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Pasting and rheological properties of waxy corn starch as affected by guar gum and xanthan gum

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Abstract

Effects of guar (GG) and xanthan (XG) gums (0.35–1.0% w/w) on pasting and rheological properties of waxy corn starch (WCS) (6.0% w/w) were studied. GG had a higher molecular weight but lower intrinsic viscosity than did XG, indicating that the GG chain was more flexible. RVA results indicated that viscosity and pasting temperature of the WCS dispersion during pasting increased with increasing GG or XG concentration. Dynamic viscoelasticity measurements indicated that the WCS/XG mixed pastes exhibited slightly superior viscoelastic properties to the WCS/GG pastes as evidenced by their higher G' and lower $\tan \delta$ values. Flow tests showed that the WCS/GG pastes exhibited mainly thixotropic hysteresis loops during a full shear cycle, whereas the WCS/XG pastes showed much less thixotropic and eventually became antithixotropic at high XG concentrations. In-shear structural recovery of the pastes increased more with increasing XG concentrations than did pastes with increasing GG concentrations. The differences in molecular characteristics of the GG and XG chains are hypothesized to be responsible for the above mentioned effects.

Keywords: Waxy corn starch; Guar gum; Xanthan gum; Pasting; Rheology

1. Introduction

Starch is widely used in the food industry, either as a main raw material or as a food additive. As an additive, starch contributes to the thickening and stabilizing effects and texture modification in food (Eliasson & Gudmundsson, 2006). However, the numerous food applications of native starches are restricted because of their tendency to retrograde and undergo syneresis. Furthermore, in their native form, gels or pastes of starches like waxy corn starch (~99% amylopectin) tend to break down either from prolonged heating, high shear or acidic conditions producing weak-bodied, cohesive, rubbery pastes and undesirable gels (Whistler & BeMiller, 1997).

Blends of native starches and other polysaccharide hydrocolloids have been used in the modern food industry to modify and control the texture, improve moisture retention, and control water mobility and eating quality of food products (Appelqvist & Debet, 1997). Guar gum and xanthan gum are among the most commonly used as thickening agents in real food systems (Norton & Foster, 2002).

Guar gum is water-soluble non-ionic polysaccharide from the ground endosperm of guar (*Cyamopsis tetragonoloba*) seeds. Guar gum has a main chain of (1 → 4)-linked β-D-mannopyranosyl units, bearing single α-D-galactopyranosyl units attached to O-6 of the main-chain units. In contrast, xanthan gum is an anionic extracellular polysaccharide produced by fermentation of the bacterium *Xanthomonas campestris*. Xanthan has a (1 → 4)-linked β-D-glucan (cellulose) backbone solubilized by attachment of charged trisaccharide side chains [β-D-mannopyranosyl-(1 → 4)-β-D-glucuronopyranosyl-(1 → 2)-6-*O*-acetyl-β-D-mannopyranosyl] at O-3 of alternate glucose residues (Whistler & BeMiller, 1997). Close alignment of the trisaccharide side chains with the main chain make the xanthan molecule a rather stiff rod with extraordinary stability to

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heat, acid, and alkali. Therefore, unlike other polysaccharides used as food thickeners, including guar gum, xanthan can exist in solution in a rigid, ordered, chain conformation. Thus the level of intermolecular interactions appears the most important difference between the guar and xanthan systems. This distinction is confirmed by the behavior of xanthan solution as a weak gel and that of guar solution as an entanglement solution (Ross-Murphy, 1995). These behaviors should be accounted for during study of the effects of these gums on pasting and rheological properties of starch.

The preceding papers reported that guar and xanthan gums affected the pasting and rheological properties of cationic (Chaisawang & Suphantharika, 2005), native, and anionic tapioca starches (Chaisawang & Suphantharika, 2006) differently. However, it has been clearly demonstrated that the starch/gum systems were complicated by interactions of leached amylose molecules and certain gums occurring before and during pasting (Christianson, Hodge, Osborne, & Detroy, 1981; Shi & BeMiller, 2002). Therefore, waxy corn starch, an essentially amylose-free starch, was chosen for this study. It also offers the possibility of studying the effect of the added hydrocolloid without having the complexities normally existing when amylose is present.

Much less work has been carried out on the effect of guar and xanthan gums on the pasting (Bahnassey & Breene, 1994; Shi & BeMiller, 2002) and rheological properties (Biliaderis, Arvanitoyannis, Izydorczyk, & Prokopowich, 1997) of waxy corn starch. The molecular characteristics, i.e. molecular weights and intrinsic viscosities, of the gums used and their effects on an in-shear structural recovery of the pastes were not presented by these authors.

This study was initiated in order to gain an insight into the properties of guar and xanthan gums and their effects on pasting and rheological properties of waxy corn starch by Rapid Visco-Analysis (RVA), dynamic and steady shear measurements, and in-shear structural recovery measurement.

2. Materials and methods

2.1. Materials

Waxy corn starch (WCS) was supplied by National Starch and Chemical (Thailand) Limited, Samutprakarn, Thailand. Hydrocolloids were purchased from commercial companies e.g. xanthan gum (CP Kelco Co., San Diego, CA, USA) and guar gum (Shree Ram Gum & Chemicals, Jodhpur, India).

2.2. Molecular weight determination of guar and xanthan gums

Molecular weight determination was performed on a Waters 600E instrument (Waters Corporation, Milford, MA, USA) equipped with a 7.8×300 mm Ultrahydrogel linear column packed with hydroxylated polymethacrylate-based gel, a 6×40 mm guard column, and a refractive index detector. Pullulan standards, ranging from 5800 to 1.6×10^6 Da of peak molecular weight (Showa Denko K.K., Tokyo, Japan) were used for calibration. Guar gum or xanthan gum (0.2% w/w) in buffer pH 11 (0.1 M NaOH and 0.05 M Na_2CO_3) was prepared. The samples were passed through a 0.45 μm nylon filter paper before injecting into a GPC column. The conditions were set as follows; injection volume 20 μl, flow rate 0.6 ml/min, and temperature 30 °C. Buffer pH 11 was used as eluent.

2.3. Determination of intrinsic viscosity of guar and xanthan gums

The intrinsic viscosity, $[\eta]$, of guar and xanthan solutions was measured by using an Ubbelohde dilution capillary viscometer (size 50, Cannon Instrument Co., State College, PA, USA) immersed in a water bath maintained at 25 ± 0.1 °C. The efflux times of distilled water and of gum solutions ranging in concentrations from 0.005% to 0.05% were measured in triplicate and averaged.

The concentration-dependence of the viscosity of each gum solution was analyzed by using the classical Huggins equation:

$$\frac{\eta_{sp}}{c} = [\eta] + k_1[\eta]^2 c \tag{1}$$

where η_{sp} is the specific viscosity and k_1 is the Huggins constant. For each concentration, the specific viscosity was determined using the equation:

$$\eta_{sp} = \frac{(\eta - \eta_s)}{\eta_s} \tag{2}$$

where η is the solution viscosity and η_s is the solvent viscosity. The plots of η_{sp}/c versus c would result in straight lines in which the $[\eta]$ was determined as the zero concentration-limit of the η_{sp}/c value.

2.4. Determination of pasting properties

Pasting properties of WCS and WCS/gum mixtures suspended in distilled water were determined by a Rapid Visco-Analyzer (model RVA-4C, Newport Scientific Pty. Ltd., Warriewood, Australia). The WCS slurry of 25 g was prepared by dispersing weighed amounts of WCS (dry basis) in distilled water at the total solids content of 6% w/w. In the case of mixtures, gum was first dispersed in water at concentrations of 0.35, 0.70, and 1.0% w/w (dry basis) under magnetic stirring, heated to 80 °C for 5 min and cooled to room temperature; then, starch (6% w/w) was slurried in the gum solution. In both cases slurries were stirred with a spatula for sufficient duration to avoid the formation of lumps. The slurries were then 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 42 s and then held at 95 °C for 2 min 30 s. It was subsequently cooled to 50 °C within 3 min 48 s and held at 50 °C for 2 min, while maintaining a rotation speed of 160 rpm.

2.5. Rheological measurements

Dynamic viscoelastic and steady flow properties of the freshly prepared WCS and WCS/gum mixed pastes obtained from the RVA were determined by using a rheometer (Physica MCR 300, Anton Paar GmbH, Stuttgart, Germany). The sample was placed into the rheometer (cone and plate geometry, 50 mm diameter, 1° cone angle, and 0.05 mm gap) which was equilibrated to 25 °C. For dynamic viscoelastic determination, two steps of rheological measurements were performed: (1) deformation sweeps at a constant frequency (10 rad/s) to determine the maximum deformation attainable by a sample in the linear viscoelastic range and (2) frequency sweeps at a constant deformation (0.5% strain) within the linear viscoelastic range. The mechanical spectra were obtained recording storage modulus (G'), loss modulus (G''), and loss tangent ($\tan\delta = G''/G'$) as a function of frequency (ω).

Next, the steady flow tests were performed on the same sample to obtain shear rate versus shear stress (flow curves) data. The cone was programmed to ramp the shear rate from 0 to 300 s^{-1} (up curve) in 3 min followed immediately by the down curve from 300 to 0 s^{-1} in 3 min. Data from the ascending and descending segments of the shear cycle were used to characterize the flow of the paste samples and to estimate the power law parameters by using the following equation:

$$\sigma = K\dot{\gamma}^n \tag{3}$$

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

2.6. In-shear structural recovery measurements

In-shear structural recovery of the paste samples was determined according to the procedure of Mezger (2002) with some modifications. The freshly prepared WCS or WCS/gum mixed paste was load onto the rheometer at 25 °C as described earlier. A three stepped shear flow test was carried out as follows: (1) constant shear rate at 1 s^{-1} for 120 s and immediately followed by (2) constant shear rate at 300 s^{-1} for 60 s and then (3) constant shear rate at 1 s^{-1} for 180 s. The in-shear recovery of the paste samples was calculated as percentage of apparent viscosity (η_a) obtained during the first 30 s of the third step based on the η_a value determined in the first step.

2.7. Statistical analysis

The pasting data reported are means of triplicate determinations. The statistical analysis of the results was conducted by the analysis of variance (ANOVA) and Tukey's test using SPSS version 12.0 for Windows program (SPSS Inc., Chicago, IL, USA). Significant differences were reported for $P \leqslant 0.05$.

3. Results and discussion

3.1. Molecular weight and intrinsic viscosity of guar and xanthan gums

Table 1 summarizes the molecular characteristics of guar gum (GG) and xanthan gum (XG) used in this study. GG had much larger molecular weight and much smaller intrinsic viscosity than XG. Since the intrinsic viscosity of a polymer is a measure of the hydrodynamic volume per gram of macromolecular substance at infinite dilution and is proportional to its chain dimension, a more flexible polymer chain which exhibits a smaller chain dimension will give smaller intrinsic viscosity (Doublier & Cuvelier, 2006). Therefore, the flexibility of GG chain was higher than that of XG, consistent with previous studies (Ross-Murphy, 1995; Wang, Wang, & Sun, 2002). A comparison of the rheological behavior of XG and GG solutions served, respectively, as paradigms for weak gel and entanglement solution behavior. This can be attributed to the flexibility and the lack of regularity of the repeating unit of the GG chain, on one hand, and the stiffness and the comparative regularity of XG, on the other hand, which possibly prevent (GG) or stabilize (XG) rheologically relevant intermolecular interactions (Ross-Murphy, 1995).

3.2. Pasting properties

The pasting characteristics of the WCS/GG and WCS/XG mixtures at various gum concentrations determined by the RVA are summarized in Table 2. Addition of GG or XG to WCS generally resulted in significant ($P \leqslant 0.05$) increases in peak, breakdown, final and setback viscosities and pasting temperatures. This effect was more pronounced as the concentrations of GG or XG increased. This result can be interpreted assuming the system to be biphasic, with the gum located in the continuous phase and its concentration increased dramatically as the volume of the phase accessible to the gum was reduced due to swelling of the starch granules during pasting. This results in the pronounced increase in the viscosity of the continuous medium and in turn the overall viscosity of the suspension itself owing to the thickening properties of these gums (Alloncle, Lefebvre, Llamas, & Doublier, 1989). The

Table 1
Molecular weight and intrinsic viscosity of guar gum (GG) and xanthan gum (XG) in aqueous solution

Sample	Molecular weight (Da)	Intrinsic viscosity (dl/g)
GG	6.12×10^6	9.4
XG	3.47×10^6	112.3

Table 2
Pasting properties of 6% w/w waxy corn starch (WCS) in the presence of various concentrations of guar gum (GG) or xanthan gum (XG)

Sample	Gum concentration (%)	Peak viscosity (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)	Pasting temperature (°C)
WCS/water	0.00	133.4 ± 1.2^{d}	$45.8 \pm 2.3^{b,c}$	95.7 ± 1.1^{f}	$8.0 \pm 0.9^{c,d}$	71.3 ± 0.4^{d}
WCS/GG	0.35	162.2 ± 1.0^{c}	60.9 ± 0.9^{b}	112.4 ± 1.3^{e}	$12.2 \pm 0.7^{c,d}$	75.1 ± 0.0^{c}
WCS/GG	0.70	$236.6 \pm 3.4^{a,b}$	104.9 ± 3.1^{a}	144.1 ± 0.5^{d}	$12.4 \pm 0.8^{c,d}$	85.8 ± 1.0^{a}
WCS/GG	1.00	245.8 ± 3.6^{a}	118.2 ± 6.9^{a}	165.7 ± 1.6^{c}	$38.1 \pm 9.4^{b,c}$	$83.4 \pm 0.5^{a,b}$
WCS/XG	0.35	168.6 ± 0.5^{c}	53.7 ± 3.8^{b}	115.8 ± 1.6^{e}	0.9 ± 2.7^{d}	$82.3 \pm 0.9^{a,b}$
WCS/XG	0.70	174.8 ± 7.4^{c}	25.0 ± 12.1^{c}	218.0 ± 1.5^{b}	68.1 ± 19.5^{b}	80.7 ± 2.9^{b}
WCS/XG	1.00	224.2 ± 12.5^{b}	112.1 ± 12.9^{a}	302.9 ± 4.5^{a}	190.7 ± 19.0^{a}	82.1 ± 1.3^{b}

Assays were performed in triplicate. Mean ± SD values in the same column followed by different superscripts are significantly different ($P \leqslant 0.05$).

increase in viscosity can make the shear forces exerted on the swollen granules in the shear field much larger than those encountered in starch/water suspensions (Christianson et al., 1981). This results in the loss of granules integrity and subsequent disruption leading to a reduction in the paste viscosity. The resultant drop in viscosity, which is called breakdown, was most evident in the starch/gum paste, indicating the possible breakdown of the granules.

The increase in peak viscosity was more pronounced for the WCS/GG than in the WCS/XG mixtures at high gum concentrations (0.7% and 1.0%). This can be attributed to the fact that XG covered most of the starch granules individually, as observed by means of scanning electron microscopy (SEM) (Chaisawang & Suphantharika, 2006) and confocal laser scanning microscopy (CLSM) (Gonera & Cornillon, 2002), and promoted granule association (Abdulmola, Hember, Richardson, & Morris, 1996), which restricted swelling of the granules and limited the increase in viscosity during pasting. GG, on the contrary, did not cover the starch granules but formed a sheet structure in the continuous phase (Chaisawang & Suphantharika, 2006). Therefore, the granules can swell freely before their physical breakdown which results in significantly ($P \leqslant 0.05$) higher peak viscosities during pasting as compared with the WCS/XG mixtures. This result is in good agreement with that previously reported for WCS/GG and WCS/XG mixtures (Bahnassey & Breene, 1994). In general, polymer chains can induce association (flocculation) of colloidal particles by two mechanisms, bridging and depletion (Walstra, 1993), both of which would be promoted by conformational rigidity. Bridging flocculation involves chains adhering to the surface of individual particles and forming a link between them. The entropic barrier to association will clearly be much lower for a rigid chain than for a flexible chain. Depletion flocculation centers on the hydrodynamic volume swept out by the polymer chains, which again will be much greater for rigid molecules. Either (or both) of these mechanisms would explain enhancement of WCS granule association by the presence of XG, and at the moment we have no basis for distinguishing between them, although previous studies of the interaction of WCS with XG (Abdulmola et al., 1996) suggest that depletion flocculation is more likely at XG concentrations of 0.25% and 0.5%.

XG exhibited a more pronounced effect on increasing the final and setback viscosities than GG at high gum concentrations (0.7% and 1.0%), indicating different interactions between amylopectin and the gum molecules. This can be attributed to the difference in molecular structure and the flexibility of the gum chains as described earlier. A significant ($P \leqslant 0.05$) shift in the gelatinization temperature to a higher temperature in the presence of hydrocolloid and excess water can be interpreted as a result of the lower heating rates and water diffusivities in a more viscous sample as pointed out by Krüger, Ferrero, and Zaritzky (2003).

3.3. Dynamic rheological properties

The dynamic mechanical spectra (frequency-dependence of G' and G'') of the WCS/GG and WCS/XG mixed pastes (Fig. 1) are typical for a biopolymer gel network (Clark & Ross-Murphy, 1987) where G' is higher than G'' throughout the measured frequency range and G' is almost independent of frequency. The G'' shows a spectrum parallel to G', but two to three times lower. Fig. 1(a) shows that G' of the WCS/GG mixed pastes increased very slightly with increasing GG concentrations in the range 0–1.0%. Fig. 1(b) shows that for XG addition, the magnitude of G' increased initially with increasing XG concentrations but then decreased at XG concentrations higher than 0.7%, such behavior agrees with the overall rheological behavior observed in the WCS/gellan (Rodríquez-Hernández, Durand, Garnier, Tecante, & Doublier, 2006), cross-linked WCS/pectin (Khondkar, Tester, Hudson, Karkalas, & Morrow, 2007), and potato maltodextrin/gum arabic (Annable, Fitton, Harris, Phillips, & Williams, 1994) mixed pastes. These can be ascribed to phase separation processes, i.e. mutual exclusion of starch and hydrocolloid so that their concentration increases in their respective microdomains, in relation to incompatibility phenomena between unlike polysaccharides (Alloncle & Doublier, 1991; Annable et al., 1994).

This result indicates that the WCS/GG mixed pastes exhibited slightly inferior viscoelastic properties to the WCS/XG pastes. The elastic character of the GG solutions is far less marked than that of the XG solutions as described earlier. This may provide a straightforward explanation for the limited effect of GG incorporation on

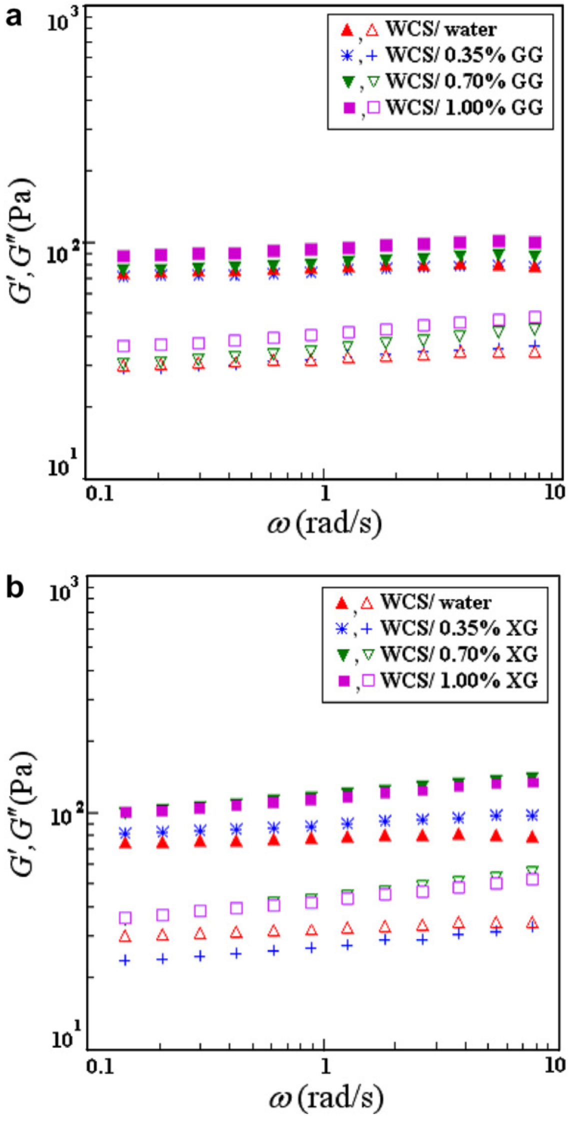

Fig. 1. Dynamic mechanical spectra of 6% w/w waxy corn starch (WCS) pastes in water (control) and in (a) guar gum (GG) or (b) xanthan gum (XG) solutions at various concentrations measured at 0.5% strain and 25 °C. Closed symbols and $*$, storage modulus (G'); open symbols and $+$, loss modulus (G'').

G' values of the mixed pastes (Allonce & Doublier, 1991). In addition, increase in association of gelatinized starch granules in the presence of XG (Abdulmola et al., 1996) appears to have contributed to the enhancement of G' values in the WCS/XG mixed pastes. The relative effectiveness of different biopolymers in inducing association will depend on the volume swept out by the individual chain, i.e. intrinsic viscosity, and this in turn will depend on molecular weight and stiffness (Mohammed, Hember, Richardson, & Morris, 1998). Considering the molecular characteristics of GG and XG (Section 3.1), we would therefore expect XG promoted association of the gelatinized WCS granules more effectively than GG.

The loss tangent (tan δ) values of the WCS/GG mixed pastes were slightly higher than that of the WCS alone paste (Fig. 2(a)), indicating that their overall structure became weaker and less gel-like. Similar findings were previously reported for waxy rice starch/GG mixed pastes, in which it was also shown that GG changed the nature of the starch network from viscoelastic to more viscous-like, presumably by reducing the number of remaining associations between the amylopectin molecules (Kulicke, Eidam, Kath, Kix, & Kull, 1996). On the contrary, XG addition resulted in lower tan δ values of the WCS/XG mixed pastes, which means that they were more structured and more solid-like compared with the WCS alone pastes (Fig. 2(b)). However, the lowest tan δ value was observed for the mixed paste with 0.35% XG concentration. This result is consistent with our previous findings that the bonding yield stress, i.e. the stress required to break the inter-particle bonding, of the WCS/XG mixed paste was highest at 0.35% XG concentration as compared with that of the WCS alone and the

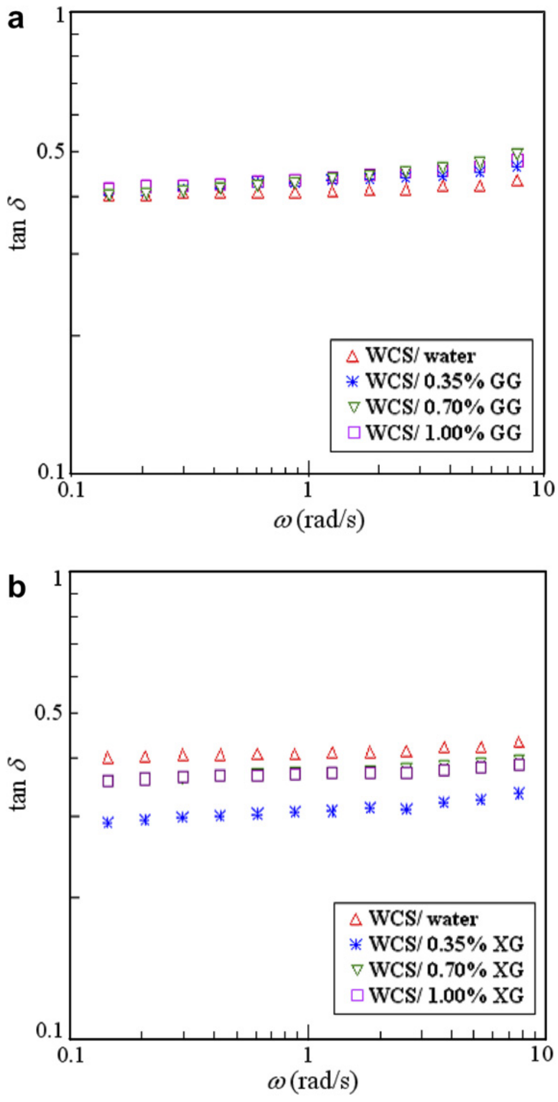

Fig. 2. Dynamic mechanical loss tangents (tan δ) of 6% w/w waxy corn starch (WCS) pastes in water (control) and in (a) guar gum (GG) or (b) xanthan gum (XG) solutions at various concentrations measured at 0.5% strain and 25 °C.

mixed pastes with 0.7% and 1.0% XG concentrations (Achayuthakan, Suphantharika, & Rao, 2006).

3.4. Steady flow properties

The flow behaviors of the WCS/GG and WCS/XG mixed pastes, together with the WCS alone paste for a comparison, are presented in Fig. 3. For the range of shear rates used in this study, the power law model accurately described flow behavior of each paste. Consistency coefficients (K) and flow behavior indices (n) along with coefficients of determination (R^2) for each flow curve are shown in Table 3. All pastes exhibited pseudoplastic, shear-thinning behavior, for which $n < 1$. In addition, hysteresis loops were found in the shear rate versus shear stress curves obtained in increasing-order of shear (up curve) and decreasing-order of shear (down curve).

Table 3
Effect of guar gum (GG) and xanthan gum (XG) concentrations on steady shear rheological properties of 6% w/w waxy corn starch (WCS) pastes at 25 °C

Sample	Gum concentration (%)	Up curve			Down curve		
		K	n	R^2	K	n	R^2
WCS/water	0.00	6.70	0.49	0.944	5.13	0.51	0.997
WCS/GG	0.35	8.57	0.54	0.967	9.16	0.51	0.998
WCS/GG	0.70	15.84	0.49	0.974	12.31	0.52	0.998
WCS/GG	1.00	39.32	0.44	0.993	22.56	0.52	0.999
WCS/XG	0.35	14.82	0.40	0.994	13.50	0.41	0.998
WCS/XG	0.70	23.37	0.36	0.987	22.22	0.37	0.998
WCS/XG	1.00	23.16	0.37	0.991	24.85	0.36	0.998

K, consistency coefficient (Pa s^n); n, flow behavior index (dimensionless).

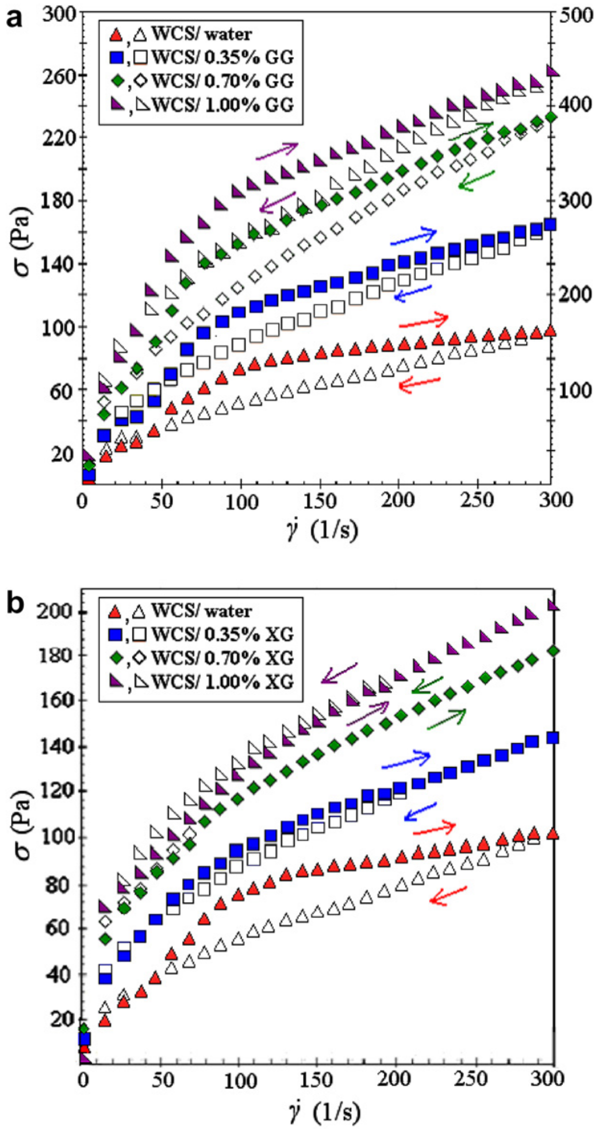

Fig. 3. Flow curves of 6% w/w waxy corn starch (WCS) pastes in water (control) and in (a) guar gum (GG) or (b) xanthan gum (XG) solutions at various concentrations measured at 25 °C. The right-hand axis of (a) is only for the flow curve of the WCS/1.00% GG mixed paste. Arrows show direction of shear rate change. Closed symbols, up curve; open symbols, down curve.

The WCS/GG mixed pastes and the WCS alone paste exhibited similar combined hysteresis loops, i.e. anticlockwise loop (antithixotropic behavior) at low shear rates and clockwise loop (thixotropic behavior) at higher shear rates ($\dot{\gamma} > 50\ \mathrm{s}^{-1}$) (Fig. 3(a)). The anticlockwise loops are not clearly visible, whereas the clockwise loops are large and dominated the hysteresis loop areas. These systems contained a large amount of amylopectin which was responsible for shear-thickening properties and shear-induced structure formation and alteration, i.e. antithixotropic behavior (Dintzis, Berhow, Bagley, Wu, & Felker, 1996), and this may explain the initial anticlockwise loops of the flow curves. On the contrary, the clockwise loops can be interpreted as structure breakdown by the shear field (thixotropic behavior) to alter a structure or form a new structure, which then maintained a shear-thinning characteristic on following shear sweeps. This is evidenced by a slight decrease in K values but increase in n values of the down curves as compared with those of the up curves (Table 3).

Thixotropy appears to be less pronounced in the presence of XG as seen by the area of the loop between the up and down curves (Fig. 3(b)). The thixotropic loop area of the WCS/XG mixed pastes markedly decreased at 0.35% XG as compared with that of the WCS alone paste and seemed to completely disappear at 0.7% XG. This result can be attributed to rather small changes in the structure of the WCS/XG mixed pastes on the shear applied, indicating that the structure of such pastes was strong and shear-resistant. In addition, for the WCS/XG mixed paste with 1.0% XG, the majority of the loop was found to be slightly antithixotropic up to a shear rate of 200 s^{-1}. This result indicates that XG addition at high levels enhanced the formation of shear-induced network structure of the mixtures and reduced breakdown of the network by shear. This occurs because of the unusual rigid rod-like conformation of XG. This evidence is confirmed by rather constant K and n values obtained from the up and down curves of the WCS/XG mixed pastes (Table 3). Rheological results reported for cross-linked WCS/κ-carrageenan mixed paste

(4% starch and 0.5% gum) at 60 °C also showed an anticlockwise loop up to a shear rate of 300 s^{-1} (Tecante & Doublier, 1999). Based on observations by phase-contrast microscopy, Dintzis et al. (1996) considered the presence of antithixotropy in dispersions of normal waxy starch in 0.2 M NaOH as an indication of a shear-induced structure.

In general, increases in GG or XG concentration increased K values and decreased n values (Table 3), indicating that the mixed pastes became more pseudoplastic as the level of gum increased. This effect was more pronounced for the WCS/XG mixed pastes than the WCS/GG pastes, indicating that the WCS/XG pastes were more shear-thinning. This result is consistent with that obtained from the small-deformation oscillatory measurements in which the more structured WCS/XG mixed pastes gave higher resistance to the applied steady shear than the less structured WCS/GG pastes.

3.5. In-shear structural recovery

This experiment was carried out to investigate the capability of the mixed pastes to recover their original structure under low-shear conditions after decomposition under high-shear conditions (Grassi, Lapasin, & Pricl, 1996; Mezger, 2002). For the purpose of illustration, the viscosity profiles as a function of time during the three-step function tests of the WCS/GG and WCS/XG mixed pastes with 0.7% gum concentration are presented in Fig. 4. Similar viscosity versus time curves were shown by the WCS/GG and WCS/XG mixed pastes with other gum concentrations and the WCS alone paste; they are not shown here. The percentage of recovery for each mixed paste and the WCS alone paste were calculated and plotted against gum concentrations as shown in Fig. 5. The recovery of the GG and XG solutions was also determined under the same conditions as controls. The recoveries of the 1.0% w/w GG and XG solutions were 80% and 96%, respectively, indicating that XG returned to its original structure more quickly after deformation than did GG. This can be due to the stiffness of XG molecule in which the intermolecular interactions are more stabilized as compared with the more flexible GG molecule as described earlier in Section 3.1. The structural recoveries of the WCS/GG and WCS/XG mixed pastes were higher than that of the WCS alone paste and increased with increasing gum concentrations. The effect was more pronounced for the WCS/XG pastes than the WCS/GG pastes, indicating that the recovery of the mixed pastes was clearly dominated by the added gums. As discussed earlier, the rigid XG molecule promoted association of the gelatinized WCS granules more efficiently than the flexible GG chain. Therefore, the WCS/XG mixed pastes were more structured and more elastic than the WCS/GG pastes as shown in Figs. 1 and 2 and in turn could recover their original structure more quickly. This result is also consistent with the steady shear data in which the high recovery property and rigid structure of XG resulted in a decrease in the hysteresis loop

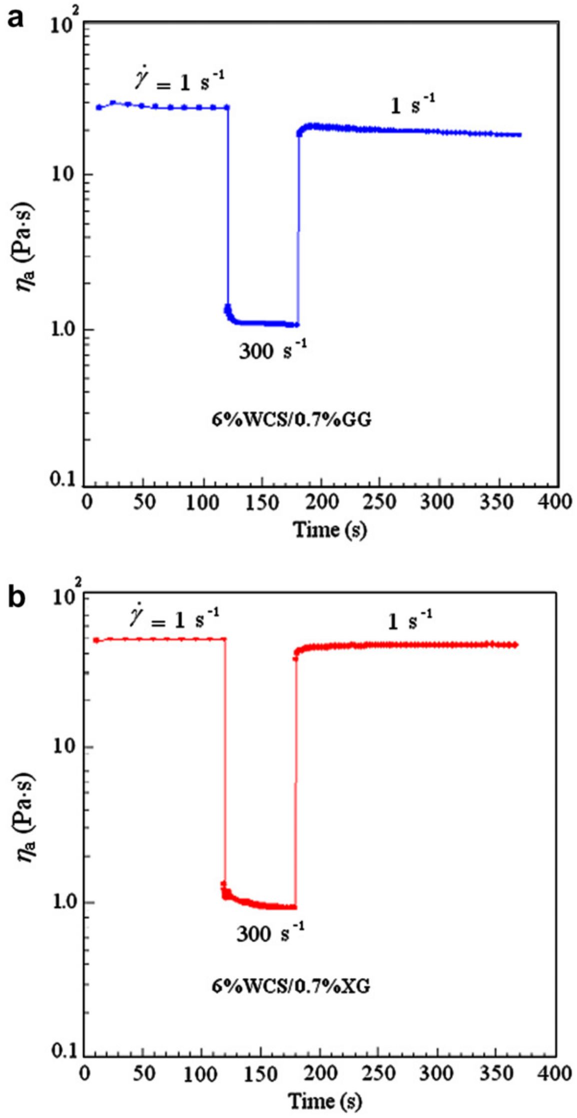

Fig. 4. Typical result of the in-shear structural recovery test of (a) the WCS/GG and (b) the WCS/XG mixed pastes measured at 25 °C.

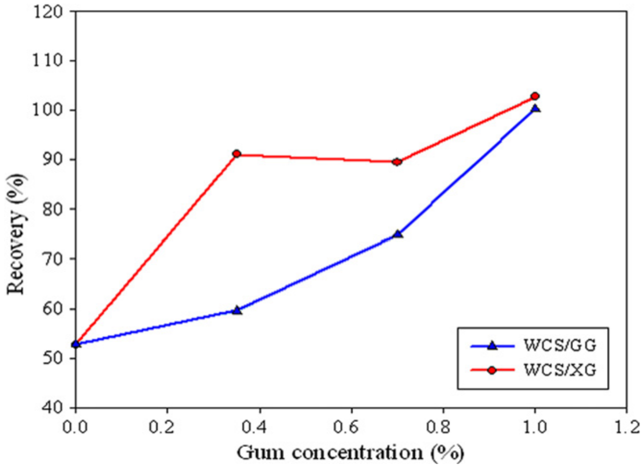

Fig. 5. Influence of gum concentrations on the in-shear structural recovery of the WCS/GG and WCS/XG mixed pastes measured at 25 °C.

areas of the WCS/XG pastes as compared with that of the WCS alone paste. In contrast, GG has lower recovery, less rigid and repeated structure as compared with XG exhibited much less effect on the flow behavior of the WCS paste.

4. Conclusions

This work clarified that the pasting and rheological characteristics of the WCS were largely affected by GG or XG addition, the extent of which depended on their concentrations and as well as their molecular characteristics. The higher molecular weight but lower intrinsic viscosity of GG as compared with XG indicated that GG chains were more flexible than XG chains. RVA results showed that peak, breakdown, final, and setback viscosities and pasting temperature of the WCS dispersion during pasting increased with increasing gum concentrations. Dynamic viscoelasticity measurements on the WCS/gum mixed pastes indicated that the WCS/XG pastes had higher G' and lower $\tan\delta$ values than the WCS/GG pastes, indicating that they were more structured and more solid-like in comparison with the WCS/GG pastes. Flow tests showed that the WCS/GG pastes exhibited a combined time-dependent shear-thickening (antithixotropic) and time-dependent shear-thinning (thixotropic) behavior in which the hysteresis loops seemed to be unaffected by GG concentrations. Thixotropic hysteresis loops of the WCS/XG pastes decreased with increasing XG concentrations and eventually changed to antithixotropic at high concentrations. In-shear structural recovery of the WCS/gum mixed pastes increased with increasing gum concentrations; a more pronounced effect was observed for XG addition. The differences in molecular weight and flexibility of the GG and XG chains are hypothesized to be responsible for the above mentioned effects.

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