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Effect of salts on pasting, thermal, and rheological properties of rice starch in the presence of non-ionic and ionic hydrocolloids

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ABSTRACT

Effects of salts on pasting, thermal, and rheological properties of rice starch (RS) in the presence of non-ionic (guar gum; GG) or ionic (xanthan; XT) hydrocolloid were studied. Rapid visco-analysis (RVA) showed that addition of salts significantly increased peak, breakdown, and final viscosities, and pasting temperatures of RS/XT blends, whereas those of RS/GG blends were varied depending on the type of salts added. Differential scanning calorimetry (DSC) demonstrated that salt addition significantly increased gelatinization temperatures of either RS/GG or RS/XT blend, whereas gelatinization enthalpy was less affected. Dynamic viscoelastic tests revealed that addition of salts had a more pronounced effect on enhancing structure formation of RS/XT gels than that of RS/GG gels. The steady shear viscosity was generally in line with the values of final viscosity obtained during pasting. These results would be used as a guideline for developing starch-based food products containing salts.

1. Introduction

Starch/hydrocolloid combinations have been widely used particularly in the food industry. The reason for using combinations is because native starches do not generally have ideal properties for the preparation of food products, such as have tendency to syneresis, retrogradation and exhibit breakdown, either from extended cooking, high shear or acidic conditions, producing weak-bodied, cohesive, rubbery pastes, and undesirable gels (BeMiller, 2007, chap. 6). There are extensive studies to overcome these shortcomings by blending of native starches with polysaccharide hydrocolloids (gums), as reviewed by Appelqvist and Debet (1997) and most recently by BeMiller (2011). Therefore, the mixtures of starch and hydrocolloids have been used to modify and control rheological and textural properties, improve moisture retention, control water mobility, and maintain overall product quality during processing and storage of food products.

In general, however, starch/hydrocolloid combinations usually co-exist with other ingredients in many food formulations. One such ingredient is salt. Studies on the effects of salts on gelatinization and paste properties of starch date from 1933 (Mangels & Bailey, 1933). Salts have been reported to have a significant effect on the gelatinization (Ahmad & Williams, 1999; Chinachoti, Kim-Shin, Mari, & Lo, 1991; Chinachoti, Steinberg, & Villota, 1990; Chungcharoen & Lund, 1987; Evans & Haisman, 1982; Jane, 1993; Jyothi, Sasikiran, Sajeev, Revamma, & Moorthy, 2005; Katsuta, 1998; Lii & Lee, 1993; Maaurf, Che Man, Asbi, Junainah, & Kennedy, 2001; Mangels & Bailey, 1933; Oosten, 1979, 1982, 1983, 1990; Wootton & Bamunuarachchi, 1980; Zhou, Wang, Li, Fang, & Sun, 2011), retrogradation (Chang & Liu, 1991; Katsuta, 1998), rheological properties (Ahmad & Williams, 1999; Katsuta, 1998), and granular swelling (Zhu, Gayin, Chatel, Dewettinck, & Van der Meeren, 2009) of various starches. The effects of salts on the molecular conformation and solution rheology of hydrocolloids have been studied mainly on ionic hydrocolloids, particularly xanthan (Carrington, Odell, Fisher, Mitchell, & Hartley, 1996; Launay, Cuvelier, & Martinez-Reyes, 1997; Ma & Barbosa-Cánovas, 1997; Meyer, Fuller, Clark, & Kulicke, 1993; Rochefort & Middleman, 1987; Sato, Norisuye, & Fujita, 1984) and scarcely on non-ionic hydrocolloids, e.g. guar gum (Gittings et al., 2001; Ma & Pawlik, 2007).

The effects of salts on starch/hydrocolloid mixtures have been reported in the literature for corn starch/xanthan (Sudhakar, Singhal, & Kulkarni, 1995), corn starch/guar gum (Sudhakar, Singhal, & Kulkarni, 1996), corn starch/iota-carrageenan (Funami et al., 2008), wheat starch/xanthan (Mandala, Michon, &

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Launay, 2004), rice starch/xanthan (Viturawong, Achayuthakan, & Suphantharika, 2008), and wheat starch/hsian-tsao leaf gum (Lai & Chao, 2000) combinations. The hydrocolloids present in those combinations studied can be classified into non-ionic (guar gum) and ionic (xanthan, iota-carrageenan, and hsian-tsao leaf gum) hydrocolloids. It is generally known that the effects of salts on starch, hydrocolloid, and a combination of starch and hydrocolloid depend on the type of salt, i.e. the type and valency of cations and anions, as well as on the concentration. In principle, different behaviors might be expected for the formulations containing non-ionic hydrocolloids and those containing ionic hydrocolloids as affected by salt addition. Surprisingly, as far as we are aware, there are no studies that compare the effect of salts on the behaviors of starch/non-ionic hydrocolloid and starch/ionic hydrocolloid combinations generally. The purpose of this investigation, therefore, was to undertake a systematic study of the effect of salts on the pasting, thermal, and rheological properties of rice starch in the presence of non-ionic (guar gum) and ionic (xanthan) hydrocolloids. The salts were chosen on the basis that they have the same type of anion, i.e. NaCl and $CaCl_2$, in order to reduce the complexity of electrolytes.

2. Materials and methods

2.1. Materials

Rice starch (RS) was supplied by Cho Heng Rice Vermicelli Factory Co., Ltd., Nakhon Pathom, Thailand. RS had amylose, protein, fat, ash, moisture, and carbohydrate (by difference) contents of 22.66%, 1.40%, 0.20%, 0.29%, 11.80%, and 86.30%, respectively, determined by following the AACC (2000) methods. Xanthan (XT) was purchased from CP Kelco Co., San Diego, CA, USA. Guar gum (GG) was purchased from Sigma–Aldrich, Inc., St. Louis, MO, USA. Sodium chloride (NaCl) and calcium chloride ($CaCl_2{\cdot}2H_2O$) were of reagent grade and purchased from Merck KGaA, Darmstadt, Germany.

2.2. Molecular weight determination of xanthan and guar gum

Weight-average molecular weight (M_w) values of XT and GG in distilled water and aqueous salt solutions (0.1 M NaCl or $CaCl_2$) were determined by gel permeation chromatography (GPC), using a Waters 600E instrument (Waters Corporation, Milford, MA, USA) equipped with a 7.8 mm × 300 mm Ultrahydrogel linear column packed with hydroxylated polymethacrylate-based gel, a 6 mm × 40 mm guard column, and a refractive index detector. Dextran standards, ranging from 4400 to 4.01×10^5 Da of peak molecular weight (Waters Corporation, Milford, MA, USA), were used for calibration. For gum 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 cutoff 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 the first four days and finally followed by distilled water. Gum solutions (0.2%, w/v) in, pH 11, buffer (0.1 M NaOH and 0.05 M $NaHCO_3$) were prepared and filtered using a 0.45 μm nylon filter membrane before injection into the GPC column. The conditions were set as follows; injection volume 20 μL, flow rate 0.6 mL/min, and temperature 30 °C. Buffer at pH 11 was used as an eluent.

2.3. Intrinsic viscosity determination of xanthan and guar gum

The intrinsic viscosity, $[\eta]$, of XT and GG solutions in the presence and absence of salts at 0.1 M concentration 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 0.005% to 0.025% were measured in triplicate and averaged. The dilutions were made with the same solvents as used in the stock solutions, namely either distilled water or aqueous salt (0.1 M NaCl or $CaCl_2$) solutions. The concentration-dependence of the viscosity of gum solutions was analyzed by using the classic Huggins equation:

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

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:

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

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 6% (w/w) RS alone and RS/gum blends (19:1, w/w ratio) as well as 0.3% (w/w) gum alone suspended in distilled water and 0.1 M salt solutions were determined by a rapid visco-analyzer (Model RVA-4C, Newport Scientific Pty. Ltd., Warriewood, Australia). RS alone slurries were prepared by dispersing weighed amounts of RS (dry basis) in distilled water or salt solutions. In the case of RS/gum blends, gum was first dispersed in distilled water containing 0.02% sodium azide as a preservative and stirred until lumps were absent. For the gum in salt solutions, calculated weight amount of NaCl or $CaCl_2{\cdot}H_2O$ was added to the gum solutions to make a final concentration of 0.1 M salt. The solutions were then heated at 80 °C for 20 min under mild stirring and cooled to room temperature. RS was then slurried in the gum solutions and stirred for 1 h until a smooth solution was obtained. The slurries weighing 28 g were then poured into aluminum canisters and stirred manually using plastic paddles for 20–30 s before insertion into the RVA instrument. 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 (i.e. a heating rate of 12 °C/min) 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. The viscosity was expressed in rapid visco units (RVU).

2.5. Determination of thermal properties

Thermal properties, namely gelatinization temperatures and enthalpy, of RS alone and RS/gum blends in the presence and absence of salts were measured by a differential scanning calorimeter (DSC 1, Mettler-Toledo GmbH, Schwerzenbach, Switzerland). The total solid content of samples was 12% (w/w, dry basis), while keeping the RS/gum ratio constant at 19:1 (w/w). 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 was exactly weighed into 40 μL aluminum crucibles, which were 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 gelatinization enthalpy (ΔH) and transition temperatures, namely the onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c), were determined, based on the DSC heating curves. The ΔH 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.

2.6. *Determination of swelling power and amylose leaching*

Swelling power and amylose leaching of RS during heating were determined by modifying the method of Chaisawang and Suphantharika (2006) and Shi and BeMiller (2002). Suspensions of 0.6% (w/w) RS alone and RS/gum blends (19:1, w/w ratio) in the presence and absence of salts at 0.1 M concentration were prepared as described above. The suspensions were put into centrifuge tubes with closed screw caps and heated in a shaking water bath at 75 °C (a temperature below the normal pasting temperature) for 3 h with minimum shear condition. The suspensions were then quickly cooled to room temperature by immersing in an ice bath for 5 min. A drop from each suspension was stained with iodine solution and examined with a light microscope (Olympus BX51, connected with an Olympus PM10-SP digital camera, Tokyo, Japan). The suspensions were also centrifuged at 6000 × g for 15 min. The supernatant was removed, and the residue was weighed, then dried to constant weight in a hot air oven at 105 °C. The swelling power is the ratio of the wet weight of the residue to its dry weight, assuming that the total amount of gum remained in the supernatant. The amylose content of the supernatant was determined by the colorimetric method (AACC, 2000, Method 61-03).

2.7. *Determination of rheological properties*

Dynamic viscoelastic and steady flow properties of the freshly prepared gels of RS alone and RS/gum blends in the presence and absence of salts, obtained from pasting in the RVA and holding at room temperature (~25 °C) for 1 h (a cooling rate of about 0.4 °C/min), were determined using a rheometer (Physica MCR 301, Anton Paar GmbH, Graz, Austria) equipped 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 region of all gel samples. The storage modulus (G'), loss modulus (G''), and loss tangent ($\tan\delta = G''/G'$) as a function of frequency (ω) were obtained.

Steady flow tests were also performed on the freshly prepared gel samples at 25 °C to obtain shear rate versus shear stress (flow curve) data. The cone was programmed to increase the shear rate from 0 to 300 s^{-1} in 3 min. Using the equipment software, the experimental data were fitted to the power law model:

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

where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency coefficient ($\mathrm{Pa\,s}^{n}$), and n is the flow behavior index (dimensionless). The apparent viscosity (η_a) was also calculated using the equation:

$$\eta_a = K\dot{\gamma}^{n-1} \tag{4}$$

2.8. *Statistical analysis*

Results are expressed as mean ± standard deviations of triplicate analyses for each sample unless otherwise stated. A one-way analysis of variance (ANOVA) and Duncan's test were used to establish the significance of differences among the mean values at the 0.05 significance level. Statistical analyses were performed using SPSS version 15.0 for Windows (SPSS Inc., Chicago, IL, USA).

Table 1
Intrinsic viscosity ([η]) and weight-average molecular weight (M_w) of xanthan (XT) and guar gum (GG) dispersed in aqueous solutions with and without salts at 0.1 M concentration.

Hydrocolloid	Salt	[η] (dL/g)[a]	M_w (Da)
XT	None	110.4 ± 14.3a	1.45×10^7
	NaCl	27.6 ± 3.8b	1.47×10^7
	$CaCl_2$	14.9 ± 1.7c	1.05×10^7
GG	None	17.7 ± 1.8a	2.63×10^6
	NaCl	15.8 ± 0.7a	2.81×10^6
	$CaCl_2$	14.3 ± 2.4a	2.76×10^6

[a] Assays were performed in triplicate. Mean ± standard deviation values in the same column for each hydrocolloid followed by different letters are significantly different ($p \leq 0.05$).

3. Results and discussion

3.1. *Intrinsic viscosity and molecular weight of xanthan and guar gum*

The molecular characteristics of xanthan (XT) and guar gum (GG) in the presence and absence of salts at 0.1 M concentration are summarized in Table 1. The addition of salts was found to greatly reduce (4–7 times) the intrinsic viscosity, [η], of XT solutions, as expected for a polyelectrolyte. At this low XT concentration (≤0.025%), the cations of the salts, i.e. Na^+ and Ca^{2+}, produced a charge screening effect, reducing segmental repulsion, to yield a more compact configuration and caused a dramatic reduction in hydrodynamic volume of the XT molecule and hence reduction in [η] (Carrington et al., 1996; Launay et al., 1997; Rochefort & Middleman, 1987). The more pronounced effect of the divalent cations (Ca^{2+}) on the [η] of XT solutions, compared with that of monovalent cations (Na^+), was possibly due to intramolecular cross-linking between XT and Ca^{2+}, which resulted in a greater extent of molecular contraction (Higiro, Herald, Alavi, & Bean, 2007). In contrast, addition of salts did not significantly affect the [η] of GG, for which values ranged between 14.3 and 17.7 dL/g in an aqueous solution and in 0.1 M of salts. GG is a non-polyelectrolyte, and salt has little effect on the hydrodynamic volume (Higiro et al., 2007; Ma & Pawlik, 2007). In addition, the weight-average molecular weight (M_w) of these hydrocolloids was unchanged in the presence of salts, indicating no intermolecular association or depolymerization occurred by increasing the ionic strength of the solutions. This can be partly explained by the fact that there are fewer molecules available for intermolecular interaction in a very dilute solution as pointed out by Rochefort and Middleman (1987).

3.2. *Pasting properties*

The pasting characteristics of RS/XT and RS/GG mixtures in the presence and absence of salts determined by RVA are depicted in Fig. 1. XT and GG alone solutions at a concentration of 0.3% in the presence and absence of salts were also run under the same RVA conditions to establish control viscosity curves and to determine whether the hydrocolloids were completely dispersed before heating. The viscosities of these hydrocolloid solutions remained almost constant throughout the RVA run, indicating a complete dissolution of the hydrocolloids. The addition of salts significantly increased the viscosity of XT solution from 7.1 RVU for the control without added salts to 8.5 and 9.0 RVU for the NaCl and $CaCl_2$ added samples, respectively. Generally, how salts affect viscosity of XT solution depends on XT concentration. At concentrations of ≤0.25%, both monovalent and divalent salts cause a slight decrease in viscosity, whereas at higher XT concentrations, viscosity increases with added salts (Sworn, 2000; Wyatt & Liberatore, 2010). This has been confirmed by our results, i.e. the addition of salts resulted

Table 2
Pasting properties of 6% (w/w) rice starch alone (RS) and rice starch in the presence of xanthan (RS/XT) or guar gum (RS/GG) (19:1, w/w ratio) dispersed in aqueous solutions with and without salts at 0.1 M concentration.[a]

Sample	Salt	Peak viscosity (RVU)	Breakdown (RVU)	Final viscosity (RVU)	Setback (RVU)	Pasting temperature (°C)
RS	None	53.5 ± 0.6b	7.4 ± 1.2b	56.2 ± 1.3b	8.2 ± 0.8a	94.6 ± 0.8a
	NaCl	47.0 ± 0.7c	11.9 ± 2.8a	41.1 ± 0.2c	5.4 ± 1.2b	94.9 ± 0.0a
	$CaCl_2$	64.1 ± 1.7a	6.6 ± 2.9b	63.3 ± 0.8a	6.1 ± 1.1b	94.8 ± 0.5a
RS/XT	None	71.8 ± 0.6c	1.9 ± 0.2b	79.1 ± 2.3c	11.3 ± 2.3a	90.9 ± 0.9b
	NaCl	94.3 ± 1.5b	6.0 ± 1.5b	92.3 ± 0.8b	5.0 ± 1.3b	94.9 ± 0.5a
	$CaCl_2$	133.6 ± 0.4a	32.0 ± 1.3a	105.4 ± 1.4a	6.8 ± 1.6b	92.0 ± 0.8b
RS/GG	None	116.0 ± 1.0a	3.4 ± 2.2a	130.9 ± 3.0a	19.4 ± 3.0a	88.7 ± 0.4b
	NaCl	87.3 ± 2.3b	4.1 ± 1.3a	95.3 ± 1.7c	8.1 ± 2.1b	91.2 ± 3.5a,b
	$CaCl_2$	114.2 ± 2.5a	1.1 ± 0.1b	123.9 ± 1.5b	11.4 ± 1.5b	95.2 ± 2.1a

[a] Assays were performed in triplicate. Mean ± standard deviation values in the same column for each sample followed by different letters are significantly different ($p \leq 0.05$).

in a reduction of viscosity at XT concentrations ≤0.025% (Section 3.1), but an increase in viscosity at a XT concentration of 0.3%. It is generally recognized that the rheology of dilute XT solutions is primarily controlled by intramolecular conformation changes, whereas that of the semi-dilute solutions is controlled by intermolecular associations. When salt is added to the dilute XT solution, an extended configuration of the polymer chain collapses and assumes a smaller, more compact conformation due to charge screening effects which reduce hydrodynamic size and in turn solution viscosity. However, in the semi-dilute solution, this compact configuration (with the electrostatic repulsions screened), the molecules are easily aligned and strongly associate due to hydrogen bonding and ionic interactions to form a highly viscous solution (Rochefort & Middleman, 1987). The divalent cations (Ca^{2+}) produced higher viscosity than monovalent cations (Na^+) possibly due to either inter- or intramolecular cross-linking of the polymer chains (Wyatt & Liberatore, 2010). In contrast, the viscosity of GG solution seemed to be unaffected by salt addition, in which its value was 4.9, 4.4, and 4.5 RVU for the control without added salts, NaCl, and $CaCl_2$ added samples, respectively.

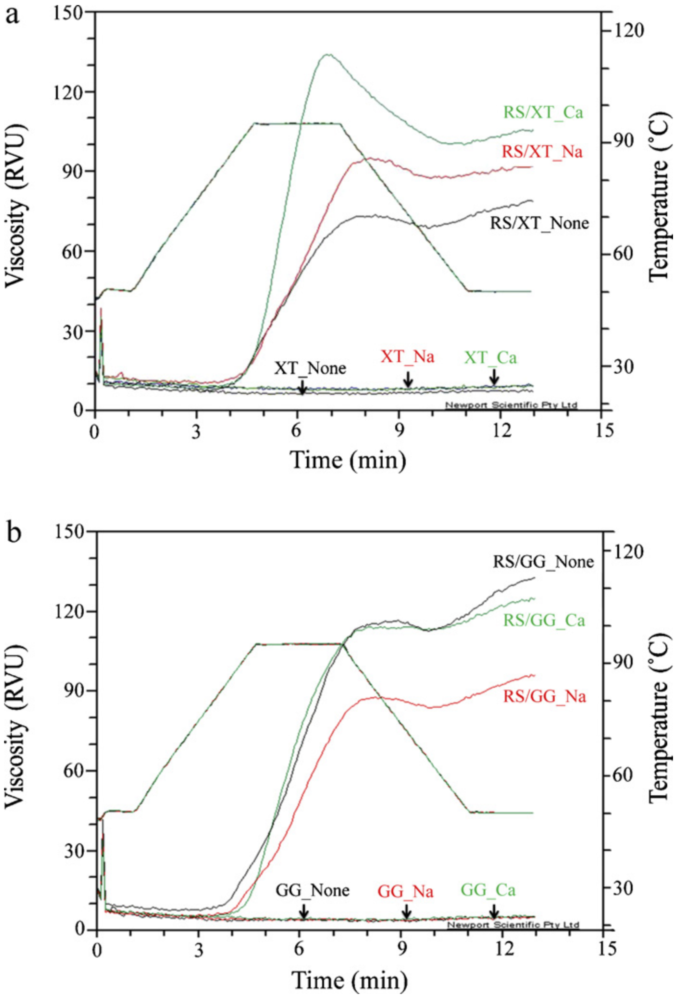

Fig. 1. Typical RVA pasting profiles of 6% (w/w) rice starch (RS) in the presence of (a) xanthan (RS/XT) or (b) guar gum (RS/GG) (19:1, w/w ratio) and 0.3% (w/w) gum alone (XT or GG) dispersed in aqueous solutions with and without salts at 0.1 M concentration.

Statistical analyses of all pasting parameters of RS alone, RS/XT, and RS/GG in the presence and absence of salts were also performed and are summarized in Table 2. Considering the effect of salts on RS alone, peak viscosity was significantly decreased by added NaCl but was significantly increased by $CaCl_2$, both at 0.1 M concentration. These data are clearly in contradiction with those previously reported for cassava starch by Jyothi et al. (2005). These authors observed no significant change in peak viscosity when the concentration of NaCl was increased from 0.05 to 1% (0.17 M) but slightly increased at 2.5 and 5% (0.86 M) concentrations, whereas $CaCl_2$ caused a gradual decrease in peak viscosity with an increase in concentration up to 5% (0.45 M). Zhou et al. (2011), on the other hand, observed a significant decrease in peak and final viscosities of *Angelica duhurica* starches at 0.5% (∼0.1 M) NaCl and a gradual increase at higher concentrations up to 3% (0.5 M). Our results are in good agreement with those reported by Zhou et al. (2011) at 0.1 M NaCl. Unlike cassava starch, RS contains proteins and lipids, where these components also influence the viscosity by interaction with the salts (Jyothi et al., 2005). Based on a significant reduction of swelling power and amylose leached out the RS granules in the presence of either 0.1 M NaCl or $CaCl_2$ (Table 4), we would expect a decrease in peak viscosity. An increase in peak viscosity of RS therefore hypothesized to be the predominant effect of interactions of $CaCl_2$ with the other components of RS. The effects of NaCl or $CaCl_2$ on breakdown and final viscosity were complicated by this hypothesis. Addition of either NaCl or $CaCl_2$ significantly decreased setback (i.e. amylose retrogradation) of RS due to a significant reduction of the amount of amylose leached out the starch granules (Table 4). According to a significant increase in gelatinization temperatures (T_o, T_p, and T_c) of RS alone caused by salt addition (Table 3), an increase in pasting temperature was expected. However, our data show no significant effect of salts on pasting temperature of RS. This could be explained by the fact that pasting temperature of RS alone was 94.6 °C which is close to the maximum attainable temperature of the RVA (95 °C) and therefore a detection of pasting temperature higher than 95 °C is impossible by this technique.

In the absence of salts, addition of any of these hydrocolloids at the concentration tested resulted in a significant increase in peak, final, and setback viscosities, whereas pasting temperature was decreased. Similar observations were reported for corn starch/xanthan (Sudhakar et al., 1995) and corn starch/guar gum

Table 3
Thermal properties of 12% (w/w) rice starch alone (RS) and rice starch in the presence of xanthan (RS/XT) or guar gum (RS/GG) (19:1, w/w ratio) dispersed in aqueous solutions with and without salts at 0.1 M concentration.[a]

Sample	Salt	T_o (°C)	T_p (°C)	T_c (°C)	ΔT ($T_c - T_o$) (°C)	ΔH_1 (J/g)
RS	None	73.0 ± 0.0c	76.9 ± 0.1c	80.6 ± 0.2c	7.6 ± 0.2a	8.7 ± 0.1a
	NaCl	76.6 ± 0.2b	80.4 ± 0.3b	83.8 ± 0.2b	7.3 ± 0.1a,b	8.9 ± 0.1a
	$CaCl_2$	78.0 ± 0.2a	81.6 ± 0.2a	85.1 ± 0.3a	7.1 ± 0.2b	9.8 ± 0.9a
RS/XT	None	73.7 ± 0.2c	77.5 ± 0.2c	81.2 ± 0.2c	7.4 ± 0.1a	7.5 ± 0.4c
	NaCl	77.0 ± 0.2b	80.6 ± 0.1b	84.1 ± 0.2b	7.2 ± 0.0c	8.2 ± 0.2b
	$CaCl_2$	78.2 ± 0.1a	81.9 ± 0.1a	85.5 ± 0.2a	7.3 ± 0.1b	9.1 ± 0.1a
RS/GG	None	73.6 ± 0.2c	77.4 ± 0.2c	81.2 ± 0.3c	7.6 ± 0.1a	8.2 ± 0.2a
	NaCl	77.1 ± 0.2b	80.8 ± 0.2b	84.4 ± 0.1b	7.3 ± 0.0b	8.6 ± 0.6a
	$CaCl_2$	78.2 ± 0.1a	81.9 ± 0.0a	85.6 ± 0.0a	7.4 ± 0.1a,b	8.3 ± 0.3a

[a] Assays were performed in triplicate. Mean ± standard deviation values in the same column for each sample followed by different letters are significantly different ($p \leq 0.05$).

Table 4
Swelling power (g/g) and leached amylose (%, w/v) of 0.6% (w/w) rice starch alone (RS) and rice starch in the presence of xanthan (RS/XT) or guar gum (RS/GG) (19:1, w/w ratio) dispersed in aqueous solutions with and without salts at 0.1 M concentration and heated at 75 °C for 3 h.[a]

Sample	Salt	Swelling (g/g)	Leached amylose (%, w/v)
RS	None	7.95 ± 1.3a	15.90 ± 1.3a
	NaCl	3.54 ± 1.4b	5.46 ± 0.7b
	$CaCl_2$	3.79 ± 1.6b	3.47 ± 1.0b
RS/XT	None	9.68 ± 0.7a	21.89 ± 2.7a
	NaCl	6.49 ± 0.2b	12.16 ± 2.9b
	$CaCl_2$	6.00 ± 0.2c	6.23 ± 1.5b
RS/GG	None	8.98 ± 0.2a	20.07 ± 4.4a
	NaCl	6.17 ± 0.2b	10.46 ± 1.4b
	$CaCl_2$	4.74 ± 1.0c	4.12 ± 1.0c

[a] Assays were performed in triplicate. Mean ± standard deviation values in the same column for each sample followed by different letters are significantly different ($p \leq 0.05$).

(Sudhakar et al., 1996) combinations. A decrease in the pasting temperature of RS in the presence of either XT or GG may be attributed to an increase in the effective concentration of leached starch molecules, primarily amylose, in the continuous phase upon heating (Alloncle, Lefebvre, Llamas, & Doublier, 1989) due to phase separation as a result of mutual exclusion between leached starch and hydrocolloid molecules based on thermodynamic incompatibility between the two polysaccharides (Alloncle & Doublier, 1991; Annable, Fitton, Harris, Phillips, & Williams, 1994). Increase in the effective concentrations of leached starch molecules as well as hydrocolloid in the continuous phase enhanced interactions between the swollen starch granules, leading to detection of pasting at a lower temperature. However, interactions between leached starch molecules and hydrocolloid in the continuous phase (Christianson, Hodge, Osborne, & Detroy, 1981; Shi & BeMiller, 2002) should not be excluded as another factor to affect the pasting temperature of the starch/hydrocolloid system. The synergistic effect on peak viscosity of starch/hydrocolloid combinations was 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 hydrocolloid (Alloncle et al., 1989) added to the thickening produced by swollen starch granules (Techawipharat, Suphantharika, & BeMiller, 2008). An increase in final viscosity and setback values suggested that retrogradation of starch should be promoted at a very early stage of storage by addition of hydrocolloids. The promotion of retrogradation was attributed to an increase in the effective concentration of starch or more specifically amylose in the continuous phase due to mutual exclusion between solubilized starch and hydrocolloid (Alloncle et al., 1989).

Addition of salts to RS/XT blend increased peak, breakdown, and final viscosities, and pasting temperatures, but decreased setback values compared to the control without added salts. The increase in peak and final viscosities could be explained by the fact that cations reduced intermolecular repulsion and promoted network formation of XT. Divalent cations (Ca^{2+}) at the same concentration produced greater effect because they are more highly charged. A decrease in setback value could be attributed to a lower amount of amylose leaching out the starch granules in the presence of salts, which will be discussed later. In the case of RS/GG systems, addition of $CaCl_2$ had a lesser effect on the pasting properties, as expected, due to the non-electrolyte characteristic of GG. Surprisingly, however a significant decrease in peak, final, and setback viscosities was observed in the presence of NaCl as compared with the control without salts. In general, however, the effect of salt on the pasting characteristics of RS/GG exhibited a similar trend to that of RS alone systems, indicating a predominant effect of starch–salt interaction. It was concluded that the pasting behaviors of starch/ionic hydrocolloid combinations were predominantly affected by hydrocolloid–salt interaction, whereas those of the starch/non-ionic hydrocolloid systems were governed by starch–salt interaction.

3.3. *Thermal properties*

The onset (T_o), peak (T_p), and conclusion (T_c) gelatinization temperatures, and the gelatinization temperature range (ΔT) and enthalpy (ΔH) of RS alone and RS/gum blends in aqueous suspensions with and without salts, determined by DSC, are summarized in Table 3.

For RS alone, addition of salts at 0.1 M concentration significantly increased the magnitudes of T_o, T_p, and T_c and decreased ΔT values without any significant effect on ΔH as compared with those of the control. Salts have been reported to increase or decrease gelatinization temperature and enthalpy, depending on the type of salts and their concentrations used (Ahmad & Williams, 1999; Chungcharoen & Lund, 1987; Jane, 1993; Jyothi et al., 2005; Maaurf et al., 2001; Oosten, 1982, 1983, 1990). It has been reported that either NaCl or $CaCl_2$, at low concentrations, slightly increased the T_p of sago starch (Ahmad & Williams, 1999; Maaurf et al., 2001), T_o of corn starch (Jane, 1993), T_p of wheat starch (Chinachoti et al., 1991; Wootton & Bamunuarachchi, 1980), and T_p of corn, rice, potato, canna, and lotus tuber starches (Lii & Lee, 1993) but, when the concentrations increased further (up to ~2 M for NaCl and ~1 M for $CaCl_2$), these temperatures decreased. The ΔH of rice starch was reported to be significantly decreased in the presence of ~0.3 M NaCl (Chungcharoen & Lund, 1987) while those of wheat starch (Wootton & Bamunuarachchi, 1980) and corn starch (Chinachoti et al., 1990) were significantly decreased when NaCl concentration was raised up to 1 M. Other studies, however, showed that as the concentration of NaCl or $CaCl_2$ increased, the ΔH of corn starch increased to a maximum and then decreased as concentration increased further up to 6 M for NaCl and 4 M for $CaCl_2$ (Jane, 1993). However, those salt concentrations are much higher than that used in the present study. 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), starch is a weak acid ion exchanger when NaCl or $CaCl_2$ is added to a starch suspension, some alcoholic groups in the starch granules are converted to sodium or calcium alcoholate groups. These compounds are better dissociated, thus causing a rise in a difference in potential between the starch granule and the water phase, called the Donnan potential. The negative potential of the starch granule attracts the cation and repels the anion. Oosten (1990) also suggested that the anion is the gelatinizing agent and could promote the gelatinization of starch by rupturing the hydrogen bond between starch molecules. However, the absorption of Na^+ or Ca^{2+} was rather limited since, in our systems, there was no agent to bind the released H^+; hence, the increase in gelatinization temperatures was also limited. Oosten (1979), however, reported that the absorption of Na^+ ions is very much enhanced by adding NaOH to the starch suspension in the NaCl solution. This is caused by the addition of the H^+ ions binding hydroxyl ions. This subsequently resulted in substantial rises of the gelatinization temperatures. The presence of $CaCl_2$ at the concentration used in this study exhibited a more pronounced effect on gelatinization of RS than did NaCl. This could be attributed to the fact that the principle component affecting the gelatinization process is the anion (Ahmad & Williams, 1999). There are twice as many Cl^- ions per mole of $CaCl_2$ than there are per mole of NaCl. This is the primary reason for the greater effectiveness of $CaCl_2$ on starch gelatinization. In concentrated $CaCl_2$ (~3 M) solutions, starch gelatinized at room temperature but did not gelatinize in NaCl solutions at any concentration (Evans & Haisman, 1982; Jane, 1993; Mangels & Bailey, 1933).

Surprisingly, the presence of either XT or GG at a concentration used in this study, did not significantly affect the T_o, T_p, T_c, and ΔT values of RS/XT or RS/GG blends as compared with those of the corresponding control samples without added hydrocolloids. It is clear that, in combinations of starch, hydrocolloid, and salt, the effect of salt on gelatinization temperatures of starch is unchanged by an increase in the viscosity of starch/hydrocolloid blends. The magnitude of ΔH values, in contrast, was significantly decreased by hydrocolloid addition. This could be attributed, at least in part, to a reduction in water availability and/or mobility, causing incomplete melting of crystalline regions in the starch granules, and the effect of starch/hydrocolloid interactions (Chaisawang & Suphantharika, 2006). Similar observations were reported by Viturawong et al. (2008) for RS/XT/salt combinations.

3.4. Swelling power and amylose leaching

In order to investigate the influence that salt and hydrocolloid might have on the morphological change of the starch granules during heating, the swelling power and amylose leaching were measured and microscopic observations were performed. The results are shown in Table 4 and Fig. 2, respectively. For RS alone, addition of any of these salts resulted in a significant decrease in swelling power and amylose leaching of RS. Jyothi et al. (2005) reported a similar effect on the swelling volume of cassava starch in the presence of either NaCl or $CaCl_2$ at various concentrations. Zhu et al. (2009), however, found that the swelling inhibitory effect of salt on wheat starch is largely temperature dependent. A pronounced swelling inhibitory effect of NaCl was observed at temperature up to 65 °C followed by a limited (rather promoting) effect at higher temperatures. The effect of salt on starch could be explained by at least 2 factors: (1) the electrostatic interaction between starch and the ions from salts (Oosten, 1982, 1983, 1990), and (2) the competition between the salts and the starch for the available water. These factors would limit the swelling of the starch granules and in turn decreased the amylose leaching. In the absence of salts, addition of either XT or GG significantly increased swelling power and amylose leaching of the starch. A similar influence of hydrocolloids on enhancing the swelling and amylose leaching of starch granules has been reported in the literature for wheat starch (Mandala & Bayas, 2004), tapioca starch (Chaisawang & Suphantharika, 2006), and rice starch (Techawipharat et al., 2008).

For RS/XT and RS/GG blends, addition of salts significantly decreased swelling power and amylose leaching of these blends, in which, $CaCl_2$ produced greater effect than did NaCl. These results showed a similar trend to that of the RS alone, indicating that the swelling power and amylose leaching of starch were predominantly affected by the added salts. In general, this finding showed that the effect of these salts on the reduction of swelling power and amylose leaching of RS follows the order of the Hofmeister series.

Microscopic examination of RS/XT and RS/GG blends in the presence and absence of salts revealed that the starch granules subjected to heating were mostly unbroken, i.e. intact and stained blue with iodine (Fig. 2). As it can be visualized for the starch/hydrocolloid blends without salts, the swollen starch granules were larger and stained less blue than those of the samples with added salts. The presence of salts resulted in the smaller granule size and stained darker blue, indicating that salts inhibited the swelling and amylose leaching of the starch granules. This is in good agreement with the previous experiment, i.e. the swelling and amylose leaching assay (Table 4). A retardation of swelling of starch granules in the presence of salts was reflected by a shift in the DSC gelatinization temperatures to higher temperatures (Table 3). On the contrary, the RVA results showed that the peak viscosity of RS/XT blends was significantly higher when salts are presented (Table 2 and Fig. 1) even though the swelling power was lower. These results imply that salt could dominantly affect the swelling power value, whereas the peak viscosity of the mixtures was greatly affected by the interaction of hydrocolloids and cations from salts as discussed earlier. A reduction in the amount of amylose leached out the starch granules in the presence of salts reduced amylose association outside the granules and was responsible for a decrease in the setback values (Sae-kang & Suphantharika, 2006).

3.5. Rheological properties

3.5.1. Dynamic viscoelastic properties

Small amplitude oscillatory shear tests of RS/XT and RS/GG gels in the presence and absence of salts were compared and demonstrated similar dynamic mechanical spectra (Fig. 3a and b). From these rheograms, the storage modulus (G') was much larger than the loss modulus (G''); both moduli show a slight variation with frequency (ω), and a crossover between these two moduli was not observed throughout the tested frequency range, demonstrating a typical weak gel structure as classified rheologically by Clark and Ross-Murphy (1987). Moreover, the dynamic mechanical loss tangent ($\tan\delta = G''/G'$) values for all the gels tested were much smaller than unity, indicating predominantly elastic or solid-like behavior (Fig. 3c). According to the highest temperature used for the RVA pasting was 95 °C which is about the pasting temperature of RS, the gelatinization of RS was therefore incomplete. This would result in a composite paste or gel containing swollen starch granules, granule fragments, and macromolecularly dispersed starch and hydrocolloid molecules. This is a typical characteristic of cereal

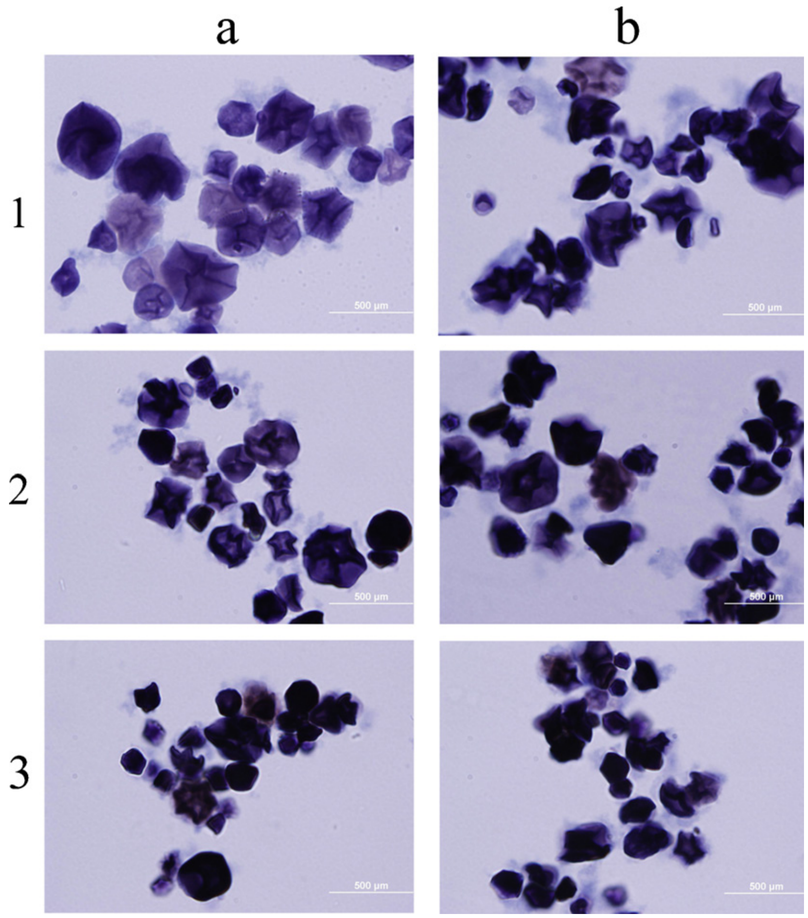

Fig. 2. Light micrographs of 0.6% (w/w) rice starch (RS) stained with iodine after heating at 75 °C for 3 h in the presence of (a) xanthan (RS/XT) or (b) guar gum (RS/GG) (19:1, w/w ratio) dispersed in (1) distilled water, (2) 0.1 M NaCl, and (3) 0.1 M $CaCl_2$ aqueous solutions (100×, bar = 500 μm).

starch pastes (Alloncle et al., 1989). The viscoelastic properties of such a system are known to be governed by the characteristics of the dispersed phase as well as the continuous phase. As soon as starch granules swell during pasting, the volume available to hydrocolloid molecules decreases and their effective concentration in the continuous phase markedly increases. Owing to the high thickening capacity and the dramatic concentration dependence of the hydrocolloid viscosity, this effect results in a spectacular rise in the viscosity of the continuous phase. As thickening properties of leached amylose are very low compared to the hydrocolloids (Alloncle et al., 1989), we assume that viscosity of the continuous phase is mainly determined by the hydrocolloid viscosity. The viscoelastic properties of the composite gels with a high volume fraction of swollen granules, like in the present study, are known to be strongly influenced by the dispersed phase. The continuous phase makes an additional contribution due to its own viscoelastic properties (Alloncle & Doublier, 1991). This could be an explanation for the similar dynamic mechanical spectra of RS/XT and RS/GG gels, which contained the same amount of RS and in turn a comparative volume fraction of swollen granules.

For RS/XT gels, addition of salts resulted in a marked decrease in tan δ values especially at low ω values, demonstrating a more solid-like behavior of the gels. This could be attributed to the mutual exclusion between leached amylose molecules and XT molecules in the continuous phase, as discussed above, which flavored the interaction of the like polymer molecules. Addition of salts enhanced the intermolecular interaction of XT molecules through the charge screening effects, promoting network formation (Wyatt & Liberatore, 2010). The characteristics of the network formed in the XT microdomain predominated the viscoelastic properties of the continuous phase and the RS/XT gels as a whole (i.e. an increase in elasticity of the gels as evidenced by a decrease in tan δ). $CaCl_2$ exhibited more pronounced effect than did NaCl due to a higher charge density of Ca^{2+} and a possibility of cross-linking between XT chains induced by Ca^{2+} (Wyatt & Liberatore, 2010). The cross-linking of XT chains resulted in a stiffer, more elastic network, leading to the strongest network structure of the RS/XT gel (i.e. highest G' in Fig. 3a and lowest tan δ in Fig. 3c) compared among all the gels tested. These results contradicted those previously reported for xanthan/konjac mannan mixture by Annable, Williams, and Nishinari (1994), who argued that xanthan/konjac mannan mixture formed a gel by synergistic interaction. The addition of salt enhanced self-association of xanthan at the expense of xanthan/konjac mannan interaction and thus weaken the gelling behavior as noted by the lower value for G'. For RS/GG gels, as expected, addition of salts showed a much less effect on tan δ values, indicating an insensitivity of GG to salt.

3.5.2. *Steady shear rheological properties*

The steady flow curves of RS/XT and RS/GG gels in the presence and absence of salts are illustrated in Fig. 3d. For a range of shear rates used in this study, all gels exhibited mainly pseudoplastic shear thinning behavior which were well fitted by the power law model (R^2 = 0.979–0.996). The power law parameters, i.e. consistency coefficients (K) and flow behavior indices (n), and apparent viscosities (η_a) at shear rates of 10 s^{-1} and 100 s^{-1} for each flow curve are summarized in Table 5.

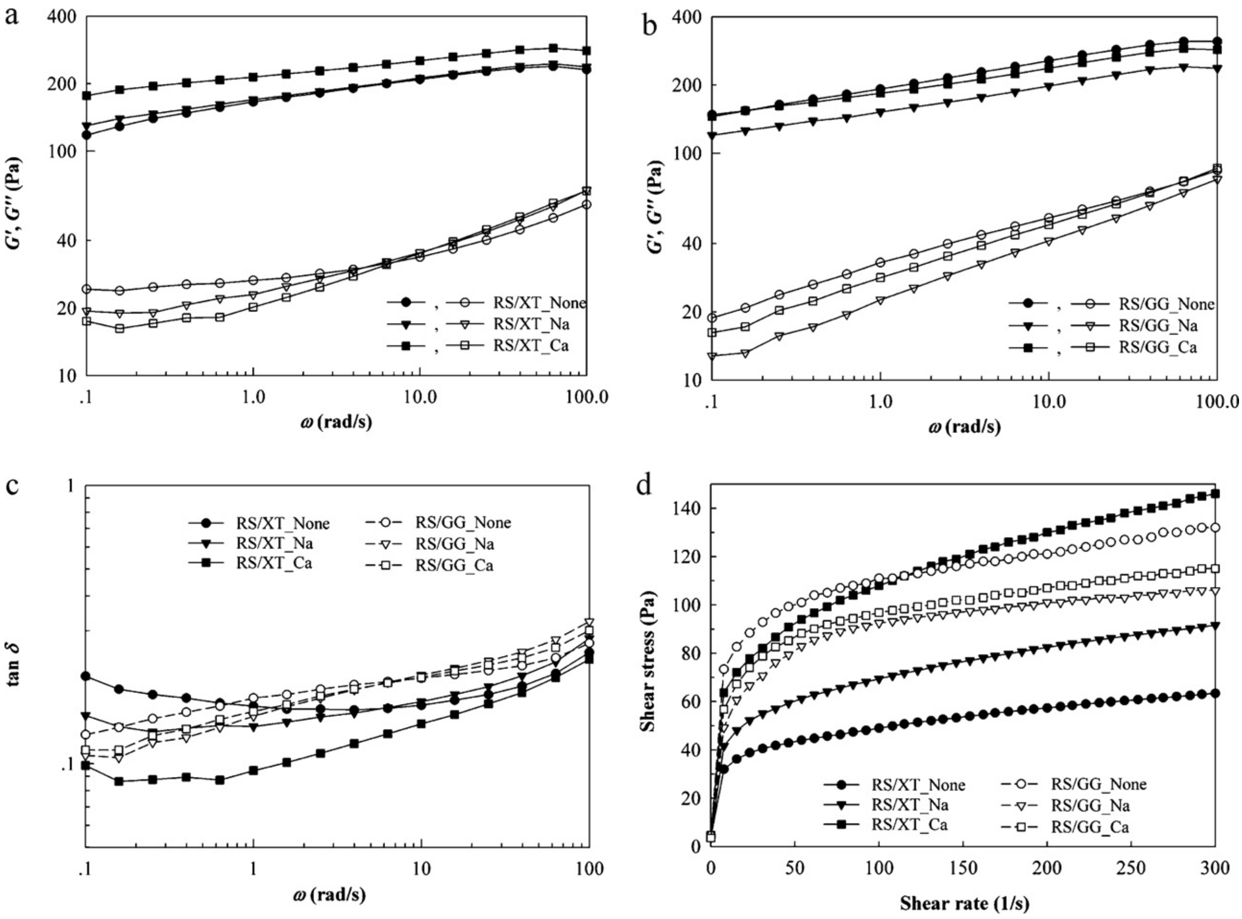

Fig. 3. Rheological properties: (a and b) dynamic mechanical spectra (closed symbols, storage modulus, G'; open symbols, loss modulus, G''), (c) dynamic mechanical loss tangents (tan δ) measured at 0.5% strain, and (d) flow curves of 6% (w/w) rice starch (RS) in the presence of xanthan (RS/XT) or guar gum (RS/GG) (19:1, w/w ratio) with and without salts at 0.1 M concentration. All measurements were made at 25 °C.

As shown in Fig. 3d, addition of salts to RS/XT gels resulted in a marked increase in the shear stress in the order $CaCl_2 > NaCl$, whereas that of RS/GG gels was only slightly decreased by the addition of salts. This could be attributed to the promotion of interactions between XT chains through charge screening effects induced by added salts. The polymer chains would experience more difficulty on moving past one another under shear resulted in an increase in shear stress and viscosity of the RS/XT gels. This result is also consistent with the dynamic viscoelastic data in which the more structured gels having lower tan δ values (Fig. 3c) exhibited higher shear stress than did the less structured ones. Table 5 shows that apparent viscosities (η_a) of all the gels measured at a high shear rate ($\dot{\gamma} = 100\,s^{-1}$) were much lower than those measured at a low shear rate ($\dot{\gamma} = 10\,s^{-1}$), indicating a shear thinning characteristic of these gels. The n values obtained for all the gels were below 1, confirming that the gels behaved as pseudoplastic shear thinning fluids. The addition of either XT or GG to RS in the absence of salts caused a decrease in the n values, suggesting that hydrocolloids make the starch gels more pseudoplastic in the order GG > XT. In contrast, the addition of salts to RS alone, RS/XT, and RS/GG blends resulted in an increase in the n values, indicating that salts lowered the psuedoplasticity of all the gels tested. The K values (which represents

Table 5
The power law parameters and the apparent viscosity (η_a) at shear rates of $10\,s^{-1}$ ($\eta_{a,10}$) and $100\,s^{-1}$ ($\eta_{a,100}$) of 6% (w/w) rice starch alone (RS) and rice starch in the presence of xanthan (RS/XT) or guar gum (RS/GG) (19:1, w/w ratio) dispersed in aqueous solutions with and without salts at 0.1 M concentration.[a]

Sample	Salt	$\eta_{a,10}$ (Pa s)	$\eta_{a,100}$ (Pa s)	Power law parameters[b]		
				K (Pa s^n)	n	R^2
RS	None	4.19 ± 0.4a	0.61 ± 0.0b	20.9 ± 2.2a	0.25 ± 0.01c	0.969
	NaCl	2.79 ± 0.2b	0.49 ± 0.0c	12.4 ± 1.2b	0.32 ± 0.01a	0.993
	$CaCl_2$	4.48 ± 0.3a	0.71 ± 0.0a	21.1 ± 1.4a	0.28 ± 0.01b	0.985
RS/XT	None	3.29 ± 0.2c	0.47 ± 0.0c	20.2 ± 1.3b	0.20 ± 0.01b	0.990
	NaCl	4.02 ± 0.4b	0.61 ± 0.1b	22.9 ± 2.6b	0.23 ± 0.01a	0.992
	$CaCl_2$	6.61 ± 0.3a	1.02 ± 0.0a	36.4 ± 2.3a	0.24 ± 0.01a	0.995
RS/GG	None	7.57 ± 0.9a	1.04 ± 0.1a	49.9 ± 7.0a	0.16 ± 0.01b	0.996
	NaCl	4.90 ± 0.4c	0.78 ± 0.1b	31.1 ± 1.2b	0.20 ± 0.00a	0.979
	$CaCl_2$	6.34 ± 0.2b	1.54 ± 0.1a	42.4 ± 1.5a	0.18 ± 0.01a	0.995

[a] Assays were performed in triplicate. Mean ± standard deviation values in the same column for each sample followed by different letters are significantly different ($p \leq 0.05$).

[b] Power law parameters: K, consistency coefficient; n, flow behavior index.

in the resistance to flow) of RS/XT gels increased in the presence of salts, whereas those of RS/GG gels decreased with NaCl addition but were unaffected by $CaCl_2$ addition. The η_a values which depend on both the K and n values exhibited a similar trend to that of the K values for all the gels tested. The η_a values are also consistent with the final viscosity of the corresponding systems obtained during pasting (Table 2).

4. Conclusions

In complex systems like starch/hydrocolloid/salt combinations, it should be assumed that the salts added can interact with both the hydrocolloids and the starch, and also that the hydrocolloids can interact with the starch. This study demonstrated that the salts added exhibited a more pronounced effect on the pasting and rheological properties of the starch/ionic hydrocolloid (RS/XT) blends in the order $CaCl_2 > NaCl$ than those of the starch/non-ionic hydrocolloid (RS/GG) blends. On the contrary, the thermal properties of the starch seemed to be unaffected by the presence of any of these hydrocolloids, but significantly affected by the presence of salts in the order $CaCl_2 > NaCl$. These results have important practical implications in applications of hydrocolloids in starch-based food products containing salts.

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