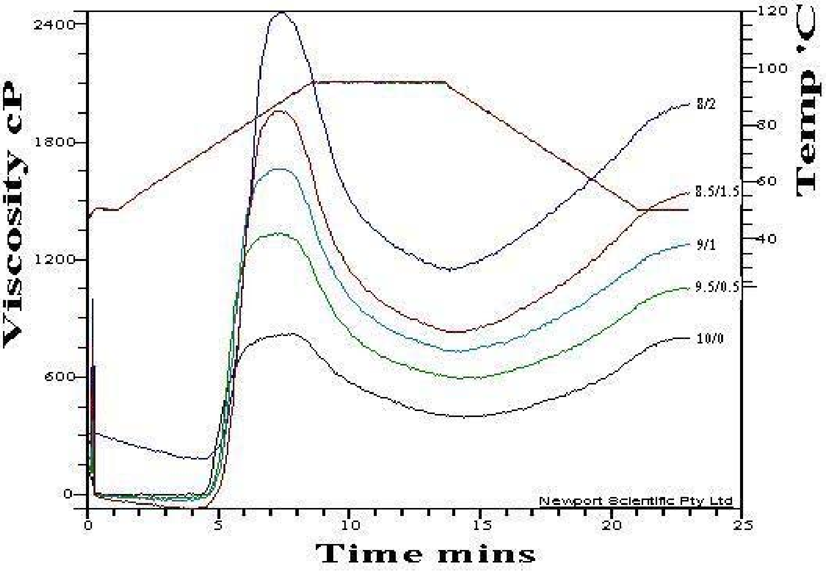


Fig. 3.6.3 Typical RVA pasting profiles of selected TS/Alg mixtures at different mixing ratios of 5 wt% total polysaccharide concentration.

Table 3.6.1 Pasting characteristics of TS/Alg (5 wt% total polysaccharide content) at different mixing ratios.

TS/Alg mixing ratio	Pasting temperature (°C)	Peak viscosity (cP)	Breakdown (cP)	Final viscosity (cP)	Setback (cP)
10/0	71.6 ± 0.1c	824 ± 6.0e	432 ± 2.9e	789 ± 7.8e	398 ± 13.1e
9.5/0.5	72.5 ± 0.2b	1347 ± 22.0d	759 ± 13.1d	1042 ± 29.4d	454 ± 17.3d
9/1	72.8 ± 0.0b	1661 ± 13.5c	939 ± 6.0c	1286 ± 31.9c	564 ± 23.7c
8.5/1.5	72.8 ± 0.5b	1962 ± 3.5b	1146 ± 16.7b	1508 ± 30.1b	692 ± 16.6b
8/2	73.9 ± 0.0a	2471 ± 9.7a	1331 ± 10.6a	2001 ± 14.0a	861 ± 15.3a

Assays were performed in triplicate. Mean ± SD values followed by the same letter in each column are not significantly different ($P > 0.05$).

The synergistic effect of tapioca starch - alginate systems reulted in higher RVA peak viscosities assuming the hydrocolloid was in the continuous phase. During heating for gelatinization process, the increase of starch granules swelling lower volume of water to interact with alginate resulted in the pronounced increase in the mixture viscosity (Alloncle, Lefebvre, Llamas, & Doublier, 1989). Peak viscosity was considered as the equilibrium point between swelling and rupture of starch granules (Newport Scientific, 1995).

When the system was at the holding temperature (95°C), the mixtures were subjected to mechanical or shear stress, which led to further disruption of the starch granules and leaching out of starch molecules. 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). The resultant drop in viscosity from peak to a holding strength (minimum viscosity after the peak, occuring around the beginning of RVA cooling stage), defined as breakdown, increased with alginate concentration, indicating the higher rupture of the granules in the starch–alginater pastes.The rusults suggest that alginate enhances the breakdown due to the higher viscous of pasted and less resistance to breakdown due to the higher shear force applied on the granules during heating and shear condition.

When the sample was subsequently cooled down to 50°C at 6°C/min, the viscosity of the pastes increased to a final viscosity at the end of RVA experiments (23 min), which was attributed to the reassociation of amylose molecules (sometimes called short-term retrogradation). The increased in viscosity of TS and TS/Alg pastes occurs not only due to the simple kinetic effect of cooling on viscosity, but also due to the reassociation of starch (particularly amylose) molecules. The setback values obtained from the RVA pasting curves were used to indicate the extent of short-term retrogradation (Table 3.6.1). Addition of Alg resulted in significant ($P \leq 0.05$) increased in setback values. These results suggest that short term retrogradation of TS/Alg mixtures enhancing by added alginate at the examined solid content in the early stages of storage immediately gelatinization.

3.6.3 Differential scanning calorimetry

The investigation of gelatinization and retrogradation of 25% TS and TS/Alg (10/0, 9.5/0.5 and 9/1) dispersions using differential scanning calorimetry (DSC) revealed the The DSC measurements were measured after they had been stored at room temperature for overnight (Fig. 3.6.4). The endothermic DSC peaks are indicative of melting of native starch structure.

During the first-run heating of TS in the absence or presence of Alg, single large endothermic peaks were observed (Fig. 3.6.4). Gelatinization temperatures (T_o, T_p, T_c) shifted to higher temperature when increasing Alg content (Table 3.6.2). The gelatinization enthalpy was evaluated from the area under endothermic curve observed during the first-run heating (ΔH_1) and summarized in Table 3.6.2. Dispersions of individual Alg did not show any peak (data not shown). The ΔH_1 values of TS/Alg mixtures slightly decreased when increasing Alg content.

After gelatinization, the samples were cooled down to 25°C at -5°C/min and kept at 5°C up to 24 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 & Nishinari, 1991) and the results are shown in Fig. 3.6.5. The retrogradation ratio of TS pastes increased with increasing storage time. In the presence of Alg, retrogradation ratios at the TS/Alg mixing ratio of 9/1 proceeded faster than those of TS alone after keeping at 5°C for longer storage time, suggesting that Alg accelerate re-ordering of starch polysaccharides.

Table 3.6.2 Gelatinization temperatures and enthalpy of the 25 wt% tapioca starch and sodium alginate mixtures (TS/Alg) at different mixing ratios.

TS/Alg	T_o (°C)	T_p (°C)	T_c (°C)	Enthalpy (J/g dry starch)
10/0	63.48 ± 0.06	70.00 ± 0.00	76.80 ± 0.04	16.77 ± 0.22
9.5/0.5	66.15 ± 0.09	72.34 ± 0.12	78.76 ± 0.28	16.67 ± 0.00
9/1	67.65 ± 0.09	74.06 ± 0.13	80.13 ± 0.13	16.20 ± 0.23

Values are average ± SD.

T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature.

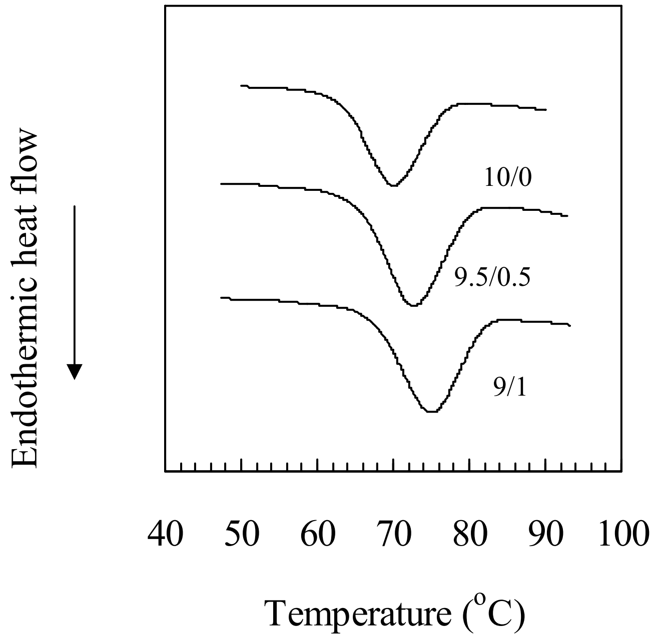


Fig. 3.6.4 First-run heating DSC thermograms of 25 wt% TS and mixtures of TS/Alg at different ratios. Heating rate was 5°C/min.

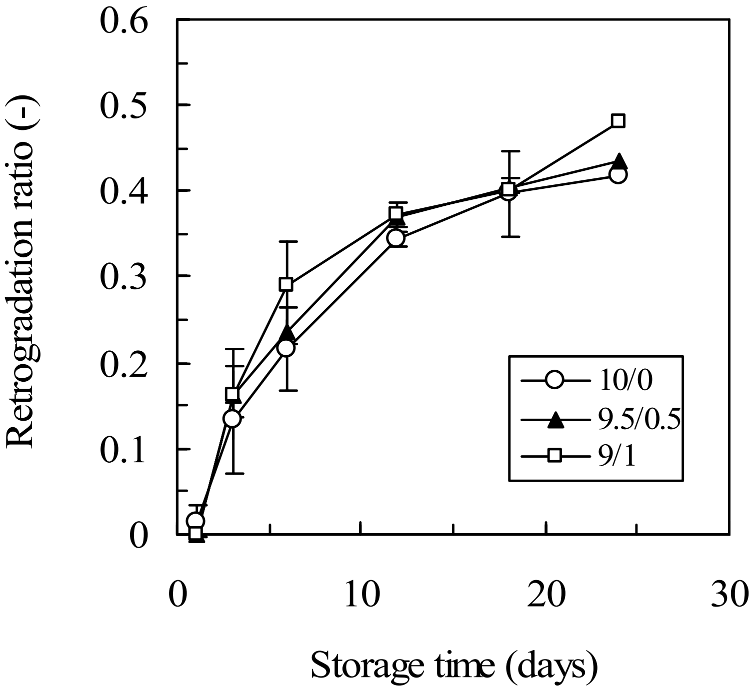


Fig. 3.6.5 Retrogradation ratio ($\Delta H_2/\Delta H_1$) of 25 wt% TS and mixtures of TS/Alg at different ratios (TS/Alg = 10/0, 9.5/0.5 and 9/1) after storage at 5°C up to 24 days.

3.6.4 Steady shear viscosity

After the preparation of TS and TS/Alg pastes, a portion of the paste kept at 40°C was put on the plate of the rheometer which had been kept at 25°C beforehand. Sample temperature was kept constant at 25 ± 0.5 °C for at least 30 s before starting the measurement. At a constant temperature (25°C), the shear rate dependence of the steady shear viscosity of gelatinized TS with and without Alg is shown in Fig. 3.6.6. The shear rate was increased from 0.1 to 1000 s^{-1}. At 5 wt% TS/Alg mixing ratios (10/0 and 9/1) showed shear-thinning flow behavior in this studied range: the higher the shear rate the lower the apparent viscosity. The viscosity of the TS paste was lower than those of the TS/Alg paste.

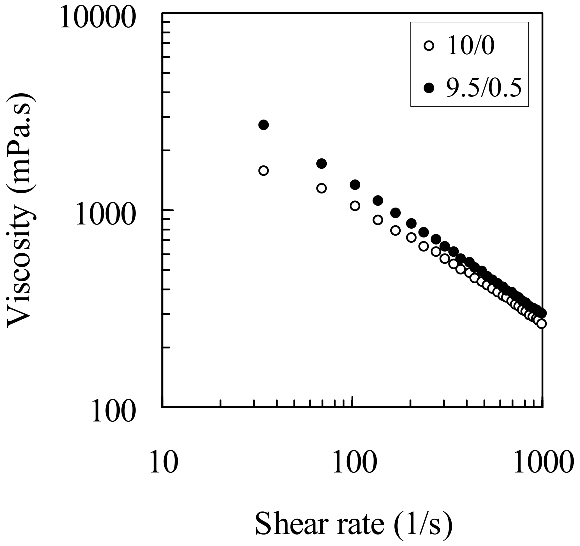


Fig. 3.6.6 Shear rate dependence of the steady shear viscosity at 25°C of TS/Alg mixtures at different mixing ratios; 10/0 (open) and 9.5/0.5 (solid).

3.6.5 Freeze-thaw stability

Freeze-thaw stability is important in the food industry. Thermal fluctuations and consequent phase changes of water during freeze-thaw treatment are the main causes of deterioration in frozen food especially in the gel matrix of starch (Lee, Baek, Cha, Park & Lim, 2002; Pongsawatmanit et al., 2006). During cold storage, the reorganization of starch molecules may result in the release of water (or syneresis) and this may affect the functional properties in terms of viscosity or gel behavior. Repeated freeze-thaw treatment is a technique proposed for measuring the syneresis of gelatinized starches to determine the cold storage stability of starch-based foods (Zheng et al., 1998) where the definition of syneresis is the spontaneous separation of a liquid form a gel or colloidal suspension due to contraction of the gel (Lapedes, 1978).

Under the present experimental conditions, the percentage of water separation from the gelatinized TS paste increased with increasing numbers of freeze-thaw cycles (Fig. 3.6.7). Water separation from the gelatinized TS paste increased from 8 to 12% after 1 and 9 freeze-thaw cycles, respectively, indicating that the starch network might be damaged due to the retrogradation of starch which resulted in higher water separation on thawing (Yuan & Thompson, 1998). For the 5 wt% TS/Alg mixture pastes at mixing ratios of 9/1 and 8/2 (containing 0.5 wt% and 1.0 wt% Alg, respectively), water separation was lower than that of the 5 wt% TS paste after 9th cycle of repeated freeze-thaw treatment. The syneresis result revealed that sodium salt of alginate was effective in stabilizing the starch gel against the repeated treatments of freeze-thaw. It was supposed that the stabilizing effect was mainly attributed to the ionic properties of the polymer. The ionic groups could immobilize adjacent water molecules, and this restricted mobility was expected to make it difficult for the water molecules to transform into ice or to incorporate the polysaccharide chain association (Sanderson, 1981). Alginate might reduce the syneresis mainly on alginate-water interactions (Lee et al., 2002).

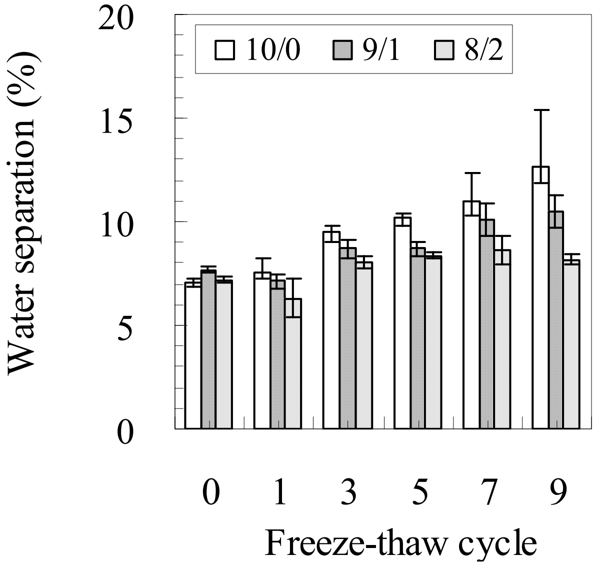


Fig. 3.6.7 Increased water separation (%) of 5 wt% gelatinized TS/Alg mixtures at selected mixing ratios of 10/0, 9/1 and 8/2 as a function of number of freeze-thaw cycles. The vertical bar represents the standard deviation.

3.7 **Changes in TPA parameters of tapioca starch gels containing alginate during storage**

The retrogradation of starch gel during storage is important for product development in food industry. Tapioca starch (TS) is a food ingredient widely used in many products. Incorporation of a proper amount of hydrocolloids may improve textural properties and stability of tapioca starch in food products**.** Therefore, the objective of this study was to evaluate the change in TPA parameters of TS gels with and without alginate during the storage at low temperature.

The hardness and stiffness values of each TS/Alg gel increased with increasing storage time but these two values were lower with increasing Alg content at the same storage time (Fig. 3.7.1). However, cohesiveness of the TS/Alg gels exhibited the lower values with increasing storage time but increased with increasing Alg substitution. The results suggest that keeping the starch gels at 5°C enhanced the strength of gel structure due to the retrogradation of starch but Alg can decrease network rigidity by reducing the structure formation of the amylose in TS during the storage..

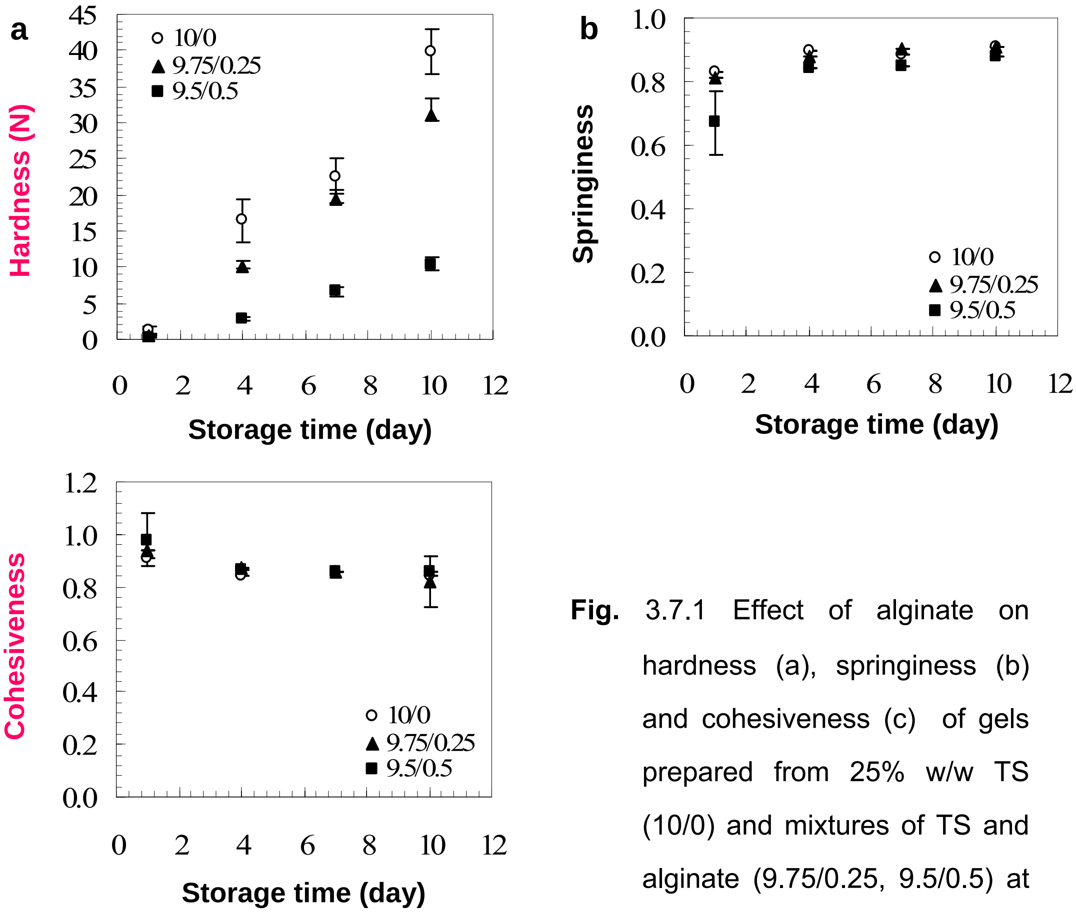


Fig. 3.7.1 Effect of alginate on hardness (a), springiness (b) and cohesiveness (c) of gels prepared from 25% w/w TS (10/0) and mixtures of TS and alginate (9.75/0.25, 9.5/0.5) at 5°C 1, 4, 7 and 10 days.

Suggestions for future work

1. More hydrocolloids should be studied since physical properties of starch and hydrocolloids systems depend on ingredient interaction and structure-function relationship.
2. Influence of sugars on the physical properties and storage stability should be emphasized due to the formulation of food products including sugars for taste improvement.

Output from the projects

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ (ระบุชื่อผู้แต่ง ชื่อเรื่อง ชื่อวารสาร ปี เล่มที่ เลขที่ และหน้า)
   a. Pongsawatmanit, R. and S. Srijunthongsiri. (2008). Influence of xanthan gum on rheological properties and freeze–thaw stability of tapioca starch. *Journal of Food Engineering*, 88, 137-143.
   b. Srijunthongsiri. S., & P. Pongsawatmanit. 2006. Effect of xanthan gum and pH on pasting properties and freeze-thaw stability of tapioca starch. *Kasetsart Journal (Nat. Sci.), 40* (5), 203-208.
   c. Chantaro, P., and R. Pongsawatmanit. Influence of xanthan gum and sucrose on the pasting properties of tapioca starch. LWT - Food Science and Technology (Submitted Jan 2009).

2. การนำผลงานวิจัยไปใช้ประโยชน์
   ในเชิงวิชาการ ได้นำความรู้จากการวิจัยไปใช้
   - ในการพัฒนาการเรียนการสอนทั้งในระดับปริญญาตรี โทและเอก ที่เกี่ยวข้องกับวิทยากระแส ส่วนประกอบอาหาร การพัฒนาผลิตภัณฑ์ และได้แสดงให้เห็นถึงองค์ความรู้ที่ได้จำเป็นต่อการพัฒนาผลิตภัณฑ์ โดยได้พัฒนาผลิตภัณฑ์และนำไปจดอนุสิทธิบัตร 1 เรื่อง
   - โครงการวิจัยนี้ สร้างนักวิจัยใหม่ที่มีความสามารถในระดับปริญญาโท 1 คน และปริญญาเอก 1 คน

3. อื่นๆ (เช่น ผลงานตีพิมพ์ในวารสารวิชาการในประเทศ การเสนอผลงานในที่ประชุมวิชาการ หนังสือ การจดสิทธิบัตร)
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อนุสิทธิบัตร

รุ่งนภา พงศ์สวัสดิ์มานิต. ผลิตภัณฑ์ขนมชั้นแช่แข็งและกระบวนการผลิตขนมชั้น. ยื่นคำขอเมื่อวันที่ 25 กุมภาพันธ์ 2551 เลขที่คำขอ 0803000292.

ภาคผนวก

บทความสำหรับการเผยแพร่

ในอุตสาหกรรมอาหาร มักมีการเติมส่วนประกอบต่างๆ เพื่อให้ผลิตภัณฑ์มีสมบัติและเนื้อสัมผัสต่างๆ ที่เป็นลักษณะเฉพาะของผลิตภัณฑ์ แป้งเป็นส่วนประกอบของอาหารที่มีการใช้เพื่อให้ความหนืดรวมทั้งความคงตัวแก่ผลิตภัณฑ์ แป้งมันสำปะหลังเป็นสารให้ความหนืดที่นิยมใช้ในผลิตภัณฑ์อาหารหลายชนิดโดยเฉพาะในประเทศไทย แต่แป้งมันสำปะหลังมักมีข้อเสียในด้านการนำไปใช้โดยเฉพาะความคงตัวในด้านความหนืด เป็นที่ทราบโดยทั่วไปว่า ไฮโดรคอลลอยด์ (หรือในอุตสาหกรรมอาหารเรียกว่า กัม) มีสมบัติในการช่วยทำให้ผลิตภัณฑ์มีความคงตัวมากขึ้น ด้วยการเพิ่มความหนืดหรือทำให้เกิดลักษณะเจลที่ต้องการในอาหาร ดังนั้นอันตรกิริยาของส่วนประกอบต่างๆ ระหว่างแป้งมันสำปะหลังและพอลิแซคคาไรด์ที่ไม่ใช่แป้งที่เกี่ยวข้องกับเจลาติไนเซชันและรีโทรกราเดชันระหว่างการให้ความร้อนและทำให้เย็น จึงมีบทบาทต่อคุณภาพสุดท้ายของผลิตภัณฑ์ที่มีแป้งเป็นส่วนประกอบ ด้วยเหตุนี้ งานวิจัยที่ต้องการความเข้าใจในเรื่องผลของไฮโดรคอลลอยด์ต่อสมบัติทางกายภาพและความคงตัวของระบบที่ใช้แป้งมันสำปะหลัง จึงสำคัญต่อการพัฒนาผลิตภัณฑ์และกระบวนการในเทอมของการเพิ่มคุณภาพและการยืดอายุการเก็บสำหรับอุตสาหกรรมอาหาร แซนแทนกัม (Xan) และอัลจีเนต (Alg) เป็นไฮโดรคอลลอยด์ที่ศึกษาที่มีผลต่อสมบัติทางกายภาพและความคงตัวของแป้งมันสำปะหลัง (TS) ด้วยวิธีการต่างๆ เช่น RVA, steady shear measurement, DSC, การละลายและแช่แข็งหลายรอบ ผลที่ได้คือ ไฮโดรคอลลอยด์ทั้งสองชนิดเพิ่มสมบัติทางเพสติง การแทนที่แป้งมันสำปะหลังบางส่วนด้วยแซนแทนกัม สามารถปรับปรุงให้สมบัติเพสติงและความคงตัวทางด้านการแช่แข็งและละลายของแป้งมันสำปะหลังได้ดีขึ้นภายใต้สภาวะที่เป็นกรด (pH 3 ถึง 7) เมื่อศึกษาสหสัมพันธ์ระหว่างค่า setback และการแยกตัวของน้ำจากของผสม TS/Xan พบว่า สามารถใช้เพื่อทำนายการแยกตัวของน้ำที่เกิดขึ้น ณ วงจรการแช่แข็งและละลายใดๆ จากค่า RVA setback นอกจากนี้ การเติมน้ำตาลยังมีผลต่อการเพิ่มอุณหภูมิเพสติง ความหนืดของพีค ความหนืดสูงสุด ค่า breakdown และ setback ของของผสม TS/Xan (p<0.05) ส่วนอัลจีเนตสามารถปรับปรุงความคงตัวทางด้านการแช่แข็งและละลายของแป้งมันสำปะหลังได้ดีขึ้นเมื่อมี pH 5 ถึง 7 การเติมอัลจีเนตมีผลให้ส่วนผสม TS/Alg มีความคงตัวทางด้านความร้อนดีกว่าของเพสต์แป้งมันสำปะหลังเท่านั้นเนื่องจากมีค่าพลังงานกระตุ้นต่ำกว่า อัตราส่วนรีโทรกราเดชันของส่วนผสม TS/Alg ที่หาจาก DSC ดำเนินไปเร็วกว่าที่ได้จาก TS เท่านั้นเมื่อเก็บไว้ที่ 5°C แสดงว่า Alg เร่งการจัดเรียงตัวของแป้ง ทำให้อุตสาหกรรมอาหารที่ต้องการให้แป้งเกิดการแข็งตัวได้เร็วเพื่อใช้ในกระบวนการผลิตต่อไป เช่น การตัด เป็นต้น จากองค์ความรู้แต่ละส่วนสามารถที่จะใช้ไฮโดรคอลลอยด์ในการปรับปรุงกระบวนการและผลิตภัณฑ์ที่มีแป้งมันสำปะหลังเป็นส่วนประกอบต่อไป

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Influence of xanthan gum on rheological properties and freeze–thaw stability of tapioca starch

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Abstract

Physical properties and storage stability of tapioca starch (TS) can be modified using hydrocolloids. Xanthan gum (Xan) was investigated in this study for further application in TS-based products. The TS and TS/Xan mixtures at a total polysaccharide concentration of 5% w/w (db) were prepared. From RVA pasting profiles, pasting temperature, peak and final viscosities of TS pastes increased with increasing Xan concentration ($p < 0.05$) whereas the setback values indicating the short-term retrogradation were lower ($p < 0.05$). Flow curves of all TS and TS/Xan pastes from steady shear measurement exhibited shear thinning behavior. Water separation values of TS/Xan pastes were also lower than those of TS pastes alone from repeated freeze–thaw experiment, indicating Xan preventing the reassociation of starch molecules. The correlation between setback and water separation was investigated and proven to be a useful approach for predicting water separation from RVA setback value at any given freeze–thaw cycles. These results have important implications for the formulation of TS-based products with improved rheological properties and freeze–thaw stability.

Keywords: Xanthan gum; Tapioca starch; Pasting profile; Rheological properties; Retrogradation; Correlation; Freeze–thaw cycle

1. Introduction

Starch is one of the most important functional food biopolymers and is added as a functional ingredient to many products such as sauces, puddings, confectionery and a variety of low-fat products (Hermansson and Svegmark, 1996). 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 and 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 et al., 2005). During distribution and storage, starch pastes may proceed the transformation of starch biopolymer molecules: namely, chain aggregation and recrystallization. Moreover, it is difficult to maintain frozen food products in a constant and optimum frozen state undergoing the repeated freeze–thaw cycles during the supply chain leading to the changes in syneresis and related rheological properties (Lee et al., 2002). This is the driving force for food industry to formulate and develop the high quality of products which can be maintained throughout the process, distribution and storage.

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 et al., 2005; Tester and Sommerville, 2003). Addition of hydrocolloids can alter both structural and rheological characteristics of starches such as gelatinization temperature and pasting properties (Shi and BeMiller, 2002; Pongsawatmanit et al., 2006). Xanthan gum (Xan) is a heteropolysaccharide produced by the fermentation of *Xanthomonas campestris* (Urlacher and Noble, 1999) and has a backbone of 1,4-linked β-D-glucose (like cellulose) with side chains consisting of two mannose molecules and

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one glucuronic acid molecule. Xanthan gum is a unique hydrocolloid that exhibits a significant yield stress value even at a low concentration, which explains the ability of xanthan solutions to stabilize emulsions or suspensions due to microgel particles or aggregates of xanthan polymer chains (Morris, 1995). This gum is also reported to provide an excellent stability in heat and acid systems (Sahin and Ozdemir, 2004). Tapioca starch (TS), produced from cassava roots, is a favorable thickener used in food industry due to its high viscosity, clear appearance, and low production cost, compared to other starches. The viscosity of the tapioca starch paste decreases when mechanically disturbed and leading to the textural instability during storage. Hence, the functional modification of the tapioca starch for improving the product quality and shelf life plays an important role in product and process development.

Recently, several studies have reported the freeze–thaw stabilization of some starch gels or pastes using biopolymers (Brennan et al., 2004; Ferrero et al., 1994; Lee et al., 2002; Sudhakar et al., 1996) including xanthan gum. However, an understanding of rheological properties and freeze–thaw stability in the systems of the partial substitution of starch with hydrocolloid at a fixed total polysaccharide is also important for improving the quality of TS-based products. Moreover, a model to demonstrate the behavior of water separation under the pasting properties encountered in the real repeated freeze–thaw cycles is necessary for controlling and maintaining the quality of TS-based frozen products. Therefore, the objective of the present study is to investigate the rheological properties of TS containing different xanthan gum contents at a fixed total polysaccharide concentration using RVA and steady shear viscosity measurements, and the water separation of TS/Xan pastes after repeated freeze–thaw treatment. A correlation between the pasting properties and freeze–thaw stability is also examined.

2. Materials and methods

2.1. Materials

Tapioca starch was supplied by Chorchaiwat Industry Co. Ltd. (Cholburi, Thailand). The moisture and amylose contents of the starch were 11.9% and 19.4% determined by the hot air oven method at 105 °C (AOAC, 1995) and HPSEC (modified method of Govindasamy et al., 1992), respectively. Xanthan gum (CP Kelco, San Diego) was donated by Winner Group Enterprise Ltd. (Bangkok, Thailand) containing 12.8% w/w moisture content determined by the hot air oven method at 105 °C (AOAC, 1995). Both polysaccharides were mixed on a dry basis and used without any further purification.

2.2. Rapid visco analyser (RVA) measurement

Pasting properties of 5% w/w TS and xanthan gum (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) were determined using a Rapid Visco Analyser (RVA) (RVA-4, Newport Scientific, Narrabeen, Australia). 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. Then, TS was added finally to achieve a total weight of 28 g for preparing pastes of 5% w/w TS/Xan mixtures. The dispersions were kept at room temperature for further 30 min to hydrate the starch. Before the measurement, each 28 g TS/Xan suspension was stirred manually to disperse the sample uniformly. The pasting profile of the sample was monitored during a thermal treatment 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 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 during the measurement was started at 960 rpm for the first 10 s and kept constant at 160 rpm until the end of experiment. Pasting profiles were determined in triplicate in order to confirm the reproducibility of the data and the average values of evaluated pasting parameters were reported.

2.3. Steady shear viscosity measurement

Gelatinized TS and TS/Xan mixtures (5% w/w total polysaccharide concentration) at five mixing ratios obtained from RVA experiment were used for steady shear viscosity measurement using a rheometer (Physica MCR 300, 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 or 50 °C for at least 30 s before starting the measurement. Apparent viscosity was recorded by increasing the shear rate from 0.1 to 100 s^{-1}. The measurements were done using at least three freshly prepared samples and each average value was reported.

2.4. Freeze–thaw stability measurement

TS and Xan mixtures were prepared at different mixing ratios (TS/Xan = 10/0, 9.5/0.5 and 9/1) with 5% w/w total polysaccharide concentration in deionized distilled water. In the case of TS/Xan dispersions, Xan dispersion was first prepared at room temperature and stirred using a magnetic stirrer for at least 6 h, and then TS was added into the Xan dispersion and mixed for at least 30 min. The dispersions of TS or TS/Xan were heated to 95 °C, held at the temperature of 95–98 °C for 30 min, and cooled down in an ice-water bath. Each mixture was poured into the freeze–thaw plastic tubes (Fig. 1a). All samples were centrifuged at 190*g* for 2 min to remove air bubbles. Sodium azide (0.04%) was also added to prevent microbial spoilage.

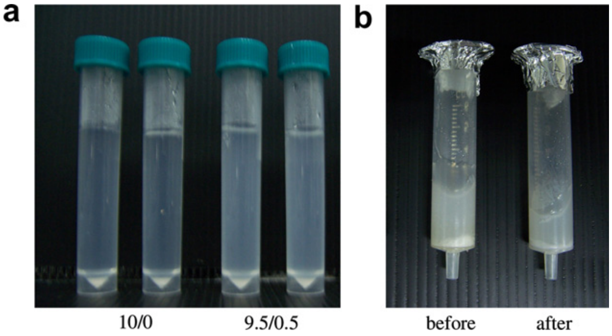

Fig. 1. Freeze–thaw plastic tubes containing 5% w/w TS/Xan pastes (10/0, 9.5/0.5) (a); plastic syringes containing thawed pastes (TS/Xan = 9.5/0.5) before and after centrifugation for water separation determination (b).

The freeze–thaw stability of TS/Xan pastes was determined by storing the gelatinized pastes in the freezer (−25 °C) for 20 h, and then thawing at 40 °C for 2 h repeatedly up to seven cycles. To measure water separation from the TS/Xan pastes at defined freeze–thaw cycles, 5-ml plastic syringes without the tip and plunger of the syringe were used (Fig. 1b) according to the methods of Pongsawatmanit et al.(2006) and Zheng and Sosulski (1998). The syringes were centrifuged at about 2100*g* for 10 min to remove excess water from the cotton and then weight (W_t). Paste samples (2.5 g) after thawing at selected freeze–thaw cycles were added into each syringe. The syringe was weighed before and after centrifugation at 2100*g* for 10 min and the weights were recorded as W_1 and W_2, respectively (Pongsawatmanit et al., 2006). The percentage of water separation was calculated as shown in the following equation:

$$\text{Water separation } (\%) = (W_1 - W_2) \times 100/(W_1 - W_t). \tag{1}$$

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

2.5. Data and statistical analysis

Each of the mentioned measurements was carried out using at least three freshly prepared samples. Statistical analysis was performed by SPSS V.12 statistical software (SPSS (Thailand) Co. Ltd.). The results are reported as the mean and standard deviation. The RVA parameters and water separation values at different freeze–thaw cycles were related by Pearson's correlation. The linear regression was also conducted to relate the RVA parameters and water separation to predict a set of response/dependent variables.

3. Results and discussion

3.1. RVA pasting properties

The pasting properties of 5% w/w TS/Xan mixtures (TS/Xan = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) were investigated during heating and cooling processes using RVA. Typical RVA pasting profiles of TS/Xan mixtures were affected by the addition of Xan (Fig. 2). Xan dispersions showed no peak or viscosity change in the RVA experiment indicating that pasting properties are related to the gelatinization of starch-based samples during the temperature change of RVA profiles. Pasting temperatures of TS/Xan were increased significantly compared with those of TS alone (about 71 °C) ($p < 0.05$, Table 1). The pasting temperatures of TS increased with increasing xanthan gum substitutions. The results suggest that xanthan gum alters the gelatinization temperature of TS, indicating that there are some interactions between xanthan gum and TS. In addition, available water for gelatinization is reduced due to the increase in hydration of xanthan gum assumed to be located in the continuous phase leading to the higher pasting temperatures (Hirashima et al., 2005).

The synergistic effect of TS/Xan systems resulted in higher RVA peak viscosities (Table 1). During heating of gelatinization process, the increase in starch granule swelling led to the lower volume of water to interact with xanthan gum assumed to be in the continuous phase resulted in a pronounced increase in the mixture viscosity (Alloncle et al., 1989) from about 820 to 1430 mPa s for TS alone and TS containing 0.5% Xan, respectively. The increase in viscosity was about 74% in comparison with that of TS paste. When the system was maintained at 95 °C, the mixtures were subjected to both thermal and shear stress, which led to both further disruption of the starch granules and leaching out of starch molecules causing a greater 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) defined as breakdown, increased from 425 to 480 mPa s for TS alone and TS containing 0.5% Xan, respectively (Table 1). The increase in viscosity of TS/Xan suspensions creates the shear forces exerted on the swollen starch granules in the

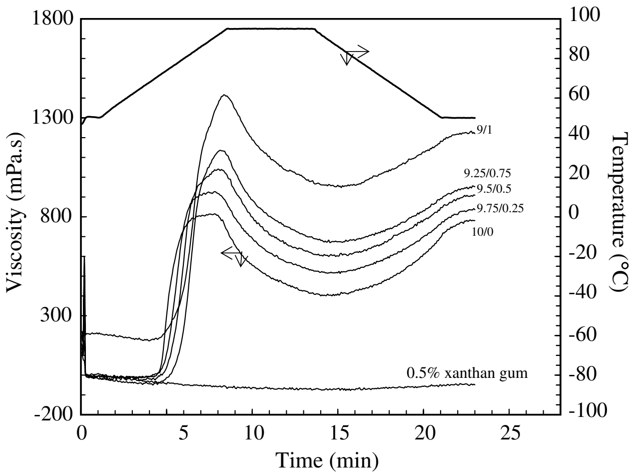

Fig. 2. Typical RVA pasting profiles of TS/Xan mixtures at different mixing ratios of 5% w/w total polysaccharide concentration.

Table 1
Pasting characteristics of TS/Xan (5% w/w total polysaccharide content) at different mixing ratios determined by Rapid visco analyser (RVA)

TS/Xan mixtures	Pasting temperature (°C)	Peak viscosity (mPa s)	Breakdown (mPa s)	Final viscosity (mPa s)	Setback (mPa s)
10/0	71.3 ± 0.5d	818 ± 2.3e	425 ± 10.0c	784 ± 16.2e	391 ± 15.1a
9.75/0.25	72.8 ± 0.9c	924 ± 21.0d	413 ± 7.0c	833 ± 16.2d	323 ± 3.9b
9.5/0.5	74.2 ± 0.3b	1036 ± 17.5c	444 ± 10.4b	905 ± 8.4c	313 ± 3.2b
9.25/0.75	76.1 ± 0.5a	1132 ± 9.8b	476 ± 9.0a	951 ± 17.7b	289 ± 6.4c
9/1	76.7 ± 1.0a	1429 ± 16.0a	482 ± 15.7a	1219 ± 24.0a	272 ± 3.0d

Mean ± SD values ($n = 3$) followed by different letters within the same column are significantly ($p < 0.05$) different by Duncan's multiple range test.

shear field greater than that encountered in TS-water system. This results in the loss of starch granule integrity and subsequent disruption leading to a reduction of the paste viscosity (Christianson et al. 1981). The viscosity reduction of TS pastes containing Xan under the influence of applied shear to TS/Xan mixtures, indicating the formed aggregates of xanthan molecules in the pastes through hydrogen bonding and polymer entanglement were disrupted under the shear with increasing gum content (Sworn, 2000).

When the sample was subsequently cooled down to 50 °C at 6 °C/min, the viscosity of the pastes increased to a final viscosity at the end of RVA experiments. Final viscosities of TS/Xan increased with increasing Xan content ($p < 0.05$). The increase in viscosities of TS and TS/Xan pastes from holding strength values to final viscosity called setback occurs not only due to the simple kinetic effect of cooling on viscosity, but also due to the reassociation of starch (particularly amylose) molecules. Addition of xanthan gum resulted in significant decrease in setback of TS/Xan pastes ($p < 0.05$, Table 1). Usually, high setback is associated with syneresis during freeze–thaw cycles and is used to indicate the extent of short-term retrogradation. These results suggest that short-term retrogradation of TS/Xan mixtures can be depressed by xanthan gum even at low concentration.

3.2. Steady shear viscosity of TS/Xan pastes

At a constant temperature (25 °C), the shear rate dependence (0.1 to 100 s^{-1}) of the steady shear viscosity of gelatinized TS with and without Xan exhibited shear thinning behavior (Fig. 3a). The viscosities of TS were lower than those containing Xan at very low shear rates but revealed the higher values at higher shear rates due to the strong pseudoplastic behavior of the xanthan gum contributing to the TS pastes.

When viscosity measurement of 5% w/w TS and TS/Xan pastes was performed at higher temperature (50 °C), the shear thinning behaviors were also obtained (Fig. 3b). However, the viscosities of TS were lower than those containing Xan in the studied shear rate range (0.1 to 100 s^{-1}). The TS/Xan pastes showed a smaller viscosity reduction with an increase in the Xan content, indicating the thermal stability of xanthan gum contributing to TS pastes.

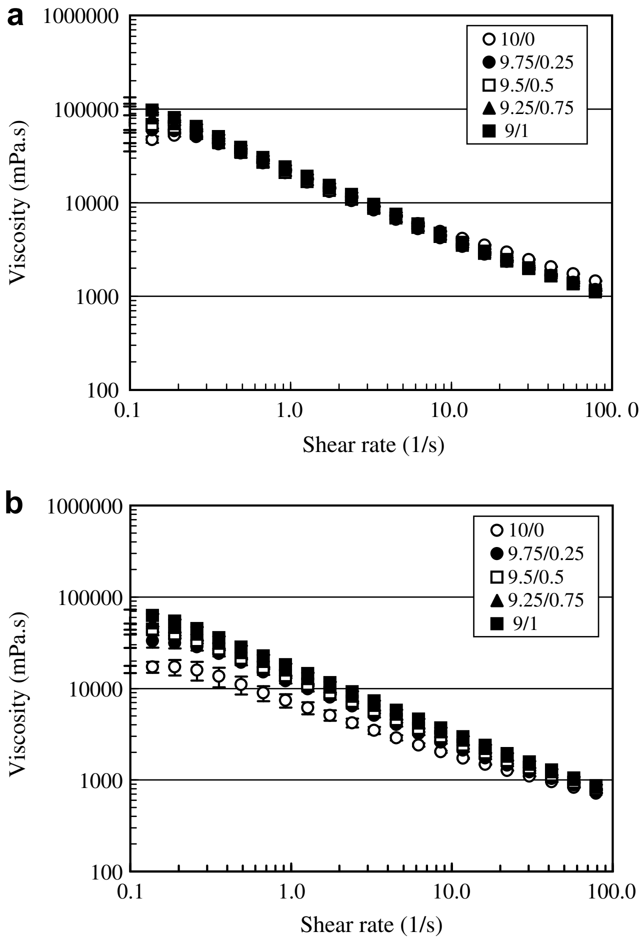

Fig. 3. Shear rate dependence of the steady shear viscosity of 5% w/w gelatinized TS/Xan mixtures at different mixing ratios of 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1 for 25 °C (a) and 50 °C (b). The vertical bar represents the standard deviation.

3.3. Freeze–thaw stability

Freeze–thaw stability is important in food industry. In cold chain storage, thermal fluctuations and consequent phase changes of water are the main causes of deterioration in frozen food especially in the gel matrix of starch (Pongsawatmanit et al., 2006). During cold storage, the reorganization of starch molecules may result in the release of water (or syneresis) and this may affect the functional properties in terms of viscosity or gel behavior. The water separation from the gelatinized TS pastes increased with increasing numbers of freeze–thaw cycles (Fig. 4a). The results suggest that the retrograded starch network or structure was easily disrupted by ice crystal formation which resulted in higher water separation on thawing (Pongsawatmanit et al., 2006; Yuan and Thompson, 1998). In this study, water separation from the gelatinized TS paste increased from 8.8% to 14.5% after 1 to 7 freeze–thaw cycles, respectively but our previous studied reported the water separation from TS pastes increased from 8% to about 20%. This difference in the water separation is expected from the difference of cassava cultivar, time and conditions at harvest leading to the difference in physicochemical properties of tapioca starch (Sriroth et al., 1999).

For the 5% w/w TS/Xan pastes at mixing ratios of 9.5/0.5 and 9/1 (containing 0.25% and 0.5% Xan, respectively), water separation was lower than that of the 5% TS paste after the first freeze–thaw cycle. In addition, the degree of water separation from gelatinized TS/Xan mixtures compared with that of TS paste decreased with an increase in the gum content, indicating that Xan dissolved in the continuous phase reduced the reassociation of starch molecules and this reduction in the damage to the network led to less syneresis. The results suggest that xanthan gum minimized freeze–thaw damage by reducing the available water to form ice crystals. This confirms that partial substitution of TS with xanthan gum formed a paste with improving freeze–thaw stability.

The increase in water separation as a function of repeated freeze–thaw cycles from TS and TS/Xan pastes is characterized in terms of the change in water separation: $\Delta w = w_i - w_0$, where w_i and w_0 are the water separation values from thawed pastes after repeated freeze–thaw cycle i and zero (before freezing), respectively. The w_0 values of TS/Xan pastes before freezing were 7.66%, 7.24% and 7.11% for pastes containing 0%, 0.25% and 0.5% Xan, respectively.

The change in water separation (Δw) from TS pastes alone was the highest compared with those containing Xan at any given freeze–thaw cycle. The Δw of TS pastes alone was more dependent on the number of freeze–thaw cycles than those containing Xan about three times evidenced by the slopes of TS (~0.93) and TS/Xan pastes (~0.32–0.35) as shown in Fig. 4b. The results again confirm the better freeze–thaw stability of xanthan gum contributing to TS pastes.

3.4. Correlation analysis and regression model

All correlations among RVA parameters and water separation from different freeze–thaw cycles for the TS/Xan mixtures (TS/Xan = 10/0, 9.5/0.5 and 9/1) are listed in Table 2. All values are significant correlation at $p < 0.05$. Xanthan gum, pasting temperature, peak viscosity, final viscosity, and breakdown have a significant positive correlation to each other and a significant negative correlation to setback and the water separation values after 1, 3, 5 and 7 freeze–thaw cycles. Setback and water separation at the specified freeze–thaw cycles have a positive correlation each other. Therefore, we plotted the experimental water separation values from TS and TS/Xan pastes as a function of setback and specified freeze–thaw cycles (Fig. 5). Since the mechanism for explaining the setback and water separation from freeze–thawed pastes is the retrogradation or starch reassociation of starch biopolymers in the TS or TS/Xan mixtures, the linear regression was conducted to relate the RVA setback and water separation to predict response/dependent variable (*Y: water separa-*

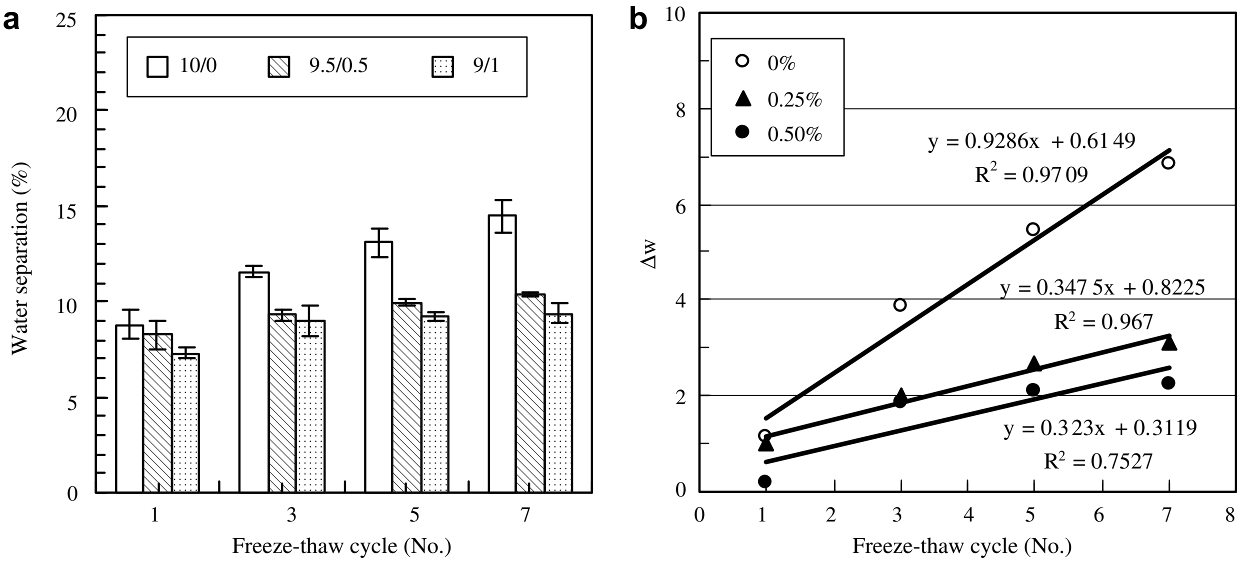

Fig. 4. Water separation (a) and the change of water separation (Δw) (b) of 5% w/w gelatinized TS/Xan mixtures at selected mixing ratios of 10/0, 9.5/0.5 and 9/1 as a function of number of freeze–thaw cycles. The vertical bar represents the standard deviation.

Table 2
Correlation matrix between RVA parameters and water separation at different freeze–thaw cycles

	Xanthan gum	Peak viscosity	Final viscosity	Setback	Pasting temperature	Trough	Breakdown	Cycle 1	Cycle 3	Cycle 5	Cycle 7
Xanthan gum	1.000										
Peak viscosity	0.986*	1.000									
Final viscosity	0.966*	0.994*	1.000								
Setback	−0.973*	−0.929*	−0.889*	1.000							
Pasting temperature	0.971*	0.954*	0.921*	−0.965*	1.000						
Trough	0.986*	0.999*	0.995*	−0.930*	0.948*	1.000					
Breakdown	0.906*	0.927*	0.905*	−0.849*	0.922*	0.910*	1.000				
Cycle 1	−0.763*	−0.739*	−0.701*	0.822*	−0.830*	−0.740*	−0.666*	1.000			
Cycle 3	−0.859*	−0.779*	−0.714*	0.932*	−0.852*	−0.775*	−0.747*	0.697*	1.000		
Cycle 5	−0.922*	−0.850*	−0.800*	0.959*	−0.895*	−0.850*	−0.781*	0.700*	0.931*	1.000	
Cycle 7	−0.887*	−0.821*	−0.758*	0.963*	−0.918*	−0.817*	−0.787*	0.865*	0.942*	0.935*	1.000

* Correlation is significant at the 0.05 level (2-tailed), $p < 0.05$.

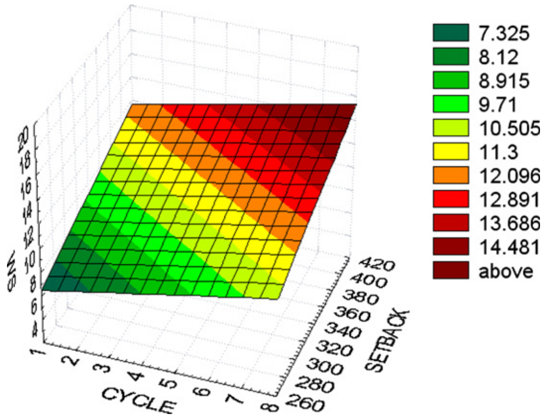

Fig. 5. Surface plot of experimental water separation as a function of freeze–thaw cycles and setback values of 5% w/w TS/Xan pastes at different mixing ratios of 10/0, 9.5/0.5 and 9/1.

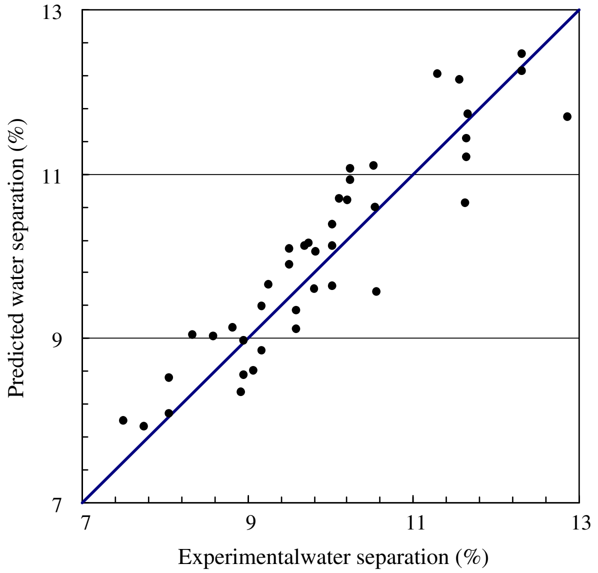

Fig. 6. Predicted water separation using Eq. (2) vs. experimental water separation from 5% w/w TS/Xan pastes at different mixing ratios (10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) ($R = 0.925$, MSE = 0.274).

tion) from a set of explanatory/independent variables (*X: RVA setback and number of* freeze–*thaw cycles*). The linear regression analysis yielded an Eq. (2) for predicting water separation as shown below:

$$\text{Water separation } (\%) = -2.269 + 0.522\ (\text{cycle}) + 0.032\ (\text{setback}). \tag{2}$$

To test the model performance, another groups of experiment data were carried out with newly prepared TS/Xan pastes (TS/Xan = 10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) for determining the water separation of the pastes after repeating freeze–thaw treatment for one to eight cycles. The experimental water separation values were plotted against those calculated from Eq. (2) using the RVA setback (Table 1) and specified freeze–thaw cycles (Fig. 6). A good predictability of the property at various freeze–thaw cycles between the modeling dataset and testing dataset was achieved, indicated by the corresponding correlation coefficient ($R = 0.925$) and small mean square error (MSE = 0.274) values between them. We did not present the quadratic regression equation due to a low correlation coefficient of the model testing.

4. Conclusion

Xanthan gum increased pasting temperatures, RVA peak and final viscosities, steady shear viscosity of TS pastes but decreased the RVA setback and the water separation from freeze–thawed pastes. Partial substitutions of TS with Xan impart more viscous, heat and freeze–thaw stability to the gelatinized TS pastes. The regression model performance in predicting water separation from setback value and a specified freeze–thaw cycle revealed a good agreement with the experimental dataset because both RVA setback and water separation values implied to the retrogradation of starch molecules were lower with increasing Xan. Therefore, xanthan gum can be used to create TS-based products with better rheological properties and freeze–thaw stability during product development in food industry. In addition, this model could be further applied to predict and control the water separation from TS-based frozen products for higher shelf life expectation.

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Article Type: Research Paper

Keywords: Rheological properties, retrogradation, Pearson's correlation, model, Rapid visco-analysis, setback, specific viscosity

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Abstract: Sugars and hydrocolloids are added into starch-based products during processing for improving the final qualities of food. Effect of xanthan gum (Xan) (0 to 0.5%) and sucrose (0 to 30%) on the pasting properties of tapioca starch (TS) was investigated using a Rapid Visco-Analyzer (RVA). RVA pasting temperatures, peak viscosity, final viscosity, breakdown and setback values of 5% w/w TS/Xan mixtures increased with increasing sucrose contents ($p<0.05$) according to the Pearson's correlation analysis. Setback values of TS/Xan pastes decreased significantly with increasing xanthan concentration during cooling ($p<0.05$) from 95 to 50°C. The rate of viscosity breakdown was increased in TS and TS/Xan mixtures with the addition of sucrose. Steady shear viscosities of TS/Xan pastes exhibited thermal stability of xanthan gum contributing to TS pastes for the systems with and without added sucrose. Specific viscosity of TS/Xan pastes containing sucrose up to 20% exhibited a single master curve. The linear regression analysis from RVA pasting profile was derived for predicting final viscosity with a good relationship and can be applied to predict the viscosities of TS/Xan/Sucrose mixtures below 2000 mPa.s from steady shear

measurement. These results have essential implications for the formulation of TS-based products containing sucrose and xanthan gum in food industry.

Cover Letter

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January 28, 2009

Dear Editor,

Refer to the guide for authors to submit a manuscript to LWT - Food Science and Technology, I would like to submit an original research paper entitled “Influence of xanthan gum and sucrose on the pasting properties of tapioca starch” by Prawta Chantaro, Rungnaphar Pongsawatmanit. Please find the attached manuscript as submitted online.

The corresponding author and address are shown below:

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If you have any questions, please do not hesitate to let me know. I look forward to hearing from you.

Yours sincerely,

Rungnaphar Pongsawatmanit
Associate Professor

Influence of xanthan gum and sucrose on the pasting properties of tapioca starch

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Abstract

Sugars and hydrocolloids are added into starch-based products during processing for improving the final qualities of food. Effect of xanthan gum (Xan) (0 to 0.5%) and sucrose (0 to 30%) on the pasting properties of tapioca starch (TS) was investigated using a Rapid Visco-Analyzer (RVA). RVA pasting temperatures, peak viscosity, final viscosity, breakdown and setback values of 5% w/w TS/Xan mixtures increased with increasing sucrose contents ($p<0.05$) according to the Pearson's correlation analysis. Setback values of TS/Xan pastes decreased significantly with increasing xanthan concentration during cooling ($p<0.05$) from 95 to 50°C. The rate of viscosity breakdown was increased in TS and TS/Xan mixtures with the addition of sucrose. Steady shear viscosities of TS/Xan pastes exhibited thermal stability of xanthan gum contributing to TS pastes for the systems with and without added sucrose. Specific viscosity of TS/Xan pastes containing sucrose up to 20% exhibited a single master curve. The linear regression analysis from RVA pasting profile was derived for predicting final viscosity with a good relationship and can be applied to predict the viscosities of TS/Xan/Sucrose mixtures below 2000 mPa.s from steady shear measurement. These results have essential implications for the formulation of TS-based products containing sucrose and xanthan gum in food industry.

Keywords: Rheological properties, retrogradation, Pearson's correlation, model, Rapid visco-analysis, setback, specific viscosity

1. Introduction

In food industry, many ingredients are added for determining the functional properties of products. Starch is one of the most important polysaccharides used in food systems. The characteristics of starch granular swelling, gelatinization and retrogradation during processing are important for controlling rheological properties of foods (Nishinari, Zhang & Ikeda, 2000). 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 (Pongsawatmanit & Srijunthongsiri, 2008). Since rheological and thermal properties of starch/hydrocolloid mixtures play an important role of texture modification, various studies on these properties of the mixtures between starches and hydrocolloids have been reported (Christianson, Hodge, Osborne & Detroy, 1981; Sudhakar, Singhal & Kulkarni, 1996; Temsiripong, Pongsawatmanit, Ikeda & Nishinari, 2005; Yoshimura, Takaya & Nishinari, 1999). In general, the viscosity of the mixed system is much higher than that of the starch alone due to the synergistic effect and the competition for water between hydrophilic biopolymers and starch (Christianson et al., 1981; Funami, Kataoka, Omoto, Goto, Asai & Nishinari, 2005; Temsiripong et al., 2005). In terms of storage, syneresis of the starch can be lower during storage by adding hydrocolloids such as the mixtures of corn starch and konjac-glucomannan (Yoshimura, Takaya & Nishinari, 1998) corn starch and xyloglucan (Yoshimura et al., 1999), tapioca starch and xyloglucan (Temsiripong et al., 2005) or tapioca starch and xanthan gum (Pongsawatmanit & Srijunthongsiri, 2008).

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 starch-based foods (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 reported (Baek, Yoo & Lim, 2004; Chungcharoen & Lund, 1987; Ikeda, Yabuzoe, Takaya & Nishinari, 2001; Kruger, Ferrero & Zaritzky, 2003). Most of sugars exhibit anti-plasticising effect leading to the lower amount of amylose leaching (Ahmad & Williams, 1999; Kohyama & Nishinari, 1991). The ingredient interactions between starch 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. In addition, The understanding of these pasting properties and rheological properties are important for process and product development in food industry in terms of process design, quality and shelf life extension. Therefore, pasting properties of the selected starch-hydrocoilloid-sucrose systems were investigated. Tapioca starch (TS), a favorable thickener used in many food products, was used for investigation. Xanthan gum is a unique hydrocolloid reported to provide an excellent stability in thermal and acid systems. Sucrose is one of the important sweeteners applied in food products. Therefore, the objective of this study was to evaluate the pasting properties of tapioca starch containing xanthan gum and sucrose using RVA during heating and cooling. The regression analysis from

RVA pasting profile was established to determine the final viscosity. Finally, steady shear viscosity was also conducted to investigate the possibility of using the regression model derived from RVA measurement to predict the viscosity from steady shear measurement since the knowledge would be useful for further application to investigate the thermal and rheological properties of starch-based products.

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 HPSEC (modified method of Govindasamy, Oates & Wong, 1992), respectively. Xanthan gum (Xan) (CP Kelco, San Diego) containing 12.73% w/w moisture content determined by the hot air oven method at 105°C (AOAC, 1995). Both polysaccharides were mixed on a dry basis and used without any further purification. Sucrose (Merck) was used as obtained.

2.2 Rapid Visco Analyser (RVA) measurement

Pasting properties of 5% w/w TS and xanthan gum (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, 10, 20 and 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 finally 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 further 30 min to hydrate the starch. Each TS/Xan/Sucrose suspension was stirred manually to disperse the sample uniformly before measurement. The pasting profile of the sample and agitation speeds of paddle were monitored during a thermal treatment according to Pongsawatmanit and Srijunthongsiri (2008) as following: 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 for the first 10 s was started at 960 rpm and kept constant at 160 rpm until the end of experiment. Pasting profiles were evaluated in triplicate to confirm the data reproducibility and the average values of evaluated pasting parameters were reported.

2.3 Steady shear viscosity measurement

Selected gelatinized TS/Xan/Sucrose mixtures obtained from RVA experiment were used for steady shear viscosity measurement using a rheometer (Physica MCR 301, Anton Paar GmbH, Stuttgart, Germany). All pastes were centrifuged at 190g 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 or 50 °C for at least 2 min before starting the measurement.

Apparent viscosity was recorded by increasing the shear rate from 0.1 to 1000 s^{-1}. The measurements were done using at least three freshly prepared samples and each average value was reported.

2.4 Data and statistical analysis

Pasting profiles were determined in triplicate in order to confirm the reproducibility of the data. 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.). The 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 RVA pasting properties

Changes in the pasting properties of starch during heating and cooling processes can alter the qualities of final starch-based products by addition of hydrocolloids and sugars. The pasting properties of 5% w/w TS/Xan mixtures (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 investigated during RVA experiment. The concentrations of xanthan gum used in the study are ranged from 0-0.5% due to the common concentration range applied in food products (Sharma, Naresh, Dhuldhoya, Merchant & Merchant, 2006). 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. 1). RVA pasting properties are related to the gelatinization and short-term retrogradation of starch-based samples during heating and cooling since no peak of curve was observed in the mixture of 1%Xan containing 30% sucrose. The correlations among sucrose and RVA parameters were analysed and revealed significant positive correlations (p<0.05) (Table 1). Pasting temperatures of TS/Xan pastes increased significantly with sucrose content (p<0.05, Table 2). The results suggest that sucrose reduces the available water in the system and exhibits as an anti-plasticising agent leading to the lower amount of amylose leaching and causing the retardation in gelatinization of TS and TS/Xan mixtures (Ahmad & Williams, 1999; Kohyama & Nishinari, 1991). In addition, a decrease in water content in TS/Xan mixtures containing higher sucrose contents requires higher energy to gelatinization due to such anti-plasticising effect of sucrose (Pongsawatmanit et al., 2007) and leading to higher pasting temperatures (Table 2) (Hirashima, Takahashi & Nishinari, 2005), Sucrose may play an important role in the inhibition of hydration for starch granules or non-starch polysaccharide fraction (Yoshimura, Takaya & Nishinari, 1996). Therefore, in the systems containing higher concentration of sugar, the competition between sucrose and xanthan gum to be hydrated by water in the 5% w/w of total polysaccharides may be critical and leading to increase the pasting temperatures of TS/Xan mixtures from 72 - 78 to 82 - 90 °C with increasing sucrose concentration from 0 to 30%, respectively (Table 2).

The viscosity at the peak of RVA profile called 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 peak and final viscosities of the gum-starch pastes ($p<0.05$) much higher than the influence of xanthan gum substitutions (Figs. 2a and 2b), indicating that the synergistic effect of sucrose and TS or TS/Xan systems is dominant.

After TS or TS/Xan mixtures 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) is determined and defined as breakdown due to the loss of starch granule integrity and subsequent disruption leading to a reduction of the paste viscosity (Christianson et al. 1981). The breakdown of TS/Xan pastes revealed almost constant with increasing Xan substitution ($p>0.05$). However, breakdown values of TS or TS/Xan pastes increased significantly with sucrose content ($p<0.05$, Fig. 2c, Table 1) 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 were more prone to be disrupted under isothermal shear with increasing sucrose content.

When the sample was subsequently cooled down to 50°C at 6°C/min, the viscosity of the pastes increased to a final viscosity at the end of RVA experiments. The increase in viscosities of TS and TS/Xan pastes from holding strength values to final viscosity called setback occurs not only due to the simple kinetic effect of cooling on viscosity, but also due to the reassociation of starch (particularly amylose) molecules. Setback values indicating short-term retrogradation increased with increasing sucrose and decreased with xanthan gum contents ($p<0.05$) (Fig. 2d). The effect of xanthan gum on the extent of decrease in setback values of TS/Xan pastes with and without added sucrose was also observed. Setback values for TS and TS/Xan (4.5% TS, 0.5% Xan) pastes without added sucrose were about 360 mPa.s, and 260 mPa.s, respectively while setback values of those pastes containing sucrose (30%) were 1050 mPa.s and 440 mPa.s, respectively. The results imply that for the TS-based formulation containing sucrose, the xanthan gum addition could reduce the setback of the TS pastes leading to lower syneresis especially in the case of frozen food (Pongsawatmanit & Srijunthongsiri, 2008).

3.2 Analysis of viscosity breakdown under RVA isothermal shear stress

Pasting viscosities of each TS/Xan paste with and without added sucrose were selected from RVA running time at 600 to 780 s during heating at 95°C for calculating the rate of viscosity breakdown from slope of the curve. The slope of each TS/Xan mixture was assumed to be linear relationship and plotted as a function of xanthan gum concentration (Fig. 3). The rates of viscosity breakdown for TS/Xan mixtures (0% sucrose) only slightly increased with xanthan gum concentration whereas relatively large increase of the values was observed from TS/Xan mixtures containing sucrose, especially from higher sucrose content. The slopes of the plots in Fig. 3 were noticeably increased with sucrose content. We have observed that the breakdown values of various TS/Xan mixtures containing the same sucrose content were almost constant (Fig. 2c). However, the effect of sucrose on the rate of viscosity breakdown of the system was more pronounced with increasing both concentrations of sucrose and xanthan gum.

3.3 Steady shear viscosity of TS/Xan pastes

Gelatinized TS and TS/Xan pastes at various mixing ratios containing sucrose (0 to 30%) from RVA experiments was used to evaluate shear rate dependence of the steady shear viscosity. At a constant temperature (25°C), the shear rate dependence (0.1 to 1000 s^{-1}) of the steady shear viscosity of gelatinized TS and TS/Xan exhibited shear thinning behavior (Fig. 4). Selected TS/Xan paste (mixing ratio = 9.5/0.3) revealed the stronger pseudoplastic behavior than that of TS paste (Fig. 4a) due to the contribution of xanthan gum to the TS pastes (Pongsawatmanit & Srijunthongsiri, 2008). Adding sucrose (30%) enhanced the viscosity values of both TS and TS/Xan pastes. In addition, the viscosities of TS paste were higher than those of TS/Xan paste at all studied shear rates (Fig. 4b).

When the viscosity measurement of 5% w/w TS and TS/Xan pastes was performed at higher temperature (50°C), the shear thinning behaviors were also obtained. However, the viscosities of only TS pates were lower than those of pastes containing xanthan gum in the studied shear rate range (0.1 to 1000 s^{-1}) (Fig. 4c). The addition of sucrose (30%) enhanced steady shear viscosity of both TS and TS/Xan pastes (Fig. 4d). However, at higher temperature, viscosities of TS/Xan were also higher than those of TS pastes at low shear rates due to higher pseudoplastic behavior of xanthan gum in TS/Xan mixtures. The results also represent the thermal stability of xanthan gum contributing to TS pastes.

3.3 Specific viscosity of TS/Xan/sucrose

Specific viscosity represents the increase in viscosity that may be contributed by the polymeric solute. For polymer dispersions, the specific viscosity (η_{sp}) is equal to the relative viscosity of the same solution minus one and can be rearranged and calculated from the following equation:

$$\eta_{sp} = (\eta - \eta_s) / \eta_s \qquad (1)$$

where η = viscosity of the TS/Xan/Sucrose system, η_s = viscosity of the solvent (sucrose and water). Values of the specific viscosity are considered to be the contribution of the polymer to viscosity (Pongsawatmanit, Ikeda & Miyawaki, 1999), reflecting the effective volume occupied by polymers in the system. In TS/Xan/Sucrose/water systems, the contribution of TS and Xan to solution viscosity can be determined using viscosity values of the sucrose solution as η_s. The specific viscosities of TS/Xan pastes containing different sucrose contents (0 to 20%) at 50 °C calculated from both RVA final viscosity (Fig. 5a) and steady shear viscosity at shear rate 57.4 s^{-1} (Fig. 5b) were plotted as a function of xanthan gum concentration in total polysaccharide concentration at 5%. An average shear rate of the RVA experiment was estimated from the value of 21.5 multiplied by the angular velocity given in revolutions per second (modified from Lai, Steffe & Ng, 2000). In this study, steady shear viscosities at 57.4 s^{-1} was used to compare with the RVA final viscosity because this shear rate is approximately corresponding to the shear rate obtained from RVA at 160 rpm. The results from both types of measurement methods exhibited a single master curve (Fig. 5), indicating the effect of sucrose (0 to 20%) on the specific viscosity values was relatively small.

3.4 Regression model and model validation of final viscosity

Final viscosity plays an important role in the colloidal system stabilization and product handling in food industry. The final viscosity of TS paste depends on both xanthan and sucrose contents in the system as discussed in the previous sections. Therefore, we plotted the experimental RVA final viscosity from TS and TS/Xan pastes as a function of xanthan gum and sucrose concentrations (Fig. 6). Since the mechanism for explaining the final viscosity depending on the amount of hydrocolloids and sucrose in the TS/Xan/Sucrose mixtures, the linear regression was conducted to relate the RVA final viscosity with xanthan gum 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 an equation (2) for predicting final viscosity as shown below:

$$\text{Final viscosity (cP)} = 712.417 + 355.267\,(\text{Xan}) + 42.303\,(\text{Sucrose}) \qquad (2)$$

Where Xan = xanthan gum concentration ranged from 0 to 0.5% and

Sucrose = sucrose concentration ranged from 0 to 30%

To test the model performance, another group of RVA experiment data was carried out 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%) for determining the final viscosity. Experimental final viscosity values were plotted against those calculated from Eq. (2) using the different xanthan gum and sucrose contents. A good predictability of the viscosity at various sucrose and xanthan gum concentrations between the modeling dataset and testing dataset was achieved, indicated by the corresponding correlation coefficient (R = 0.980) and small root mean square error (RMSE = 84.4) values between them as shown in the Fig. 7a.

We also tested the model from Eq. (2) for predicting the steady shear viscosity of TS/Xan/Sucrose/water system, the result revealed that model from

Eq. (2) predict the steady shear viscosity values of TS/Xan pastes containing sucrose 0 to 20% (lower than 2000 mPa.s) slightly lower than those from the experimental data with the R = 0.9039 and RMSE = 170.9 (Fig. 7b).

4. Conclusion

Strong influence of sucrose on pasting properties of TS and TS/Xan mixtures at a total polysaccharide concentration of 5%w/w. Partial substitutions of TS with xanthan gum impart more stability to the gelatinized TS pastes in terms of heat and setback reduction. The rate of viscosity breakdown in TS pastes was more prominent with increasing both concentrations of sucrose and xanthan gum. The regression model performance from RVA measurement in predicting final viscosity revealed a good agreement with the experimental dataset. Therefore, xanthan gum and sucrose can be used to create TS-based products with better pasting properties during product development in food industry.

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Figure captions

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

Fig. 2 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 3 Rate of viscosity breakdown calculated from RVA pasting profiles 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 containing different sucrose contents during heating at 95 °C with RVA paddle speed at 160 rpm.

Fig. 4 Shear rate dependence of the steady shear viscosity of 5% w/w gelatinized TS/Xan mixtures (mixing ratios = 10/0, 9.5/0.5) with and without sucrose at 25 and 50°C: Measurement at 25°C without sucrose (a), at 25°C with 30% sucrose (b), at 50°C without sucrose (c) and at 50°C with 30% sucrose (d). The vertical bar represents the standard deviation.

Fig. 5 Specific viscosity of 5% w/w TS/Xan pastes containing different sucrose contents measured at 50 °C from RVA (a) and steady shear (b) measurement. The viscosity of solvent used to calucate specific viscosity obtained from the viscosity of sucrose solution (0 to 30%) at 50 °C.

Fig. 6 Surface plot of experimental final viscosity of 5% TS/Xan pastes at different mixing ratios (10/0, 9.75/0.25, 9.5/0.5, 9.25/0.75 and 9/1) as a function of xanthan gum (0 to 0.5%) and sucrose (0 to 30%) concentrations

Fig. 7 Predicted final viscosity using Eq. (2) against experimental RVA final viscosity (a) and steady shear viscosity (b) from 5% w/w gelatinized 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 various sucrose concentrations.

Table 1 Pearson's correlation between selected RVA parameters and 5% TS/Xan mixtures containing different sucrose contents (0 to 30%).

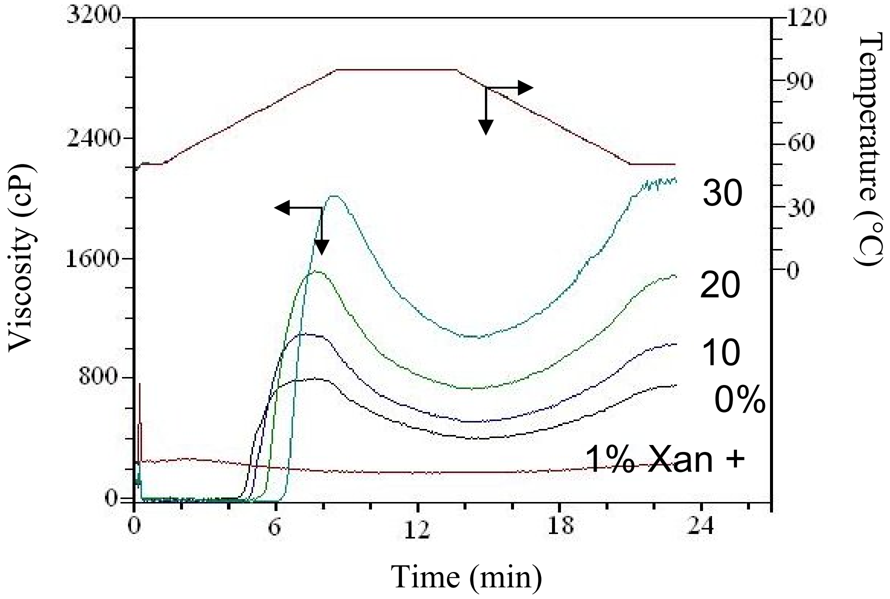
RVA parameters	Sucrose
Pasting temperature	0.850*
Peak viscosity	0.903*
Breakdown	0.985*
Final viscosity	0.954*
Setback	0.723*

* Correlation is significant at the 0.05 level (2-tailed), $p<0.05$.

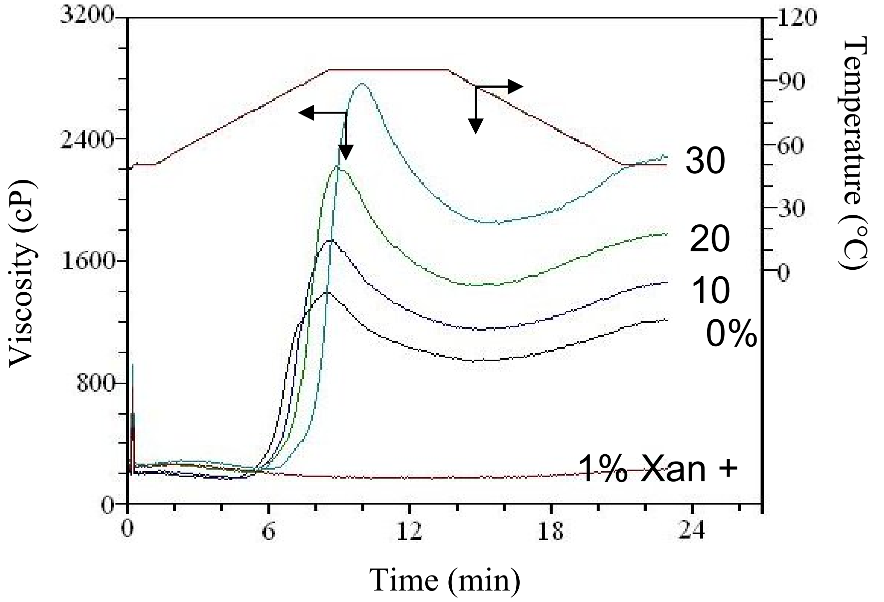
Table 2 Effect of sucrose on pasting temperatures of 5% w/w TS alone and 5% w/w TS/Xan mixtures at various mixing ratios from RVA analysis

Xanthan gum concentration	Pasting temperature (°C)			
	0%	10%	20%	30%
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.



(a) TS only



(b) TS/Xan = 9/1

Fig. 1

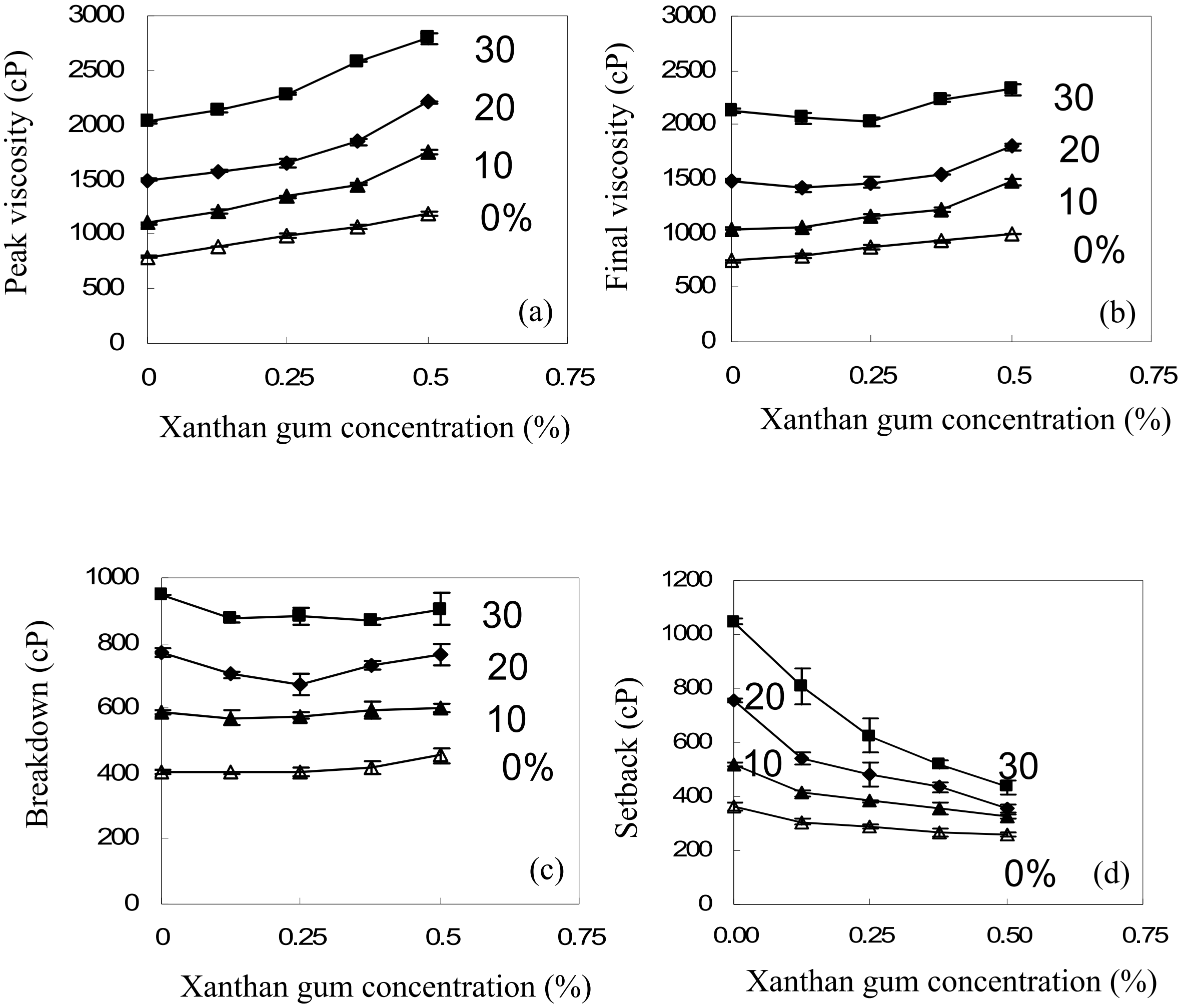

(a)
Peak viscosity (cP)
3000
2500
2000
1500
1000
500
0
0
0.25
0.5
0.75
Xanthan gum concentration (%)
30
20
10
0%
(b)
Final viscosity (cP)
3000
2500
2000
1500
1000
500
0
0
0.25
0.5
0.75
Xanthan gum concentration (%)
30
20
10
0%
(c)
Breakdown (cP)
1000
800
600
400
200
0
0
0.25
0.5
0.75
Xanthan gum concentration (%)
30
20
10
0%
(d)
Setback (cP)
1200
1000
800
600
400
200
0
0.00
0.25
0.50
0.75
Xanthan gum concentration (%)
20
10
30
0%

Fig. 2

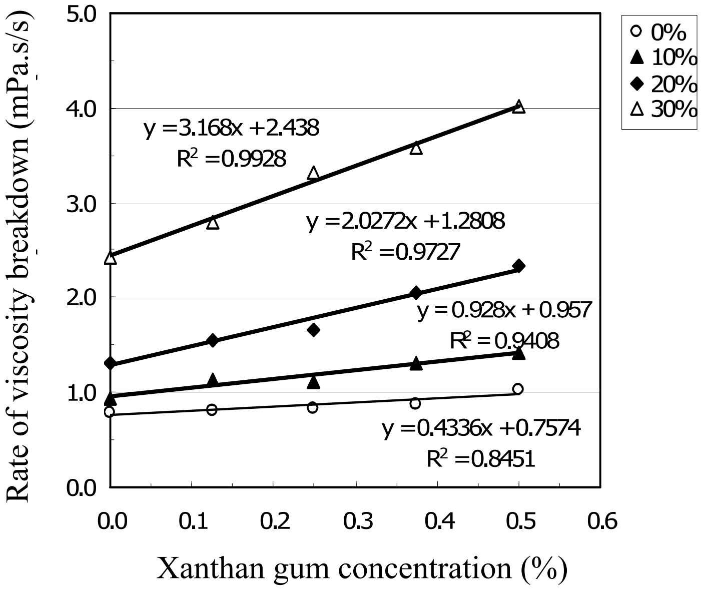
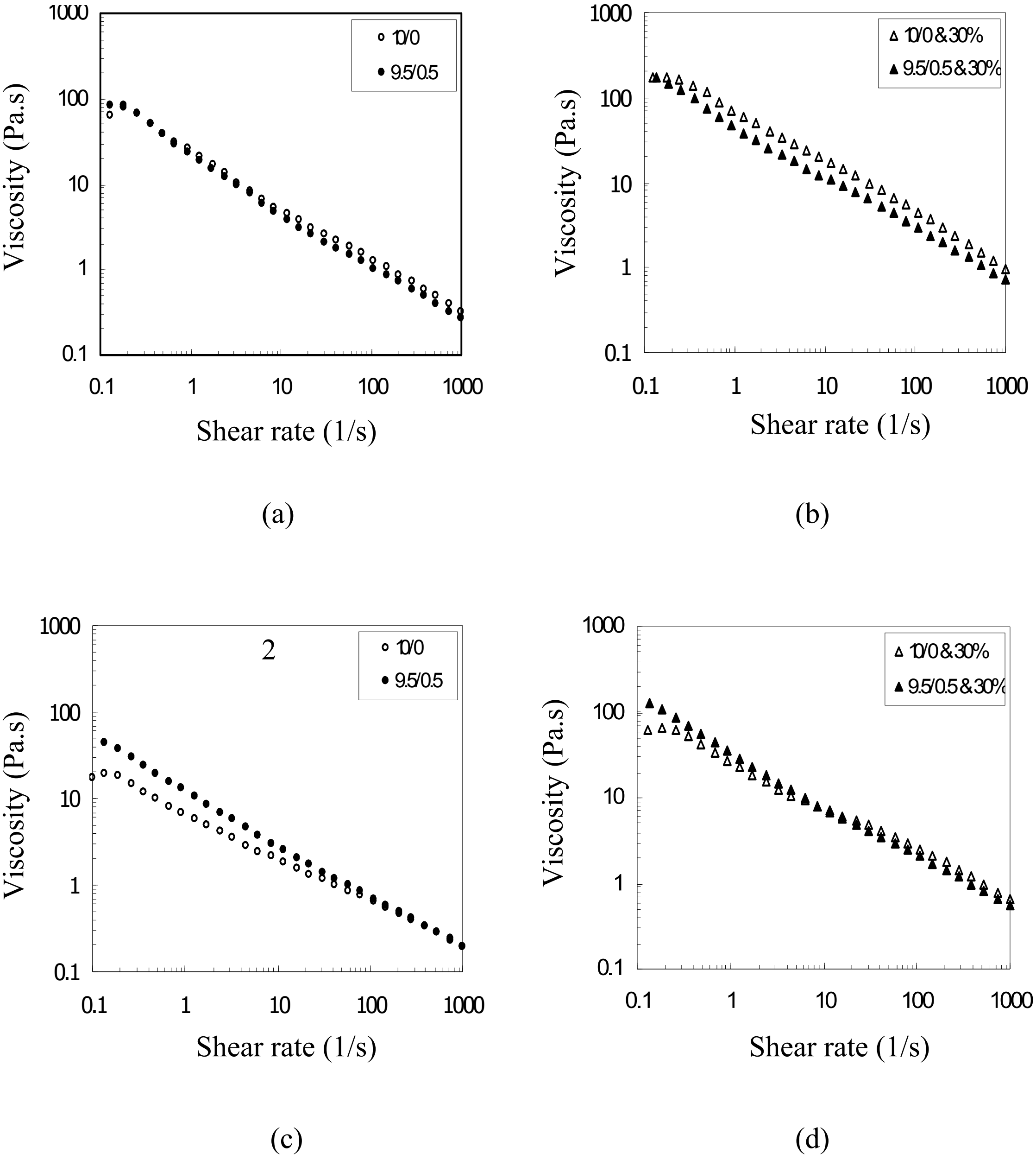

Rate of viscosity breakdown (mPa.s/s)
5.0
4.0
3.0
2.0
1.0
0.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Xanthan gum concentration (%)
○ 0%
▲ 10%
◆ 20%
△ 30%
y = 3.168x + 2.438
R^2 = 0.9928
y = 2.0272x + 1.2808
R^2 = 0.9727
y = 0.928x + 0.957
R^2 = 0.9408
y = 0.4336x + 0.7574
R^2 = 0.8451

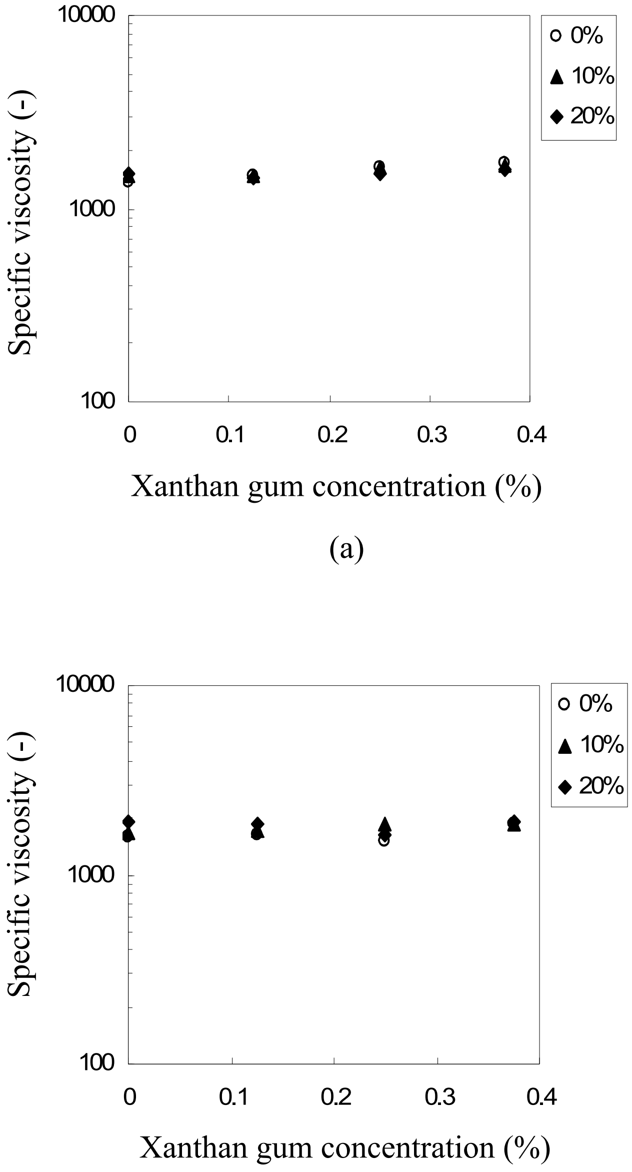
Fig. 3


Viscosity (Pa.s)
Shear rate (1/s)
0.1
1
10
100
1000
1/0
9.5/0.5
1/0&30%
9.5/0.5&30%
2

(a) (b)

(c) (d)

Fig. 4


Specific viscosity (-)
10000
1000
100
0
0.1
0.2
0.3
0.4
Xanthan gum concentration (%)
○ 0%
▲ 10%
◆ 20%

(a)

(b)

Fig. 5

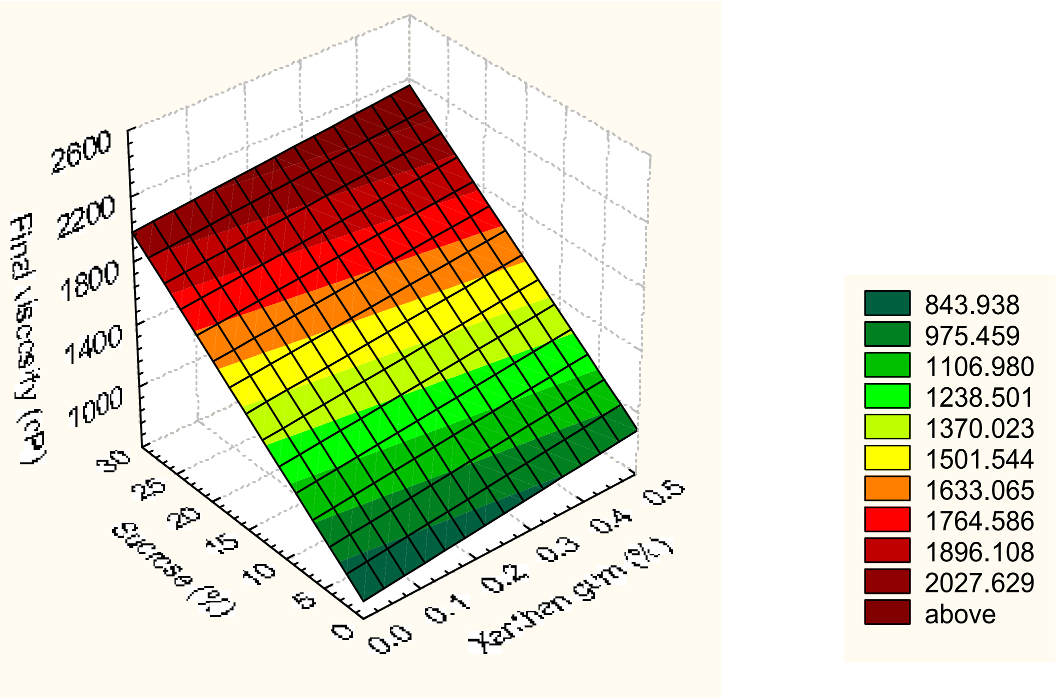
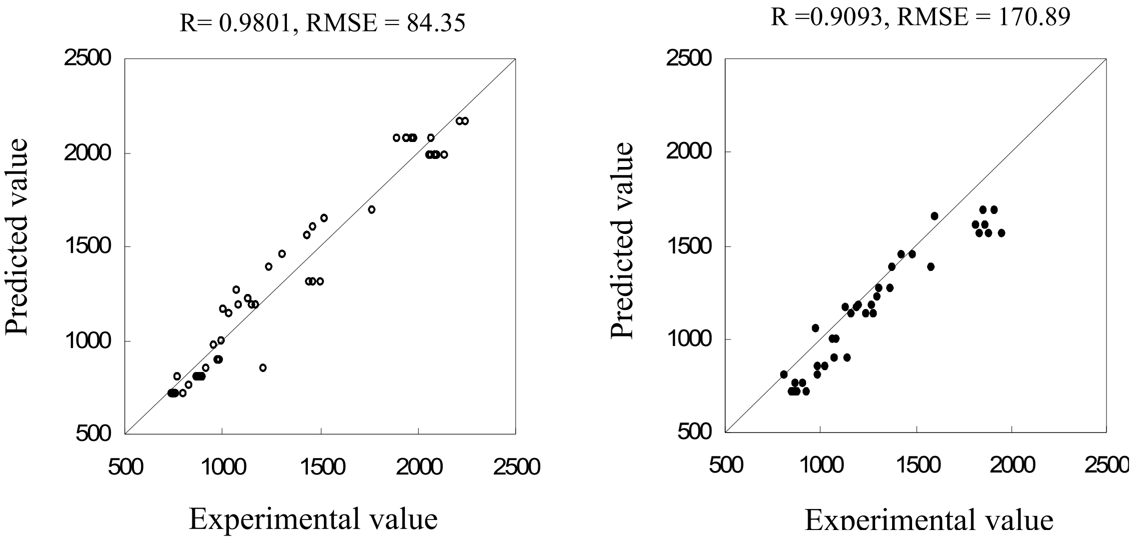

Final viscosity (cP)
2600
2200
1800
1400
1000
Sucrose (%)
30
25
20
15
10
5
0
Xanthan gum (%)
0.0
0.1
0.2
0.3
0.4
0.5
843.938
975.459
1106.980
1238.501
1370.023
1501.544
1633.065
1764.586
1896.108
2027.629
above

Fig. 6


R= 0.9801, RMSE = 84.35
2500
2000
1500
1000
500
Predicted value
500
1000
1500
2000
2500
Experimental value
R =0.9093, RMSE = 170.89
2500
2000
1500
1000
500
Predicted value
500
1000
1500
2000
2500
Experimental value

(a) (b)

Fig. 7

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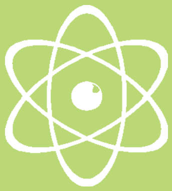

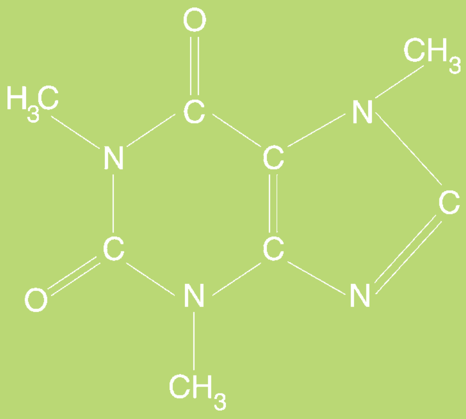

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Effect of Xanthan Gum and pH on Pasting Properties and Freeze-Thaw Stability of Tapioca Starch

Suwapat Srijunthongsiri and Rungnaphar Pongsawatmanit*

ABSTRACT

Effect of xanthan gum on the viscosity and thermal stability of tapioca starch (TS) at different mixing ratios of TS and xanthan gum under different pH values was investigated using a Rapid Visco-Analyzer (RVA) and repeated freeze-thaw treatment. At a total polysaccharide concentration of 5% (w/w) tapioca starch (TS) and TS/xanthan gum mixtures, the RVA peak and final viscosity values increased with xanthan gum concentration. Final viscosity of gelatinized TS alone under pH 3 exhibited the lowest value compared with those of TS at pH 5 and 7 but the extent of difference between those of pH 3 and pH 5 or 7 was lower with increasing gum content. Freeze-thaw stability of TS pastes containing xanthan gum exhibited lower water separation (<10%) compared with that of TS pastes alone (>10%) after 3 cycles of repeated freeze-thaw treatment. This study shows that the substitution of a part of tapioca starch with xanthan gum can improve pasting properties and the freeze–thaw stability of tapioca starch under acidic systems which could be applied to food industry.

Key words: tapioca starch, xanthan gum, pasting properties, pH, freeze-thaw stability

INTRODUCTION

Tapioca starch or cassava starch is a favorable thickener used in food industries especially in Thailand due to its high viscosity, clear appearance, and low production cost, compared to other starches. In food production, the starch-based products may suffer from low stability against shear, or other mechanical stimuli (Temsiripong *et al*., 2005). Starch stability at different pH values is another parameter to be considered for food preparation. 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 stability during a long storage period (Yoshimura *et al*., 1996; Tester and Sommerville, 2003; Pongsawatmanit *et al*., 2006). However, there are a few reports related to the stability of tapioca starch and hydrocolloids such as xyloglucan (Temsiripong *et al*., 2005; Pongsawatmanit *et al*., 2006) in terms of temperature, shear and freeze-thaw stability.

Xanthan gum is a heteropolysaccharide produced by fermentation using *Xanthomonas campestris*. Xanthan gum has a backbone of 1, 4-linked β-D-glucose (like cellulose) with side chains consisting of two mannose and one glucuronic acid. The mannose residue attached to the cellulosic backbone is acetylated, and half of the terminal mannose units contain a pyruvic acid

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residue (Urlacher and Noble, 1999). The gum is reported to provide an excellent stability in heat and acid systems (Sahin and Ozdemir, 2004). Therefore, the objectives of this study were to investigate the influence of xanthan gum (Xan) on the viscosity and thermal stability of tapioca starch (TS) at different mixing ratios and pH values using a Rapid Visco-Analyzer (RVA) and repeated freeze-thaw treatment.

MATERIALS AND METHODS

Materials

Tapioca starch (TS) was purchased from a manufacturer located in the area of Chonburi province, Thailand. The moisture contents of TS and commercial xanthan gum (Xan) (Thai food and chemical Co., Ltd, Thailand) were 12.1 and 11.9% w/w determined by the hot air oven method at 105°C (AOAC, 1995) for 6 h. Amylose content of TS was 22.0% determined by HPSEC (modified method of Govindasamy, Oates and Wong, 1992). The samples were used without any further purification. HCl was analytical grade for adjusting required pH of the mixture suspensions.

Sample preparations

TS and Xan were prepared at different mixing ratios (TS/Xan = 10/0, 9.5/0.5 and 9/1) of 5% total polysaccharide concentration for all measured samples in distilled water adjusted to be at various pH values (3, 5 and 7) using 0.1 N HCl or NaOH. Xanthan gum dispersions were first prepared at room temperature, stirred using magnetic stirrer at least 2 h and kept at 5°C at least 6 h to ensure complete hydration. Then TS powder was added into the gum dispersion, and continuously mixed for 1 h before RVA measurement and freeze-thaw stability test. All samples were prepared in the closed system for preventing moisture loss during preparation.

Determination of RVA pasting properties and freeze-thaw stability

Pasting properties of TS/Xan mixtures were determined using a Rapid Visco-Analyser (RVA-4, Newport Scientific, Narrabeen, Australia), interfaced with a personal computer equipped with Thermocline software (Newport Scientific) according to the method and temperature profile of Pongsawatmanit *et al.* (2006). Pasting profiles were determined in triplicate and the evaluated parameters were averaged.

For the determination of freeze–thaw stability, dispersions of TS or TS/Xan were heated to 95°C, held at the temperature 95-98°C for 30 min, and cooled down to 40°C in ice-water bath. The gelatinized TS/Xan pastes (5% w/w total polysaccharide concentration) with three mixing ratios (10/0, 9.5/0.5 and 9/1) and different pH values (3, 5 and 7) were investigated by storing the pastes in the freezer (-25°C) for 20 h, and then thawing at 40°C for 2 h repeatedly from 1 to 3 cycles according to the method of Pongsawatmanit *et al.* (2006). Sodium azide (0.04% w/w) was added to prevent microbial spoilage. The percentage of water separation using centrifugation at 2100 g for 10 min was calculated from the following equation:

$$\text{Water separation (\%)} = (W_1 - W_2) \times 100 / (W_1 - W_o) \qquad (1)$$

When : W_o = weight of syringes without paste samples after centrifugation at 2100 g for 10 min

W_1 = weight of syringes with paste samples before centrifugation

W_2 = weight of syringes with paste samples after centrifugation at 2100 g for 10 min

Statistical analysis

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

RESULTS AND DISCUSSION

Influence of xanthan gum and pH on RVA pasting properties of TS

The Rapid Visco-Analyser (RVA) was used to investigate the pasting properties of TS and TS/Xan mixtures during heating and cooling processes. Typical RVA pasting profiles of selected TS/Xan mixtures at pH 7 were shown in Figure 1.

When starch granules are heated above the gelatinization temperature in a sufficient amount of water, the granules absorb a large amount of water and swell to many times their original size and the viscosity increases. When most of the tapioca starch granules became swollen, a rapid increase in viscosity occurred. As the temperature increased further, the starch granules began to rupture and the amylose molecules leached out into the continuous phase until reaching a viscosity called the peak viscosity. The peak viscosity is considered to represent the equilibrium point between swelling and rupture of starch granules (Newport Scientific, 1995). Swelling of granules, accompanied by leaching of starch biopolymers, increased the viscosity and during further heating, granules would rupture further which resulted in a decrease in the viscosity. When the system was at the holding temperature (95°C), the sample was subjected to mechanical shear stress, which led to further disruption of the starch granules and amylose leaching, followed at a slower rate by leaching of the amylopectin fraction. The leached-out polymer molecules were more or less aligned in the direction of flow, which contributes to a breakdown in viscosity at a constant temperature. Therefore, the reduction in the viscosity after appearance of the peak was likely to be caused by mechanical rupture of starch granules. As the sample was subsequently cooled down to 50°C, the viscosity increased to a final viscosity at the end of RVA experiments, which was attributed to reassociation of amylose molecules or short-term retrogradation. Peak viscosity increased with xanthan gum concentration and showed no difference in the mixtures containing different pH (Figure 2a). However, final viscosity of gelatinized TS (Figure 2b) under higher acidic conditions (pH = 3)

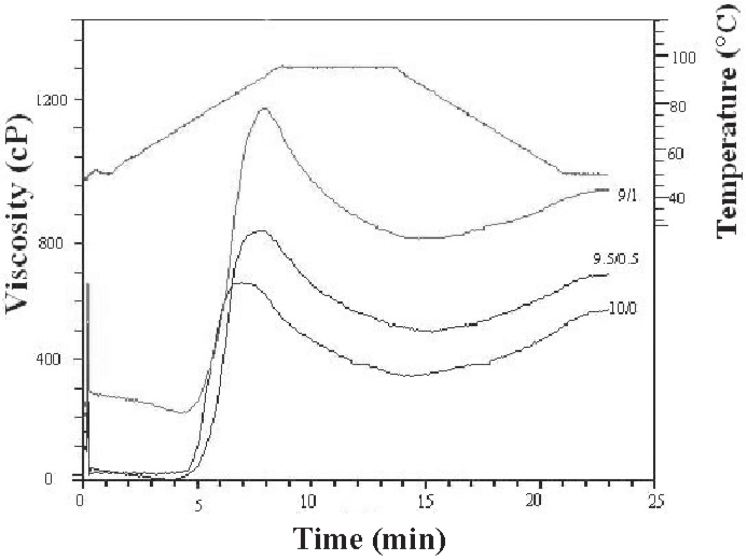

Figure 1 Typical RVA pasting profiles of tapioca starch/xanthan gum mixtures at pH 7 with mixing ratios of 10/0, 9.5/0.5 and 9/1 (a total polysaccharide concentration of 5%).

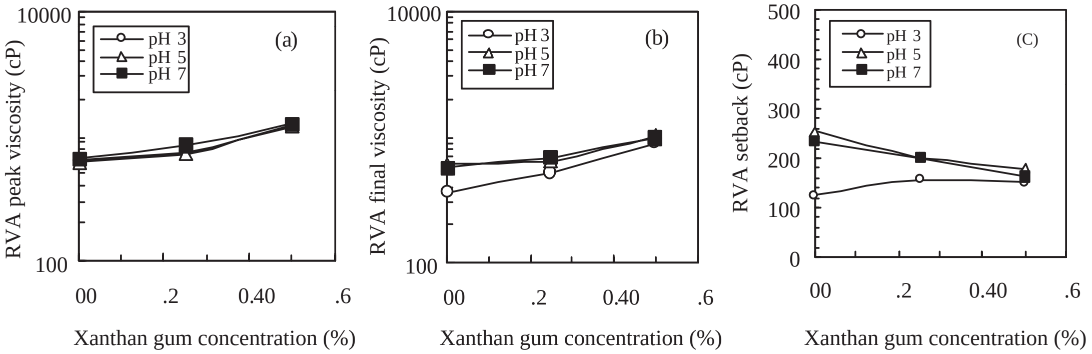

Figure 2 RVA peak (a), final (b) viscosities and setback (c) of 5% w/w tapioca starch/xanthan gum mixtures as a function of gum concentration for different pH.

exhibited the lowest final viscosity ($p \leq 0.05$) compared with those at with pH 5 and 7 probably related to a more damaged granule structure at low pH. The final viscosity values of TS pastes at pH 3 increased with gum concentration and showed a lower extent of difference from those at pH 5 and 7 with increasing gum concentration. The results suggest that xanthan gum provides a good stability of TS in acidic systems. Setback values, referred to short-term retrogradation, of TS and TS/Xan pastes at pH 3 were lower than those at pH 5 and 7 ($p \leq 0.05$). Considering the pastes at pH 5 and 7, setback values of TS pastes were lower with increasing xanthan concentration, indicating that xanthan gum decreases the retrogradation of TS pastes at these pH.

Influence of xanthan gum and pH on freeze–thaw stability of gelatinized TS

Freeze–thaw stability is important in the food industry. In cold chain storage, thermal fluctuations and consequent phase changes of water are the main causes of deterioration in frozen food especially in the gel matrix of starch (Pongsawatmanit *et al.*, 2006). During cold storage, the reorganization of starch molecules may result in the release of water (or syneresis) and this may affect the functional properties in terms of viscosity or gel behavior. Repeated freeze–thaw treatment for one cycle of TS paste at pH 3 showed the highest water separation (17%) compared with those at pH 5 and 7 (10 to 11%) as shown in Figure 3 due to the damaged granule structure during heating and starch hydrolysis promoted by acidic heat treatment (Rogols, 1986). The damage of starch network resulted in higher water separation after thawing. However, the water separations of gelatinized TS containing xanthan gum (for mixing ratios at 9.5/0.5 and 9/1) were lower than 10% for all studied pH (Figure 3)

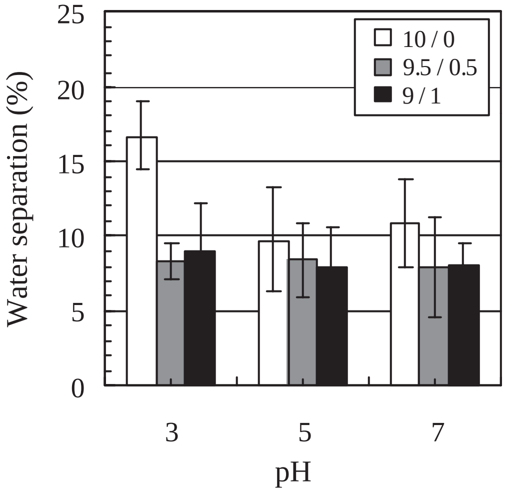

Figure 3 Water separation of 5% w/w gelatinized tapioca starch/xanthan gum mixtures at mixing ratios of 10/0 (a), 9.5/0.5 (b) and 9/1 (c) for different pH values after freezing and thawing.

The thermal stability of gelatinized TS and TS/Xan pastes was investigated further with higher number of freeze–thaw cycles. After the third cycle of repeated freeze–thaw treatment, again the percentages of water separation of TS (pH 3, 5 and 7) containing xanthan gum were almost lower than 10% (Figure 4). Percentages of water separation from TS pastes alone at pH 3 gave the highest value. This results also confirm that the substitution of a part of tapioca starch with xanthan gum improve the freeze–thaw stability of tapioca starch system under acidic condition.

CONCLUSION

At a total polysaccharide concentration of 5% (w/w) TS and TS/Xan mixtures, the peak and final viscosities increased with xanthan gum concentration. Final viscosity of gelatinized TS alone under pH 3 exhibited the lowest value compared with those of pH 5 and 7 but increasing xanthan gum content decreased the extent of such difference. TS pastes containing xanthan gum showed the lower water separation compared with those of TS pastes alone for both one and three cycles of repeated freeze-thaw treatment especially at pH 3.

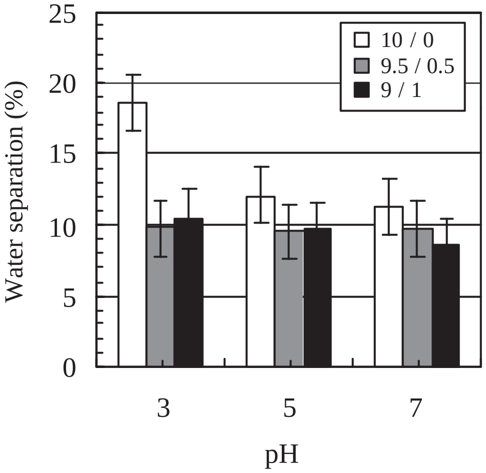

Figure 4 Water separation of 5% w/w gelatinized tapioca starch/xanthan gum mixtures at mixing ratios of 10/0, 9.5/0.5 and 9/1 for different pH values after three cycles of repeated freeze–thaw treatment.

ACKNOWLEDGEMENTS

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Influence of Temperature on Viscosity of Tapioca Starch containing Sodium Alginate

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ABSTRACT

Hydrocolloids have been widely used for improving textural properties and stability of starch during the storage. Viscosity is one of the important physical properties of hydrocolloid and starch mixture in the product development. The objective of this study was to investigate the effect of temperatures (5 to 55°C) on viscosity of tapioca starch (TS) and sodium alginate (Alg) at different mixing ratios to gain more understanding for applications in food products. Gelatinized TS/Alg mixtures were evaluated using a rheometer. Apparent viscosity and consistency index (*K*) values of TS and TS/Alg pastes were decreased with increasing temperatures. The viscosities of mixed TS/Alg pastes were higher than that of TS at temperature >25°C but lower at 5°C. The activation energy values of TS/Alg mixtures were lower than that of TS alone according to the Arrhenius plot, indicating the heat stability of TS/Alg mixtures. The results suggested that sodium alginate could be applied to modify the viscosity and temperature stability of tapioca starch based food product.

Keywords: Tapioca starch, Sodium alginate, Temperature, Viscosity, Activation energy

1. Introduction

Starch is among the most abundant of plant products and is a major food reserve providing a bulk nutrient and energy source in the human diet (Zobel and Stephen, 1995). Among the vast sources of starch, tapioca starch has been commercially exploited for some time and continues to be major sources of starch (Moorthy, 2004). Tapioca starch obtained from cassava roots is widely used as a thickener in the food industry compared to other starches, especially in Southeast Asia (Rapaille and Vanhemelrijck, 1997) because of its high viscosity, clear appearance, and low production cost. However, the physical properties of native starch pastes often limit commercial applications in products due to low stability against heat or shear. During storage, aggregation or recrystallization of starch biopolymers in starch granules can occur and lead to increase rigidity and syneresis (Lie *et al.*, 2003), affecting the texture of starch-based food products. In addition, temperature during distribution and storage before consumption is another environmental factor determining the final stability of the required texture attributes of starch pastes. This leads to difficulty in predicting and controlling the change of physical properties of starch-based foods during the time before consumption. A well-known technique to modify viscosity/texture or maintain desirable viscosity/texture during storage is to blend starches with other hydrocolloids or biopolymers (Funami *et al.*, 2005; Hernandez *et al.*, 2006; Pongsawatmanit *et al.*, 2006; Pongsawatmanit *et al.*, 2007; Shi and BeMiller, 2002; Temsiripong *et al.*, 2005). When a starch/hydrocolloid mixture is used as a texture modifier, understanding of its rheological properties is important to improve the formulation of starch-based foods. Thus, many investigations on rheological properties of mixtures between starches and hydrocolloids have been reported (Funami *et al.*, 2005; Pongsawatmanit *et al.*, 2007; Shi and BeMiller, 2002; Sudhakar *et al.*, 1996; Temsiripong *et al.*, 2005). In general, the viscosity of a starch/hydrocolloid mixed system is much higher than that of starch or hydrocolloid alone because most biopolymers are strongly hydrophilic and compete with starch for water (Pongsawatmanit *et al.*, 2006). This can be described by synergistic interactions between starch and hydrocolloids. Since a wide range of temperature is encountered during processing and storage of food, the effect of temperature on rheological properties in terms of either apparent viscosity at a specified shear rate or the consistency index, *K*, of the power law model of a liquid food can be described by the Arrhenius relationship (Rao, 1999). This leads to an understanding which allows prediction and controls the quality of the final product which such are of commercial importance for food manufacturers, potentially leading to cost reduction in the processing of starch-based food products or to the control of their overall qualities during storage (Funami *et al*., 2005).

Alginates are salts of alginic acids (Morris, 1998). They occur naturally as the major structural polysaccharides of brown marine algae (*Phaeophyceae*) and as extracellular mucilages secreted by certain species of bacteria. They are linear polymers of (1 → 4)-β-D-mannuronopyranosyl and (1 → 4)-α-L-guluronopyranosyl units in a copolymer that contains homopolymeric sequences. The dissociation constants for mannuronic acid (M) and guluronic acid (G) monomers are 3.38 and 3.65, respectively (Draget, 2000). Alginate solutions are in general highly viscous because the extended conformation of the alginate molecule gives the alginate a large hydrodynamic volume and high ability to form viscous solution (Moe *et al.*, 1995). Sodium alginate is soluble in water, producing viscous solutions, and is used in both food and non-food systems (Sime, 1990). Sodium alginates are used as stabilizers, thickeners and gelling agents in several foods, such as sauces, soups, beverages and deserts (Whistler and BeMiller, 1997).

Understanding the properties of starch/hydrocolloid mixtures would improve the development of high quality starch-based products. However, there are few reports related to viscosity of tapioca starch in the presence of sodium alginate. Therefore, in this study, sodium alginate was combined with tapioca starch to investigate the effect of temperature (5 to 55°C) on viscosity of tapioca starch and sodium alginate at different mixing ratios.

2. Materials and methods

2.1 Materials

Tapioca starch (TS) was obtained from Chorchaiwat Industry Co., Ltd. (Three Elephants Brand, Cholburi, Thailand). Food grade sodium alginate (Alg) was kindly donated by TIC gums (TIC Pretested® Colloid 488T). The supplier reported that this product had an M : G ratio of about 55 : 45, was of "medium" viscosity, and had a molecular mass of 216 kDa. The samples were used without further purification.

2.2 Methods

Weighed amounts of TS and Alg were dispersed into deionized distilled water at the total polysaccharide content of 5 wt% with various mixing ratios (TS/Alg = 10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2). Sodium alginate solution was first prepared and stirred using a magnetic stirrer for 2 h prior mixing with TS to ensure fully hydration of polysaccharide. The mixtures were stirred using a magnetic stirrer for 1 h at room temperature, heated in a boiling-water bath, and then further stirred for 30 min while the sample temperature was maintained at 95 – 98°C and cooling immediately. The mixtures were centrifuged at 190 g for 2 min to remove air bubbles.

Gelatinized TS/Alg pastes with different mixing ratios of 10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2 (5 wt% total polysaccharide concentration) were studied. Steady shear viscosity of gelatinized TS and Alg mixtures was measured using a rheometer (Physica MCR300, Anton Paar GmbH, Stuttgart, Germany), equipped with a cone-plate test fixture (50 mm diameter, 1° cone angle and 0.05 mm gap). Sample was loaded onto the plate of the rheometer and allowed to reach equilibrium on the plate. Apparent viscosity was recorded by increasing the shear rate from 0.1 to 1000 s^{-1}. Measurements were done at 5, 15, 25, 35, 45, and 55°C. The Arrhenius equation was also used to investigate the temperature dependency of the apparent viscosity of all mixtures.

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

3. Results and Discussion

The shear viscosity of gelatinized TS/Alg was measured using a rheometer. Sample temperature was kept constant at 25 ± 0.1°C for at least 30 s before starting the measurement. At a constant temperature (25°C), the shear rate dependence of the steady shear viscosity of 5 wt% gelatinized TS/Alg mixtures at different mixing ratios (10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) and dispersion of 1 wt% Alg is shown in Figure 1. The shear rate was increased from 0.1 to 1000 s^{-1}. All 5 wt% TS/Alg mixing ratios (10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) showed shear-thinning flow behavior in this studied range: the higher the shear rate the lower the apparent viscosity. The viscosity of the TS pastes was lower than those of the TS/Alg pastes. The TS/Alg pastes gave higher apparent viscosity with increasing Alg concentration; indicate that the steady flow behavior of TS/Alg pastes was dominated by those of Alg dissolving in the continuous phase as shown in the previous study of tapioca starch and xyloglucan mixtures (Pongsawatmanit *et al.*, 2006).

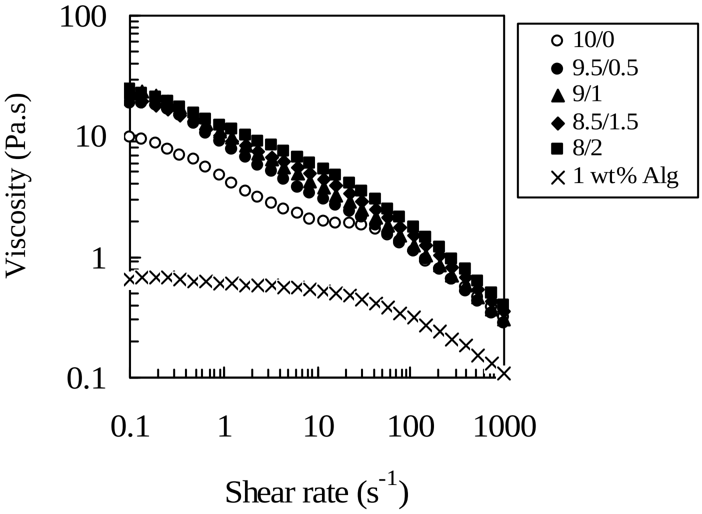

Figure 1 Shear rate dependence of the steady shear viscosity of 5 wt% gelatinized TS/Alg mixtures at different mixing ratios of 10/0, 9.5/0.5, 9/1, 8.5/1.5, 8/2 and dispersion of 1 wt% Alg at constant temperature 25°C.

Since a wide range of temperatures are usually encountered during processing and storage of fluid foods, therefore, the influence of temperature on the apparent viscosity was studied (Figure 2). The sample temperatures were studied at 5, 15, 25, 35, 45, and 55°C. Apparent viscosity was plotted at a shear rate of 50 s^{-1} because it has been reported as an effective oral shear rate (Morris, 1983; Marcotte *et al.*, 2001). We found that the apparent shear viscosity was decreased with increasing temperature as expected. The change in the apparent viscosity with temperature of the TS paste alone showed a higher change than those of the TS/Alg pastes.

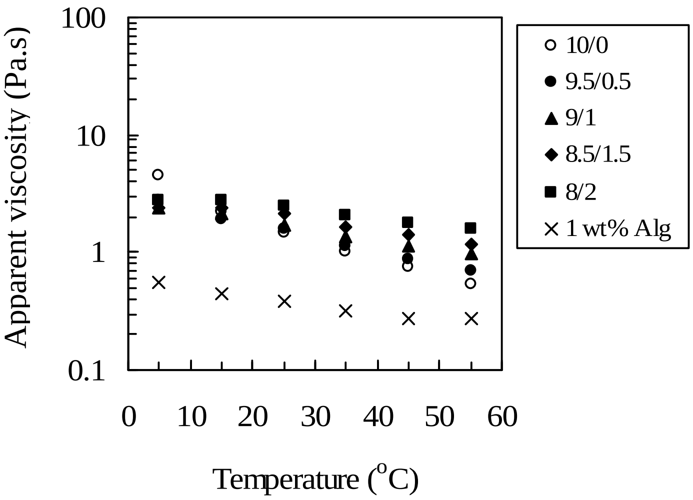

Figure 2 Temperature dependence of apparent viscosity of 5 wt% gelatinized TS/Alg mixtures (10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) and dispersion of 1 wt% Alg for a fixed shear rate of 50 s^{-1}.

The relationship between the steady shear stress and shear rate for all mixing ratios of TS/Alg pastes at different temperatures was analyzed by using a power law model as shown in the following equation:

$$\tau = K \dot{\gamma}^{n} \tag{1}$$

where τ is shear stress (Pa or N/m^2), $\dot{\gamma}$ is steady shear rate (s^{-1}), K is consistency index ($Pa.s^n$), and n is flow behavior index (-). The consistency index K is defined as the shear stress at a shear rate of 1.0 s^{-1} and the exponent n, the flow behavior index, is dimensionless that reflects the closeness to Newtonian flow (Rao, 1999). The n value is sometimes called the power law index where $n = 1$ corresponds to Newtonian fluid and the lower n value reflects a higher degree of pseudoplastic properties of the fluid. The power law parameters (K and n) were calculated by linear regression from a plot of log τ and log $\dot{\gamma}$ and values of K and n for all mixing ratios of 5 wt% TS/Alg are summarized in Table 1.

Table 1 Power law parameters (*n* = power index; *K* = consistency index) for 5 wt% total polysaccharide content of TS/Alg at different mixing ratios and temperature determined from the shear rate range from 0.5 to 100 s^{-1}.

Dispersions	Temperature (°C)	*K* (Pa s^n)	*n* (-)	R^2
5% TS/Alg (10/0)	5	35.17 ± 0.88	0.60 ± 0.11	0.94
	15	8.22 ± 1.74	0.68 ± 0.05	0.99
	25	4.46 ± 0.88	0.72 ± 0.04	0.99
	35	3.75 ± 1.04	0.69 ± 0.05	0.99
	45	2.96 ± 0.68	0.66 ± 0.05	0.99
	55	1.98 ± 0.37	0.67 ± 0.03	0.99
5% TS/Alg (9.5/0.5)	5	28.11 ± 2.19	0.50 ± 0.05	0.93
	15	14.03 ± 0.27	0.53 ± 0.03	0.99
	25	8.70 ± 0.37	0.57 ± 0.01	0.99
	35	6.69 ± 0.09	0.58 ± 0.04	0.99
	45	4.47 ± 0.79	0.59 ± 0.04	0.99
	55	3.43 ± 0.64	0.60 ± 0.04	0.99
5% TS/Alg (9/1)	5	23.27 ± 1.09	0.48 ± 0.03	0.97
	15	14.60 ± 0.05	0.53 ± 0.01	0.99
	25	10.88 ± 1.17	0.58 ± 0.04	0.99
	35	6.79 ± 0.75	0.60 ± 0.02	0.99
	45	5.28 ± 0.50	0.61 ± 0.02	0.99
	55	4.24 ± 0.35	0.63 ± 0.01	0.99
5% TS/Alg (8.5/1.5)	5	20.45 ± 1.28	0.49 ± 0.01	0.98
	15	15.81 ± 0.51	0.55 ± 0.00	0.99
	25	10.48 ± 0.87	0.61 ± 0.00	0.99
	35	7.60 ± 0.49	0.63 ± 0.00	0.99
	45	5.76 ± 0.31	0.65 ± 0.01	0.99
	55	4.41 ± 0.18	0.67 ± 0.01	0.99
5% TS/Alg (8/2)	5	21.94 ± 1.52	0.49 ± 0.03	0.99
	15	18.45 ± 1.11	0.55 ± 0.02	0.99
	25	12.68 ± 1.04	0.61 ± 0.02	0.99
	35	9.40 ± 0.98	0.63 ± 0.02	0.99
	45	6.95 ± 0.71	0.66 ± 0.02	0.99
	55	5.63 ± 0.56	0.68 ± 0.02	0.99
1 % Alg	5	1.28 ± 0.02	0.81 ± 0.00	0.99
	15	1.15 ± 0.04	0.85 ± 0.00	0.99
	25	1.57 ± 0.08	0.88 ± 0.00	0.99
	35	2.04 ± 0.20	0.90 ± 0.02	0.99
	45	2.73 ± 0.09	0.93 ± 0.01	0.99
	55	3.12 ± 0.08	0.97 ± 0.01	0.99

The correlation coefficients for all determinations were higher than 0.9. Considering only 1 wt% Alg dispersion, *K* values of Alg dispersion were mostly much lower than those of the 5 wt% TS and TS/Alg pastes. The *K* values of all TS and TS/Alg pastes and Alg dispersion decreased with increasing temperature. The change of *K* as a function of temperature of the gelatinized TS sample was higher than those of all gelatinized TS/Alg pastes (Figure 3), suggest that Alg increased the thermal stability of TS/Alg pastes in terms of viscosity change with temperature.

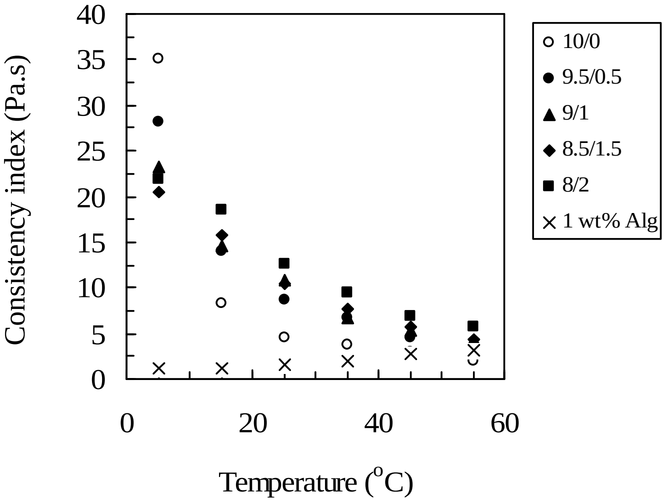

Figure 3 Dependence of the consistency index (*K* value) on the temperature of 5 wt% gelatinized TS/Alg mixtures (10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) and dispersion of 1 wt% Alg.

For the flow behavior index, *n* values of the Alg dispersion (1 wt%) were about 0.81 - 0.97, while the magnitude of the *n* values of TS and TS/Alg pastes were lower ranging from 0.48 - 0.72, indicating that only Alg had a flow behavior which was close to Newtonian. However, this result is limited to the intermediate shear rate range because the power law model does not describe the low shear and high shear rate constant – viscosity data of shear thinning foods (Rao, 1999).

The temperature dependency of the apparent viscosity at specified shear rates of liquid or semi-solid foods can be described by the Arrhenius relationship:

$$\eta_a = \eta_{\infty A} \exp(E_a/RT) \qquad (2)$$

where η_a is the apparent viscosity at a specific shear rate, $\eta_{\infty A}$ is the frequency factor, E_a is the activation energy (J/mol), *R* is the gas constant (J/mol K), and *T* is the absolute temperature (K) (Rao, 1999). Activation energies (E_a) and correlation coefficients for the determination are shown in Table 2. Since E_a is a parameter reflecting the sensitivity of the viscosity change due to the temperature change, gelatinized TS/Alg mixtures had a smaller temperature dependence indicated by lower E_a compared to that of TS alone. These results again suggest that Alg improved the heat stability of the TS/Alg mixtures and the viscosity of TS showed a higher sensitivity to a change in temperature compared to that of TS/Alg mixtures. Activation energies of Alg dispersion (1 wt%) were also determined at shear rate 50 s^{-1} and they were lower than that of the TS paste alone. However, we can observe that the apparent viscosity values for Alg dispersion without TS were lower than those of the 5 wt% TS/Alg mixtures.

4. Conclusion

The influence of temperature (5 to 55°C) on viscosity of tapioca starch containing sodium alginate at different mixing ratios was determined. The flow curve of all 5 wt% TS/Alg mixtures showed shear thinning behavior and the viscosity of the mixtures increased with increasing Alg content. Apparent viscosity and consistency index (K) values of TS and TS/Alg pastes were decreased with increasing temperatures. The influence of Alg on thermal stability can be described by the Arrhenius plot with lower activation energy (E_a) on gelatinized TS/Alg mixtures compared to that of TS alone.

Acknowledgements

This material is based upon work supported by Thailand Research Fund and Kasetsart University Research and Development Institute (KURDI). We gratefully thank Chorchaiwat Industry Co., Ltd. And TIC gums for providing tapioca starch and sodium alginate, respectively.

Table 2 Activation energy for 5 wt% TS/Alg mixtures at different mixing ratios (10/0, 9.5/0.5, 9/1, 8.5/1.5, and 8/2) and for dispersions of Alg (1 wt%) derived from the Arrhenius relationship and evaluated at shear rates 50 s^{-1}.

Dispersions	Total concentration (wt%)	E_a (kJ/mol)	R^2
TS 10/0	5	27.43 ± 1.21	0.96
TS/Alg 9.5/0.5	5	20.72 ± 0.60	0.99
TS/Alg 9/1	5	15.96 ± 1.04	0.99
TS/Alg 8.5/1.5	5	14.24 ± 0.46	0.99
TS/Alg 8/2	5	11.67 ± 1.10	0.99
Alg	1	10.31 ± 0.34	0.95

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ความคงตัวทางด้านการแช่แข็งและละลายของสารผสมแป้งมันสำปะหลังกับอัลจีเนตที่มี pH แตกต่างกัน

FREEZE-THAW STABILITY OF TAPIOCA STARCH AND ALGINATE MIXTURES AT DIFFERENT pH

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บทคัดย่อ: ความคงตัวทางด้านการแช่แข็งและละลายของแป้งมันสำปะหลัง (TS) สามารถปรับได้ด้วยการใช้ไฮโดรคอลลอยด์ โดยศึกษาผลของอัลจีเนต (Alg) ต่อความคงตัวดังกล่าว ด้วยการเตรียมดิสเพอร์ชันของแป้งมันสำปะหลังและอัลจีเนตความเข้มข้นรวม 5% (สัดส่วน 10/0, 9/1, 8/2) ที่มีความเป็นกรดด่างต่างกัน (pH 5, 6, 7) ผลการทดลองพบว่า ปริมาณน้ำที่แยกออกมาจากเพสต์แป้งมันสำปะหลังหลังวงจรการแช่แข็งและละลาย 7 รอบ ที่ pH 5 มีค่าสูงสุดเมื่อเปรียบเทียบกับเพสต์ของแป้งที่ pH 6 และ 7 ส่วนปริมาณน้ำที่แยกออกมาจากเพสต์ของ TS/Alg (9/1 และ 8/2) มีค่าต่ำกว่าของเพสต์จากแป้งอย่างเดียวหลังผ่านวงจรการแช่แข็งและละลาย 7 รอบที่ทุก pH โดยปริมาณน้ำที่แยกออกมานั้นจะมีค่าต่ำกว่าเมื่อ pH มีค่าสูงขึ้น ผลการศึกษาชี้ให้เห็นว่า อัลจีเนตสามารถใช้ในการปรับปรุงสมบัติทางด้านความคงตัวที่ pH 5 ถึง 7 ในผลิตภัณฑ์ที่ใช้แป้งมันสำปะหลังเป็นส่วนประกอบ

Abstract: Freeze-thaw stability of tapioca starch (TS) can be modified using hydrocolloids. Alginate (Alg) was investigated in this study using a repeated freeze-thaw treatment. The gelatinized 5% TS/Alg dispersions (10/0, 9/1, 8/2) at different pH values (5 to 7) were prepared. The results showed that water separation of TS paste alone after 7 freeze–thaw cycles at pH 5 was the highest value compared with those of TS pastes at pH 6 and 7. The water separations of gelatinized TS/Alg (9/1 and 8/2) were lower than those of TS pastes alone after seven freeze-thaw cycles for all studied pH whereas water separation was lower with higher pH. The results suggest that alginate can be used for improving the freeze-thaw stability at the studied pH (5 to 7) in TS-based products.

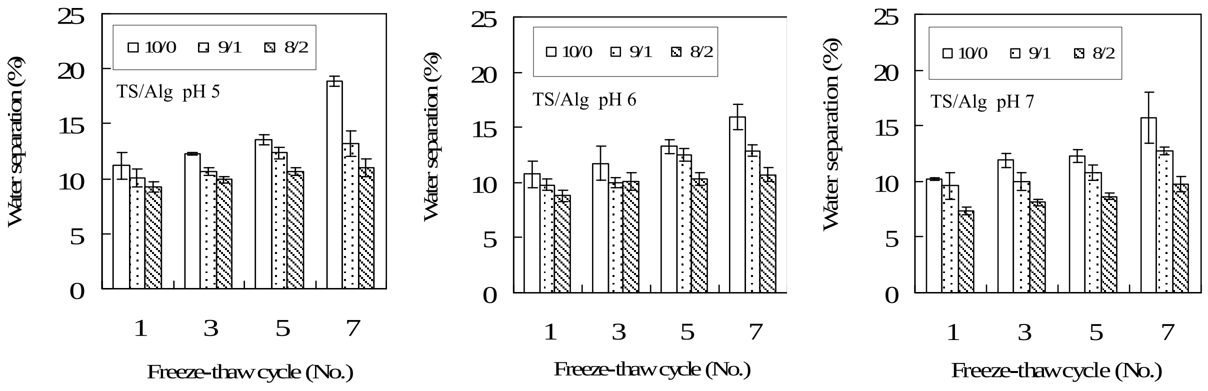
Introduction: Tapioca starch is a favorable thickener used in food products especially in Thailand due to its high viscosity, clear appearance, and low production cost, compared to other starches. In food production, the starch-based products may suffer from low stability against shear, or other mechanical stimuli [1]. In addition, starch stability at different pH values is another parameter to be considered for food preparation. Incorporation of a proper amount of hydrocolloids may improve textural properties and stability of tapioca starch in food products in frozen storage [2, 3, and 4]. Alginate occurs naturally as the major structural polysaccharides of brown marine algae (*Phaeophyceae*) are used in this study. Alginate with high guluronic acid content results in strong and brittle microparticles with good heat stability but likely to syneresis after freeze-thaw treatment, whereas alginates with high manuronic acid content result in weaker and more elastic gels with good freeze-thaw stability [5]. The objective of this study was to evaluate the influence of alginate on the freeze-thaw stability of tapioca starch at different pH.

Methodology: Tapioca starch (TS) and sodium alginate (Alg) were prepared at three mixing ratios (TS/Alg = 10/0, 9/1 and 8/2). The 5 % total polysaccharide concentrations of all mixtures were prepared for the freeze-thaw stability measurement. Alginate dispersions were first prepared at room temperature, stirred using magnetic stirrer at least 2 h to ensure complete hydration. Then TS powder was added into the gum dispersion, and continuously mixed for 30 min. Then, all TS/Alg mixture were adjusted to various pH values (5, 6 and 7) using 0.1 N HCl or NaOH. The dispersions of TS or TS/Alg were heated to 95°C, held at the temperature 95-98°C for 30 min, and cooled down in ice-water bath. All samples were prepared in the closed system for preventing moisture loss during preparation. The gelatinized TS/Alg pastes were investigated by storing the pastes in the freezer (-25°C) for 20 h, and then thawing at 40°C for 2 h repeatedly from 1 to 7 cycles. Water separation from the TS/Alg pastes at defined freeze-thaw cycles was carried out according to the method of Pongsawatmanit et al. (2006) [2].

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

Results, Discussion and Conclusion: Freeze–thaw stability is important in the food industry. During cold storage, the reorganization of starch molecules may result in the release of water (or syneresis) and this may affect the functional properties in terms of viscosity or gel behavior. Water separation of TS paste alone after the seventh cycle at pH 5 showed the highest value (19%) compared with those of TS pastes at pH 6 and 7 (about 16%) (Fig. 1) suggest that the retrograded starch network or structure was easily disrupted by ice crystal formation which resulted in higher water separation on thawing [2, 6]. The water separations of gelatinized TS containing Alg (for mixing ratios at 9/1 and 8/2) were lower than 13% after the seventh cycle for all studied pH values. Water separation values of 5% TS and TS/Alg pastes at pH 5 were higher than those at pH 6 and 7, indicating the degraded starch network occurring at the low pH resulting in larger ice crystal formation evidenced by higher water separation. These results suggest that partial substitution of TS with alginate formed a paste with improving freeze-thaw stability for pH range from 5 to 7.

Therefore, alginate can be used to formulate TS-based products containing different pH (5 to 7) with better freeze-thaw stability during product development in food industry.



(a) (b) (c)

Figure 1 Water separation of 5% w/w gelatinized tapioca starch/alginate mixtures at mixing ratios of 10/0, 9/1 and 8/2 for different pH values pH 5 (a), pH 6 (b) and pH 7 (c) values after freezing and thawing.

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Keywords: Tapioca starch, alginate, pH, freeze-thaw stability, retrogradation

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T-1364	CHANGES IN TPA PARAMETERS OF TAPIOCA STARCH GELS CONTAINING ALGINATE DURING STORAGE	Nawaporn Kumpai,, Suwapat Srijunthongsiri, Thepkanya Harnsilawat, Rungnaphar Pongsawatmanit
T-1365	EFFECTS OF DIFFERENT ATMOSPHERES ON QUALITY OF STORED KUERLE FRAGRANT PEAR FRUIT	Junmao Tong, Guogang Chen, Zhenli Wang, Ying Jiang, Jiluan Chen

CHANGES IN TPA PARAMETERS OF TAPIOCA STARCH GELS CONTAINING ALGINATE DURING STORAGE

Nawaporn Kumpai, Suwapat Srijunthongsiri, Thepkanya Harnsilawat,
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Introduction

The retrogradation of starch gel during storage is important for product development in food industry. Tapioca starch (TS) is a food ingredient widely used in many products. Incorporation of a proper amount of hydrocolloids may improve textural properties and stability of tapioca starch in food products**.** Therefore, the objective of this study was to evaluate the change in TPA parameters of TS gels with and without alginate during the storage at low temperature.

Materials and Methods

TS dispersions containing alginate (Alg) (0 to 1.25 wt%) were prepared at the mixing ratios of 10/0, 9.75/0.25 and 9.5/0.5. Gelatinized pastes containing 25% w/w polysaccharide were obtained in plastic cases to form cylindrical gels with 22 mm in diameter. The gels were kept at 5 ^{o}C and cut into 20 mm in height for texture profile analysis (TPA) after storage for 1, 4 and 7 day.

Results and Discussion

The hardness and stiffness values of each TS/Alg gel increased with increasing storage time but these two values were lower with increasing Alg content at the same storage time. However, cohesiveness of the TS/Alg gels exhibited the lower values with increasing storage time but increased with increasing Alg substitution. The results suggest that keeping the starch gels at 5°C enhanced the strength of gel structure due to the retrogradation but Alg can decrease network rigidity by reducing the structure formation of the amylose in TS during the storage.

Changes in TPA parameters of tapioca starch gels containing alginate during storage

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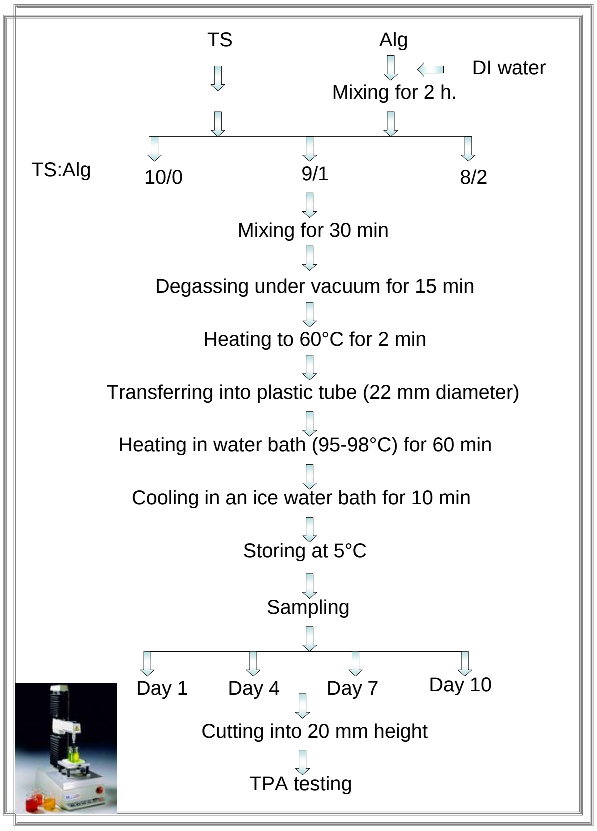
Introduction

The retrogradation of starch gel during storage plays an important role in food quality for both processing and storage stages. Incorporation of a proper amount of some hydrocolloids may change textural properties and stability of starch-based products [1, 2]**.** Tapioca starch (TS) is an widely used ingredient in many products. Alginate occurs naturally as the major structural polysaccharides of brown marine algae (*Phaeophyceae*) and was used in this study. The objective of this work was to evaluate the change in TPA parameters of TS gels with and without alginate during the storage at low temperature.

Materials and methods

TS dispersions containing alginate (Alg) (0 to 1.25 wt%) were prepared at the mixing ratios of 10/0, 9.75/0.25 and 9.5/0.5. Gelatinized pastes (25% w/w polysaccharide) were prepared in plastic cases to form cylindrical gels with 22 mm. diameter (Fig. 1). The gels were kept at 5 °C and cut into 20 mm. in height for texture profile analysis (TPA) after storage for 1, 4, 7 and 10 day. The gel sample was compressed for a distance of 6 mm (30% compression) at a speed of 0.5 mm/s with a 50 mm-diameter probe using flat plate of the Texture Analyzer (TA.XT.plus, UK.). Force-deformation curves were obtained with a 5 kN load cell. The attributes reported are: hardness (N), springiness (dimensionless), cohesiveness (dimensionless) (Fig. 2).


TS

Alg

DI water

Mixing for 2 h.

TS:Alg

10/0

9/1

8/2

Mixing for 30 min

Degassing under vacuum for 15 min

Heating to 60°C for 2 min

Transferring into plastic tube (22 mm diameter)

Heating in water bath (95-98°C) for 60 min

Cooling in an ice water bath for 10 min

Storing at 5°C

Sampling

Day 1

Day 4

Day 7

Day 10

Cutting into 20 mm height

TPA testing

Fig. 1. The preparation of tapioca starch with alginate gels.

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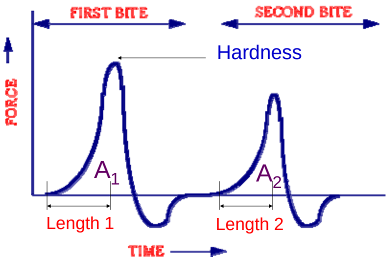

Fig. 2. Standard TPA profile of gel sample [3]

Hardness is the maximum force during the first compression cycle ("first bite").

Cohesiveness is the ratio of the positive force area during the second compression to that during the first compression (A_2/A_1).

Springiness (sometimes also referred to as "elasicity") is the distance of the detected height of the product on the second compression (Length 2), divided by the original compression distance (Length 1).

Results and Discussion

The hardness (an indicator of samples structure strength) and springiness (a perception of gel "rubberiness" in the mouth) of each TS/Alg gel increased with increasing storage time but these two values were lower with increasing alginate content at the same storage time (Fig. 1a and b).

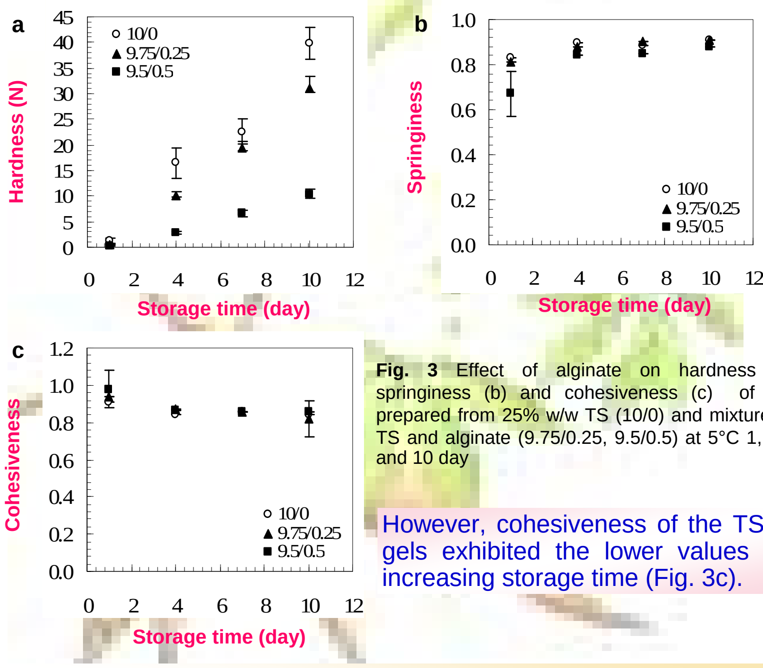

Fig. 3 Effect of alginate on hardness (a), springiness (b) and cohesiveness (c) of gels prepared from 25% w/w TS (10/0) and mixtures of TS and alginate (9.75/0.25, 9.5/0.5) at 5°C 1, 4, 7 and 10 day

However, cohesiveness of the TS/Alg gels exhibited the lower values with increasing storage time (Fig. 3c).

In conclusion, the results suggest that keeping the starch gels at 5°C enhanced the strength of gel structure due to the retrogradation but Alg addition decrease network rigidity by reducing the structure formation of the amylose in TS during the storage.

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