



Effects of hydrocolloids on the pasting and paste properties of commercial pea starch

Hyun-Seok Kim¹, James N. BeMiller*

Whistler Center for Carbohydrate Research, Department of Food Science, Purdue University, West Lafayette, IN 47907-2009, USA

ARTICLE INFO

Article history:

Received 31 August 2011

Received in revised form 18 January 2012

Accepted 19 January 2012

Available online 28 January 2012

Keywords:

Dynamic rheology

Hydrocolloids

Pea starch

RVA parameters

Starch–hydrocolloid composites

ABSTRACT

Twenty-one members of five families of hydrocolloids were used. Xanthan alone increased the temperature at which the rapid increase in viscosity was observed; all other hydrocolloids lowered the temperature of initiation of the rapid viscosity increase. Addition of all hydrocolloids (guar gum, methylcellulose (MC), sodium alginate, carboxymethylcellulose (CMC), xanthan) other than hydroxypropylmethylcellulose (HPMC) increased peak viscosities. Increases in final viscosities were generally more modest. Final viscosities increased with increasing MW for CMC and MC products. HPMC appeared to have an optimum size for increasing final viscosity. Both starch-alone and starch–hydrocolloid composite pastes exhibited gel-like characteristics. Addition of any of the hydrocolloids made the pastes/gels less solid-like. G' increased upon addition of increasing MW preparations of guar gum and HPMC. Both G' and G'' increased as the MW of CMC increased. Addition of the carrageenans increased peak and final viscosities, G' , G'' , $\tan \delta$, and η^* in the order $\lambda > \iota > \kappa$.

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1. Introduction

Because the inherent properties of native starches are undesirable/unsuitable for most food products, because many food processors would like to avoid using chemically modified starches in their products, and because it has been shown that combinations of starches and certain hydrocolloids improve the properties of starch-based foods, many studies have been conducted to attempt to determine the best hydrocolloid (both type and concentration) to use with a particular starch to achieve a particular result (e.g., increased or decreased viscosity, gel strength, or paste elasticity) and/or to determine the mechanism(s) producing the particular effect. As it has been shown that the interactions are specific for a particular starch and particular hydrocolloid combination (Autio, Vesterinen, & Stolt, 2002; Chaudemanche & Budtova, 2008; Fanta & Christianson, 1996; Shi & BeMiller, 2002; Song, Kim, & Shin, 2008), more than one mechanism may be involved.

In a review of starch hydrocolloid interactions, it was determined that studies of 21 different native starches had been reported in more than 150 basic research papers up to July 2010 (BeMiller, 2011). Only four of the papers covered a legume starch. Liu and Eskin (1998) examined combinations of pea starch and acetylated pea starch with locust bean gum and yellow mustard mucilage

(YMM) and reported that addition of the hydrocolloids resulted in an earlier onset of the viscosity increase (RVA) without any change in the gelatinization temperature and increases in the final viscosity. Liu, Eskin, and Cui (2006) further examined the interaction of YMM with pea starch and reported that the addition of YMM effected increases in peak viscosity, storage modulus (G'), loss modulus (G''), and dynamic viscosity (η^*) and decreased the loss tangent ($\tan \delta$) and granule swelling. Hongsprabhas, Israkarn, and Rattanawattanapakit (2007) studied the combination of mung-bean starch and sodium alginate and found that the hydrocolloid increased the time required to reach peak viscosity, increased peak and final viscosities, reduced setback, and affected the shear-thinning behavior of the starch pastes. They also found that protein migrated toward the outer surface of the starch granules during gelatinization. In addition, Lafargue, Lourdin, and Doublier (2007) studied the combination of modified pea starch and κ -type carrageenan with and without K^+ ions.

As field pea starch is now commercially available, a more thorough study of pea starch–hydrocolloid interactions is warranted. Ratnayake, Hoover, and Warkentin (2002) reviewed information available on the extraction, composition, structures, properties, and modified forms of smooth- and wrinkled-seeded field pea starches (see also Ratnayake, Hoover, Shahidi, Perera, & Jane, 2001). The supplying company of the yellow pea starch used in this study (Roquette Freres, Lestrem, France) provided the following information about the starch: amylose content, 35% (amylopectin content 65%); granule size, 5–35 μm ; swelling temperature, 70 °C; protein, 0.2%; fatty acids, 0.2%; ash, <0.1%; phosphorus, 0.05%; moisture, 14%; X-ray diffraction crystal type, C. Pea starch granules

* Corresponding author. Tel.: +1 765 494 5684; fax: +1 765 494 7953.

E-mail address: bemiller@purdue.edu (J.N. BeMiller).

¹ Department of Food Science and Biotechnology, Andong National University, 1375 Gyeongsong-ro, Andong-si, Gyeongsangbuk-do 760-749, Republic of Korea.

contain blocklets throughout (Ridout, Parker, Hedley, Bogracheva, & Morris, 2003, 2004). Ratnayake et al. (2002) concluded, from their review of the literature, that its high extent of retrogradation is a major negative factor in its widespread use in the food industry, an inherent property that might be alleviated by combining it with certain hydrocolloids in formulations. This study was conducted to determine the effects of hydrocolloids on the pasting and paste properties of commercial pea starch.

2. Materials and methods

2.1. Materials

Commercial field pea starch was obtained as a gift from Roquette Freres (Lestrem, France). Food-grade xanthan, was obtained as a gift from CPKelco (Atlanta, GA, USA) (Keltrol, 1400 mPa s (for 1% gum in 1% KCl)). Sodium carboxymethylcellulose (CMC) and guar gum were obtained as gifts from Hercules Inc. (Wilmington, DE, USA); types obtained and used are outlined in Table 1.

Methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) were obtained as gifts from Dow Chemical Co. (Midland, MI, USA); types obtained and used are outlined in Table 2.

Sodium alginate (400–600 mPa s, pH 6.0–8.0) was obtained as a gift from FMC BioPolymer (Girran, Ayrshire, UK). κ -, ι -, and λ -type carrageenans were obtained as gifts from FMC Biopolymer (Philadelphia, PA, USA).

2.2. Preparation of hydrocolloid solutions

All hydrocolloids were used as received. All hydrocolloid solutions were prepared as 0.448 wt.% solutions. Xanthan and guar gum were hydrated for 3 h at room temperature ($\sim 22^\circ\text{C}$) with vigorous stirring in reverse osmosis and distilled (ROD) water. Xanthan was also hydrated in a 1.0% (w/v) NaCl solution. Cellulose derivatives (i.e., MC, HPMC, CMC) were dissolved in ROD water at room temperature with vigorous stirring for 2 h. Sodium alginate and carrageenan (κ , ι , and λ) were dispersed independently in ROD water, and the dispersions were heated under constant stirring to 80°C for 30 min, during which time the solutions became clear. Upon completion of dissolution, the hot solutions were cooled in a water bath to room temperature ($\sim 22^\circ\text{C}$). 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 pea starch–hydrocolloid mixtures were analyzed using a Rapid ViscoAnalyzer (RVA-4V, Newport Scientific Pty. Ltd., Warriewood,

Australia). Pea starch (2.128 g, db) was added to an aluminum canister containing the hydrocolloid solution (25.0 g), after which the pea starch–hydrocolloid slurry was adjusted to 28.0 g by adding ROD water. The mixing ratio of pea starch to hydrocolloid was 19:1 (w/w); the total solids content was 8.0 wt.%. 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. 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 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 properties of starch alone were determined at total solid contents of 8.0 and 7.6 wt.% under the same conditions to elucidate the impact of both replacement of the starch and addition to the starch of hydrocolloids on the pasting and paste properties of the pea 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 ($\sim 22^\circ\text{C}$). The resultant paste (or gel) was loaded onto the platen of an ARES-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 0.63–62.8 rad/s at 1% strain (in the linear viscoelastic region as determined from preliminary strain sweep tests). Storage modulus (G') and loss modulus (G'') were obtained from TA rheometer Data Analysis Software (version 5.7.1) and used to calculate complex viscosity ($\eta^* = \sqrt{(G')^2 + (G'')^2}$) and loss tangent ($\tan \delta = G''/G'$). Two replicates of each mixture were run.

2.5. Experimental design and statistical analysis

The paste preparation was replicated at least twice for each pea 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 9.1 for Windows (SAS Institute, Cary, NC, USA). Experimental data were analyzed using Analysis of Variance (ANOVA) and expressed as mean values \pm standard deviations. Significant differences among experimental mean values were assessed using a least square difference (LSD) test ($\alpha < 0.05$).

3. Results and discussion

3.1. Pasting properties of the pea starch–hydrocolloid mixtures

None of the hydrocolloid solutions at the 0.448 wt.% concentration at which they were prepared gave any viscosity reading in the RVA instrument. (Their final concentrations in the RVA analyses were 0.4 wt.%.) It should also be noted that none of the hydrocolloids was used with any cations, other than xanthan being used with Na^+ ions.

Data obtained by RVA analysis from pea starch (7.6%)–hydrocolloid (0.4%) composite systems are given in Table 3. Considering apparent pasting temperature (app. T_p), i.e., the

Table 1
Carboxymethylcellulose (CMC) and guar gum preparations used.

Company designation	Our designation	Viscosity (mPa s)	DS
CMC			
CMC 7LF	CMC-LV	31 ^a	0.76
CMC 7MF	CMC-MV	490 ^a	0.74
CMC 7HF	CMC-HV	1860 ^b	0.83
CMC 7H3SF	CMC-H3S	2100 ^b	0.89
Guar gum			
Supercol K1	GG-LV	1380 ^c	
Supercol G2S	GG-MV	3850 ^c	
Supercol GF	GG-HV	4500 ^c	
Supercol U	GG-VHV	5100 ^c	

^a 2 wt.% aqueous solution at 25°C .

^b 1 wt.% aqueous solution at 25°C .

^c 1 wt.% aqueous solution at 25°C after 2 h hydration.

Table 2
Methylcellulose (MC) and hydroxypropylmethylcellulose preparations used.

Company designation	Our designation	Viscosity (mPa s) ^a	Methyl (%)	Hydroxypropyl (%)
MC				
Methocel A15	MC-LV	17	30.1	
Methocel A4M	MC-MV	5440	30.1	
Methocel A40M	MC-HV	39,979	30.6	
HPMC				
Methocel F50	HPMC-LV	45	28.8	6.1
Methocel F4M	HPMC-MV1	5020	27.5	6.6
Methocel K4M	HPMC-MV2	5364	23.4	8.9
Methocel K100M	HPMC-HV	116,640	23.3	9.8
Methocel SX ^b	HPMC-SX	109	^c	^c

^a 2 wt.% in water 20 °C.

^b Sulfate ash 0.4%.

^c Not reported.

temperature of initiation of the rapid viscosity increase observed with the RVA instrument, only xanthan effected an increase, regardless of the presence of NaCl. Others that reported that xanthan delayed the rapid viscosity increase were Pongsawatmanit and Srijunthongsiri (2008) (tapioca starch) and Weber, Clerici, Collares-Queiroz, and Chang (2009) (waxy maize starch (WMS)). An increase in the temperature of the initiation of the rapid viscosity increase is consistent with the inhibition of granule swelling found with other starches (Abdulmola, Hember, Richardson, & Morris, 1996 (WMS); Chaisawang & Supphantharika, 2006 (tapioca

starch); Gonera & Cornillion, 2002 (NMS, WMS, potato starch); Sekine, 1996). The other hydrocolloids reduced the app. T_p , the approximate order of effectiveness being MC > HPMC > CMC > Na alginate > guar gum > carrageenans. A lowering of the temperature of initiation of the rapid viscosity increase was first reported by Bean and Yamazaki (1978) (CMC; wheat starch), followed (in order) by Christianson, Hodge, Osborne, and Detroy (1981) (CMC and guar gum; wheat starch), Alloncle, LeFebvre, Llamas, and Doublier (1989) (guar gum; normal maize and wheat starches), Sudhakar, Singhal, and Kulkarni (1996) (guar gum; normal maize

Table 3
RVA pasting and paste characteristics of pea starch–hydrocolloid mixtures.

Sample ^a	Peak viscosity (mPa s)	Final viscosity (mPa s)	Breakdown (%) ^b	Setback (%) ^c	"Pasting temp." (°C) ^d
Pea starch					
(8.0%) ^e	2025(31) ^f	3607(90)	20	122	73.9(0.5)
(7.6%) ^g	1670(27)	2979(39)	12	102	74.3(0.1)
Xanthan					
(water)	2056(38)	3125(55)	7.1	64	77.7(1.2)
(1% NaCl)	2883(5)	3505(13)	24	59	79.9(0.0)
Na alginate					
	2966(7)	4332(31)	22	86	71.91(1.1)
CMC					
LV	1913(6)	3441(37)	7.9	95	70.7(0.6)
MV	2466(17)	4000(28)	19	101	71.6(0.4)
HV	2833(16)	4179(24)	15	73	70.2(0.0)
H3S	2862(33)	4160(35)	11	64	73.9(0.5)
Carrageenan					
κ-	1856(23)	3277(57)	9.2	94	73.0(0.6)
ι-	2134(30)	3549(56)	16	98	72.7(1.2)
λ-	2425(23)	3712(6)	5.3	60	73.5(0.0)
Guar gum					
LV	3080(54)	4297(74)	31	101	69.8(0.6)
MV	3278(23)	4334(27)	32	95	72.7(1.1)
HV	3266(9)	4263(17)	35	100	71.8(0.0)
VHV	3373(42)	4343(73)	35	98	72.3(0.6)
MC					
LV	2147(57)	3302(34)	17	86	69.3(0.0)
MV	3301(146)	4471(224)	17	62	68.7(0.0)
HV	3196(158)	4945(333)	14	79	68.4(0.5)
HPMC					
LV	1703(8.5)	2624(17)	4.4	61	71.0(0.0)
MV1	1842(11)	3912(30)	9.8	135	69.7(0.5)
MV2	1821(17)	3934(48)	17	161	70.2(1.1)
HV	1629(7)	4294(105)	3.3	173	69.8(0.6)
SX	1578(38)	2795(43)	6.4	89	70.2(1.1)

^a See Section 2.1. Total polysaccharide = 8.0 wt.% (db). Starch–hydrocolloid ratio = 19:1 (w/w).

^b Percent loss of peak viscosity.

^c Percent increase over trough viscosity.

^d Temperature of initial rapid viscosity increase recorded by the instrument.

^e Same total polysaccharide content as in starch–hydrocolloid mixtures.

^f Numbers in parentheses are standard deviations.

^g Percent starch without added hydrocolloid.

starch (NMS)), Funami et al. (2005a) (guar gum as a function of molecular weight; normal, waxy, and amylo maize starches), and Sikora, Kowalski, and Tomasik (2008) (xanthan; normal maize, potato, tapioca, and oat starches in a generally concentration-dependent manner), and Sikora, Tomasik, and Krystyan (2010) (guar gum and κ - and λ -type carrageenans; potato starch). In order, Christianson et al. (1981), Christianson (1982) (guar gum, xanthan, CMC; normal maize and wheat starches), Sajjan and Rao (1987) (guar and locust bean gums, xanthan; wheat starch), Alloncle et al. (1989), Bahanassey and Breene (1994) (guar and locust bean gums, xanthan, gellan, konjac flour; normal maize, waxy maize, wheat, tapioca, and amaranth starches), Eidam, Kulicke, Kuhn, and Stute (1995) (guar and locust bean gums, xanthan, CMC, κ - and ι -type carrageenans; NMS), Abdulmola et al. (1996) (xanthan; WMS, crosslinked WMS), Liu and Eskin (1998) (locust bean gum, yellow mustard mucilage; pea and acetylated pea starch), Shi and BeMiller (2002) (guar gum, xanthan, CMC, HPMC, sodium alginate, κ - and ι -type carrageenans; normal and waxy maize, wheat, potato, tapioca, normal and waxy rice starches), Freitas, Gorin, Neves, and Sierakowski (2003) (galactoxyloglucan; waxy and amylo maize starches), Funami et al. (2005a), Liu et al. (2006) (yellow mustard mucilage; pea and buckwheat starches), and Funami et al. (2008) (fenugreek gum; NMS) all concluded that the earlier onset of rapid viscosity increase (app. T_p) was due to associations between leached starch molecules (primarily amylose) and hydrocolloid molecules. Alternatively or in addition, the observed results could be due to an increase in viscosity of the continuous phase as a result of an increasing concentration of the hydrocolloid in the continuous phase as a result of increased hydration and swelling of the starch granules as the temperature increases as proposed (in order) by Alloncle et al. (1989), Liu and Lelievre (1992) (gellan, locust bean gum + gellan; rice starch), Lai, Huang, and Lii (1999) (κ - and ι -type carrageenans, agarose; rice starch), Liu, Eskin, and Cui (2003) (yellow mustard mucilage; wheat and rice starches), Mandala, Michon, and Launay (2004) (xanthan; wheat starch), Yoo, Kim, and Yoo (2005) (guar and locust bean gums; rice starch), Rodríguez-Hernández, Durand, Garnier, Tecante, and Doublier (2006) (deacylated gellan + Ca^{2+} ; WMS), Huang, Kennedy, Li, Xu, and Xie (2007) (κ -type carrageenan, konjac glucomannan, high-acyl gellan; rice and waxy rice starches), Lafargue et al. (2007) (κ -type carrageenan + K^+ ; modified pea starch), Achayuthankan and Supphantharika (2008) (guar gum, xanthan; WMS), Chaudemanche and Budtova (2008) (κ -type carrageenan; NMS), and Savary, Handschin, Conde-Petit, Cayot, and Doublier (2008) (κ -type carrageenan, LM-pectin; modified WMS). However, Abdulmola et al. (1996) concluded that, in a system containing either native or crosslinked WMS plus xanthan, the observed increase in dynamic moduli could not be completely explained by an increase in the hydrocolloid concentration in the continuous phase and speculated that depletion flocculation might be at least part of the reason for the increase. Weber et al. (2009) reported that guar gum delayed pasting of normal maize starch in a concentration-dependent manner.

Addition of all viscosity grades of guar gum gave considerable increases in peak viscosity (1.8–2.0 \times that of the 7.6% starch-alone paste), with only a modest increase with increase in viscosity grade (i.e., molecular weight (MW)) of the gum (Table 4). An increase in peak viscosity upon addition of guar gum was previously reported by Alloncle et al. (1989), followed (in order) by Alloncle and Doublier (1991) (NMS), Bahanassey and Breene (1994), Sudhakar et al. (1996), Korus, Juszczak, Witczak, and Achremowicz (2004) (triticale starch), Chaisawang and Supphantharika (2006) (tapioca starch), Achayuthankan and Supphantharika (2008), Song et al. (2008) (NMS and wheat starch), and Huang (2009) (potato, yam, yam bean, sweet potato, and taro starches). Funami et al. (2005a) reported that the peak viscosity increased as the molecular weight

Table 4

Selected values for pasting and paste properties obtained using 7.6 wt.% pea starch and 0.4 wt.% hydrocolloid (19:1, w/w) divided by those obtained using 7.6 wt.% starch alone.

Hydrocolloid ^a	Peak viscosity	Final viscosity	G'	G''	Tan δ	η^*
Xanthan						
(water)	1.23	1.05	1.28	1.45	1.12	1.28
(1% NaCl)	1.73	1.18	1.37	1.79	1.30	1.37
Na alginate	1.78	1.45	1.10	1.38	1.25	1.10
CMC						
LV	1.15	1.16	0.96	1.17	1.21	0.96
MV	1.48	1.34	1.09	1.26	1.16	1.09
HV	1.70	1.40	1.13	1.54	1.37	1.13
H3S	1.71	1.40	1.21	1.61	1.33	1.21
Carrageenan						
κ -	1.11	1.10	0.99	1.14	1.16	0.99
ι -	1.28	1.19	1.11	1.28	1.14	1.12
λ -	1.45	1.25	1.16	1.55	1.33	1.16
Guar gum						
LV	1.84	1.44	1.33	2.10	1.56	1.34
MV	1.96	1.45	1.44	2.19	1.51	1.44
HV	1.95	1.43	1.47	2.12	1.44	1.47
VHV	2.02	1.46	1.46	2.12	1.44	1.68
MC						
LV	1.28	1.11	0.85	1.11	1.30	0.85
MV	1.98	1.50	1.56	2.97	1.89	1.57
HV	1.91	1.66	1.80	3.91	2.16	1.81
HPMC						
LV	1.02	0.88	0.94	1.38	1.47	0.94
MV1	1.09	1.32	1.04	2.10	2.02	1.05
MV2	0.98	1.44	1.07	2.00	1.82	1.07
HV	0.94	0.94	1.26	3.03	2.40	1.27
SX	1.10	1.31	1.02	1.53	1.49	1.02

^a See Section 2.1.

of the guar gum increased. Thus, the effect of guar gum on pea starch peak viscosity was congruent with the effect of guar gum on the peak viscosities of both cereal and other non-cereal starches.

Addition of the medium-viscosity (MV) grade of methylcellulose (MC) produced essentially the same increase in peak viscosity as guar gum (2.0 \times), with addition of the high-viscosity (HV) grade producing only slightly less (1.95 \times), while addition of the low-viscosity (LV) grade produced much less (1.3 \times); so in the case of MC, there seems to be an optimum molecular size for increasing peak viscosity. An increase in peak viscosity affected by the addition of MC was also reported by Techawipharat, Supphantharika, and BeMiller (2008) (rice and waxy rice starches).

Sodium alginate was next most effective in increasing peak viscosity (1.8 \times), followed closely by xanthan in 1% NaCl (1.8 \times), while xanthan in water effected a smaller increase (1.2 \times). An increase in peak viscosity upon addition of sodium alginate was reported by Hongsprabhas et al. (2007) (mungbean starch). Lee, Baek, Cha, Park, and Lim (2002) (sweet potato starch) reported a general increase in paste viscosity upon addition of sodium alginate. Those that reported an increase in peak viscosity upon addition of xanthan were (in order) Bahanassey and Breene (1994), Mali et al. (2003) (yam starch), Chaisawang and Supphantharika (2006), Achayuthankan and Supphantharika (2008) (WMS), and Sikora et al. (2008) (NMS and tapioca starch). Viturawong, Achayuthakan, and Supphantharika (2008) reported that addition of xanthan to rice starch increased the peak viscosity, both in the presence and absence of salts, and that the effect was more pronounced with increasing molecular weight of the xanthan. A decrease in peak viscosity upon addition of xanthan was first reported by Song, Kwon, Choi, Kim, and Shin (2006) (rice starch), followed (in order) by Song et al. (2008) and Weber et al. (2009). Weber et al. (2009) reported that xanthan had no effect on the peak viscosity of WMS.

Addition of CMC gave a range of peak viscosity increases ($1.15\text{--}1.7\times$), with its effectiveness increasing with increases in viscosity type/MW. That addition of CMC increased peak viscosity was also reported by Christianson et al. (1981) and Techawipharat et al. (2008). The effectiveness of carrageenans in increasing peak viscosity was in the order $\lambda\text{-type} > \iota\text{-type} > \kappa\text{-type}$. The same pattern of increasing peak viscosity was reported by Techawipharat et al. (2008). Addition of hydroxypropylmethylcellulose (HPMC) had essentially no effect on peak viscosity ($1.0\text{--}1.1\times$). Techawipharat et al. (2008) reported that HPMC decreased the peak viscosity of rice and waxy rice starches.

The greatest increase in final viscosity was given by addition of the HV grade of MC ($1.7\times$), followed by addition of the MV grade ($1.5\times$). The LV grade of MC produced only a small increase in final viscosity ($1.1\times$). An increase in final viscosity upon addition of MC was also reported by Techawipharat et al. (2008). This result could be related to the thermogelation property of MC. Addition of sodium alginate, one of the MV grades of HPMC, and guar gum (all 4 viscosity grades) produced the same increase in final viscosity (ca. $1.45\times$). The other MV grade of HPMC increased the final viscosity $1.3\times$, while the LV and HV grades decreased it slightly ($0.9\times$), so it appeared that there might be an optimum viscosity grade/MW of HPMC for increasing the final viscosity of pea starch pastes. An increase in final viscosity upon addition of sodium alginate was reported by Hongsprabhas et al. (2007). A decrease in final viscosity upon addition of HPMC was reported by Techawipharat et al. (2008). Increases in final viscosity upon addition of guar gum were reported (in order) by Alloncle and Doublier (1991), Sudhakar et al. (1996), Chaisawang and Supphantharika (2006), Achayuthankan and Supphantharika (2008), Huang (2009), and Weber et al. (2009). In order, Lee et al. (2002), Mali et al. (2003), and Juszczak, Witczak, Fortuna, and Banachowicz (2004) (rye starch) reported general increases in paste viscosity. Mali et al. (2003) also reported that guar gum was more effective than xanthan in increasing peak viscosity, congruent with this work. Final viscosity increased with addition of increasing viscosity grades of CMC ($1.2\text{--}1.4\times$). An increase in final viscosity upon addition of CMC was reported by Techawipharat et al. (2008). The effectiveness of the carrageenans in increasing final viscosity was in the order $\lambda\text{-type} > \iota\text{-type} > \kappa\text{-type}$. The same effect was reported by Techawipharat et al. (2008). Addition of xanthan in a water system increased the final viscosity only slightly ($1.05\times$); xanthan in 1% NaCl increased it a little more ($1.2\times$). Increases in final viscosity upon addition of xanthan were reported (in order) by Brennan et al. (2006) (WMS), Chaisawang and Supphantharika (2006), Viturawong et al. (2008), and Achayuthankan and Supphantharika (2008). General increases in paste viscosity upon addition of xanthan were reported (in order) by Mali et al. (2003), Korus et al. (2004), and Song et al. (2006), while decreases in paste viscosity were reported by Lee et al. (2002) and Weber et al. (2009). Weber et al. (2009) also reported that addition of xanthan had no effect on the final viscosity of WMS. Our and other information leads to the conclusion that addition of xanthan has little and a variable effect on final viscosity of pea starch pastes.

3.2. Dynamic rheological properties of pea starch–hydrocolloid pastes/gels

Dynamic rheological parameters of pastes/gels made from pea starch–hydrocolloid mixtures (total polysaccharide concentration 8%; starch–hydrocolloid ratio (19:1, w/w) compared to the same parameters for pastes/gels made from pea starch alone (7.6%) are given in Table 4. The data used to construct Table 4 are given in Table 5.

Addition of HPMC, except for the HV grade ($1.3\times$), changed the storage modulus (G') very little ($0.9\text{--}1.1\times$), but what change there was increased with increasing viscosity grade/MW.

Increases in G' upon addition of the carrageenan products were in the order $\lambda\text{-type} > \iota\text{-type} > \kappa\text{-type}$. Addition of CMC-LV did not change G' ; the other CMC products increased it slightly as a function of increasing MW ($1.1\text{--}1.2\times$). Addition of MC-LV resulted in a decrease in G' ($0.85\times$), while MC-MV ($1.6\times$) and MC-HV ($1.8\times$) substantially increased it as a function of MW, indicating that any synergistic interaction between starch molecules and MC molecules is dependent on the average molecular weight of the MC. Addition of guar gum increased G' $1.5\text{--}1.3\times$ in the order $\text{VHV} = \text{HV} > \text{MV} > \text{LV}$. Increases in G' upon addition of guar gum were first reported by Alloncle and Doublier (1991) (fresh NMS pastes), followed (in order) by Yoo et al. (2005), Kim, Lee, and Yoo (2006) (rice starch), and Choi and Yoo (2008) (sweet potato starch), while Biliaderis, Arvanitoyannis, Izydorczyk, and Prokopowich (1997) found that addition of guar gum had no effect on the rheology of wheat starch gels. Increases in G' were also found upon addition of xanthan ($1.3\text{--}1.4\times$) and sodium alginate ($1.1\times$). Increases in G' upon addition of xanthan were previously reported (in order) by Abdulmola et al. (1996), Kim and Yoo (2006) (rice starch), Chaisawang and Supphantharika (2006), Wang et al. (2009) (WMS), Choi and Yoo (2009) (sweet potato starch), and Kim, Lee, and Yoo (2009) (waxy rice starch).

Addition of all 21 hydrocolloid preparations increased the loss modulus (G'') $1.1\text{--}3.9\times$, the two extremes being the LV and MV types of MC. Increases in G'' paralleled increases in MW (viscosity grade) only for CMC ($1.2\text{--}1.6\times$) and MC ($1.1\text{--}3.9\times$). Increases in G'' upon addition of guar gum were reported (in order) by Yoo et al. (2005), Kim et al. (2006), and Choi and Yoo (2008) and upon addition of xanthan by Kim and Yoo (2006), Wang et al. (2009), Choi and Yoo (2009), and Kim et al. (2009). The order of increases in G'' upon addition of carrageenans was $\lambda\text{-type} > \iota\text{-type} > \kappa\text{-type}$.

In every case, increases in G'' were greater than were increases in G' , so the loss tangent ($\tan \delta$) increased, indicating that the cooled pastes were more liquid-like after hydrocolloid addition. $\tan \delta$ increased with increasing viscosity grade only for MC ($1.3\text{--}2.2\times$). An increase in $\tan \delta$ upon addition of MC, CMC, and HPMC was reported by Techawipharat et al. (2008) (rice starch) and upon addition of guar gum by Kulicke, Eidam, Kath, Kix, and Kull (1996) (waxy rice starch) and Nagano, Tamaki, and Funami (2008) (NMS). Little or no effect on $\tan \delta$ upon addition of guar gum was reported by Choi and Yoo (2008) and upon addition of CMC and MC by Techawipharat et al. (2008) (waxy rice starch). Decreases in $\tan \delta$ values upon addition of xanthan were reported (in order) by Chaisawang and Supphantharika (2006), Wang et al. (2009), and Choi and Yoo (2009), indicating that addition of xanthan made the starch gels more solid-like.

In this work, the increases in $\tan \delta$ resulting from carrageenan addition were in the order $\lambda\text{-type} > \iota\text{-type} > \kappa\text{-type}$ ($1.3\text{--}1.2\times$). Techawipharat et al. (2008) reported that all 3 types of carrageenan increased $\tan \delta$ values of rice starch gels, but had no effect on $\tan \delta$ values of waxy rice starch gels. In every case, G'' values were much less than G' values, giving $\tan \delta$ values that were much smaller than 1 (0.057 for the control 7.6% paste and 0.064 (addition of xanthan in water)) to 0.123 (addition of MC-HV), indicating that the 7.6% pea starch paste was much more solid-like than liquid-like and that addition of any of the hydrocolloids made the paste somewhat less solid-like, which is consistent with the fact that increases in G'' were always greater than increases in G' . Eidam et al. (1995), Ahmad and Williams (2001) (guar and locust bean gums; sago starch), Funami et al. (2005a), Funami et al. (2005b) (guar gum; normal, waxy, and amylo maize starches), Yoo et al. (2005), Kim et al. (2006), Nagano et al. (2008), and Ravindran and Matia-Merino (2009) (fenugreek gum; normal maize starch). Alloncle and

Table 5

Dynamic rheology parameters of pea starch hydrocolloid composite pastes at 6.28 rad/s.

Sample ^a	G' (Pa) ^b	G'' (Pa) ^b	η^* (Pa s) ^b	$\tan \delta^b$
Pea starch (water)				
(8.0%) ^c	1617(87)i	86.7(5.1)n	257.7(14.0)h	0.054(0.001)r
(7.6%) ^d	1393(33)op	78.9(0.1)o	222.1(5.2)no	0.057(0.001)q
Pea starch (1% NaCl)				
(8.0%) ^c	1343	88.6	214.2	0.066
+Xanthan				
(water)	1783(12)f	114.4(0.8)i	284.3(1.9)f	0.064(0.000)p
(1% NaCl)	1904	141	303.9	0.074
+Na alginate	1536(52)kl	108.5(0.2)j	245.2(8.2)ijk	0.071(0.002)m
+CMC				
LV	1341(6)q	92.6(1.3)l	213.9(1.0)op	0.069(0.001)n
MV	1515(38)l	99.8(4.1)k	241.7(6.0)jkl	0.066(0.004)o
HV	1575(30)j	121.8(5.2)h	251.4(4.7)hi	0.078(0.005)j
H3S	1681(17)h	127.4(4.6)g	268.4(2.8)g	0.076(0.002)k
+Carrageenan				
κ -	1375(47)p	90.1(4.2)lm	219.3(7.5)no	0.066(0.001)o
ι -	1553(35)jk	101.2(2.5)k	247.7(5.7)ij	0.065(0.000)op
λ -	1614(36)i	122.3(3.6)h	257.6(5.7)h	0.076(0.001)k
+Guar gum				
LV	1859(5)e	165.9(3.4)e	297.0(0.8)e	0.089(0.001)f
MV	2007(13)d	172.8(1.0)d	320.5(2.1)d	0.086(0.001)g
HV	2050(11)c	167.5(4.8)e	327.3(1.7)d	0.082(0.002)i
VHV	2037(33)c	167.0(0.6)e	372.4(61.5)b	0.082(0.001)i
+MC				
LV	1188(23)s	87.3(3.6)mn	189.6(3.7)q	0.074(0.002)l
MV	2173(9)b	234.3(5.1)c	347.8(1.6)c	0.108(0.001)d
HV	2502(91)a	308.7(11.7)a	401.2(14.6)a	0.123(0.000)b
+HPMC				
LV	1307(26)r	109.0(1.8)j	208.8(4.0)p	0.084(0.001)h
MV1	1450(25)n	165.6(5.6)e	232.2(4.0)lm	0.115(0.002)c
MV2	1484(26)m	157.8(4.4)f	237.5(4.1)kl	0.104(0.001)e
HV	1750(22)g	239.2(10.2)b	281.0(3.7)f	0.137(0.004)a
SX	1414(1)o	120.4(1.6)h	225.9(0.2)mn	0.085(0.001)g

^a See Section 2.1. Total polysaccharide = 8.0 wt.% (db) except for the 7.6 wt.% starch control. Starch–hydrocolloid ratio = 19:1 (w/w).^b Mean values of 2 or 3 measurements. Values sharing the same lower-case letters within a column are not significantly different ($p < 0.05$). Numbers in parentheses are standard deviations.^c Same total polysaccharide content as in starch–hydrocolloid mixtures.^d Percent starch without added hydrocolloid.

Doublier (1991) suggested that less firm/rigid gels were due to the increased viscosity of the continuous phase which inhibited phase separation between amylose and amylopectin molecules, resulting in less amylose molecules in the gel network. Those who concluded that interactions between hydrocolloid molecules and amylose molecules interfered with network formation and, hence, resulted in weaker gels were (in order) Kim and D'Appolonia (1977) (wheat flour pentosans; wheat flour), Kohyama and Nishinari (1992) (CMC; normal maize starch), Ferrero et al. (1993a,b) (xanthan; normal maize starch), Eidam et al. (1995), Biliaderis et al. (1997) (guar gum, xanthan, arabinoxylan, β -glucan; waxy maize and wheat starches), Mali et al. (2003), Funami et al. (2005a,b), Temsiripong, Pongsawatmanit, Ikeda, and Nishinari (2005) (xyloglucan; tapioca starch), Yoo et al. (2005), Kim et al. (2006), Tan, Li, Li, Dong, and Qin (2008) (soluble soybean polysaccharides), Weber, Queiroz, and Chang (2008) (guar gum, xanthan; normal, waxy, and amylomaize starches), and Pongsawatmanit and Srijunthongsiri (2008).

Addition of the κ -type carrageenan did not change the complex viscosity (η^*), while the ι - and λ -types increased it in the order λ -type ($1.2\times$) > ι -type ($1.1\times$). Addition of MC-LV, HPMC-LV, and CMC-LV reduced η^* . Since the starch concentration was constant, reduced viscosity would indicate prevention of starch polymer, especially amylose, molecular associations by the hydrocolloid molecules. All other hydrocolloid additions increased η^* , with all products available in different viscosity grades (CMC, guar

gum, MC, HPMC) increasing η^* as MW increased. An increase in η^* upon addition of xanthan was also reported by Choi and Yoo (2009), while Yoo et al. (2005) reported a decrease in η^* upon addition of guar gum.

4. Summary

The objective of this study was to determine interactions of commercial field pea starch with hydrocolloids and effects of molecular weight (MW) of the hydrocolloids on pasting and paste parameters. Commercial pea starch and 5 families of hydrocolloid products were used in a 19:1 (w/w) ratio. None of the hydrocolloids used in this study produced detectable RVA viscosity when used without starch in the same concentration used in the combinations. Only did addition of xanthan delay the apparent pasting, i.e., increase the apparent pasting temperature (app. T_p); addition of xanthan (in water) also produced less breakdown and setback, phenomena attributed to the inhibition of granule swelling and maintenance of granule integrity as found when xanthan was mixed with other starches. All other hydrocolloids decreased app. T_p in the approximate order MC > HPMC > CMC > Na alginate > guar gum > the carrageenans, a phenomenon consistent with an association of leached starch molecules and hydrocolloid molecules as proposed for other starches.

Four viscosity types of guar gum (a neutral gum) were used. All types produced considerable increases in peak and final viscosities, with only modest increases with increases in MW. Three viscosity types of methylcellulose (MC) (also a neutral hydrocolloid), all possessing the same methyl ether content (30.1–30.6%), were used. The largest increase in peak viscosity was given by the MV type of MC, indicating an optimum molecular size for this phenomenon. Increases were seen in peak and final viscosities as the MW of the MC increased, probably due to thermal thickening. Sodium alginate increased the final viscosity as much as did guar gum and was third most effective in increasing the peak viscosity. Increases in peak and final viscosities as the MW increased were also found for CMC addition. The five types of hydroxypropylmethylcellulose (HPMC) with different amounts and ratios of methyl and hydroxypropyl ether groups had used little effect on peak or final viscosities, with the exception of the two MV types, which increased final viscosities 1.3× and 1.4×, while having no effect on peak viscosities, indicating that there might be an optimum MW of HPMC for increasing the final viscosity of a pea starch paste. The effectiveness of the carrageenans in increasing peak viscosity was in the order λ -type > ι -type > κ -type.

It is concluded that the enhanced viscosities observed for the starch–hydrocolloid composite pastes (except for the lowest viscosity types) indicate synergistic effects between pea starch and the hydrocolloids that increased the peak viscosity more than 1.5× (1.7–2.0×) roughly in the order guar gum (all MWs) = MC (higher MWs) > Na alginate > CMC (higher MWs) > xanthan in 1% NaCl. Increases in final viscosity were generally more modest, with MC (MV and HV types) > guar gum (all MWs) = Na alginate > CMC (MV and HV types) = HPMC (MV types) > λ -type carrageenan increasing it 1.6–1.25×; the other types of carrageenan and xanthan increased it less.

All 21 hydrocolloid preparations increased G' and $\tan \delta$, and all starch-alone and starch–hydrocolloid composite pastes exhibited gel-like characteristics ($G' \gg G''$, $\tan \delta < 1$), with those containing a hydrocolloid being less solid-like, i.e., less structured, probably due to interactions between amylose and hydrocolloid molecules that inhibit network formation by amylose molecules. An increase in MWs of the hydrocolloids, except for guar gum, enhanced dynamic rheology attributes (G' , G'' , η^* , $\tan \delta$) of the composite pastes.

All CMCs (except for the product producing the least viscosity) increased G' 1.1–1.2×; and for all CMC products, G'' of the composite pastes relative to starch-alone pastes was 1.2–1.6× greater, with both parameters increasing with increasing viscosity grade of the CMC, indicating that the pastes became more liquid-like as the MW of the hydrocolloid increased. G' and G'' also increased with increasing MW of MC. Addition of guar gum increased G' 1.5–1.3× in the order VHV = HV > MV > LV. The order of increases in G' , G'' , and $\tan \delta$ for the carrageenans was λ -type > ι -type > κ -type.

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