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# Gelatinization and rheological properties of rice starch/xanthan mixtures: Effects of molecular weight of xanthan and different salts

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# ABSTRACT

Effects of molecular weight ( $M_w$ ) of xanthan (XG) and salts (0.1 M NaCl or CaCl<sub>2</sub>) on the pasting, thermal, and rheological properties of rice starch (RS) were studied. A series of five XG samples, having various  $M_w$ , was prepared by homogenization of native XG solutions in the presence or absence of salts. The presence of salts greatly reduced the intrinsic viscosities, [ $\eta$ ], of all XG solutions. Rapid visco-analysis (RVA) data showed that XG addition increased the peak, breakdown, final, and setback viscosities of RS, either in the presence or absence of salts, whereas the pasting temperatures were unaffected. Differential scanning calorimetry (DSC) demonstrated that the gelatinization temperatures of RS were unaffected by XG addition but slightly increased by CaCl<sub>2</sub> addition, whereas the gelatinization enthalpies ( $\Delta H$ ) were significantly decreased by additions of XG and salts. Dynamic shear data revealed weak gel-like behaviour in all paste samples in which their rigidity was decreased by XG addition. Flow tests showed that all pastes exhibited time-dependent shear-thinning (thixotropic) with yield stress behaviour in which the hysteresis loop areas were significantly decreased by XG addition, whereas the other rheological parameters varied differently among the samples, with and without added salt. In general, the effects of XG addition on the pasting and rheological properties of RS were more pronounced with increasing  $M_w$  of XG and these effects depended on salts added.

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# 1. Introduction

Rice (*Oryza sativa* L.) starch has many unique attributes that make it one of the most interesting starches in the food industry. Rice starch is hypoallergenic for many, bland in taste, white in colour and, as a gel, is smooth in texture (Bao & Bergman, 2004). However, rice starch, in common with other cereal starches, has negative aspects, such as gel syneresis, retrogradation, and tendency to exhibit breakdown, either from extended cooking, high shear or acidic conditions, producing weak-bodied, cohesive, rubbery pastes, and undesirable gels (BeMiller, 2007). These shortcomings can be overcome by the blending of native starches with polysaccharide hydrocolloids, as reviewed by Appelqvist and Debet (1997). The mixtures of starch and hydrocolloids have been widely used in food products to modify and control rheological and textural properties, improve moisture retention, control water mobility, and maintain overall product quality during storage.

Xanthan is a branched, anionic microbial heteropolysaccharide produced by aerobic fermentation of the bacterium *Xanthomonas campestris*. The polysaccharide is known commercially as xanthan gum (XG). Xanthan is widely and more extensively used as a food gum than is any polysaccharide, other than starch, because of its unique and useful properties. Xanthan is soluble in hot or cold water and solutions exhibit high viscosities at low concentrations and are highly pseudoplastic. These characteristics show excellent stability over a wide pH and temperature range and the polysaccharide is resistant to action of enzymes found in food systems (BeMiller, 2007; Sworn, 2000).

Addition of xanthan to rice starch is known to modify and control the pasting (Shi & BeMiller, 2002; Song, Kwon, Choi, Kim, & Shin, 2006) and rheological properties (Kim & Yoo, 2006) of starch. In general, however, starch and hydrocolloids usually co-exist with other ingredients in many food formulations. One such ingredient is salt. Salts have been shown to have a significant effect on the gelatinization (Ahmad & Williams, 1999, 2002; Chungcharoen & Lund, 1987; Jane, 1993; Jyothi, Sasikiran, Sajeev, Revamma, & Moorthy, 2005; Maaurf, Che Man, Asbi, Junainah, & Kennedy, 2001; Oosten, 1982, 1983, 1990) and rheological properties (Ahmad & Williams, 1999) of various starches. Eliasson and Gudmundsson (2006) have reviewed the effects of salts on these properties of starch and found that they depend on the type of salt as well as on the concentration. The effects of salts on xanthan conformation and the solution rheology have been studied by many researchers (Carrington, Odell, Fisher, Mitchell, & Hartley, 1996; Ma & Barbosa-Cánovas, 1997; Meyer, Fuller, Clark, & Kulicke, 1993; Rochefort & Middleman, 1987; Sato, Norisuye, & Fujita, 1984). In the presence of salts, xanthan undergoes a disorder to





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order conformational transition from a random coil to a helix which affects its solution rheology. Additionally, the molecular weight of hydrocolloids such as guar gum have been found to affect the pasting characteristics of starch (Funami et al., 2005). However, there are very few reports in the literature concerning the effect of salts on starch/hydrocolloid mixtures such as corn starch/xanthan (Sudhakar, Singhal, & Kulkarni, 1995), wheat starch/xanthan (Mandala, Michon, & Launay, 2004), and corn starch/iota-carrageenan (Funami et al., in press) combinations. In particular, no attempt has been made to study the effect of molecular weight of hydrocolloids on these combinations. Therefore, the main objective of this study was to investigate the effect of molecular weight of xanthan and salts on the pasting, thermal, and rheological properties of rice starch/xanthan mixtures.

#### 2. Materials and methods

#### 2.1. Materials

Commercial normal rice starch (RS) was supplied by Cho Heng Rice Vermicelli Factory Co. Ltd., Nakhon Pathom, Thailand. Moisture and amylose contents for the RS sample were 12.7% and 33.0%, respectively. Xanthan (XG) used in this study was a food grade sample and obtained from Jungbunzlauer Austria AG, Wulzeshofen, Austria. All salts used, namely sodium chloride (NaCl) and calcium chloride (CaCl<sub>2</sub>), were of reagent grade and purchased from Merck KGaA, Darmstadt, Germany.

#### 2.2. Preparation of xanthan with different molecular weights

Xanthan preparations with different average molecular weights were prepared by shearing solutions of native xanthan in distilled water or in salt solutions, using a high-pressure homogenizer (Type Panda, Niro-Soavi S. p. A., Parma, Italy). Xanthan solutions (1% w/w) were obtained by dispersing a weighed amount of XG powder in distilled water or an aqueous salt (0.1 M NaCl or CaCl<sub>2</sub>) solution while stirring at room temperature (~25 °C). Sodium azide (0.02%) was used as a preservative. The solutions were heated for 20 min at 80 °C in a water bath to completely solubilize the gum and then were cooled to room temperature. These solutions were then passed through the homogenizer at a pressure of 700 bar for 1, 2, 4, or 12 passes which were denoted as XG1, XG2, XG4, or XG12, respectively. The non-homogenized XG solutions (XG0) were used as controls. The average molecular weights and intrinsic viscosities of the xanthan preparations were determined.

#### 2.3. Molecular weight determination of xanthan

Weight-average molecular weight  $(M_w)$  values of XG in distilled water and salt solutions were determined by gel permeation chromatography (GPC), using a Waters 600E instrument (Waters Corporation, Milford, MA, USA) equipped with a  $7.8 \times 300 \text{ mm}$ Ultrahydrogel linear column packed with hydroxylated polymethacrylate-based gel, a  $6 \times 40$  mm guard column, and a refractive index detector. Pullulan standards, ranging from 5800 to  $1.6 \times 10^6$  Da of peak molecular weight (Showa Denko K.K., Tokyo, Japan), were used for calibration. For XG solutions containing salts, the salts were removed from the samples by dialysis at 4 °C using a cellulose dialysis membrane (Spectra/Por®1, Spectrum Laboratories Inc., CA, USA) with a molecular weight cut off of 6000-8000 Da. An aqueous sodium azide solution (0.02%) was used as a dialysis solution and was changed every 3-5 h for four days and finally followed by distilled water. Xanthan solutions (0.2% w/v) in, pH 11, buffer (0.1 M NaOH and 0.05 M NaHCO<sub>3</sub>) were prepared and filtered using a 0.45  $\mu$ m nylon filter membrane before injection into the GPC column. The conditions were set as follows; injection volume 20  $\mu$ l, flow rate 0.6 ml/min, and temperature 30 °C. Buffer at pH 11 was used as an eluent.

#### 2.4. Intrinsic viscosity determination of xanthan

The intrinsic viscosity,  $[\eta]$ , of XG 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 solvents and of gum solutions, ranging in concentrations from 0.01% to 0.05% were measured in triplicate and averaged. Additional dilutions of the 1% XG solutions were made with the same solvents as used in the stock solutions, namely either distilled water or an aqueous salt (0.1 M NaCl or CaCl<sub>2</sub>) solution.

The concentration-dependence of the viscosity of XG solutions was analyzed by using the classic Huggins equation:

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

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

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

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

#### 2.5. Determination of pasting properties

Pasting properties of rice starch (RS) alone and RS/XG mixtures suspended in distilled water or salt solutions were determined by a rapid visco-analyzer (Model RVA-4C, Newport Scientific Pty. Ltd., Warriewood, Australia). Rice starch slurry alone (6% w/w) was prepared by dispersing weighed amounts of RS (dry basis) in distilled water or salt solutions. In the case of mixtures (5.7% RS and 0.3% XG), RS was slurried in the weighed amounts of dilute homogenized or non-homogenized XG in distilled water or salt solutions. In both cases, the slurries were stirred for 15 min at room temperature to avoid lump formation. The slurries (28 g) were then poured into aluminium canisters and stirred manually using plastic paddles for 20-30 s before insertion into the RVA machine. The heating and cooling cycles were programmed, following the general pasting method (STD 1). 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.

#### 2.6. Determination of thermal properties

Thermal properties, namely gelatinization temperatures and enthalpy, of RS alone, RS/salt, RS/XG, and RS/XG/salt systems, were measured by a differential scanning calorimeter (DSC 822<sup>e</sup>, Mettler-Toledo GmbH, Schwerzenbach, Switzerland). The total solids content of samples was selected to be 12% w/w (dry basis), while keeping the RS/XG mixing ratio constant at 5.7/0.3. The samples were prepared by the procedure described above. After hydration for 1 h at room temperature, 10–15 mg of the well-stirred sample suspensions were exactly weighed into 40 µl aluminium crucibles and immediately hermetically sealed to prevent moisture loss. Scans were performed from 25 to 100 °C at a controlled constant rate of 10 °C/min. A sealed empty crucible was used as a reference and the DSC was calibrated using indium. The enthalpy and transition temperatures, namely the onset temperature ( $T_{\rm o}$ ), peak temperature ( $T_{\rm p}$ ), and conclusion temperature ( $T_{\rm c}$ ), were determined, based on the DSC heating curves. The gelatinization enthalpy was evaluated, based on the area of the main endothermic peak, and expressed in terms of J/g of dry starch using the equipment software.

#### 2.7. Determination of rheological properties

Dynamic viscoelastic and steady flow properties of the freshly prepared pastes of RS alone and RS/XG mixtures, in the presence or absence of salts obtained from pasting in the RVA and keeping at room temperature ( $\sim$ 25 °C) for 1 h, were determined by using a rheometer (Physica MCR 301, Anton Paar GmbH, Graz, Austria) with a cone and plate geometry sensor (1° cone angle, 50 mm diameter, and 0.05 mm gap). The sample was placed in the rheometer 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 over a range of 0.1–100 rad/s at a constant deformation (0.5% strain) within the linear viscoelastic range. The storage modulus (G'), loss modulus (G''), and loss tangent (tan  $\delta = G''/G'$ ) as a function of frequency ( $\omega$ ) were obtained.

Steady flow tests were also performed on the freshly prepared paste samples at 25 °C to obtain shear rate versus shear stress (flow curves) data. The cone was programmed to increase the shear rate from 0 to  $300 \text{ s}^{-1}$  in 3 min (upward flow curve), followed immediately by a reduction from 300 to  $0 \text{ s}^{-1}$  in the next 3 min (downward flow curve). Using the equipment software, the areas of the hysteresis loops were found and the Herschel–Bulkley rheological model expressed by Eq. (3) was fitted to the experimental data.

$$\sigma = \sigma_0 + K \dot{\gamma}^n \tag{3}$$

where  $\sigma$  is the shear stress (Pa),  $\sigma_0$  is the yield stress (Pa),  $\dot{\gamma}$  is the shear rate (s<sup>-1</sup>), *K* is the consistency coefficient (Pa s<sup>*n*</sup>), and *n* is the flow behaviour index (dimensionless).

### 2.8. Statistical analysis

All measurements were made in triplicate for each sample. Results are expressed as means ± standard deviations. A one-way analysis of variance (ANOVA) and Tukey's test were used to establish the significance of differences among the mean values at the 0.05 level of confidence. The statistical analyses were performed using SPSS (2003) version 12.0 for Windows program (SPSS Inc., Chicago, IL, USA).

# 3. Results and discussion

### 3.1. Molecular weight and intrinsic viscosity of xanthan

It is known that strong mechanical effects, such as sonication (Holzwarth, 1978; Sato et al., 1984) or homogenization (Koczo, Wasan, Borwankar, & Gonsalves, 1998), split xanthan (XG) molecules into smaller fragments. Table 1 shows that homogenization of 1% XG solutions in the presence or absence of salts resulted in a decrease in weight-average molecular weight ( $M_w$ ) with increasing number of passes during homogenization. The presence of salts caused about a double increase in  $M_w$  of XG in the non-homogenized solutions. This can be attributed to a salt induced self-aggregation of XG molecules, as pointed out by Meyer et al. (1993).

When salt is added to the solution, XG, like other polyelectrolytes, undergoes a disorder (random coil) to order (helix) conformational transition in which the backbone takes on a helical conformation and the charged trisaccharide side chains collapse down onto the backbone (due to charge screening effects) and stabilize the ordered conformation. In this rod-like configuration, with the electrostatic repulsions screened, the molecules are easily aligned and strongly associate (due to hydrogen bonding and ionic interactions) to form (nonpermanent) intermolecular associations (Rochefort & Middleman, 1987). By using light scattering measurement, Sato et al. (1984) found that XG in 0.1 M aqueous NaCl consisted of paired chains having  $M_w$  about two times higher than that of single chain molecules. In fact, differences in  $M_w$  have been attributed to the degree of aggregation of XG by Meyer et al. (1993). However, these XG aggregates were easily ruptured by only a few passes through the homogenizer. When homogenization was performed for more than four passes. XG molecules in both distilled water and salt solutions were disrupted, by the same extents, to about  $2.0 \times 10^6$  Da at 12 passes.

The intrinsic viscosity,  $[\eta]$ , of XG solutions, with and without added salts significantly ( $P \leq 0.05$ ) decreased with decreasing  $M_w$ of XG. This is expected since the  $[\eta]$  is a measure of the hydrodynamic volume occupied by a macromolecule, which is closely related to the size and conformation of the macromolecular chains in a particular solvent (Higiro, Herald, Alavi, & Bean, 2007). Furthermore, the addition of salts was found to greatly reduce (5–10 times) the  $[\eta]$  of XG, providing further proof that XG molecules have a highly expanded conformation at low ionic strength (in distilled water) due to electrostatic repulsions of the negatively charged side chains (Carrington et al., 1996). When salt is added, charge screening causes the side chains to collapse down to the backbone, hence giving the XG molecule a more compact structure and reducing the hydrodynamic volume (Rochefort & Middleman, 1987).

#### 3.2. Pasting properties

The pasting and paste characteristics of RS alone and RS/XG mixtures, with various  $M_w$  of XG suspended in distilled water or aqueous salt solutions, determined by RVA analysis, are summarized in Table 2. Addition of 0.1 M NaCl or CaCl<sub>2</sub> to RS, alone, suspensions resulted in a significant ( $P \leq 0.05$ ) increase in peak viscosities as compared with the control. This could be attributed to the starch/salt interactions which reduced mobility of the starch granules, leading to higher viscosity, as pointed out by Bircan and Barringer (1998). Oosten (1983) proposed that starch, being a weak acidic ion-exchanger, adsorbs the more voluminous cations, namely sodium or calcium ion, from the solution in exchange with the smaller hydrogen ion. A consequence is that the starch matrix is stretched to some extent, resulting in an increase of granule volume. This also seems to be responsible for the increase in viscosity of a starch suspension by adding salts. Jyothi et al. (2005) reported that a higher peak viscosity of a starch suspension during pasting in the presence of salts generally indicates a higher swelling power of the starch granules due to the weakening of the granule structure by those salts. These slightly weakened granules are more affected by prolonged stirring at high temperature, and this leads to the large breakdown value and lower final and setback viscosities. This also explains a significant increase in breakdown viscosities and decrease in final and setback viscosities of RS alone in the presence of salts, with the exception of CaCl<sub>2</sub>, which increased final viscosity and did not affect setback viscosity of RS alone. There was no significant change in pasting temperatures of RS alone in the presence of either NaCl or CaCl<sub>2</sub> as compared with the control.

In the case of RS/XG mixtures in the presence or absence of salts, addition of XG generally resulted in a significant ( $P \le 0.05$ )

# Table 1

Effect of high pressure homogenization on weight-average molecular weight ( $M_w$ ) and intrinsic viscosity ([ $\eta$ ]) of xanthan (XG) in aqueous solutions with or without salts

Homogenization <sup>A</sup>	Molecular we	Molecular weight (Da) $\times 10^{-6}$			Intrinsic viscosity <sup>B</sup> (dl/g)			
Number of passes	No salt	0.1 M NaCl	0.1 M CaCl <sub>2</sub>	No salt	0.1 M NaCl	0.1 M CaCl <sub>2</sub>		
0 (XG0)	4.05	8.96	8.17	$110.34 \pm 3.59^{a}$	$21.22 \pm 1.21^{a}$	$18.92 \pm 0.68^{a}$		
1 (XG1)	3.33	5.11	4.99	96.84 ± 3.19 <sup>b</sup>	12.56 ± 0.12 <sup>b</sup>	13.93 ± 1.08 <sup>b</sup>		
2 (XG2)	3.10	3.67	3.64	$94.46 \pm 5.27^{b}$	$10.10 \pm 0.43^{\circ}$	10.59 ± 0.71 <sup>c</sup>		
4 (XG4)	2.70	2.83	2.73	78.53 ± 3.50 <sup>c</sup>	$8.30 \pm 0.71^{\circ}$	$9.03 \pm 0.39^{cd}$		
12 (XG12)	2.01	2.06	1.99	$65.10 \pm 5.16^{d}$	$6.14 \pm 0.80^{d}$	$7.22 \pm 0.38^{d}$		

<sup>A</sup> The sample codes are denoted in parentheses.

<sup>B</sup> Assays were performed in triplicate at 25 °C. Mean  $\pm$  standard deviation values in the same column followed by different superscripts are significantly different ( $P \leq 0.05$ ).

Fable 2	
Pasting properties of 6% rice starch (RS) alone and RS (5.7%)/xanthan (XG; 0.3%) mixtures dispersed in aqueous solutions with or without salts at 0.1 M concentration <sup>A</sup>	

Salt	Hydrocolloid <sup>B</sup>	Peak viscosity (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)	Pasting temperature (°C)
None	None	$43.9 \pm 1.1^{\circ}$	$2.7 \pm 1.3^{d}$	$62.2 \pm 0.3^{\circ}$	$21.2 \pm 0.3^{d}$	$94.7 \pm 1.0^{a}$
	XG0	$69.4 \pm 1.8^{a}$	$15.4 \pm 0.9^{a}$	83.7 ± 2.3 <sup>a</sup>	29.7 ± 2.3 <sup>ab</sup>	$86.4 \pm 1.4^{b}$
	XG1	$49.7 \pm 0.6^{b}$	$9.7 \pm 0.9^{b}$	$71.8 \pm 1.5^{b}$	$32.0 \pm 0.4^{a}$	$95.0 \pm 0.4^{a}$
	XG2	$42.8 \pm 0.2^{\circ}$	$7.8 \pm 0.8^{bc}$	62.1 ± 1.3 <sup>c</sup>	27.1 ± 2.1 <sup>bc</sup>	$94.3 \pm 1.2^{a}$
	XG4	38.6 ± 1.8 <sup>c</sup>	7.5 ± 0.3 <sup>bc</sup>	$57.0 \pm 4.0^{cd}$	25.9 ± 2.1 <sup>bc</sup>	92.5 ± 3.4 <sup>a</sup>
	XG12	$37.5 \pm 0.4^{\circ}$	6.1 ± 0.7 <sup>c</sup>	$55.8 \pm 1.3^{d}$	$24.4 \pm 0.6^{cd}$	$94.4 \pm 0.1^{a}$
NaCl	None	$48.0 \pm 0.4^{d}$	$9.9 \pm 0.4^{bc}$	$45.7 \pm 0.4^{\rm f}$	$7.6 \pm 0.6^{e}$	$95.1 \pm 0.2^{a}$
	XG0	$86.4 \pm 0.8^{a}$	$27.2 \pm 0.7^{a}$	$98.3 \pm 1.7^{a}$	39.3 ± 2.1 <sup>a</sup>	$92.2 \pm 0.4^{a}$
	XG1	$60.0 \pm 0.9^{b}$	$12.2 \pm 2.6^{b}$	$73.2 \pm 1.0^{b}$	$25.5 \pm 2.3^{b}$	$94.9 \pm 0.4^{a}$
	XG2	$53.1 \pm 0.2^{bc}$	$9.6 \pm 0.9^{bc}$	$65.7 \pm 0.7^{\circ}$	$22.2 \pm 0.5^{bc}$	$95.1 \pm 0.2^{a}$
	XG4	49.1 ± 0.3 <sup>cd</sup>	8.2 ± 0.8 <sup>c</sup>	$59.9 \pm 0.4^{d}$	$19.0 \pm 1.0^{cd}$	$95.0 \pm 0.1^{a}$
	XG12	$43.9 \pm 1.9^{d}$	$6.8 \pm 0.5^{\circ}$	$53.8 \pm 4.3^{e}$	$16.7 \pm 0.8^{d}$	$94.9 \pm 0.3^{a}$
CaCl <sub>2</sub>	None	$52.1 \pm 1.2^{f}$	5.9 ± 0.1 <sup>e</sup>	$67.3 \pm 1.6^{f}$	21.1 ± 1.7 <sup>d</sup>	$94.9 \pm 0.5^{a}$
	XG0	$118.6 \pm 0.3^{a}$	$21.8 \pm 0.2^{a}$	$124.7 \pm 0.2^{a}$	$28.0 \pm 0.5^{bc}$	93.7 ± 1.4 <sup>a</sup>
	XG1	$79.0 \pm 0.8^{b}$	$16.3 \pm 0.6^{d}$	$100.0 \pm 1.4^{\rm b}$	$37.2 \pm 0.3^{a}$	91.2 ± 1.5 <sup>a</sup>
	XG2	$73.6 \pm 0.5^{\circ}$	$19.6 \pm 0.7^{b}$	$88.5 \pm 0.5^{\circ}$	$34.5 \pm 0.7^{a}$	$93.0 \pm 1.9^{a}$
	XG4	$68.2 \pm 1.0^{d}$	$17.8 \pm 0.4^{\circ}$	$80.7 \pm 1.5^{d}$	$30.4 \pm 1.1^{b}$	$91.2 \pm 1.4^{a}$
	XG12	64.1 ± 2.3 <sup>e</sup>	$17.1 \pm 0.3^{cd}$	72.8 ± 1.2 <sup>e</sup>	26.7 ± 1.1 <sup>c</sup>	$92.5 \pm 2.0^{a}$

<sup>A</sup> Assays were performed in triplicate. Mean  $\pm$  standard deviation values in the same column for each solution followed by different superscripts are significantly different ( $P \leq 0.05$ ).

<sup>B</sup> Refer to Table 1 for the sample codes of XG (XG0–XG12) having various  $M_w$  values.

increase in peak, breakdown, final, and setback viscosities, whereas pasting temperatures were not significantly affected. This result can be interpreted by assuming that the system is biphasic, with the hydrocolloid located entirely in the continuous phase. Its concentration would then increase as the volume of the phase accessible to the hydrocolloid was reduced due to swelling of the starch granules during pasting. This resulted in a pronounced increase in the viscosity of the continuous phase and in turn the overall viscosity of the suspension itself, owing to the thickening properties of these hydrocolloids (Alloncle, Lefebvre, Llamas, &

Table 3

Thermal properties of 12% rice starch (RS) and RS/xanthan (XG; 5.7/0.3, w/w	w ratio) mixtures c	dispersed in aqu	ueous solutions with	h or without salts at 0.1	M concentration
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Salt	Hydrocolloid <sup>B</sup>	<i>T</i> <sub>o</sub> (°C)	$T_{\rm p}$ (°C)	$T_{\rm c}$ (°C)	$\Delta T (T_{\rm c} - T_{\rm o})$	$\Delta H$ (J/g)
None	None	$75.5 \pm 0.6^{a}$	$80.7 \pm 0.3^{a}$	$87.1 \pm 0.8^{a}$	$11.6 \pm 1.2^{a}$	$15.3 \pm 0.2^{a}$
	XG0	$75.5 \pm 0.6^{a}$	$81.3 \pm 0.4^{a}$	$87.7 \pm 0.7^{a}$	$12.3 \pm 1.3^{a}$	$10.1 \pm 0.7^{b}$
	XG1	75.5 ± 1.3 <sup>a</sup>	$81.0 \pm 0.2^{a}$	87.3 ± 0.3 <sup>a</sup>	$11.7 \pm 1.2^{a}$	$9.9 \pm 0.2^{b}$
	XG2	$74.7 \pm 0.3^{a}$	$81.0 \pm 0.1^{a}$	$87.4 \pm 0.2^{a}$	$12.7 \pm 0.3^{a}$	$8.2 \pm 0.5^{\circ}$
	XG4	$76.2 \pm 0.2^{a}$	$81.0 \pm 0.3^{a}$	86.7 ± 0.3 <sup>a</sup>	$10.6 \pm 0.4^{a}$	$7.6 \pm 0.4^{\circ}$
	XG12	$75.9 \pm 1.2^{a}$	$81.3 \pm 0.3^{a}$	$87.1 \pm 0.6^{a}$	$11.2 \pm 1.5^{a}$	$8.5 \pm 0.4^{\circ}$
NaCl	None	$77.0 \pm 2.1^{a}$	$81.9 \pm 2.1^{a}$	$86.5 \pm 2.8^{a}$	$9.5 \pm 1.1^{a}$	$12.2 \pm 2.1^{a}$
	XG0	$77.3 \pm 1.2^{a}$	$82.2 \pm 2.4^{a}$	$86.6 \pm 3.4^{a}$	$9.3 \pm 2.3^{a}$	$7.4 \pm 0.3^{b}$
	XG1	$78.4 \pm 0.1^{a}$	$83.8 \pm 0.1^{a}$	$89.3 \pm 0.3^{a}$	$10.8 \pm 0.3^{a}$	$7.4 \pm 0.2^{b}$
	XG2	$78.6 \pm 0.1^{a}$	$84.0 \pm 0.3^{a}$	$89.5 \pm 0.1^{a}$	$10.8 \pm 0.2^{a}$	7.5 ± 0.1 <sup>b</sup>
	XG4	$79.2 \pm 0.5^{a}$	$84.3 \pm 0.1^{a}$	$89.5 \pm 0.7^{a}$	$10.4 \pm 1.2^{a}$	$8.0 \pm 0.5^{b}$
	XG12	$78.5 \pm 0.6^{a}$	$83.8 \pm 0.2^{a}$	$89.1 \pm 0.1^{a}$	$10.5 \pm 0.7^{a}$	$7.5 \pm 0.4^{b}$
CaCl <sub>2</sub>	None	$79.5 \pm 0.5^{a}$	$85.0 \pm 0.2^{b}$	$90.6 \pm 0.2^{a}$	$11.1 \pm 0.6^{a}$	8.8 ± 0.3ª
	XG0	$80.3 \pm 1.1^{a}$	$85.1 \pm 0.1^{ab}$	$90.5 \pm 0.7^{a}$	$10.2 \pm 1.8^{a}$	$7.5 \pm 0.8^{a}$
	XG1	$79.6 \pm 0.6^{a}$	$85.1 \pm 0.1^{ab}$	$91.0 \pm 0.4^{a}$	$11.5 \pm 0.9^{a}$	$8.8 \pm 1.6^{a}$
	XG2	$80.1 \pm 0.7^{a}$	$85.4 \pm 0.2^{a}$	$90.9 \pm 0.1^{a}$	$10.8 \pm 0.8^{a}$	$8.6 \pm 1.6^{a}$
	XG4	$79.5 \pm 0.3^{a}$	$85.0 \pm 0.1^{b}$	$90.4 \pm 0.4^{a}$	$10.9 \pm 0.7^{a}$	$7.5 \pm 0.5^{a}$
	XG12	$79.7 \pm 0.2^{a}$	$85.0 \pm 0.0^{b}$	$90.6 \pm 0.1^{a}$	$10.9 \pm 0.9^{a}$	$7.3 \pm 0.6^{a}$

<sup>A</sup> Assays were performed in triplicate. Mean  $\pm$  standard deviation values in the same column for each solution followed by different superscripts are significantly different ( $P \leq 0.05$ ).

<sup>B</sup> Refer to Table 1 for the sample codes of XG (XG0–XG12) having various  $M_{\rm w}$  values.

Doublier, 1989) added to the thickening produced by swollen starch granules. Therefore, the thickening capacity of the tested hydrocolloids could dominate the viscosity of the starch/hydrocolloid pastes. This hypothesis was confirmed by the fact that the effect of XG on viscosity of RS/XG mixtures significantly decreased with a decrease in their  $M_w$  (Table 2) due to their lower viscosities (Table 1).

Addition of salts significantly increased peak, breakdown, final, and setback viscosities of RS/XG mixtures with various  $M_w$  of XG. As discussed earlier, salts caused a disorder to order conformational transition of XG molecules which affected the solution viscosity (Carrington et al., 1996). However, this effect depends on the concentration of XG in solution. At low gum concentrations (<0.25%), salt causes a decrease in viscosity whereas, at high gum concentrations, as used in this study (0.3%), viscosity increases with added salt (Sworn, 2000). Within each RS/XG blend, divalent cations from CaCl<sub>2</sub> showed a more pronounced effect on the peak and final viscosities than did monovalent cations from NaCl. This was possibly due to molecular cross-linking of XG by calcium ions, which resulted in a greater extent of molecular contraction (Higiro et al., 2007). The opposite trend to this result was observed for addition of NaCl or CaCl<sub>2</sub> to corn starch/xanthan mixtures, which may be attributed to the lower concentration of XG used  $(\leq 0.25\%)$  in those experiments (Sudhakar et al., 1995). For the pasting temperature, it is generally known that the pasting temperature of starch is lowered by gum addition, due to the interactions between gum and leached starch molecules, primarily amylose (Christianson, Hodge, Osborne, & Detroy, 1981; Shi & BeMiller, 2002). These molecular interactions were found to become stronger with increasing  $M_w$  of gum (Funami et al., 2005). However, there were no significant differences in the pasting temperatures of any systems studied in the present work, indicating negligible interactions between leached amylose and XG with various  $M_{\rm w}$ in either the presence or absence of salts. These findings were similar to those previously reported for the pasting temperatures of 5% corn starch alone (86.6 °C) and 5% corn starch/0.25% XG/ 0.5%(~0.1 M) NaCl or 1.0%(~0.1 M) CaCl<sub>2</sub> combinations (86.0 °C; Sudhakar et al., 1995).

#### 3.3. Thermal properties

The onset ( $T_o$ ), peak ( $T_p$ ), and conclusion ( $T_c$ ) gelatinization temperatures, and the gelatinization temperature range ( $\Delta T$ ) and enthalpy ( $\Delta H$ ) of RS alone, and RS/XG aqueous suspensions in the presence or absence of salts, determined by the DSC, are summarized in Table 3.

For RS alone, addition of 0.1 M NaCl did not significantly  $(P \leq 0.05)$  affect the magnitudes of  $T_{\rm o}$ ,  $T_{\rm p}$ ,  $T_{\rm c}$  and  $\Delta T$ , whereas 0.1 M CaCl<sub>2</sub> addition significantly increased  $T_{o}$  and  $T_{p}$  values without any effect on  $T_c$  and  $\Delta T$  as compared with those of the control. The  $\Delta H$  was found to be significantly decreased by the addition of both salts used in this study. Salts have been reported to cause an elevation or depression of gelatinization temperature and gelatinization enthalpy, depending on the types of salt and their concentrations used (Ahmad & Williams, 1999, 2002; Chungcharoen & Lund, 1987; Jane, 1993; Jyothi et al., 2005; Maaurf et al., 2001; Oosten, 1982, 1983, 1990). It has been reported that NaCl and CaCl<sub>2</sub>, at low concentrations, slightly increased the  $T_p$  of sago starch (Ahmad & Williams, 1999, 2002; Maaurf et al., 2001) and T<sub>o</sub> of corn starch (Jane, 1993) but, when the concentrations increased further (up to  $\sim$ 2 M for NaCl and  $\sim$ 1 M for CaCl<sub>2</sub>), these temperatures decreased. The  $\Delta H$  showed a behaviour similar to the gelatinization temperature. In the case of various rice flours and their isolated starches, Chungcharoen and Lund (1987) found that gelatinization temperatures of rice flour or starch suspension shifted to higher temperatures and enthalpy decreased in the presence of NaCl. The

presence of CaCl<sub>2</sub> at the concentration used in this study seemed to exhibit a more pronounced effect on gelatinization of RS than did NaCl. This could be attributed to the fact that the effect of salts on starch gelatinization generally follows the order of the Hofmeister series (Ahmad & Williams, 1999, 2002; Jane, 1993). It is known that cations, coupled with the same anion counterpart, Cl<sup>-</sup> in this case, affect the gelatinization process in the following order  $Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+$ .

Various explanations have been proposed to elucidate the mechanism of starch gelatinization affected by various salts. It seems that the influence of salts on the gelatinization properties of starch can be attributed to various factors, especially the influence on polymer–solvent interaction, the effects on water structure and the electrostatic interaction between starch and the ions. According to Oosten (1982, 1983, 1990), when NaCl or CaCl<sub>2</sub> was added to a starch suspension, some alcoholic groups in the starch granules were converted to sodium or calcium alcoholate groups. These compounds were better dissociated, thus causing a



**Fig. 1.** Dynamic mechanical spectra of 6% rice starch (RS) and rice starch (5.7%)/ xanthan (XG; 0.3%) pastes in (a) distilled water (DW), (b) 0.1 M NaCl, and (c) 0.1 M CaCl<sub>2</sub> solutions. Measurements were made at 0.5% strain and 25 °C. Closed symbols represent storage modulus (*G'*) and open symbols represent loss modulus (*G''*). Refer to Table 1 for the sample codes of XG (XG0–XG12) having various  $M_w$  values.

rise in the Donnan potential, which more effectively excluded the gelatinizing Cl<sup>-</sup> from the granules. However, the absorption of Na<sup>+</sup> or Ca<sup>2+</sup> was rather limited since, in our systems, there was no agent to bind the released H<sup>+</sup>; hence, the increase in gelatinization temperature was also limited. Consequently, once gelatinization began (at a higher temperature), Cl<sup>-</sup> assisted gelatinization by breaking hydrogen bonds between starch chains, as evidenced by a reduction of the magnitude of  $\Delta H$ . Jane (1993) proposed that starch gelatinization in such salts seems to be controlled by two effects: water structure and electrostatic interaction between starch and ions. These two effects conflict with one another and result in complex effect patterns, depending on the type and concentration of salts.

Surprisingly, addition of XG with various  $M_w$ , at a concentration used in this study, did not significantly ( $P \le 0.05$ ) affect the  $T_o$ ,  $T_p$ ,  $T_c$ , and  $\Delta T$  values of RS/XG blends as compared with those of the corresponding control samples without XG. It is clear that, in combinations of RS, XG, and salt, the effect of salt, particularly CaCl<sub>2</sub> in increasing the  $T_o$  and  $T_p$  values of RS, and in turn the Donnan potential, is unchanged by an increase in the viscosity of RS/XG systems. The magnitude of  $\Delta H$  values, in contrast, was significantly decreased by XG addition, except for the systems with added CaCl<sub>2</sub>, and this effect seemed to be independent of  $M_w$  of XG. Xanthan is an anionic polysaccharide. Hydrocolloids that are polyanions have been found to alter gelatinization characteristics of starch. There is no change in anion concentration with changes in  $M_w$  of XG. The decrease in  $\Delta H$  values could be attributed, at least in part, to a reduction in water availability and/or mobility, causing partial gelatinization of crystalline regions in the starch granules, and the effect of starch/gum interactions. These were pointed out in our earlier investigation for tapioca starch/XG systems (Chaisawang & Suphantharika, 2006).

### 3.4. Dynamic viscoelastic properties

Small amplitude oscillatory shear measurements of RS alone and RS blended with XG having different  $M_w$ , both in the presence and absence of salts, were compared and demonstrated





**Fig. 2.** Dynamic mechanical loss tangents (tan  $\delta$ ) of 6% rice starch (RS) and rice starch (5.7%)/xanthan (XG; 0.3%) pastes in (a) distilled water (DW), (b) 0.1 M NaCl, and (c) 0.1 M CaCl<sub>2</sub> solutions. Measurements were made at 0.5% strain and 25 °C. Refer to Table 1 for the sample codes of XG (XG0–XG12) having various  $M_w$  values.

**Fig. 3.** Flow curves of 6% rice starch (RS) and rice starch (5.7%)/xanthan (XG; 0.3%) pastes in (a) distilled water (DW), (b) 0.1 M NaCl, and (c) 0.1 M CaCl<sub>2</sub> solutions measured at 25 °C. Solid lines represent upward curves and dashed lines represent downward curves. Refer to Table 1 for the sample codes of XG (XG0–XG12) having various  $M_w$  values.

similar dynamic mechanical spectra (Fig. 1). These rheograms show that the storage modulus (G') was much larger than the loss modulus (G'') and both moduli show only slight variation with frequency  $(\omega)$ ; moreover, a crossover between these two moduli was not observed throughout the measured frequency range. The fact that the dynamic mechanical loss tangent (tan  $\delta = G''/G'$ ) values for all the gels tested were much smaller than unity indicates predominantly elastic behaviour (Fig. 2). This behaviour may be classified rheologically as a typical weak gel structure, as popularized by Clark and Ross-Murphy (1987). The magnitudes of G' of RS/XG0 gels were comparable to those of RS alone gels, whereas those of G'' were about 2.4–4.6 times higher at a  $\omega$  of 1 rad/s, indicating that RS/XG0 gels were more viscous than RS alone gels. This result is consistent with a substantial increase in tan  $\delta$  observed for all RS/XG gels as compared with RS alone gels. However, the effects appeared to be less pronounced when  $M_{\rm w}$  of XG was decreased but the gel strengths of the pure RS pastes having the lowest tan  $\delta$  values are never attained. From this it can be deduced that the hydrocolloids employed are not able to provide an effective contribution to the further structural build-up of the starch network. This finding supports the hypothesis that these systems involve mixtures in which intermolecular interactions between like molecules are favoured, which locally at least results in a macroscopic phase separation (Alloncle & Doublier, 1991; Annable, Fitton, Harris, Phillips, & Williams, 1994; Eidam, Kulicke, Kuhn, & Stute, 1995).

Interestingly, there were almost no differences in the viscoelastic properties of RS alone and RS/XG pastes in distilled water when compared to those with the addition of sodium or calcium ions. This may be attributed, at least in part, to the relatively low level (0.1 M) of salts used in this study. All previous research on the effects of various salts, including NaCl and CaCl<sub>2</sub>, on the viscoelastic properties of starch gels occurred at much higher concentrations (0.5 M; Ahmad & Williams, 1999) than those that were effective for xanthan gels (0.01 M; Ma & Barbosa-Cánovas, 1997). Our results demonstrated that, in combinations of RS, XG, and salt, XG dominates the viscoelastic behaviour of the mixed gels and the addition of salts only slightly affects these properties. This is in accordance with an earlier report for wheat starch/XG/NaCl mixed systems (Mandala et al., 2004).

#### 3.5. Steady shear rheological properties

The steady flow characteristics of RS alone and RS/XG pastes with various  $M_w$  of XG in the presence or absence of salts are presented in Fig. 3. For the range of shear rates used in this study, all pastes exhibited mainly time-dependent shear-thinning (thixotropic) with yield stress behaviour. Both the upward and downward flow curves were adequately described by the Herschel–Bulkley model. Consistency coefficients (*K*), flow behaviour indices (*n*), and yield stresses ( $\sigma_0$ ), along with coefficients of determination ( $R^2$ ) for each upward or downward flow curve, and hysteresis loop areas between these two curves are summarized in Table 4.

As shown in Table 4, a hysteresis loop area was observed in all pastes studied, which can be interpreted as structural breakdown by the shear field to alter a structure or form a new structure, which then maintained a shear-thinning characteristic on following shear sweeps (Achavuthakan & Suphantharika, 2008). However, the hysteresis loop of RS alone pastes was significantly  $(P \leq 0.05)$  reduced when XG was added to the systems, indicating that XG apparently promoted re-association after destruction of structure due to high shear. In general, it is known that XG has high shear stability and extremely short times for recovery of its original structure after alteration (Achayuthakan & Suphantharika, 2008; Rochefort & Middleman, 1987). This effect was more pronounced for XG with high  $M_w$  and in the presence of salts, possibly due to their ordered configuration, removing any hindrance to reassociation between molecules. Similar findings were previously reported for other starch/hydrocolloid mixed pastes, in which it was also shown that hydrocolloids enhanced the in-shear structural recovery of the starch pastes (Achayuthakan & Suphantharika, 2008; Tye, 1988). This result is also consistent with the dynamic viscoelastic data in which the more structured gels having low tan  $\delta$  values (Fig. 2) exhibited higher hysteresis loop areas than did the less structured ones.

Another important flow characteristic observed for all pastes studied was the presence of yield stress ( $\sigma_0$ ), which represents a finite stress required to achieve flow. Its existence indicates that there is a cross-linked or other interactive structure in a material which must be broken down before flow can occur at an appreciable rate (Achayuthakan, Suphantharika, & Rao, 2006; Cheng, 1986).

#### Table 4

The Herschel-Bulkley parameters for 6% rice starch (RS) pastes and RS (5.7%)/xanthan (XG; 0.3%) mixed pastes in the presence or absence of salts at 0.1 M concentration<sup>A,B</sup>

Salt	Hydrocolloid <sup>C</sup>	Hysteresis loop area (Pa/s)	Upward curve				Downward curve			
			$\sigma_0$ (Pa)	K (Pa s <sup><math>n</math></sup> )	n (-)	$R^2$	$\sigma_0$ (Pa)	K (Pa s <sup><math>n</math></sup> )	n (-)	$R^2$
None	None	5126 ± 131 <sup>a</sup>	$60.3 \pm 4.3^{a}$	$0.8 \pm 0.3^{d}$	$0.78 \pm 0.06^{a}$	0.972	$23.6 \pm 1.8^{a}$	$4.7 \pm 0.5^{d}$	$0.52 \pm 0.02^{a}$	0.862
	XG0	1058 ± 43 <sup>e</sup>	$30.6 \pm 5.3^{b}$	$12.6 \pm 4.7^{b}$	$0.27 \pm 0.04^{\circ}$	0.952	$8.8 \pm 2.7^{d}$	$21.3 \pm 3.2^{a}$	$0.23 \pm 0.01^{d}$	0.941
	XG1	$2086 \pm 80^{d}$	$25.9 \pm 4.9^{b}$	11.7 ± 2.3 <sup>bc</sup>	$0.36 \pm 0.03^{bc}$	0.990	$19.9 \pm 0.7^{ab}$	$11.4 \pm 0.9^{b}$	$0.38 \pm 0.01^{\circ}$	0.968
	XG2	2538 ± 113 <sup>c</sup>	$29.9 \pm 2.2^{b}$	$10.4 \pm 1.5^{bc}$	$0.38 \pm 0.03^{b}$	0.995	$18.1 \pm 1.0^{bc}$	$10.8 \pm 0.7^{bc}$	$0.39 \pm 0.01^{bc}$	0.960
	XG4	2657 ± 108 <sup>bc</sup>	32.4 ± 1.7 <sup>b</sup>	7.8 ± 1.8 <sup>bc</sup>	$0.43 \pm 0.04^{b}$	0.993	$18.4 \pm 1.1^{bc}$	$9.6 \pm 1.0^{bc}$	$0.41 \pm 0.02^{bc}$	0.963
	XG12	$2826 \pm 88^{b}$	$29.8\pm0.4^{\rm b}$	$6.0 \pm 0.7^{cd}$	$0.46 \pm 0.02^{b}$	0.987	$15.2 \pm 0.4^{c}$	7.9 ± 0.5 <sup>c</sup>	$0.43 \pm 0.01^{b}$	0.952
NaCl	None	3422 ± 137 <sup>a</sup>	$65.4 \pm 0.9^{a}$	0.01 ± 0.01 <sup>c</sup>	$1.51 \pm 0.13^{a}$	0.970	23.4 ± 1.2 <sup>c</sup>	$4.2 \pm 0.2^{c}$	$0.50 \pm 0.02^{a}$	0.818
	XG0	$-453 \pm 78^{d}$	$62.9 \pm 0.5^{a}$	0.1 ± 0.1 <sup>c</sup>	$1.08 \pm 0.10^{b}$	0.995	$46.3 \pm 0.1^{a}$	3.3 ± 0.6 <sup>c</sup>	$0.48 \pm 0.02^{ab}$	0.971
	XG1	977 ± 516 <sup>c</sup>	$63.8 \pm 1.2^{a}$	$1.1 \pm 0.5^{bc}$	$0.74 \pm 0.10^{\circ}$	0.996	$34.9 \pm 3.8^{b}$	$8.4 \pm 2.2^{b}$	$0.42 \pm 0.04^{b}$	0.976
	XG2	$1904 \pm 187^{b}$	$49.2 \pm 1.6^{b}$	$3.7 \pm 0.8^{ab}$	0.52 ± 0.03 <sup>cd</sup>	0.995	$16.3 \pm 0.9^{d}$	$14.4 \pm 1.6^{a}$	$0.34 \pm 0.01^{\circ}$	0.962
	XG4	$1942 \pm 36^{b}$	45.7 ± 1.4 <sup>b</sup>	$4.4 \pm 0.5^{a}$	$0.50 \pm 0.02^{d}$	0.996	$16.2 \pm 1.0^{d}$	$13.9 \pm 0.4^{a}$	$0.36 \pm 0.01^{\circ}$	0.967
	XG12	2290 ± 190 <sup>b</sup>	$38.7 \pm 2.6^{\circ}$	$5.9 \pm 2.1^{a}$	$0.45 \pm 0.06^{d}$	0.997	$7.7 \pm 2.8^{e}$	$15.4 \pm 2.0^{a}$	$0.33 \pm 0.02^{\circ}$	0.950
CaCl <sub>2</sub>	None	4181 ± 260 <sup>a</sup>	$43.0 \pm 0.6^{\circ}$	$4.7 \pm 0.3^{ab}$	$0.48 \pm 0.01^{b}$	0.986	17.3 ± 1.0 <sup>c</sup>	7.3 ± 0.1 <sup>c</sup>	$0.46 \pm 0.01^{a}$	0.948
	XG0	822 ± 95 <sup>e</sup>	$89.4 \pm 3.1^{a}$	1.5 ± 0.3 <sup>c</sup>	$0.69 \pm 0.04^{a}$	0.992	45.7 ± 14.9 <sup>a</sup>	$14.3 \pm 6.4^{ab}$	$0.38 \pm 0.05^{bc}$	0.984
	XG1	$1862 \pm 104^{d}$	$58.8 \pm 2.9^{b}$	5.1 ± 1.3 <sup>ab</sup>	$0.51 \pm 0.04^{b}$	0.997	$28.7 \pm 9.8^{bc}$	$14.0 \pm 3.5^{ab}$	0.38 ± 0.03 <sup>bc</sup>	0.987
	XG2	$3095 \pm 67^{\circ}$	$40.4 \pm 3.1^{\circ}$	$14.4 \pm 1.9^{a}$	$0.36 \pm 0.02^{b}$	0.996	$17.4 \pm 2.8^{\circ}$	$20.1 \pm 1.5^{a}$	$0.33 \pm 0.01^{\circ}$	0.963
	XG4	$3589 \pm 104^{b}$	36.3 ± 1.0 <sup>c</sup>	$14.1 \pm 9.7^{a}$	$0.39 \pm 0.12^{b}$	0.995	11.9 ± 4.8 <sup>c</sup>	$19.5 \pm 5.6^{a}$	0.33 ± 0.03 <sup>c</sup>	0.958
	XG12	3399 ± 96 <sup>bc</sup>	$41.2 \pm 5.1^{\circ}$	$8.1 \pm 1.8^{ab}$	$0.47\pm0.04^{\rm b}$	0.993	21.2 ± 3.5 <sup>c</sup>	$12.7 \pm 1.2^{ab}$	$0.41 \pm 0.02^{ab}$	0.970

<sup>A</sup> Assays were performed in triplicate. Mean ± standard deviation values in the same column for each solution followed by different superscripts are significantly different ( $P \leq 0.05$ ).

<sup>B</sup> Herschel–Bulkley parameters:  $\sigma_0$ , yield stress; *K*, consistency coefficient; *n*, flow behaviour index.

<sup>C</sup> Refer to Table 1 for the sample codes of XG (XG0–XG12) having various  $M_{\rm w}$  values.

Our results demonstrated that a significantly ( $P \le 0.05$ ) higher magnitude of  $\sigma_0$  was observed in the upward flow than in the downward flow curve. Many researchers termed the former one as static and the latter one as dynamic yield stress (Achayuthakan et al., 2006; Cheng, 1986). These observations on  $\sigma_0$  implied that there could be more than one type of structure of these thixotropic gels. Some structures become insensitive to shear and serve to define the equilibrium flow curve while others are broken-down by the least shear but the weak structure can be formed again over a certain period of time during rest (Cheng, 1986). The  $\sigma_0$  of RS/ XG gels decreased with decreasing  $M_w$  of XG and slightly increased with the addition of salts.

Inspection of the consistency coefficients (K) and the flow behaviour indices (n) of RS/XG pastes without salt showed that the *K* values significantly ( $P \le 0.05$ ) decreased and the *n* values increased with decreasing  $M_{\rm w}$  of XG for both the upward and downward curves, indicating a decrease in pseudoplasticity of these gels. This could be explained by the hypothesis that XG, especially those with low  $M_w$  values, realized a smooth flow and prevented the abrasion of the starch granules by existing in the continuous phase without interacting with amylose or amylopectin leached (Funami et al., 2005). Similar findings were previously reported for the other starch/XG gels and their flow curves fitted well to the Herschel-Bulkley model (Sikora, Kowalski, & Tomasik, 2008). However, the cited authors found that their K and n values changed non-linearly with the starch/gum composition. In the presence of salts, the opposite trends were apparently observed for both salts, possibly due to the more rigid molecular structure of the small XG molecules as compared with the semiflexible structure of the larger molecules (Sato et al., 1984). However, it has been reported that a salt has a considerable effect on both starch and XG, as well as their interaction in complicated patterns, depending on the type and concentration of the salt (Sudhakar et al., 1995).

From these dynamic and steady shear results, it was concluded that all the paste samples had a weak gel-like structure that can readily be broken to give a free flowing solution, and that their steady shear properties were apparently influenced by  $M_w$  of XG and salt addition.

#### 4. Conclusions

Under the conditions used in this study, it was evident that the pasting and rheological properties of RS were more pronouncedly affected by XG and salt additions than were the gelatinization properties. The effects of XG addition were more pronounced with increasing  $M_{w_{e}}$  especially in the presence of salts. This work suggested strategies for controlling the rheological behaviour of starch encountered in real starch-based food products through the addition of XG having various  $M_{w}$ , as well as by the addition of different salts.

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