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Effects of guar gum and xanthan gum additions on physical and rheological properties of cationic tapioca starch

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Abstract

The gelatinization of cationic tapioca starch embedded in gum matrices was investigated by using a Rapid Visco-Analyzer (RVA), differential scanning calorimeter (DSC), scanning electron microscope (SEM), and rheometer. In addition, swelling power and solubility indices were measured. Xanthan and guar gum increased the RVA peak viscosity of cationic tapioca starch during pasting synergistically in different ways. Guar gum was more effective than xanthan gum in terms of increasing peak viscosity due to its ability to increase the swelling power and solubility index. Both xanthan gum and guar gum induced association between the gelatinized granules probably due to bridging. Association was much more extensive with xanthan. DSC studies showed that the presence of gums influenced the gelatinization characteristics of starch significantly by increasing the onset gelatinization temperature and decreasing the gelatinization enthalpy. Dynamic rheological measurement showed a strong interaction occurred in the cationic tapioca starch–xanthan gum mixture resulting in a decrease in the loss tangent (tan δ) as compared with guar gum addition or starch alone. The ionic interaction of gums and starch was found to play an important role in the gelatinization characteristics of the mixtures and also rheological properties of the pastes.

Keywords: Cationic tapioca starch; Gums; Starch–gum mixtures; Swelling power; Solubility; Gelatinization characteristics; Viscoelasticity

1. Introduction

Hydrocolloids (gums) are used in starch-based products to improve stability, modify texture, facilitate processing, reduce costs, control moisture and show a variety of gelatinization and rheological properties (Krüger, Ferrero, & Zaritzky, 2003; Rojas, Rosell, & Benedito de Barber, 1999; Shi & BeMiller, 2002; Sudhakar, Singhal, & Kulkarni, 1996). The use of such combinations was found in food products such as bakery and cereal products, fruit fillings, sauces, frozen foods, and confectionary products (Ward & Andon, 2002; Wei, Wang, & Wu, 2001).

Hydrocolloids have been shown to influence the gelatinization of starches. It is well known that addition of hydrocolloids to starch suspensions causes a synergistic increase in viscosity (Alloncle, Lefebvre, Llamas, & Doublier, 1989; Liu, Eskin, & Cui, 2003). There are a few reports about the interactions between starch and gum that discuss the mechanism. Christianson, Hodge, Osborne, and Detroy (1981) found that guar, xanthan, and carboxymethyl cellulose (CMC) gum gave a two-stage increase in viscosity of wheat starch during gelatinization. An initial increase in paste viscosity was attributed to the first stage of swelling and was dependent on media viscosity only. A subsequent increase in final peak viscosity was due to interactions of gums, leached component and swollen starch granules. On the contrary, Shi, & BeMiller (2002) reported that the initial increase in viscosity occurring before pasting of dilute normal maize starch–gum systems was attributed to interactions between certain leached molecules, primarily amyloses, and certain gums, i.e. CMC, gellan, xanthan, guar gum and sodium alginate. Lee, Baek, Cha, Park, and Lim (2002) reported that xanthan gum reduced the paste viscosity of sweet potato starch significantly, possibly through strong network formation with starch, whereas guar gum and alginate increased the viscosity. This result is consistent with those of Shi, & BeMiller (2002), who suggested that the greatly decreased peak viscosity when

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negatively charged gums were added to potato starch was due to the repulsion between phosphate groups on potato starch and the negative charges on the gum molecules. However, there are few reports on the interaction between gums and modified starch (Abdulmola, Hember, Richardson, & Morris, 1996; Shi, & BeMiller (2002); Tecante & Doublier, 1999) and on the morphology of gelatinization of starch–gum mixtures by using scanning electron microscopy (Jing-ming & Sen-lin, 1990; Mandala, Palogou, & Kostaropoulos, 2002).

The aim of this research was to determine the effect of hydrocolloids, i.e. guar gum (neutral gum) and xanthan gum (negatively charged gum), addition at the levels commonly used in food formulations on the pasting and viscoelastic properties of cationic tapioca starch. Cationic starch is used in numerous industrial applications, including as a thickening agent for food products and as an adhesive for paper products. Nevertheless, it is evident here that the selected types of starches and gums play an important role in the understanding of gelatinization mechanism. Recently, several effects were examined to achieve the understanding of mechanisms of starch gelatinization in the presence of gums. However, to the best of our knowledge no study has been published on the interactions of cationic starch and gums.

2. Materials and methods

2.1. Materials

Commercial cationic tapioca starch used (Batch No. 121165, General Starch Co., Ltd, Bangkok, Thailand) had 0.35% nitrogen content and 11.64% moisture content. The cationic tapioca starch was a quaternary ammonium starch ether. Xanthan gum and guar gum were obtained from Union Chemical 1986 Co., Ltd, Bangkok, Thailand. Moisture contents of xanthan and guar gums were 10.06 and 13.68%, respectively.

2.2. Pasting properties

The pasting properties of starch or starch–gum mixtures suspended in distilled water were determined by a Rapid Visco-Analyzer (Model RVA-4C, Newport Scientific Pty. Ltd, Warriewood, Australia). The slurry concentration of 6% w/v (dry basis) cationic tapioca starch was dispersed in 25 ml distilled water or 0.35% w/v (dry basis) gum solutions. In the case of starch–gum mixtures, gums were first dispersed in distilled water under magnetic stirring, heated to 80 °C for 5 min and cooled to room temperature; then, starch was slurried in the gum solutions. The dispersions were stirred with a spatula for sufficient duration to avoid the formation of lumps, especially in the xanthan gum solution. The starch–gum suspensions were poured into aluminum containers and stirred manually using a plastic paddle for 20–30 s before insertion into the RVA machine. The heating and cooling cycles were programmed in the following manner. The slurry was held at 50 °C for 1 min, heated to 95 °C within 3 min and then held at 95 °C for 2 min. It was subsequently cooled to 50 °C within 3 min and then held at 50 °C for 2 min, while maintaining a rotation speed of 160 rpm.

2.3. Swelling power and solubility index

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

2.4. Scanning electron microscopy (SEM)

In this assay, 0.6 g (dry basis) of starch was dispersed in 10 ml distilled water or 0.35% (dry basis) gum solutions. The samples were put in centrifuge tubes and heated in a water bath at a temperature of 64 °C for 5 min under minimum shear condition. After heating, the samples were mixed with an equal volume (10 ml) of 2% agarose solution of same temperature as fast as possible and were immediately immersed in an ice bath. For the SEM observation, the samples were prepared by the technique of the critical point drying modified from the method of Egelandsdal et al. (2001). The samples were chemically fixed in 6% glutaraldehyde in 0.1 M phosphate buffer (pH 7) and were post-fixed overnight in 2% osmium tetraoxide with 0.1 M imidazole and then dehydrated through a graded series of ethanol before being critical point dried through CO_2 in a critical point dryer (Hitachi HCP-2). The agars were cut with a razor blade and torn before observation by SEM. Finally, the samples were mounted on aluminum nails and coated with platina/palladium. For the observation of the sample, the SEM (SEM S-2500, Hitachi Science Systems, Ibaraki, Japan) was used. The images were captured at magnification 1500× and at an accelerating voltage of 15 kV.

2.5. *Differential scanning calorimetry (DSC)*

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

2.6. *Viscoelastic behavior*

Fresh pastes obtained from the RVA were used for dynamic oscillatory rheological measurement by a rheometer (Physica MCR 300, Anton Paar GmbH, Stuttgart, Germany). Samples were placed into the rheometer measuring system (cone and plate geometry, 50 mm diameter, 1° cone angle, and 0.05 mm gap) which was equilibrated to 25 °C. Two steps of rheological measurements were performed: (a) deformation sweeps at a constant frequency (10 rad/s) to determine the maximum deformation attainable by a sample in the linear viscoelastic range and (b) frequency sweeps at a constant deformation (0.5% strain) within the linear viscoelastic range. The mechanical spectra were obtained recording the dynamic moduli G', G'' and $\tan \delta$ as a function of frequency. G' is the dynamic elastic or storage modulus, related to the material response as a solid. G'' is the dynamic viscous or loss modulus, related to the material response as a fluid.

2.7. *Statistical analysis*

The data reported in the tables are an average of triplicate observations. The data were subjected to statistical analysis using SPSS (SPSS Inc., 1998, Chicago, IL, USA) version 9.0 for windows (Duncan's test). Significant differences were reported for $P < 0.05$.

3. Results

3.1. *Pasting profiles*

The RVA gelatinization profiles of cationic tapioca starch with and without gums are shown in Fig. 1. Pasting properties of cationic tapioca starch were greatly affected by the addition of gums. From the physico-chemical point of view, it is well known that addition of gums can increase viscosity of starch pastes. Synergistic effects in viscosity existed between cationic tapioca starch and gums. The rapid increasing in viscosity for suspensions of starch–gum mixtures were detected as the temperature increased from 50 to 95 °C. Starch–guar gum mixture exhibited significantly ($P \leq 0.05$) higher peak viscosity than starch–xanthan gum mixture, whereas the opposite trend was observed with final viscosities as shown in Table 1. Addition of xanthan gum resulted in significant ($P \leq 0.05$) increases in setback viscosity and pasting temperatures of cationic tapioca starch, whereas guar gum addition showed no effect ($P > 0.05$) on these values.

3.2. *Swelling power and solubility index*

The effects of gum addition on the swelling power (SP) and solubility index (SOL) of starch are shown in Figs. 2 and 3, respectively. All samples exhibited a sharp increase in SP with increasing heating temperatures from 60 to 70 °C followed by a slight increase for cationic tapioca starch and a decrease for starch–gum mixtures from 70 to 90 °C. The reduction of SP at higher temperatures was likely to be due to the existence of some cloudy solids, which were poured out along with clear supernatant. However, the SP profiles obtained from this study were similar to those previously reported by Li and Yeh (2001) for native tapioca starch. Statistical analysis was performed comparing SP and SOL values of starch alone and starch–gum mixtures at each temperature from 60 to 90 °C. The SP and SOL profiles of

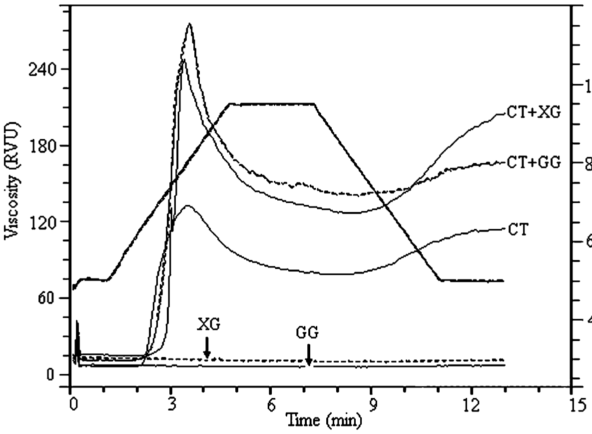

Fig. 1. RVA viscosity profiles of xanthan gum (XG), guar gum (GG), cationic tapioca starch (CT), and cationic tapioca starch in the presence of guar gum (CT+GG) or xanthan gum (CT+XG).

Table 1
Pasting characteristics of cationic tapioca starch alone (CT) and CT in the presence of guar gum (CT+GG) or xanthan gum (CT+XG) determined by the Rapid Visco-Analyzer (RVA)

Sample	Peak viscosity[a] (RVU)	Breakdown[b] (RVU)	Setback[c] (RVU)	Final viscosity[d] (RVU)	Pasting temperature[e] (°C)
CT	130.89 ± 1.83c	53.43 ± 1.62c	34.08 ± 1.01b	111.56 ± 1.83c	62.87 ± 1.49b
CT+GG	278.14 ± 8.93a	133.48 ± 4.27a	25.75 ± 0.85b	158.41 ± 6.95b	63.78 ± 0.78b
CT+XG	251.61 ± 14.42b	115.17 ± 11.44b	199.66 ± 7.42a	199.66 ± 7.43a	68.07 ± 1.17a

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

[a] Maximum viscosity during pasting.

[b] Peak viscosity minus minimum viscosity during pasting.

[c] Maximum viscosity during cooling minus minimum viscosity during pasting.

[d] Final viscosity at 50 °C.

[e] Temperature indicating an initial increase in viscosity.

starch–guar gum mixture were nearly the same as those of starch alone. The starch–xanthan gum mixture, however, exhibited a significantly ($P \leq 0.05$) lower SP and SOL values than those of the starch alone in the temperature range tested. This result demonstrated that xanthan gum inhibited starch swelling and prevented amylose leach out, whereas guar gum seemed to have no effect on these properties.

3.3. Morphology of cationic tapioca starch with and without hydrocolloids

Scanning electron micrographs of cationic tapioca starch samples with and without gums are shown in Fig. 4. The starch granules dispersed in distilled water showed large open holes at one end of the granules following gelatinization (Fig. 4(a)). As shown in Fig. 4(b) and (c), both guar gum and xanthan gum promoted granule association probably by bridging, but this was more extensive for xanthan gum. From the SEM observation, we can visualize that xanthan gum enwrapped several granules to promote aggregates within the gel matrix (Fig. 4(c)). The granular size of starch within the gel matrix promoted by xanthan gum was smaller than those within the continuous phase.

3.4. Gelatinization temperatures and enthalpy

Onset (T_o), peak (T_p), conclusion (T_c) gelatinization temperatures, and enthalpy (ΔH) determined by the DSC for the starch with and without gum addition are shown in Table 2. The T_p and T_c values were not significantly ($P > 0.05$) different among the samples with and without gum addition. The T_o values were significantly ($P \leq 0.05$) increased by the addition of gum, the highest value was observed for the starch–xanthan gum mixture. This result was consistent with the pasting temperature determined by the RVA (Table 1). A significantly ($P \leq 0.05$) decrease in gelatinization enthalpy (ΔH) and phase transition temperature range ($T_c - T_o$) was observed, however, when gums were added as compared to the control.

3.5. Viscoelastic behavior

The mechanical spectra for dispersions of cationic tapioca starch with and without gums are shown in Fig. 5. Viscoelastic properties can be used to characterize the three-dimensional network structure of starches and starch–gum mixtures. The rheological parameters, G' and G'' showed

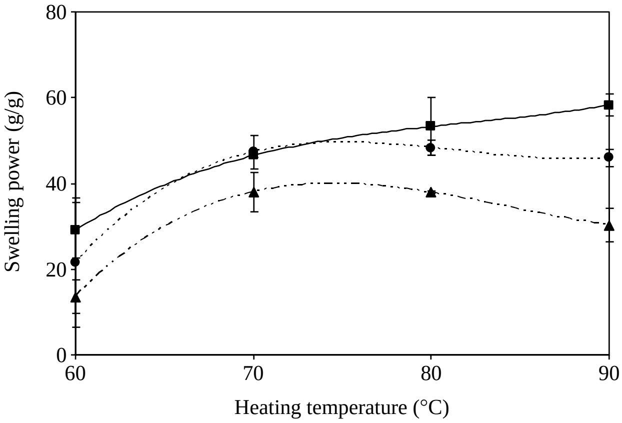

Fig. 2. Swelling power (g/g) at different heating temperature for cationic tapioca starch (■), cationic tapioca starch in the presence of guar gum (●) or xanthan gum (▲). Error bars represent standard deviations.

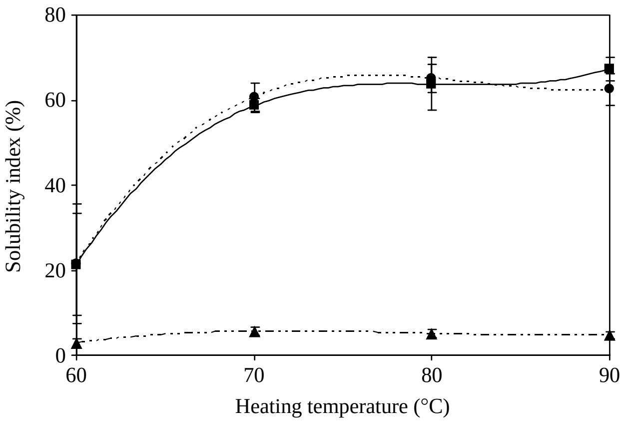

Fig. 3. Solubility at different heating temperature for cationic tapioca starch (■), cationic tapioca starch in the presence of guar gum (●) or xanthan gum (▲). Error bars represent standard deviations.

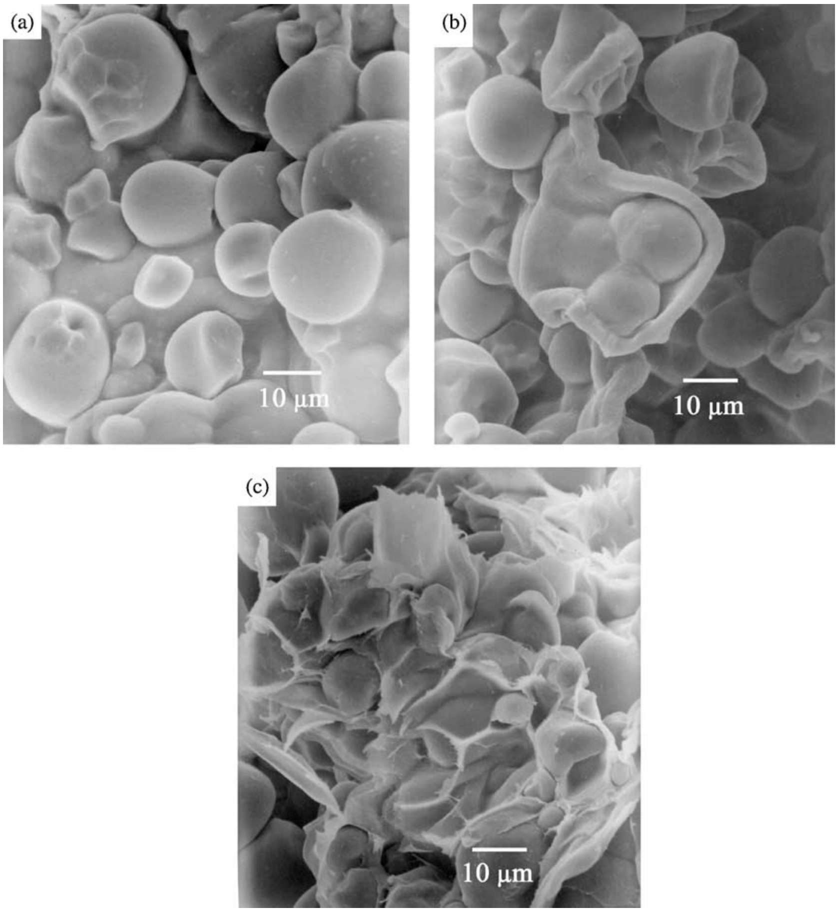

Fig. 4. Scanning electron micrographs (SEM) of cationic tapioca starch with and without gums: (a) cationic tapioca starch, (b) cationic tapioca starch–guar gum mixture, (c) cationic tapioca starch–xanthan gum mixture (1500×, Bar = 10 μm).

significant variation among starch dispersions with and without gum addition when subjected to frequency testing ranging from 1 to 100 rad/s under a deformation of 0.5% strain. Oscillatory rheological assays were not performed on gum systems without starch because of the very low magnitude of the storage modulus when compared with starch. For all samples, the magnitudes of G' were higher than those of G'' over a range of oscillatory frequencies studied. The increase in G' was accompanied by a corresponding increase in G''. The G' and G'' curves of all combinations were almost parallel in the frequency range studied. Addition of xanthan and guar gums increased the G' values of starch paste up to 14- and 5-fold at an angular frequency of 1 rad/s, respectively. Freitas, Gorin, Neves, and Sierakowski (2003) reported that mixing of galactoxyloglucan–corn starch rich in amylose increased the G' values five-fold at all the chosen frequencies. Fig. 6 shows that addition of xanthan gum resulted in a decrease of the tan δ (G''/G') values from 0.52 for starch alone to 0.37 at 1 rad/s frequency and remained roughly constant across the range of angular frequencies studied, whereas guar gum exhibited slightly lower tan δ at low frequencies but higher at high frequencies due to the reduction of tan δ of starch at high frequencies. Therefore, the starch–xanthan gum mixture exhibited seemingly more solid like behavior than the starch–guar gum mixture or starch alone.

Table 2
Thermal properties of cationic tapioca starch alone (CT) and CT in the presence of guar gum (CT + GG) or xanthan gum (CT + XG) obtained from the DSC thermograms

Sample	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	$T_c - T_o$ (°C)
CT	53.90 ± 0.80c	65.65 ± 0.89a	73.22 ± 0.54a	11.06 ± 0.51a	19.33 ± 1.26a
CT + GG	55.85 ± 0.55b	65.26 ± 0.47a	71.97 ± 0.47a	8.33 ± 0.17b	16.12 ± 0.38b
CT + XG	58.27 ± 1.03a	65.52 ± 0.50a	71.94 ± 0.81a	5.17 ± 1.09c	13.67 ± 0.70c

T_o, T_p, T_c and ΔH are onset, peak, conclusion temperatures, and enthalpy, respectively. Assays were performed in triplicate. Mean ± SD values followed by the same letter in each column are not significantly different ($P > 0.05$).

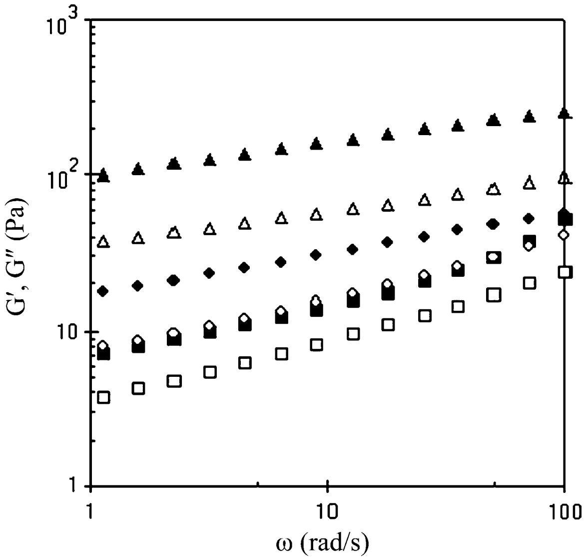

Fig. 5. Dynamic mechanical spectra of 6% cationic tapioca starch paste alone (CT: ■,□) and CT in the presence of 0.35% guar gum (CT+GG: ●,○) or xanthan gum (CT+XG: ▲, △) measured at 0.5% strain and 25 °C. Closed symbols: storage modulus (G'), open symbols: loss modulus (G'').

4. Discussion

Gums are known to influence gelatinization and retrogradation of starch. In this work, both of guar gum (neutral gum) and xanthan gum (negatively charged gum) affected an increasing of pasting peak viscosity of cationic tapioca starch (Fig. 1). In starch system, Miller, Derby, and Trimbo (1972) reported that complex filamentous network of released components of starch in an aqueous dispersion had a high positive correlation with paste viscosity, and believed that it was the principal reason for the large increase in viscosity at high temperature. In the case of starch–gum mixture, Christianson et al. (1981) found that the early onset of initial viscosity was attributed to the first stage of swelling which was dependent on media viscosity only. The later stage increase of paste viscosity was due to interactions of solubilized starch, gums, and swollen starch granules. In this study, the addition of gums synergistically increased the viscosity observed during pasting (Fig. 1) reflects the contribution of media viscosity. This can also make the shear forces exerted on granules much larger than those encountered in starch–water suspensions (Christianson et al., 1981). This significantly affects the breakdown of granules leading to a significantly ($P \leq 0.05$) higher breakdown viscosity of starch–gum systems as compared with starch alone (Table 1).

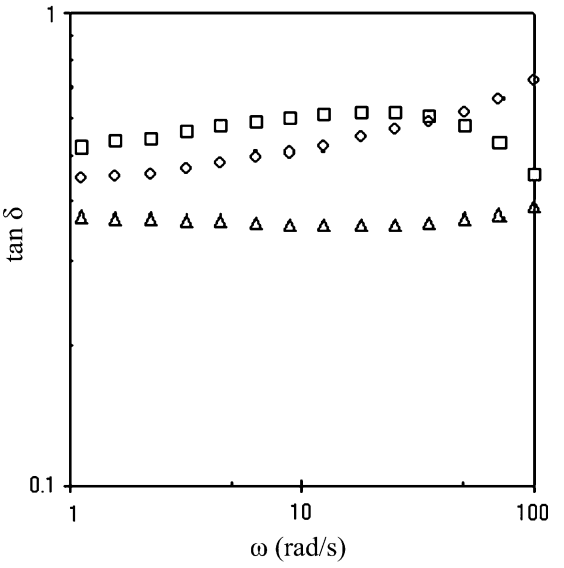

Fig. 6. Loss tangents (tan δ) of 6% cationic tapioca starch paste alone (CT: □) and CT in the presence of 0.35% guar gum (CT+GG: ○) or xanthan gum (CT+XG: △) measured at 0.5% strain and 25 °C.

According to the swelling power measurement by the method of Mandala, & Bayas (2004), the assumption that the whole amount of gum remains in the continuous phase is not completely true due to sedimentation of gum with the starch granules. For the control, the holes of starch granule at one end are considered as first breaks of granule envelope and to be the passage for amylose removal (Shi, & BeMiller 2002) as shown in Fig. 4(a). The swelling of cationic tapioca starch was highest in an aqueous dispersion due to the fact that granules could swell freely.

Xanthan gum was more effective than guar gum for depression of swelling power (Fig. 2). It was suggested that swelling power is greatly influenced by the species of gums. Cationic tapioca starch underwent very slow and restricted swelling at high temperature, indicating strong electrostatic interactions between positive charges on the surface of starch granules and negative charges on the molecules of xanthan gum. Macromolecules of xanthan gum are unable to penetrate the granule, and consequently, adsorbed on the surface and stabilized the granular shape (Gonera & Cornillon, 2002). It is clear that xanthan gum promoted association of several granules of cationic tapioca starch preventing water penetration and inhibiting the swelling of granules as shown in Fig. 4(c). We observed that the aggregation process of cationic tapioca starch by xanthan gum was very fast—practically instantaneous—after the starch and the xanthan gum dispersion were blended. It seems to be an ion bridging which occurs when xanthan gum simultaneously binds to the surface of adjacent starch granules that have the same charge (McClements, 1999). Moreover, it suggests that this strong interaction occurrence also existed between aggregated granules (Lii, Tsai, & Tseng, 1996). Mandala et al. (2002) found that each granule of potato starch was covered by xanthan gum but there was no aggregation. The creation of a xanthan gum film around each granule is also reported by Mandala, & Bayas (2004), who claimed that this film influenced the behavior of granules on further swelling and also the polymer leaking out in wheat starch. Swelling was demonstrated to be positively related to the amount of soluble solids leached outside the granules during heating. In this study, the significantly ($P \leq 0.05$) lower peak viscosity of starch–xanthan gum mixture as compared with starch–guar gum mixture (Table 1) was probably due to their interactions which restricted swelling and limited increase in viscosity.

Guar gum did not affect the swelling power of the starch dispersion. Guar gum partially and loosely wrapped the granules and some guar gum formed sheet structure as shown in Fig. 4(b). The higher concentration of starch solubles in the continuous phase of guar gum dispersion gave the higher possibilities for solubles to undergo molecular interaction with gum components which resulted in the higher ($P \leq 0.05$) peak viscosity as compared with starch–xanthan gum system. According to previous investigations, gum molecules interacted with amylose which is dominating in guar gum system (Sudhakar et al., 1996), however, a contrast was observed to xanthan gum system (Mandala, & Bayas 2004).

This current study shows that starch dispersed in guar gum can absorb more water, has enhanced swelling, and a higher concentration of gum and leached amylose in the continuous phase, whereas in xanthan gum, starch absorbs less water, has suppressed swelling, and gives a slightly increase concentration of gum in the continuous phase. The SEM micrograph reveals the association of starch granules in the xanthan gum matrix. These results are consistent with those of Abdulmola et al. (1996), who used small deformation oscillatory measurements to characterize the effect of xanthan gum on the rheological properties of gelatinized waxy maize starch.

Studies by Rao (1999) on corn starch, DSC data were compared with dynamic rheological data. The initial temperature of gelatinization from both methods was about the same. In our case, however, the T_p from DSC (Table 2) was about the same as the pasting temperature from RVA (Table 1). It was suggested that energy was required for reversible swelling of starch granules before pasting temperatures were reached. A significant shift of T_o (up to 4.37 °C) to higher values was observed due to gum additions; this can be attributed to different factors: lower ratios of free water to starch due to immobilization of water molecules by gums (Biliaderis, Maurice, & Vose, 1980; Chungcharoen & Lund, 1987), lower heat transfer rates (Krüger et al., 2003), and mass transfer of water, which could make starch gelatinization more difficult in the presence of the gum. The enthalpy (ΔH) was significantly ($P \leq 0.05$) decreased by addition of gums suggesting a partial gelatinization of crystalline regions in the starch granules due to limited amounts of water (Biliaderis et al., 1980). The gums may interact with the starch to produce an increase (Liu et al., 2003) or decrease (Rojas et al., 1999) of the temperature gelatinization ranges ($T_c - T_o$), depending on the type of gums. The overall effect of gums was a decrease in the gelatinization enthalpy in the range of 2.73–5.89 J/g starch d.b.

Xanthan gum was more effective than guar gum in terms of increasing the final viscosity (Fig. 1). This result agreed very well with the viscoelastic behavior of the paste. Based on dynamic shear data, cationic tapioca starch pastes with and without gums were rheologically classified as weak gels (Fig. 5). The main properties of weak gels are given by Clark and Ross-Murphy (1987) as $G' > G''$ throughout the accessible frequency range, both G' and G'' are slightly increased with increasing frequency and the separation of the two moduli ($\tan \delta = G''/G'$) is smaller than 0.1 for typical polysaccharide gels. The increase of G' values were also related with the rate of amylose and amylose–gum associations that occurred during cooling. The increase of G' cannot be attributed to the aggregation of amylopectin because amylopectin retrogradation occurs over long time periods (Biliaderis & Prokopowich, 1994). As suggested by Ferrero, Martino, and Zaritzky (1994), gum–amylose associations may compete with amylose–amylose interactions which are essential for retrogradation. From the rheological point of view, the decrease of $\tan \delta$ corresponded to a more solid like behavior, that is, a stronger three-dimensional network was constructed by amylose and amylose–gum system (Hsu, Lu, & Huang, 2000). The difference between guar gum and xanthan gum can be partly explained by an ionic characteristic and a lower molecular weight of guar gum with respect to xanthan gum. Christianson et al. (1981) suggested that the strength of amylose–galactomannan interaction depended on the chemical structure of the gums. Oscillatory test showed that dispersions exhibited a predominantly solid-like behavior which was attenuated on cationic tapioca starch when guar and xanthan gums were added (Fig. 5). This is in contrast to Yoshimura, Takaya, and Nishinari (1999), who suggested that xyloglucan inhibits the formation of three-dimensional network structures with corn starch due to incompatibility between unlike polymers, amylose and gums.

The magnitudes of $\tan \delta$ decreased in the following order: starch alone (control) > guar gum addition > xanthan gum addition. Xanthan gum decreased $\tan \delta$ of starch paste, possibly through strong network formation with starch. It is likely that the ionic interaction of the opposite charges of starch and gum molecules influenced the increasing of elastic modulus (G') during cooling. When the starch–gum pastes contain many oppositely charged groups, it is more likely to fold up into a compact structure that maximizes the favorable electrostatic attractions (McClements, 1999). This interaction has been ascribed to electrostatic attraction between the positively charged quaternary ammonium groups of the cationic tapioca starch and a predominantly negatively charged region in the side chain of xanthan gum. For the guar gum, galactose branches of non-ionic hydrocolloid inhibit the formation of intra-molecular hydrogen bondings. Either branched or linear molecules of guar gum can interact with amylose molecules via non-covalent hydrogen bonding (Sudhakar et al., 1996). This results suggested that guar gum was an extended conformation in starch–guar gum mixture paste. Addition of guar gum increased the starch paste rigidity but less than xanthan gum due to their chemical structure.

5. Conclusions

Guar gum and xanthan gum increased viscosity and viscoelasticity of cationic tapioca starch suspensions during and after heating, respectively. The ionic interactions between starch and gum molecules play an important role on these properties. The strong electrostatic interactions between cationic starch and anionic xanthan gum resulted in an instantaneous aggregation of granules, whereas non-ionic guar gum formed sheet structure and loosely wrapped the granules. These observations can be related to the decrease in swelling power, solubility index, peak viscosity, and loss tangent (tan δ) but increase in pasting temperature and rheological parameters G' and G'' of starch–xanthan gum mixture with respected to the starch–guar gum system.

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