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

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ABSTRACT

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

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

INTRODUCTION

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

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

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

MATERIALS AND METHODS

Materials

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

Preparation of the TS/Xan mixtures

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

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

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

Freeze-thaw stability measurement

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

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

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

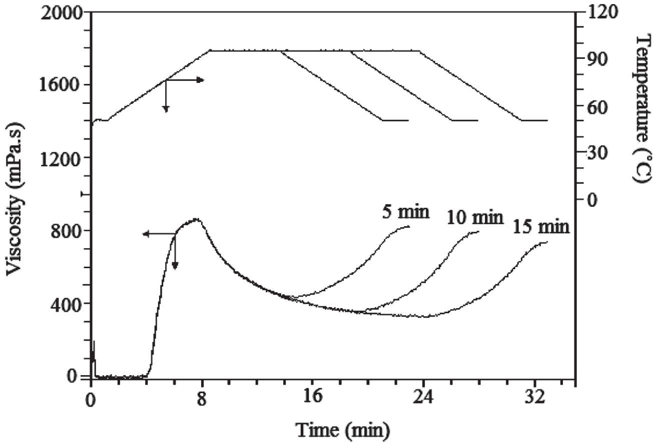
Statistical analysis

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

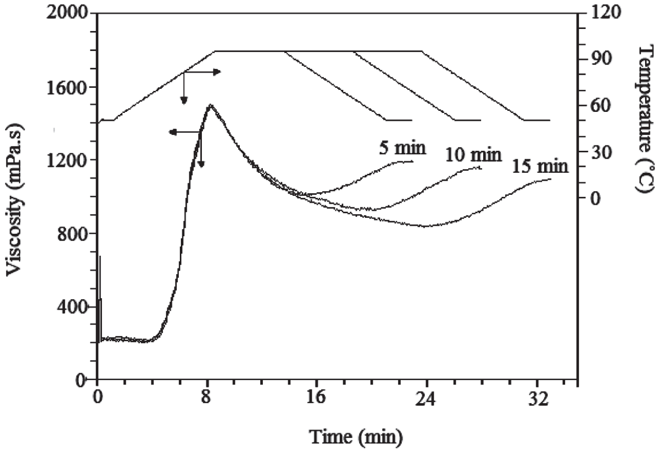
RESULTS AND DISCUSSION

Pasting properties from rapid visco-analyser measurement

The rapid visco-analyser was used to investigate the effect of thermal treatment under constant shear on the pasting properties of the TS and TS/Xan (mixing ratio = 9/1) mixtures heated at 95°C for 5-15 min. The pasting profiles of the 5% w/w TS and TS/Xan mixtures at pH 7 are shown in Figure 1 and indicate that the viscosities of the mixtures from the initial pasting to the peak (the highest apparent viscosity obtained) were almost identical among the different holding times. Pasting temperatures of the TS and TS/Xan mixtures with different heating times (5, 10 and 15 min) at 95°C were 68.6-69.3°C and 72.4-73°C, respectively, whereas peak viscosities from these three heating times were about 851-861 mPa.s and 1476-1495 mPa.s for the TS and TS/Xan mixtures, respectively. Pasting temperatures and peak viscosities for the TS and TS/Xan mixtures compared within different heating times at 95°C were not significantly ($p>0.05$) different, as expected, due to the same heating profile for the first 13.5 min of each total RVA sequence. However, the pasting temperatures and peak viscosities of the TS/Xan mixtures were higher than those of TS alone, due to the contribution of the Xan in the continuous phase of the mixtures (Temsiripong *et al.*, 2005). When the system was maintained at 95°C, the mixtures were subjected to both thermal and shear stresses, leading to further disruption of the starch granules and leaching out of starch molecules. A greater decrease in viscosity was observed in the systems with higher holding times at 95°C. The breakdown values of the TS and TS/Xan mixtures increased with heating time (Figure 2a, $p<0.05$). The greater increase in the breakdown of the TS/Xan suspensions under the shear forces indicated that the aggregates of xanthan molecules in the pastes (formed through hydrogen bonding and polymer entanglement) were disrupted with increasing heating time (Sworn, 2000; Pongsawatmanit and Srijunthongsiri, 2008).



(a)



(b)

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

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

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

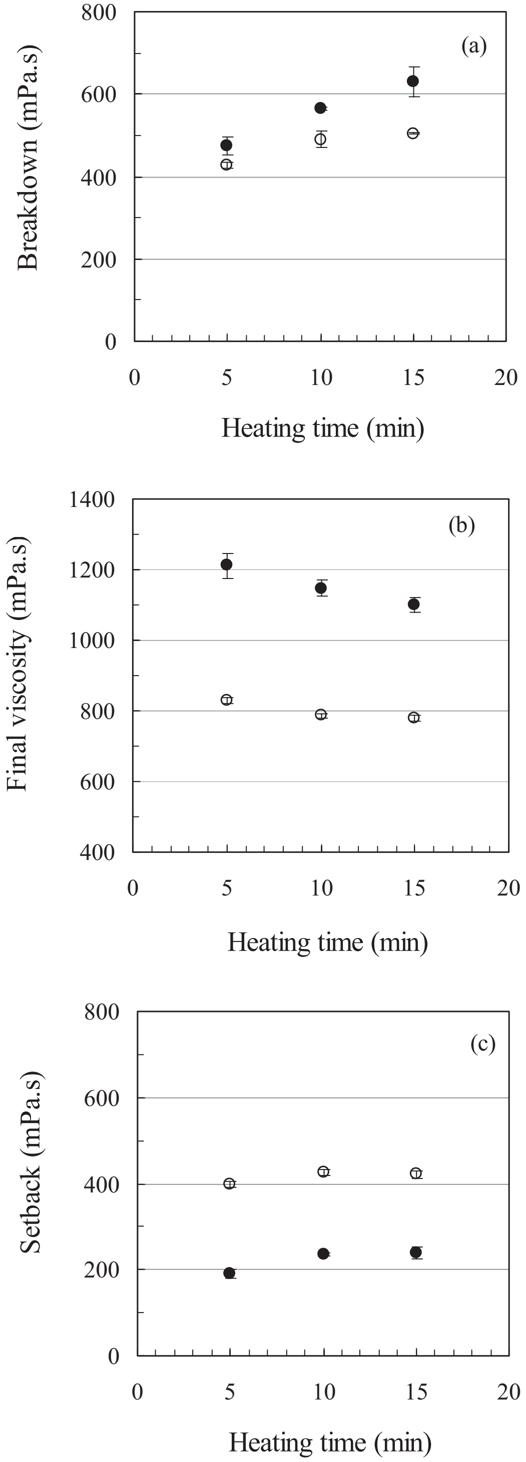


Figure 2 Plots as a function of RVA heating time at 95°C for TS (○) and TS/Xan (●): (a) breakdown; (b) final viscosity; and (c) setback.

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

Freeze-thaw stability measurement

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

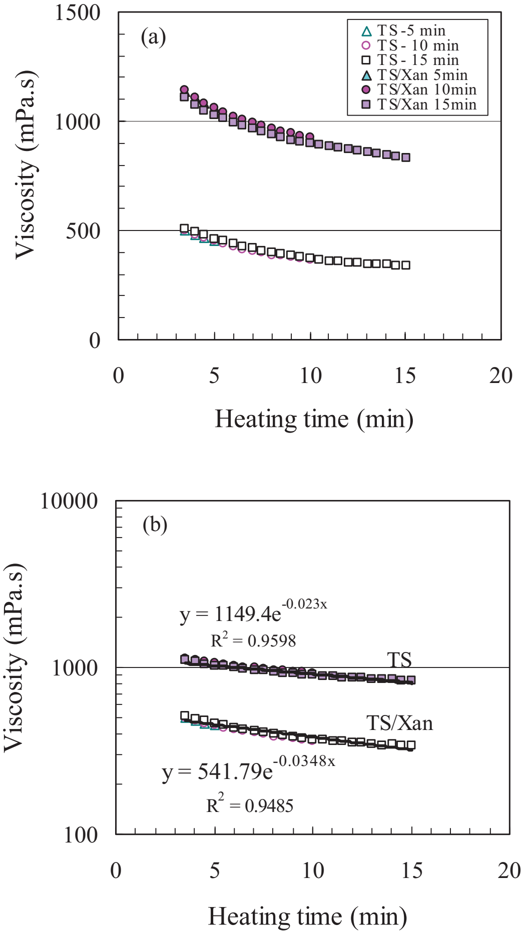
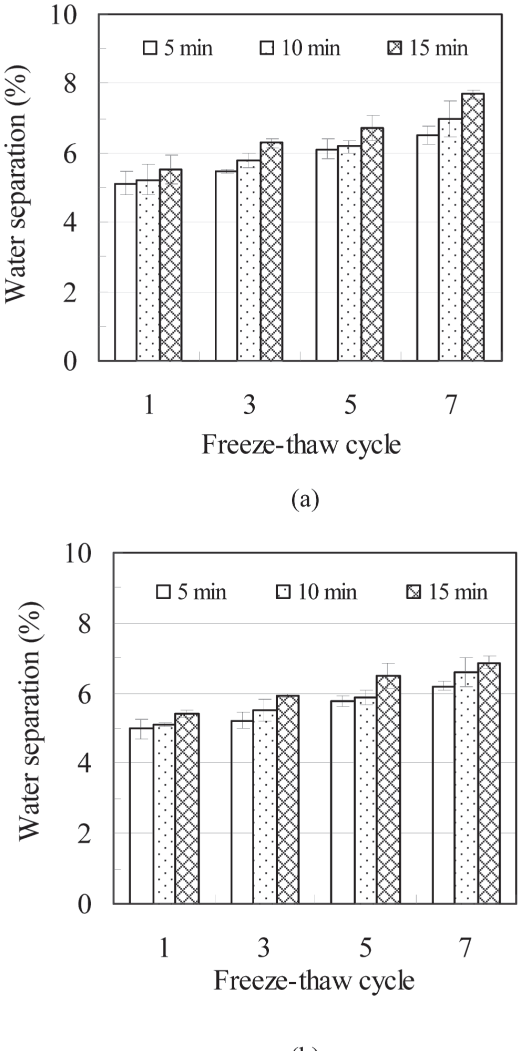


Figure 3 Plots of 5% TS (open symbol) and TS/Xan (filled symbol) pastes as a function of RVA heating time at 95°C: (a) viscosity; and (b) first order plot of viscosity.



(a)

(b)

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

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

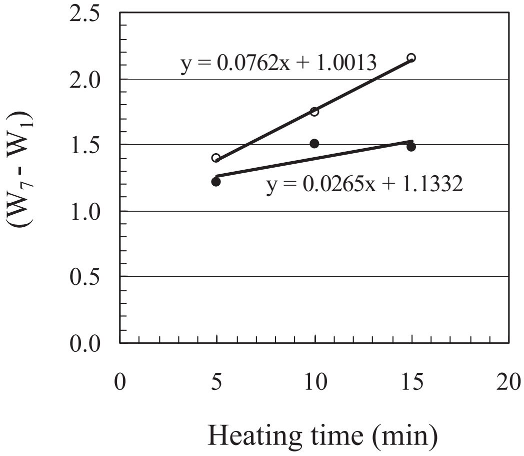


Figure 5 Difference of water separation obtained from freeze-thaw cycle 7 and 1 of 5% TS (○) and TS/Xan (●) pastes as a function of RVA heating time.

CONCLUSION

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

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