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Effects of the amylose–amylopectin ratio on starch–hydrocolloid interactions

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ABSTRACT

Combinations of 4 rice starches with amylose (AM) contents of 0%, 15%, 22%, and 28% and 8 hydrocolloids (xanthan, guar gum, CMC, sodium alginate, HPMC, κ-, ι-, λ-carrageenan) were used (4.75% starch and 0.25% hydrocolloid). With a few exceptions, addition of a hydrocolloid increased peak and final η, breakdown, setback, G'', and η^*, K, and $\eta_{a,100}$ values. It is concluded that the AM content of the starch was a greater determinant of pasting, paste, and gel properties than was the added hydrocolloid at the 19:1 (w/w) starch–hydrocolloid ratio used. Reinforced is the previous conclusion that the properties of a starch–hydrocolloid combination are determined by the specific combination.

1. Introduction

Because native starches in general do not have the properties desired for use in processed foods, they are often chemically modified to improve their properties, e.g., to increase their tolerance to processing conditions, to improve paste and gel textures, to provide cold storage and/or freeze–thaw stability, and/or to control water mobility. It has been found that certain hydrocolloids in combination with certain starches provide some improvement of properties without chemical modification. Only a few of the more than 150 basic research studies covered in a review (BeMiller, 2011) of starch–hydrocolloid interactions were designed to examine the effect of the amylose content of the starch on starch–hydrocolloid systems. In order, Crossland and Favor (1948), Sandstedt and Abbott (1965), Descamps, Langevin, and Combs (1986), Bahnassey and Breene (1994), Liehr and Kulicke (1996), Shi and BeMiller (2002), Gonera and Cornillon (2002), and Tester and Sommerville (2003) compared responses of normal and waxy maize starches. In order, Gudmundsson, Eliasson, Bengtsson, and Åman (1991), Fanta and Christianson (1996), Funami et al. (2005a, 2005c), Tischer, Noseda, de Freitas, Sierakowski, and Duarte (2006), Weber, Queiroz, and Chang (2008), Kaur, Singh, Singh, and McCarthy (2009) and Weber, Clerici, Collares-Queiroz, and Chang (2009) compared responses of normal maize, waxy maize, and amylomaize starches. Freitas, Gorin, Neves, and Sierakowski (2003) compared responses of waxy maize and amylomaize starches. Kaur et al. (2009) compared responses of normal maize and amylomaize starches. In order, Shi and BeMiller (2002) and Huang, Kennedy, Li, Xu, and Xie (2007) compared responses of rice (unspecified amylose content) and waxy rice starches. Techawipharat, Suphantharika, and BeMiller (2008) compared responses of rice (12% amylose, intermediate-amylose type) and waxy rice starches; Sasaki, Yasui, and Matsuki (2000a) compared responses of normal and waxy wheat starches, and Sasaki, Yasui, and Matsuki (2000b) compared responses of normal and low-amylose wheat starches. Funami et al. (2005b) mixed normal maize, waxy maize, and amylomaize starches to achieve amylose contents of 14%, 26%, and 50%, but their paper is not included in our discussion because of the different granule types in the mixtures.

It is known that rice starch can have a considerable range of amylose (AM) contents (see, e.g., Fitzgerald et al., 2009). Therefore, rice starches with a range of AM contents were isolated and used in combination with various hydrocolloids to determine any effects of the hydrocolloids on their pasting, paste, and gel properties.

2. Materials and methods

2.1. Materials

Rice flours were obtained as gifts from the International Rice Research Institute, The Philippines. The rice varieties and the

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approximate percent AM as determined by iodine binding were as follows: IR65 (0%), IR24 (15%), IR64 (22%), IR74 (28%) (Melissa A. Fitzgerald, personal communication). Starch was isolated from the flours via method II of Han and Hamaker (2002).

Xanthan (company description: Keltrol, 1400 mPa s (for 1% gum in 1% KCl)) was obtained as a gift from CP Kelco (Atlanta, GA, USA). Guar gum (company description: Supercol U, 5100 mPa s for 1% gum after 2 h hydration) and sodium carboxymethylcellulose (CMC) (company description: CMC 7H3SF, DS 0.89, smooth-type, 2100 mPa s for 1% gum at 25 °C) were obtained as gifts from Ashland Aqualon Functional Ingredients (Hopewell, VA, USA). Sodium alginate (company description: 400–600 mPa s at pH 6.0–8.0) was obtained as a gift from FMC BioPolymer (Girran, Ayrshire, UK). Hydroxypropylmethylcellulose (HPMC) (company description: Methocel K100M, 23.3% methyl ether groups, 9.8% hydroxypropyl ether groups, 116,640 mPa s for 2% gum at 20 °C) was obtained as a gift from Dow Chemical Co. (Midland, MI, USA). Kappa-, iota-, and lambda-type carrageenans (κC, ιC, and λC, respectively) were obtained as gifts from FMC BioPolymer (Philadelphia, PA, USA). All hydrocolloid preparations were food grade.

2.2. Preparation of hydrocolloid solutions

All hydrocolloids were used as received. All hydrocolloid solutions were prepared as 0.280% (w/w; dry weight basis (db)) solutions. Guar gum was hydrated for 3 h at room temperature (~22 °C) with vigorous stirring in reverse osmosis and distilled (ROD) water. Xanthan was hydrated for 3 h at room temperature (~22 °C) with vigorous stirring in a 100 mM NaCl solution. Cellulose derivatives (i.e., HPMC, CMC) were dissolved in ROD water at room temperature with vigorous stirring for 2 h. Sodium alginate and the carrageenans (κ-, ι-, and λ-types) were dispersed independently in ROD water, and the dispersions were heated under constant stirring at 80 °C, until the solutions became clear. Upon completion of dissolution, the hot solutions were cooled in a water bath to room temperature (~22 °C). To the resulting hydrocolloid solutions was added sufficient ROD water to replace that lost through evaporation during hydration and/or dissolution.

2.3. Pasting and paste properties

Pasting viscosity profiles and characteristics of rice starch–hydrocolloid mixtures were analyzed using a Rapid Visco Analyzer (RVA-4V; Newport Scientific Pty. Ltd., Warriewood, Australia). Starch (1.33 g, db) was added to an aluminum canister containing the hydrocolloid solution (25.0 g), after which the starch–hydrocolloid slurry was adjusted to 28.0 g by adding ROD water. The mixing ratio of starch to hydrocolloid was 19:1 (w/w). The total solids content was 5.0% (w/w). The resultant slurry was thoroughly stirred with a spatula to remove starch clumps and then carefully scraped from the spatula with a plastic paddle. Further, prior to insertion into the RVA, the slurry was manually stirred for 30 s using the plastic paddle. In the RVA, the rotation speed of the plastic paddle was maintained at 160 rpm. The heating and cooling cycles were slightly modified from standard method 1 offered by the supplier. The slurry was held at 50 °C for 120 s to minimize, if any, starch aggregates, heated to 95 °C within 222 s, held at 95 °C for 150 s, subsequently cooled to 50 °C within 228 s, and held at 50 °C for 240 s to fully develop final paste viscosity. Thermocline for Windows (version 2.0) was used to obtain pasting viscosity profiles and parameters. For comparison, pasting characteristics and paste viscosity profiles of the starch alone were determined at total solid contents of 5.0 and 4.75% (w/w) under the same conditions to elucidate the impact of both replacement of the starch with a hydrocolloid and addition of a hydrocolloid to the starch on the properties of the rice starch–hydrocolloid mixtures. Two to four replicates of each mixture were run.

2.4. Dynamic rheological measurements

The freshly prepared pastes of starch alone and starch–hydrocolloid mixtures were held 1 h at room temperature (~22 °C). The resultant paste (or gel) was loaded onto the platen of an AR/G2 rheometer (TA Instruments, New Castle, DE, USA) and held for 5 min at 30 °C prior to analysis. A frequency sweep test was conducted using a cone and plate geometry system (40 mm diameter, 2° cone angle, and 0.055 mm gap) over an angular frequency of 0.1–10 rad/s (0.0159–1.59 Hz) at 1% strain (which was in the linear viscoelastic region as determined from preliminary strain sweep tests). Storage modulus (G') and loss modulus (G'') were obtained from Rheology Advantage Data Analysis Software (version 5.7.1) (TA Instruments, New Castle, DE, USA) and used to calculate complex viscosity (η^*) and loss tangent ($\tan\delta$). Two replicates of each mixture were run.

2.5. Differential scanning calorimetry (DSC)

Thermal properties of starch samples were investigated with a differential scanning calorimeter (Q2000 DSC; TA Instruments, New Castle, DE, USA). The starch sample (5.0 mg, db) was placed in a pan and ROD water was added to a total weight of 20.0 mg (starch to water ratio = 1:3 (w/w)). The pan was hermetically sealed and equilibrated at room temperature for at least 2 h before the scan. Samples were heated from 5 °C to 95 °C at a heating rate of 5 °C/min. A sealed empty pan was used as a reference, and indium was used for temperature calibration. Duplicate analyses were performed on each sample.

2.6. Experimental design and statistical analysis

The paste preparation was replicated at least twice for each rice starch–hydrocolloid combination, and mean values of all measured pasting parameters and rheological attributes were determined at least once for each replicate paste. All statistical computations and analyses were achieved using SAS version 9.2 for Windows (SAS Institute, Cary, NC, USA). Experimental data were analyzed using Analysis of Variance (ANOVA) and expressed as mean values ± standard deviations. Significant differences among experimental mean values were assessed using a least square difference (LSD) test ($p < 0.05$).

3. Results and discussion

The four rice starches used had amylose (AM) contents of 0, 15, 22, and 28%. The 0%AM starch is comparable to other all-amylopectin cereal starches such as waxy maize starch, and the 28%AM starch is comparable to, for example, normal corn starch. Each was used in a starch–hydrocolloid w/w ratio of 19:1 (4.75% starch + 0.25% hydrocolloid). This means that AM concentrations in the RVA canisters were 0% (for the 0%AM starch), 0.71% (for the 15%AM starch; an AM-hydrocolloid w/w ratio of 2.9:1), 1.0% (for the 22%AM starch; an AM-hydrocolloid w/w ratio of 4.2:1), and 1.3% (for the 28%AM starch; an AM-hydrocolloid w/w of 5.3:1). None of the controls of 0.28% hydrocolloid solutions alone showed any RVA viscosity. It is especially noted that the 0.28% HPMC solution did not exhibit thermogelation.

Table 1
Mean[a] values for RVA paste attributes of rice starch alone and rice starch–hydrocolloid mixtures.

Sample	AM content of starch (%)	Peak η[b]	Breakdown[b]	% Breakdown[c]	Setback[b]	% Setback[d]	Final η[b]
Starch (5.00%)	0	580.0 ± 6.2a	235.8 ± 9.4a	41	78.0 ± 4.8d	18	422.3 ± 8.4b
	15	305.5 ± 3.7b	63.5 ± 4.9b	21	244.3 ± 6.1b	50	486.3 ± 12.4a
	22	253.0 ± 3.2c	54.5 ± 8.0b	22	288.3 ± 7.6a	59	486.8 ± 8.3a
	28	186.8 ± 4.6d	19.0 ± 3.4c	10	157.5 ± 5.8c	49	325.3 ± 5.6c
Starch (4.75%)	0	500.5 ± 6.2a	196.0 ± 2.3a	39	68.5 ± 2.1d	18	373.0 ± 7.9c
	15	250.5 ± 6.8b	47.3 ± 3.9b	19	214.3 ± 4.8b	51	417.5 ± 8.2a
	22	202.5 ± 6.0c	42.3 ± 3.9c	21	251.0 ± 4.1a	61	411.3 ± 9.0b
	28	144.0 ± 4.2d	17.3 ± 2.2d	12	113.3 ± 4.5c	47	240.0 ± 5.4d
Starch–xanthan[e,f]	0	687.7 ± 5.5a	291.3 ± 3.2a	42	89.3 ± 4.2d	18	485.7 ± 5.7d
	15	586.0 ± 5.7b	54.0 ± 1.4b	9.2	166.0 ± 0.0b	24	698.0 ± 7.1a
	22	528.4 ± 8.0c	45.2 ± 11.0b	8.5	192.0 ± 12.7a	28	675.2 ± 7.3b
	28	501.8 ± 4.3d	53.6 ± 10.5b	11	124.4 ± 5.9c	22	572.6 ± 8.9c
Starch–guar gum[e]	0	735.8 ± 2.6a	311.0 ± 3.6a	42	116.8 ± 10.9d	22	541.5 ± 12.3c
	15	558.0 ± 6.2b	180.3 ± 3.1b	32	293.0 ± 2.0c	44	670.7 ± 10.0b
	22	509.5 ± 8.3c	158.3 ± 6.6c	31	377.8 ± 2.6a	52	729.0 ± 6.5a
	28	417.8 ± 9.1d	32.8 ± 3.0d	7.9	348.5 ± 9.5b	48	733.5 ± 14.3a
Starch–CMC[e]	0	883.0 ± 6.6a	305.3 ± 7.8a	35	147.5 ± 8.7b	20	725.3 ± 4.3b
	15	537.3 ± 7.7c	101.3 ± 9.9b	19	277.0 ± 10.7a	39	713.0 ± 4.1c
	22	516.3 ± 11.7d	44.7 ± 6.8c	8.7	264.3 ± 10.7a	36	736.0 ± 10.0a
	28	355.4 ± 2.3b	47.6 ± 4.0c	14	147.8 ± 9.7b	32	455.6 ± 5.3d
Starch–alginate[e]	0	783.4 ± 10.3a	301.6 ± 6.7a	39	139.0 ± 4.2d	22	620.8 ± 9.3c
	15	460.5 ± 6.6b	65.0 ± 4.1b	14	252.8 ± 9.3b	39	648.3 ± 6.8b
	22	431.0 ± 13.4c	42.4 ± 6.1c	9.7	279.2 ± 9.6a	42	667.8 ± 7.9a
	28	283.0 ± 6.3d	23.8 ± 5.4d	8.5	161.8 ± 5.4c	38	421.0 ± 8.8d
Starch–HPMC[e]	0	586.5 ± 6.4a	283.5 ± 4.8a	48	213.0 ± 7.4c	41	516.0 ± 7.3d
	15	238.5 ± 11.5b	59.0 ± 9.1b	25	445.5 ± 18.3d	71	625.0 ± 16.1c
	22	193.5 ± 6.8c	50.0 ± 2.9b	26	556.3 ± 9.5b	79	699.8 ± 13.5b
	28	110.0 ± 2.3d	19.3 ± 1.7c	17	647.0 ± 5.4a	88	737.8 ± 4.6a
Starch–κC[e,g]	0	425.0 ± 1.7a	169.0 ± 2.0a	40	79.3 ± 2.5d	24	335.3 ± 1.5c
	15	270.7 ± 6.7b	20.0 ± 5.2c	7.4	181.7 ± 3.2b	42	432.3 ± 8.0b
	22	235.3 ± 11.1c	31.3 ± 4.5b	13	256.0 ± 6.0a	56	460.0 ± 12.5a
	28	158.3 ± 6.0d	14.7 ± 2.3c	9.3	140.0 ± 3.6c	49	283.7 ± 0.6d
Starch–ιC[e,g]	0	481.3 ± 5.9a	206.3 ± 10.1a	43	81.0 ± 3.0d	23	356.0 ± 7.0c
	15	349.7 ± 3.5b	58.7 ± 11.2b	17	211.7 ± 3.8b	42	502.7 ± 7.0b
	22	322.3 ± 3.1c	47.7 ± 2.5b	15	283.3 ± 3.2a	51	558.0 ± 5.3a
	28	203.7 ± 6.1d	13.3 ± 3.2d	6.5	178.3 ± 15.5c	48	368.7 ± 12.7c
Starch–λC[e,g]	0	606.3 ± 9.6a	239.3 ± 7.4a	39	93.7 ± 8.1d	20	460.7 ± 7.4c
	15	494.5 ± 6.4b	61.0 ± 1.4b	12	209.5 ± 3.5b	33	643.0 ± 11.3b
	22	492.3 ± 0.6b	53.0 ± 5.0b	11	263.0 ± 8.9a	37	702.3 ± 3.8a
	28	342.0 ± 2.6c	37.3 ± 3.2c	11	154.3 ± 6.4c	34	459.0 ± 3.5c

[a] Mean values for 3 or 4 replicate measurements. Values sharing the same lowercase letters within columns of a given starch–hydrocolloid mixture are not significantly different at $p < 0.05$.
[b] mPa s.
[c] Breakdown as a percent of the peak viscosity.
[d] Setback as a percent of the final viscosity.
[e] Starch–hydrocolloid ratio = 4.75%:0.25% (19:1, w/w). Total solid content = 5% (w/w).
[f] In 100 mM NaCl.
[g] κC, ιC, and λC are respective designations of kappa-, iota-, and lambda-type carrageenans.

3.1. *Effect of amylose content of rice starch on pasting characteristics and paste viscosity profiles of the starch–hydrocolloid mixtures*

Peak viscosity (Table 1). For the control pastes, peak η steadily decreased from that of the 0%AM starch to that of the 28%AM starch. The same was true when a hydrocolloid was added. We speculate that this phenomenon is caused by a reduction in granule swelling as the AM content increases, which is congruent with the conclusion of Tester and Morrison (1990) that AM inhibits granule swelling. The difference (in this case, a decrease) in the values going from the paste made from the 0%AM starch to that of the 15%AM starch was generally greater than that going from the 15%AM starch to the 28%AM starch, whether or not a hydrocolloid was present, which was also the case with other examined parameters for the controls (with the exception of final viscosity). Peak η of the 28%AM starch system as a percent of the peak η of the 0%AM starch system were as follows: starch–HPMC, 19%; 4.75% starch control, 29%; starch–alginate, 36%; starch–κC, 37%; starch–CMC, 40%; starch–ιC, 42%; starch–λC, 56%; starch–guar gum, 57%; starch–xanthan, 73%, which reveals differences in the effects of the different hydrocolloids on the peak η of the different rice starches – a finding repeated with all other parameters. (Data of this type are reported throughout the manuscript as indications of differences in the effects of the hydrocolloids on properties imparted by AM.)

Rosell, Yokayama, and Shoemaker (2011) found that the presence of xanthan and guar gum increased the peak η of rice starch (AM content unknown), while HPMC did not change the peak η. Techawipharat et al. (2008) found no change in peak η of a 11.9%AM rice starch and a decrease in peak η of a 0%AM rice starch effected by the presence of HPMC. We observed increases in peak η of all 4 rice starches when xanthan or guar gum were present, and increases

in peak η of 0%AM rice starch and decreases in peak η of the 3 AM-containing starches when HPMC was present.

Breakdown (Table 1). Breakdown was analyzed in two ways: (1) as the absolute value (mPa s) of peak viscosity minus trough/hot-paste viscosity, and (2) as a percentage of peak viscosity. Breakdown as recorded by the RVA increased over that of the 4.75% starch control, except for all 4 rice starch–κC combinations and the 28%AM rice starch–ιC combination. When data from the instrument readings were examined, it was found that, in every case, breakdown decreased greatly as the AM content of the starch increased from 0% to 15% and that, with two exceptions, breakdown decreased as the AM content of the starches increased. We speculate that, because the granules probably did not swell as much as their AM contents increased, they did not become as fragile; hence, less breakdown. The two exceptions were when xanthan or CMC was present. In those two cases, there was a decrease in recorded breakdown as the AM content of the starches increased from 0% to 22%, and an increase as the AM content increased from 22% to 28%. Values for breakdown of the 28%AM starch system as a percent of breakdown for the 0%AM starch system were as follows: starch–ιC, 6.5%; starch–HPMC, 6.8%; starch–sodium alginate, 7.9%; starch–κC, 8.7%; 4.75% starch control, 8.8%; starch–guar gum, 11%; starch–λC, 16%; starch–CMC, 16%; starch–xanthan, 18%.

When xanthan, guar gum, or CMC were added to the rice starches, there was no consistent pattern to trough viscosity as a function of AM content. For the controls and when sodium alginate or HPMC was added, trough viscosity decreased as the AM content increased. Therefore, breakdown was calculated as a percent of peak viscosity. The most consistent pattern found for breakdown as a percent of peak η (Table 1) was a decrease as the AM content of the starch increased, with the values for the 15%- and 22%AM starch pastes being similar. This pattern was found for the controls and the starch–xanthan, –guar gum, –HPMC, –ιC, and –λC combinations, and is an indication that there were differences in the natures of the starch polymer molecules and/or granules other than the AM content and especially so with the 15%- and/or the 22%AM starches. (Unfortunately, it was not possible to obtain starches with different amylose contents that were all from the same genetic background.) With the exception of the starch–guar gum composite system, the largest decrease was found in going from the 0%AM starch to the 15%AM starch. Values of breakdown as a percent of peak η of pastes containing the 28%AM starch expressed as a percentage of the corresponding values for pastes containing the 0%AM starch were in the order: starch–ιC, 15%; starch–guar gum, 19%; starch–sodium alginate, 22%; starch–κC, 23%; starch–xanthan, 26%; starch–λC, 28%; 4.75% starch control, 31%; starch–HPMC, 35%; starch–CMC, 40%, which is different from the order of absolute values (mPa s) of breakdown.

Setback (Table 1). Setback was also analyzed in two ways: (1) as the absolute value (mPa s) of final viscosity minus trough viscosity, and (2) as a percentage of final viscosity. When data from the instrument readings were examined, the same pattern was seen for the controls and the starch–hydrocolloid composite pastes (with the exception of the starch–HPMC combination), and that was that setback increased as the AM contents of the starches increased from 0% to 22%, then decreased substantially in going from the 22%AM starch to the 28%AM starch, but to a value that was still greater than that of the 0%AM starch (with the exception of the starch–CMC combination). An interpretation might be that, since the granules of the 28%AM starch were probably not as swollen, not as much AM leached from them; hence, there could be less setback. The starch–HPMC composite pastes exhibited a steady increase in setback as the AM contents of the starches increased. (Note that this is an increase in viscosity as the paste was cooled from 95 °C to 50 °C, so it is not related to thermogelation and might indicate a synergistic interaction between one or both of the starch molecules and HPMC.) With the starch–CMC composite pastes, setback increased going from the paste of the 0%AM to that of the 15%AM starch, then decreased so that the setback of the 28%AM starch–CMC composite paste was the same as that of the 0%AM starch–CMC paste. When setback of the 28%AM rice starch pastes were calculated as a percent of setback for the 0%AM starch pastes, the values were as follows: starch–CMC, 100%; starch–sodium alginate, 120%; starch–xanthan, 140%; starch–λC, 160%; 4.75% starch control, 160%; starch–κC, 180%; starch–ιC, 220%; starch–guar gum, 300%; starch–HPMC, 300%.

Setback as a percent of final η was calculated for the same reason that breakdown as a percent of peak η was calculated. When the data for setback as a percent of final η were examined, similar patterns for the effect of the AM content of the starch, but a different pattern for the order of the starch–hydrocolloid pastes, were found. For the controls and all rice starch–hydrocolloid combinations (with two exceptions, viz., the starch–CMC and –HPMC combinations), setback as a percent of final η increased as the AM content of the starch increased from 0% to 22%, then decreased as the AM content increased from 22% to 28%. For the rice starch–HPMC combinations, setback as a percent of final η increased continuously as the AM content of the starch increased. Values of setback as a percentage of final η of pastes containing the 28%AM starch expressed as a percentage of the corresponding values for the 0%AM starch were in the order: starch–xanthan, 120%; starch–CMC, 160%; starch–sodium alginate and starch–λC, 170%; starch–κC, 200%; starch–ιC, 210%; starch–HPMC, 210%; starch–guar gum, 220%; 4.75% starch control, 260%, which is different than the order given by the absolute values (mPa s) of setback.

Final viscosity (Table 1). Final η is determined by the peak η, breakdown, and setback. With the exceptions of the 0%AM rice starch–κC and –ιC combinations, all final η values were greater than those of the 4.75% controls. Four different patterns of final η were observed for the controls and the five starch–hydrocolloid combinations. For the controls, final η increased as the AM content of the rice starch increased from 0% to 15%, was little changed as the AM content increased from 15% to 22%, and decreased as the AM content increased from 22% to 28%. None of the starch–hydrocolloid combinations exhibited this pattern. With xanthan present, final η increased as the AM content of the starch increased from 0% to 15%, then decreased steadily as the AM content increased from 15% to 28%, with the final η of the paste containing the 28%AM starch still being greater than the paste of the 0%AM starch. With guar gum or HPMC (the two neutral hydrocolloids) present, the final η increased steadily as the AM content of the starch increased from 0% to 28%. With CMC or sodium alginate present, the final η increased slightly as the AM content of the starch increased from 0% to 22%, then decreased dramatically as the AM content increased from 22% to 28%, so that the paste of the 28%AM starch had a final η that was less than that of the paste containing the 0%AM starch. Final η values of the 28%AM starch paste as a percent of final η of the 0%AM starch paste were starch–CMC, 63%; 4.75% starch control, 64%; starch–sodium alginate, 68%; starch κC, 85%; starch–λC and starch–ιC, 100%; starch–xanthan and starch–HPMC, 120%; starch–guar gum, 140%; so both increases and decreases in final η of the 28%AM starch pastes as compared to final η of the 0%AM starch pastes were found.

3.2. Effect of amylose content of the rice starch on dynamic rheological properties of the starch–hydrocolloid mixtures

Elastic/storage modulus (G') (Table 2). Dynamic rheological measurements were done on gels produced by holding the pastes obtained from the RVA analysis at room temperature for 1 h, so properties after only short-term processes had occurred were determined, i.e., after only AM–AM intermolecular interactions had

Table 2
Mean[a] values for dynamic rheological properties of cooled gels from rice starch alone and rice starch–hydrocolloid mixtures (at 25 °C and 6.28 rad/s).

Sample	AM content of starch (%)	G' (Pa)	G'' (Pa)	tan δ	η^* (Pa s)
Starch (5.00%)	0	12.2 ± 0.2c	5.8 ± 0.0c	0.48 ± 0.01a	2.1 ± 0.0c
	15	35.5 ± 1.1b	8.6 ± 0.1a	0.24 ± 0.00b	5.8 ± 0.2b
	22	36.8 ± 2.6b	8.2 ± 0.1b	0.22 ± 0.01b	6.0 ± 0.4b
	28	50.9 ± 2.5a	6.0 ± 0.2c	0.12 ± 0.00c	8.2 ± 0.4a
Starch (4.75%)	0	11.5 ± 0.2d	5.5 ± 0.0b	0.47 ± 0.00a	2.0 ± 0.0d
	15	31.7 ± 0.3c	7.7 ± 0.1a	0.24 ± 0.01b	5.2 ± 0.0c
	22	33.6 ± 0.1b	7.5 ± 0.1a	0.22 ± 0.00c	5.5 ± 0.0b
	28	36.4 ± 1.2a	4.5 ± 0.2c	0.12 ± 0.00d	5.8 ± 0.2a
Starch–xanthan[b,c]	0	19.7 ± 1.0b	8.3 ± 0.4c	0.37 ± 0.00a	2.3 ± 0.1b
	15	72.4 ± 2.5a	16.6 ± 0.4b	0.20 ± 0.00b	9.4 ± 0.3a
	22	69.9 ± 1.2a	15.9 ± 0.7b	0.19 ± 0.00c	9.0 ± 0.2a
	28	72.1 ± 2.9a	18.6 ± 0.3a	0.21 ± 0.00b	9.2 ± 0.4a
Starch–guar gum[b]	0	15.8 ± 0.5d	8.6 ± 0.2d	0.55 ± 0.00a	2.9 ± 0.1d
	15	41.3 ± 1.8c	14.0 ± 0.4c	0.34 ± 0.01c	6.9 ± 0.3c
	22	53.6 ± 2.8b	16.3 ± 0.2b	0.30 ± 0.01b	8.9 ± 0.4b
	28	73.3 ± 4.8a	24.0 ± 1.0a	0.33 ± 0.01c	12.3 ± 0.8a
Starch–CMC[b]	0	19.5 ± 0.4c	10.9 ± 0.0d	0.56 ± 0.01a	3.6 ± 0.1c
	15	51.0 ± 0.1a	22.2 ± 0.0a	0.44 ± 0.00c	8.8 ± 0.0a
	22	52.6 ± 0.4a	20.4 ± 0.3b	0.39 ± 0.01d	9.0 ± 0.0a
	28	33.0 ± 0.1b	16.1 ± 0.0c	0.49 ± 0.01b	5.8 ± 0.0b
Starch–alginate[b]	0	15.3 ± 0.1d	8.9 ± 0.1d	0.58 ± 0.01a	2.8 ± 0.0c
	15	40.5 ± 0.0a	15.8 ± 0.2a	0.39 ± 0.01b	6.9 ± 0.0a
	22	39.9 ± 1.1a	14.5 ± 0.4b	0.36 ± 0.00c	6.8 ± 0.2a
	28	34.3 ± 1.1b	11.5 ± 0.3c	0.34 ± 0.00d	5.8 ± 0.2b
Starch–HPMC[b]	0	13.9 ± 0.1d	9.0 ± 0.0d	0.65 ± 0.01a	2.6 ± 0.0d
	15	30.9 ± 0.8c	14.1 ± 0.3c	0.46 ± 0.00b	5.4 ± 0.1c
	22	42.4 ± 2.0b	16.7 ± 0.3b	0.39 ± 0.01c	7.3 ± 0.3b
	28	69.4 ± 2.8a	25.4 ± 0.6a	0.37 ± 0.01d	11.8 ± 0.4a
Starch–κC[b,d]	0	8.7 ± 0.0c	5.7 ± 0.0c	0.66 ± 0.00a	1.7 ± 0.0c
	15	28.4 ± 0.8b	9.7 ± 0.4a	0.34 ± 0.01b	4.8 ± 0.1b
	22	29.6 ± 0.2b	9.4 ± 0.0a	0.32 ± 0.00c	4.9 ± 0.0b
	28	32.4 ± 0.7a	6.7 ± 0.2b	0.21 ± 0.00d	5.3 ± 0.1a
Starch–ιC[b,d]	0	9.8 ± 0.2c	7.0 ± 0.1d	0.72 ± 0.01a	1.9 ± 0.0c
	15	32.7 ± 0.0b	13.0 ± 0.1c	0.40 ± 0.00b	5.6 ± 0.0b
	22	39.6 ± 0.6b	13.8 ± 0.3b	0.35 ± 0.01c	6.7 ± 0.1a
	28	39.4 ± 0.2a	15.5 ± 0.1a	0.39 ± 0.00b	6.7 ± 0.0a
Starch–λC[b,d]	0	10.9 ± 0.2d	8.3 ± 0.0d	0.76 ± 0.01a	2.2 ± 0.0c
	15	40.6 ± 0.7c	17.8 ± 0.2a	0.44 ± 0.00b	7.1 ± 0.1b
	22	44.5 ± 0.9b	17.3 ± 0.3b	0.39 ± 0.00c	7.6 ± 0.2b
	28	48.4 ± 0.0a	16.6 ± 0.4c	0.34 ± 0.01d	8.1 ± 0.0a

[a] Mean values for 2 or 3 replicate measurements. Values sharing the same lowercase letters within columns of a given starch–hydrocolloid mixture are not significantly different at $p < 0.05$.
[b] Starch–hydrocolloid ratio = 4.75%:0.25% (19:1, w/w). Total solid content = 5% (w/w).
[c] In 100 mM NaCl.
[d] κC, ιC, and λC are respective designations of kappa-, iota-, and lambda-type carrageenans.

occurred (Doublier & Choplin, 1989; Eidam, Kulicke, Kuhn, & Stute, 1995; Ellis & Ring, 1985; Gidley, 1989; Silverio, Svensson, Eliasson, & Olofsson, 1996). The controls and the 8 starch–hydrocolloid combinations produced several different patterns of G' values as a function of the AM contents of the starches. One pattern was that exhibited by the controls and the rice starch–guar gum, –HPMC, –κC, and –λC combinations, in which G' values increased as the AM contents of the starches increased. The presence of the other 4 hydrocolloids (xanthan, CMC, sodium alginate, ιC) also resulted in increases in G' with an increase in the AM content of the starch from 0% to 28%; however, the value for the 28%AM-containing starch was not the highest value. (In the presence of xanthan, the values for the 15%- and 26%AM starches were the same and the highest values. In the presence of ιC, the values for the 22%- and 28%AM starches were the same and the highest values. In the presence of CMC and sodium alginate, the values for the 15%- and 22%AM starches were about the same and the highest values.) The patterns varied in every case, but when G' of the 28%AM starch gel was calculated as a percent of G' of the 0%AM starch gel, the following results were obtained: starch–CMC, 170%; starch–sodium alginate, 220%; 4.75% starch control, 320%; starch–xanthan, 370%; starch–κC, 370%; starch–ιC, 400%; starch–λC, 440%; starch–guar gum, 460%; starch–HPMC, 500%.

Loss modulus (G'') (Table 2). The controls and the 8 starch–hydrocolloid combinations also produced several different patterns of G'' values as a function of the AM contents of the starches. For the rice starch–guar gum, –HPMC, and –ιC combinations, G'' increased as the AM content of the starch increased. For the controls and the rice starch–CMC, –sodium alginate, –κC, and –λC combinations, G'' values increased as the AM content of the starch increased from 0% to 15%, decreased slightly as the AM content increased from 15% to 22%, and then decreased as the AM content increased further to 28%. For rice starch–xanthan combinations, G'' increased as the AM content of the starch increased from 0% to 15%, decreased slightly as the AM content increased from 15% to 22%, and then increased again as the AM content increased to 28%. When G'' of the 28%AM starch gels were calculated as a percent of G'' of the 0%AM starch gels, the following results were obtained:

Table 3
DSC parameters of native rice starches.

AM content of starch (%)	T_o [a] (°C)	T_p [a] (°C)	ΔH (J/g)	Temperature range[b] (°C)
0	60.5	69.5	11.97 ± 1.19	12.67
15	63.0	69.1	8.62 ± 0.08	8.83
22	72.1	76.2	10.60 ± 0.00	6.00
28	57.5	65.0	7.26 ± 0.31	9.72

[a] T_o and T_p indicate gelatinization onset and peak temperatures, respectively.
[b] Temperature range at half peak height.

4.75% starch control, 82%; starch–κC, 120%; starch–sodium alginate, 130%; starch–CMC, 150%; starch–λC, 200%; starch–ιC and starch–xanthan, 220%; starch–HPMC and starch–guar gum, 280%.

Loss tangent ($\tan\delta$; G''/G') (Table 2). In comparison with the controls, only the presence of xanthan reduced $\tan\delta$ values of gels of the 0%-, 15%-, and 22%AM starches, indicating that it made the gels more solid-like and possibly indicating xanthan–amylopectin intermolecular interactions. In every other case, $\tan\delta$ values were greater than those of the controls, indicating that the gels became more fluid upon addition of a hydrocolloid. For the controls and 4 of the rice starch–hydrocolloid (sodium alginate, HPMC, κC, λC) combinations, $\tan\delta$ decreased, i.e., the pastes became more solid-like, as the AM contents of the rice starches increased. For 3 rice starch–hydrocolloid (guar gum, CMC, ιC) combinations, the pastes became more solid-like as the AM content of the starch increased from 0% to 22%, but then $\tan\delta$ increased as the AM content increased from 22% to 28%. For the rice–starch–xanthan combinations, $\tan\delta$ values decreased greatly as the AM content of the starch increased from 0% to 15%, then changed little as the AM content increased from 15% to 28%. The values for $\tan\delta$ of the 28%AM starch gels calculated as a percent of $\tan\delta$ for the 0%AM starch gels were as follows: 4.75%AM starch control, 26%; starch–κC, 32%; starch–λC, 45%; starch–ιC, 54%; starch–HPMC and starch–xanthan, 57%; starch–sodium alginate, 59%; starch–guar gum, 60%; starch–CMC, 88%, appearing to indicate that all the hydrocolloids used decreased network formation.

The fact that the G'' and $\tan\delta$ values of the 15%- and 22%AM starches were often similar is another indicator of the unique natures of the two starches. Zhang et al. (2007), in an examination of 4 rice cultivars with different AM contents, found that relative crystallinity decreased (and setback increased) with increasing AM content. In the current study, we used DSC analysis as another method of determining similarities or differences between the 4 rice starches. No patterns were found for any DSC parameters (Table 3), either for all 4 rice starches or for the 3 AM-containing starches, again indicating that the starches, because of their different genetic backgrounds, were structurally different in ways that were not simply related to AM content. (There are multiple literature reports on the fine structures of AM and/or AP in starches of varying AM contents and, in particular, in starches from various rice cultivars because of an interest in correlating fine structures to cooking quality, texture/eating quality, and/or digestibility of the rice. See, e.g., Chung, Liu, Lee, & Wei, 2011; Igarashi, 2010; Igarashi, Hanashiro, & Takeda, 2008; Inouchi, 2010.) Interesting findings from this study were that the width of the endotherm peaks ($T_o - T_p$) and temperature range at half peak height, both of which are indications of the relative perfection of crystallites, were in the order 22%- < 15%- < 28%- < 0%AM starch, indicating that the AP molecules in the 22%AM starch were the most regularly arranged. Also, the 28%AM starch gave the lowest values for T_o, T_p, and ΔH, and the order of ΔH values (an indication of the relative quantity of crystallites) was 28%- < 15%- < 22%- < 0%AM, seemingly indicating differences in AP structures (ability to crystallize), rather than the quantity of AP, in the AM-containing starches because differences in gelatinization parameters indicate differences in granular organization, which in turn indicate differences in molecular structures.

Complex (frequency-dependent) viscosity (η^*) (Table 4). Few patterns were evident for complex viscosity. For the controls and 5 of the starch–hydrocolloid (guar gum, HPMC, κC, ιC, λC) combinations, η^* increased as the AM contents of the rice starches increased. For the starch–xanthan combination, η^* increased as the AM content of the starch increased from 0% to 15%, then varied little as the AM content increased from 15% to 28%. In the presence of CMC and sodium alginate, η^* increased as the AM content of the starch increased from 0% to 15%, changed little as the AM content increased from 15% to 22%, and then decreased as the AM content increased from 22% to 28%. In the presence of ιC, η^* increased as the AM content of the starch increased from 0% to 22%, then remained constant as the AM content increased from 22% to 28%. When η^* of the 28%AM starch gels was calculated as a percent of η^* of the 0%AM starch gels, the following values were obtained: starch–CMC, 160%; starch–sodium alginate, 210%; 4.75% starch control, 290%; starch–κC, 310%; starch–ιC, 350%; starch–λC, 370%; starch–xanthan, 400%; starch–guar gum, 420%; starch–HPMC, 450%. Comparing all 10 sets of data of this type, we arrived at two conclusions: (1) placements of the control (4.75% starch alone) and xanthan in the orders were by far the most variable, and (2) interactions of the hydrocolloid molecules with AM molecules is probably indicated by η^*, i.e., CMC and sodium alginate (2 hydrocolloids containing carboxylate groups) interfered with network formation and decreased the effects of increasing AM content, whereas the other 6 hydrocolloids promoted network formation, i.e., increased the effects of increasing AM content, with κC, ιC, and λC being the least effective, HPMC and guar gum (the 2 neutral hydrocolloids) being the most effective, and xanthan being either more or less effective than the carrageenans, depending on the attribute being determined.

Frequency dependence of dynamic rheological parameters (Figs. 1 and 2). Upon examining the relationship of the dynamic moduli and $\tan\delta$ to angular frequency (from 0.1 rad/s to 10 rad/s), we found the following trends. For 4.75% rice starch control gels, G' values for the 3 starches containing AM changed little with angular frequency and were considerably greater than the G' values of the 0%AM starch gel, either with or without added hydrocolloid. Only the 0%AM + λC, and to a lesser degree ιC, showed significant frequency dependence of G'. Also, for the 4.75% rice starch control gels, the values for the 0%AM starch gel increased the most as the frequency increased, and the data points for the curves of the 15%- and 22%AM starch gels were almost superimposed. When sodium alginate was present in the gels, this pattern was different only in that the values for the 0%AM starch gel were higher and the values for the 28%AM starch gel were lower, making the curves almost superimposed on those of the 15%- and 22%AM starch gels, and the curve was flatter. When xanthan was present in the gels, all G' values were higher (especially so for the 0%AM starch gel), the curves for all 3 AM-containing starch gels were superimposed, and all 4 curves were essentially parallel. When guar gum or HPMC, the 2 neutral hydrocolloids, were present in the gels, the curve for the 15%AM starch gel was lowered and that for the 28%AM starch gel was raised so that the 3 curves for the AM-containing starch gels were spread out and distinct. Kulicke, Eidam, Kath, Kix, and Kull (1996) found that incorporation of guar gum into a waxy rice starch gel slightly increased G' at higher frequencies, but reduced G' at lower frequencies. We found that, when guar gum was present in the 0%AM starch gel, G' was unchanged at 0.1 rad/s, but was increased at 10 rad/s. When CMC was present in the gels, the curve for the 28%AM starch gel was shifted downward so that it was below that for the 15%AM starch gel, which became superimposed with that of the 22%AM starch gel at higher frequencies.

Table 4
Mean[a] values of steady shear parameters of cooled gels from rice starch alone and rice starch–hydrocolloid mixtures (at 25 °C).

Sample	AM content of starch (%)	Power law model parameters[b]			Apparent viscosity[c] (Pa s)
		K (Pa s^n)	n	R^2	
Starch (5.00%)	0	6.3 ± 0.2d	0.50 ± 0.00b	0.998	0.63 ± 0.02c
	15	13.7 ± 0.8b	0.34 ± 0.01c	0.998	0.66 ± 0.01b
	22	16.1 ± 0.7a	0.32 ± 0.00d	0.994	0.69 ± 0.02a
	28	8.1 ± 0.7c	0.63 ± 0.01a	0.996	0.43 ± 0.01d
Starch (4.75%)	0	5.7 ± 0.0c	0.49 ± 0.00a	0.998	0.54 ± 0.00c
	15	11.4 ± 0.2b	0.34 ± 0.00c	0.998	0.56 ± 0.00b
	22	13.1 ± 1.4a	0.33 ± 0.02c	0.992	0.60 ± 0.02a
	28	5.8 ± 0.3c	0.38 ± 0.01b	0.996	0.33 ± 0.01d
Starch–xanthan[d,e]	0	12.0 ± 0.1c	0.39 ± 0.00a	0.998	0.73 ± 0.00b
	15	25.3 ± 0.2a	0.26 ± 0.00b	0.999	0.83 ± 0.00a
	22	25.6 ± 1.9a	0.25 ± 0.01b	0.998	0.81 ± 0.03a
	28	21.7 ± 2.4b	0.26 ± 0.01b	1.000	0.72 ± 0.04b
Starch–guar gum[d]	0	8.0 ± 0.0c	0.52 ± 0.00a	0.997	0.86 ± 0.00c
	15	18.6 ± 0.5b	0.35 ± 0.00b	0.999	0.91 ± 0.02b
	22	24.4 ± 0.1a	0.30 ± 0.00c	1.000	0.97 ± 0.00a
	28	24.3 ± 0.5a	0.28 ± 0.00d	0.987	0.86 ± 0.01c
Starch–CMC[d]	0	13.4 ± 0.1c	0.44 ± 0.00a	0.999	1.01 ± 0.01a
	15	17.1 ± 0.0b	0.38 ± 0.00b	1.000	0.97 ± 0.00b
	22	20.8 ± 1.0a	0.34 ± 0.01c	0.999	0.98 ± 0.00b
	28	9.7 ± 0.3d	0.43 ± 0.00a	1.000	0.72 ± 0.01c
Starch–alginate[d]	0	9.8 ± 0.1c	0.48 ± 0.00a	0.997	0.91 ± 0.01a
	15	13.6 ± 0.1b	0.41 ± 0.00c	1.000	0.90 ± 0.00a
	22	15.2 ± 0.3a	0.39 ± 0.00d	0.999	0.92 ± 0.01a
	28	7.9 ± 0.2d	0.46 ± 0.00b	0.999	0.65 ± 0.01b
Starch–HPMC[d]	0	7.1 ± 0.1c	0.54 ± 0.00a	0.998	0.84 ± 0.00d
	15	14.5 ± 1.2b	0.40 ± 0.01b	1.000	0.94 ± 0.05c
	22	21.1 ± 1.3a	0.36 ± 0.02c	0.999	1.09 ± 0.03ab
	28	22.5 ± 1.0a	0.35 ± 0.00c	0.999	1.15 ± 0.03a
Starch–κC[d,f]	0	6.3 ± 0.4c	0.43 ± 0.01a	0.995	0.46 ± 0.01c
	15	9.2 ± 0.0b	0.42 ± 0.00a	0.999	0.62 ± 0.00b
	22	13.0 ± 0.7a	0.36 ± 0.01b	0.995	0.68 ± 0.01a
	28	6.3 ± 0.4c	0.43 ± 0.01a	0.995	0.46 ± 0.01c
Starch–ιC[d,f]	0	6.0 ± 0.6c	0.51 ± 0.01a	1.000	0.64 ± 0.02c
	15	12.6 ± 0.1b	0.38 ± 0.00b	1.000	0.74 ± 0.00b
	22	17.4 ± 0.2a	0.34 ± 0.00c	0.997	0.81 ± 0.01a
	28	12.1 ± 0.8b	0.37 ± 0.01b	0.999	0.67 ± 0.01c
Starch–λC[d,f]	0	6.7 ± 0.2d	0.51 ± 0.00a	1.000	0.70 ± 0.01c
	15	15.2 ± 0.0b	0.37 ± 0.00c	1.000	0.85 ± 0.00b
	22	19.2 ± 0.1a	0.34 ± 0.00d	0.999	0.91 ± 0.01a
	28	10.7 ± 0.4c	0.40 ± 0.01b	1.000	0.69 ± 0.00c

[a] Mean values for 2 or 3 replicate measurements. Values sharing the same lowercase letters within columns of a given starch–hydrocolloid mixture are not significantly different at $p < 0.05$.
[b] Shear stress = K(shear rate)^n.
[c] At 100 s^{-1}.
[d] Starch–hydrocolloid ratio = 4.75%:0.25% (19:1, w/w). Total solids content = 5.0%.
[e] In 100 mM NaCl.
[f] κC, ιC, and λC are respective designations of kappa-, iota-, and lambda-type carrageenans.

G'' values were always less than the G' values, indicating that the gels were more solid-like than liquid-like. For the 4.75% starch-alone gel, the order of values at 1 rad/s were 28%- < 0%- < 15%- = 22%AM starch, with the curves for the 28%- and 0%AM starch gels coming together at lower frequencies and the highest frequency (10 rad/s), and the curves for the 15%- and 22%AM starch gels being superimposed. (This and the G' vs. angular frequency curves indicate that there was more similarity between these 2 starches than there were differences in AM content.) The presence of sodium alginate or CMC (2 hydrocolloids containing carboxylate groups) raised the curve for the 15%AM starch gel so that it was slightly higher than that of the 22%AM starch gel and the highest of the 4 curves. The curve for the 28%AM starch gel was below that of the 0%AM starch gel and the lowest of the 4 curves at low frequencies, but there was a crossover between 1 and 10 rad/s, putting the values for it between those of the 0%- and 22%AM starch gels at frequencies approaching 10 rad/s. When xanthan was present in the gel, the curves for all AM-containing starch gels were raised, with the curve for the 28%AM starch gel being raised the most to the point that the 3 curves for the AM-containing starch gels were superimposed, especially at lower frequencies. When HPMC was present in the gels, the curves for the 22%- and 28%AM starch gels were raised, that of the 28%AM starch gel again being raised the most. The result was that the curves were spread out, with that of the 28%AM starch gel being on top, followed in order by the curves for the 22%-, 15%-, and 0%AM starch gels. When guar gum was the added hydrocolloid, the curves for the gels of the 3 AM-containing starches were again raised, but in this case, the curve for the 28%AM

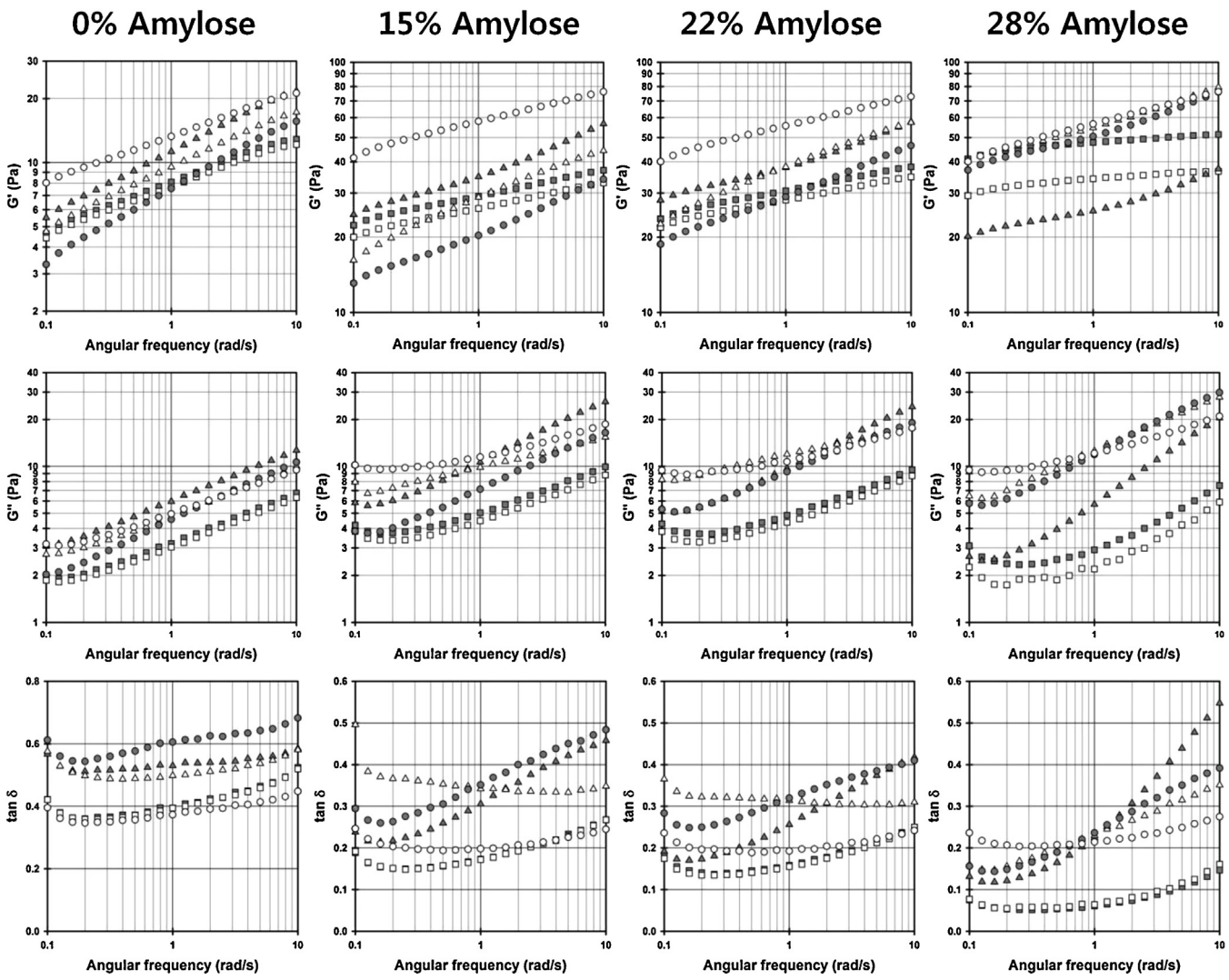

Fig. 1. Plots of dynamic rheological characteristics versus angular frequency of gels (obtained by holding the pastes produced in the RVA at room temperature (~22 °C) for 1 h) of rice starches and rice starch–hydrocolloid mixtures. Filled squares: rice starch alone (TS [total solid content] = 5.00%); open squares: rice starch alone (TS = 4.75%); filled triangles: rice starch–CMC(7H3SF) mixture (TS = 5.00%); open triangles: rice starch–guar gum(U) mixture (TS = 5.00%); filled circles: rice starch–HPMC(K100M) mixture (TS = 5.00%); open circles: rice starch–xanthan mixture (TS = 5.00%).

starch gel was below those of the 15%- and 22%AM starch gels at low frequencies and then crossed over the other 2 and was the highest curve above about 1 rad/s.

When $G' \gg G''$ and the 2 parameters are virtually frequency-independent, a network, such as an AM network, is suggested, while frequency dependence in a system in which $G' > G''$ over a broad range of frequencies suggests a system with molecular entanglements that behaves more like a liquid (higher tan δ) at lower frequencies and more like a solid (lower tan δ) at higher frequencies (Williams & Phillips, 2009). Only gels made with 0%AM rice starch + λC and with 15%- and 22%AM rice starch + guar gum displayed decreases in tan δ with increases in frequency and G' values that were somewhat greater than G'' values. For the 4.75% control starch paste, after a small initial drop with increasing frequency at low frequencies, tan δ values increased with increasing frequency. The 28%AM starch gel gave the lowest curve (lowest values). Above it was the curve for the 22%AM starch gel, and only very slightly above it was the curve for the 15%AM starch gel. These 3 curves were essentially parallel. Much higher was the curve for the 0%AM starch gel. The only changes in tan δ observed when xanthan was added were a slightly flatter curve for the 0%AM starch gel, slight increases in tan δ values for the 15%- and 22%AM starch gels, which curves were superimposed, and a greater increase in tan δ values for the 28%AM starch gel so that its curve was slightly above those of the other 2 AM-containing starch gels. Addition of HPMC raised all 4 curves, effected a greater increase in tan δ of the 15%- and 28%AM starch gels as the frequency increased, and made tan δ of the 28%AM starch gel almost the same as that of the 22%AM starch gel at 10 rad/s. Addition of sodium alginate had almost the same effect. Addition of CMC made the increase of the 28%AM starch gel as the frequency increased even steeper. It also made the curve for the 0%AM starch gel somewhat flatter, so that at 10 rad/s, tan δ values for the 28%- and 0%AM starch gels were close to each other. Addition of guar gum raised all 4 curves. In this case, the curves for the 15%- and 22%AM starch gels had a slight negative slope, and the tan δ values for the 28%AM starch gel increased more steeply as the frequency increased, so that the values for the 28%- and 15%AM starch gels were essentially the same as the frequency approached 10 rad/s. So it is indicated that all the hydrocolloids used reduced network formation involving AM, with perhaps CMC and ιC being the most effective and κC being the least effective. Perhaps, more than anything else, the different effects of the various hydrocolloids on gels of the 4 rice starches with different AM contents on the dynamic moduli as a function of angular frequency demonstrate

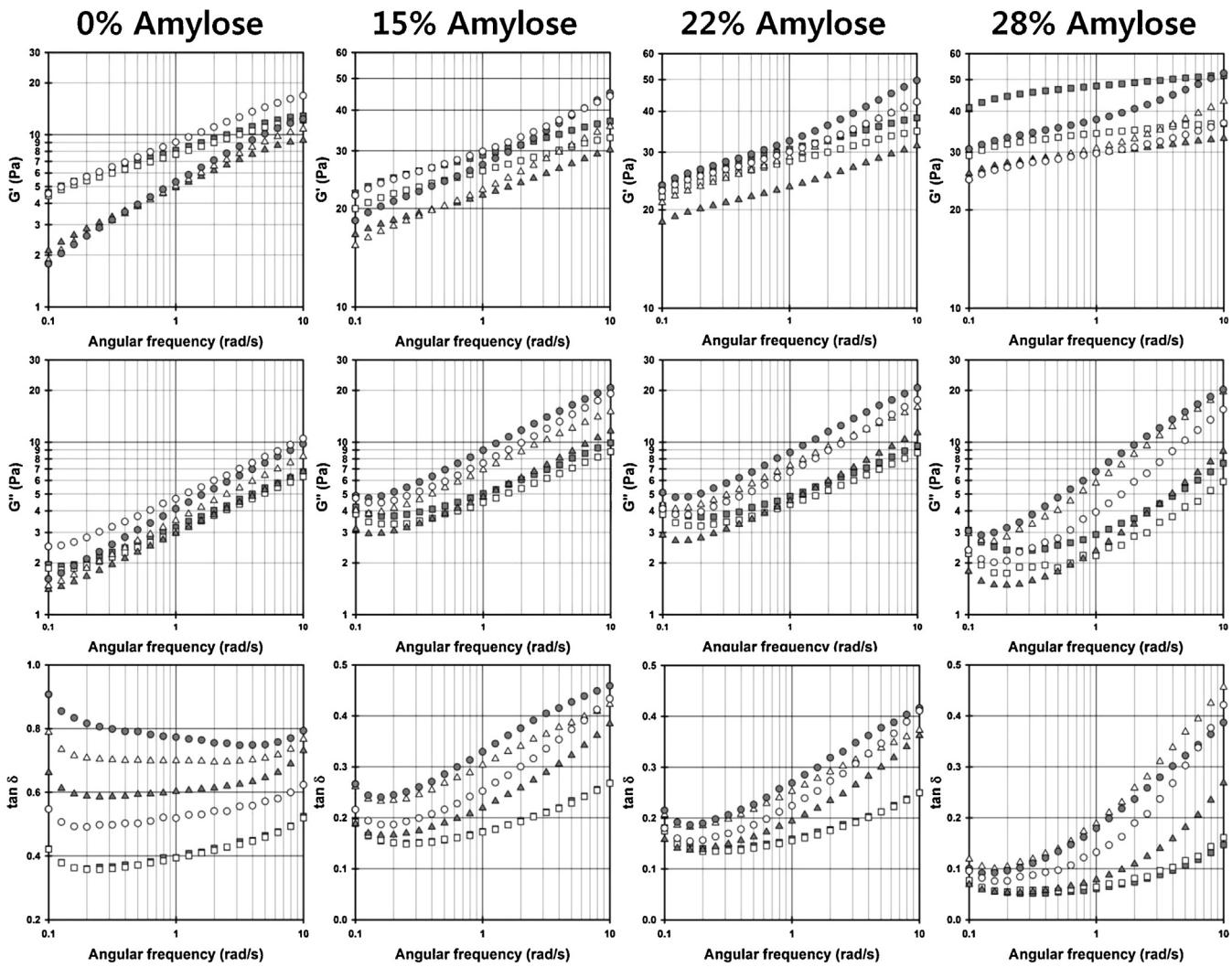

Fig. 2. Plots of dynamic rheological characteristics versus angular frequency of gels (obtained by holding the pastes produced in the RVA at room temperature (~22 °C) for 1 h) of rice starches and rice starch–hydrocolloid mixtures. Filled squares: rice starch alone (TS [total solid content] = 5.00%); open squares: rice starch alone (TS = 4.75%); filled triangles: rice starch–κ-carrageenan mixture (TS = 5.00%); open triangles: rice starch–ι-carrageenan mixture (TS = 5.00%); filled circles: rice starch–λ-carrageenan mixture (TS = 5.00%); open circles: rice starch–sodium alginate mixture (TS = 5.00%).

that each starch–hydrocolloid combination had unique properties.

Steady shear rheological properties (Table 4). In every case, the flow behavior index (n) was less than 1, indicating shear-thinning behavior. The only consistent pattern found in n values was that the 0%AM starch gels had the highest values, indicating that they were the least pseudoplastic. Three different patterns in K values were found. For the two control gels and the gels containing CMC, sodium alginate, κC, ιC, or λC, K increased as the AM content of the starch increased from 0% to 15%, increased again as the AM content increased from 15% to 22%, and then decreased as the AM content increased from 22% to 28%. For the gels containing guar gum or HPMC, K increased as the AM content of the starch increased from 0% to 15%, increased again as the AM content increased from 15% to 22%, and then was unchanged as the AM content increased from 22% to 28%. The presence of xanthan gave the third pattern, in which K increased as the AM content of the starch increased from 0% to 15%, was unchanged as the AM content of the starch increased from 15% to 22%, and decreased as the AM content increased from 22% to 28%. For the control pastes, apparent viscosity at 100 s^{-1} ($\eta_{a,100}$) was little changed as the AM content of the starch increased from 0% to 22%, but greatly reduced as the AM content increased from 22% to 28% to the point that the $\eta_{a,100}$ value for the 28%AM gel was considerably less than that the of 0%AM starch gel. Similar patterns were found for the rice starch–CMC and –alginate gels. When xanthan or guar gum was present, $\eta_{a,100}$ values for the 0%AM and 28%AM starch gels were the same. When HPMC was present, $\eta_{a,100}$ values increased steadily as the AM content of the starch increased from 0% to 28%. When κC or λC were present, $\eta_{a,100}$ increased as the AM content of the starch increased from 0% to 15%, increased to a lesser extent as the AM content of the starch increased from 15% to 22%, and then decreased considerably (to values equal to those given by the gels of the 0%AM starch) as the AM content of the starch reached 28%. When ιC was present, $\eta_{a,100}$ increased steadily as the AM content of the starch increased from 0% to 22%, then decreased as the AM content of the starch reached 28% (to a value only slightly greater than that given by the 0%AM starch gel).

Increasing values of $\eta_{a,100}$ in the presence of the hydrocolloids and the controls were in the orders (for the 0%AM starch): κC < 4.75% control < 5.00% control = ιC < λC < xanthan < HPMC < guar gum < sodium alginate < CMC; (for the 15%AM starch): 4.75% control < κC < 5.00% control < ιC < xanthan < λC < sodium alginate = guar gum < HPMC < CMC; (for the 22%AM starch): 4.75% control < κC = 5.00% control < ιC = xanthan < λC = sodium alginate < guar gum < CMC < HPMC; (for the 28%AM starch): 4.75% control < 5.00% control < κC < sodium alginate < ιC < λC < CMC =

xanthan < guar gum < HPMC, which reveals that the presence of any of 7 hydrocolloids increased $\eta_{a,100}$ values, the exception being κC, which reduced the values below those of both controls for the 0%AM starch and below that of the 5.00% control for the 15%AM starch. The effect of the two cellulosics (CMC and HPMC) on increasing $\eta_{a,100}$ was high, with the effect of CMC decreasing as the AM content increased and the effect of HPMC increasing the value as the AM content increased. The apparent viscosity in the presence of sodium alginate (an ionic polysaccharide similar in charge to CMC) was unchanged as the AM content of the starch increased from 0% to 22%, but decreased as the AM content increased from 22% to 28%. Guar gum was more effective than was xanthan in increasing $\eta_{a,100}$. The effectiveness of the carrageenans in increasing $\eta_{a,100}$ was in the order λC > ιC > κC.

4. Conclusions

The data revealed that the AM content of the starch was a greater determinate of paste and gel properties than was the added hydrocolloid (in a starch–hydrocolloid ratio of 19:1, w/w). RVA peak viscosity decreased as the AM content of the rice starch increased, whether or not a hydrocolloid was present, i.e., the presence of a hydrocolloid did not change the pattern of peak viscosity as a function of AM content. For most every rice starch–hydrocolloid combination, breakdown as recorded by the RVA increased over the control values, the principal exception being the starch–κC combinations. Only the presence of CMC or HPMC (the two cellulosics) changed the pattern of setback as a percent of final viscosity as a function of the AM content of the starch, which was that the values increased as the AM content of the starch increased from 0% to 22%, then decreased as the AM content increased from 22% to 28%. For most rice starch–hydrocolloid combinations, final η values were greater than those of the controls.

Gels of the controls and all rice starch–hydrocolloid combinations, except the starch–xanthan combinations, became more solid-like as the AM contents of the starches increased. For the controls and the rice starch–sodium alginate, –HPMC, –κC, and –λC combinations, tan δ values decreased steadily as the AM content increased. The other 4 hydrocolloids changed this pattern somewhat. With the exception of the CMC-28%AM rice starch gel, complex viscosity increased as the AM content of the starch increased. Values for G', G'', η^*, and tan δ for rice starch–guar gum composite gels all increased as the AM content of the starch increased. For rice starch–HPMC composite gels, G', G'', and η^* values increased as the AM content of the starches increased. For rice starch–carrageenan composite gels, G' and η^* values increased and tan δ values decreased as the AM content of the starch increased. All four dynamic rheology values were increased by the carrageenans in the order λC > ιC > κC.

It is likely that there are more differences between the starches in polymer and granular structures than the AM content, because unfortunately, the four rice starches did not have the same genetic background. This is most evident in the similarities in values between the 15%- and 22%AM starches. So we believe that it is possible, and very likely, that the average fine structures of the starch polymer molecules of the 4 rice starches used differed, which would give different properties to the granules and could result in different interactions with hydrocolloid molecules.

All 8 hydrocolloids increased RVA final η and $\eta_{a,100}$ values, not quite in identical orders, but in the general order κC < ιC, sodium alginate < λC, CMC < xanthan < guar gum < HPMC, the major difference being the position of CMC. (Two hydrocolloids separated by a comma is an indication that their order is variable.)

With the exception of the 0%-, 15%-, and 22%AM rice starch–xanthan combinations, tan δ values of the rice starch–hydrocolloid combinations were greater than those of the controls, indicating that the resulting gels were less solid-like.

G', G'', tan δ, and η^* values were increased when any of the carrageenan types were present in the order λC > ιC > κC.

It was concluded that two hydrocolloids containing carboxylate groups (CMC and sodium alginate) decreased the effects of increasing AM content and that the other 6 hydrocolloids increased the effects of increasing AM content, with the carrageenans being the least effective, the two neutral hydrocolloids (HPMC and guar gum) being the most effective, and the effect of xanthan being variable, i.e., in some cases it was less and in other cases more effective than the carrageenans, depending on the attribute being determined.

No two of the patterns of effects of the 8 hydrocolloids on the various parameters examined were the same. This result supports the conclusion that effects of hydrocolloids in starch–hydrocolloid systems depends on the specific starch–hydrocolloid combination as concluded (in order) by Fanta and Christianson (1996), Autio, Vesterinen, and Stolt (2002), Shi and BeMiller (2002), Yoo, Kim, and Yoo (2005), Song, Kim, and Shin (2008), and Chaudemanche and Budtova (2008). It also seems to provide evidence against general effects brought about by the presence of another water-soluble polymer, such as an increase in the effective concentration of starch molecules in the continuous phase, phase separation of the various polymer molecules, and association of swollen granules via depletion flocculation (BeMiller, 2011). Perhaps, more than one mechanism operates, and the degrees of participation of the mechanisms involved depends on the specific starch-specific hydrocolloid combination (including the viscosity grade/molecular weight of the hydrocolloid), probably the starch–hydrocolloid ratio, and possibly the overall concentration.

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