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Impact of A/B-type granule ratio on reactivity, swelling, gelatinization, and pasting properties of modified wheat starch. Part I: Hydroxypropylation

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ABSTRACT

The impact of granule type (A/B-type granule ratio) on the reactivity and physical properties of chemically-modified wheat starch was investigated. Waxy and normal wheat starches were fractionated into highly-purified A- and B-type granule fractions, and reconstituted into fractions possessing pre-defined A/B-type granule ratios (weight basis). Starch granule fractions were derivatized with either propylene oxide (PO) or PO analog (POA), and assessed with respect to molar substitution (MS), swelling, gelatinization, and pasting properties. For POA (MS < 0.025) and PO (MS $\approx$ 0.1) starch derivatives, no differences in the relative reactivities of A-type and B-type granules or among the reconstituted wheat starches of varied A/B-type granule contents were observed within a genotype. Despite the similar reactivities of reconstituted wheat starch fractions possessing varied A/B-type granule contents, variations in swelling, gelatinization, and pasting properties were observed across the modified reconstituted starch granule fractions. Thus, substitution did not completely eradicate inherent property differences observed between unmodified reconstituted wheat starch granule fractions (based on differing A/B-type granule contents).

1. Introduction

Wheat starch consists of two distinct granule populations: large A-type (>10 μm) and small B-type (<10 μm) granules, differentiated by their chemical and morphological characteristics (Kim & Huber, 2008). Wheat starch A- and B-type granules are known to possess differential compositions, amylopectin molecular structures, relative crystallinities, and microstructures (e.g., surface pores, channels, cavities), which have been summarized in detail (Bertolini, Souza, Nelson, & Huber, 2003; Chiotelli & Le Meste, 2002; Fortuna, Januszewska, Juszczak, Kielski, & Palasinski, 2000; Geera, Nelson, Souza, & Huber, 2006; Kim, 2009; Kim & Huber, 2008; Salman et al., 2009; Shinde, Nelson, & Huber, 2003; Soulaka & Morrison, 1985; Van Hung & Morita, 2005). These characteristic differences lead to variations in swelling, gelatinization, and pasting properties for the two wheat starch granule types (Chiotelli & Le Meste, 2002; Fortuna et al., 2000; Geera et al., 2006; Kim, 2009; Shinde et al., 2003; Soh, Sissons, & Turner, 2006). Both Shinde et al. (2003) and Soh et al. (2006) observed peak and final viscosities of wheat starch pastes to be reduced as the proportion of B-type granules within wheat starch increased. Thus, the proportion of A-type and B-type granules impacts wheat starch characteristics and properties. Consequently, noted differences in inherent starch characteristics and the impact of A/B-type granule ratios on wheat starch properties enhance the probability that in starch modification processes: (1) wheat starch A- and B-type granules could exhibit differential relative reactivities, and (2) wheat starch reactivity could vary according to the A/B-type granule ratio. However, available information is equivocal regarding the influence of granule type on wheat starch reactivity in chemical modification reactions.

Several studies have been conducted to assess the relative reactivities of wheat starch A- and B-type granules in substitution reactions with either propylene oxide (PO) or a propylene oxide analog (POA). Stapley and BeMiller (2003) reported slightly greater molar substitution (MS) values for the small (relative to the large) granule fraction of hydroxypropylated wheat starch modified at their low PO level (MS $\approx$ 0.123), though their high PO derivatization level (MS $\approx$ 0.206) did not result in MS value differences between the two granule fractions. In this experiment, hydroxypropylated starch granules were fractionated into their respective large and small granule fractions in an aqueous acetone medium (to prevent leaching of derivatized starch molecules from granules) following modification. Bertolini et al. (2003) reacted normal and waxy wheat starch with POA, and fractionated the derivatized wheat starches into their respective A- and B-type granule fractions (using 80% sucrose solution and/or deionized water). No reactivity

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preference in regard to granule type was observed in POA reactions. In contrast, Van Hung and Morita (2005) modified pre-fractionated A- and B-type granule populations independently with PO, and reported that A-type granule fractions were 24% more hydroxypropylated than B-type granule fractions. While conflicting relative reactivities for wheat starch A- and B-type granules have been reported, all studies to date possess some inherent limitation (i.e., undocumented A- and B-type granule fraction purities, potential leaching of derivatized starch from granules during fractionation, lack of experimental replication and/or design) that prevents full reconciliation of the contradictory reports.

The objectives of this work were to: (1) investigate the relative reactivities of A- and B-type granules of waxy and normal wheat starch in substitution reactions with POA and PO, (2) relate A- and B-type granule reactivities to their respective modified starch properties, and (3) investigate the impact of the A/B-type starch granule ratio on reactivity, swelling, gelatinization, and pasting properties of substituted wheat starch. To enhance the validity of the study, highly-purified A- and B-type granule fractions, as well as documented ratios of A- and B-type granule mixtures, of waxy and normal wheat starch were used as substrates for all substitution reactions. Two previous studies (Kim, 2009; Kim & Huber, 2008) have elucidated both the granule microstructures and starch characteristics of highly-purified A- and B-type starch granule fractions, providing a reliable foundation for investigation of wheat starch A- and B-type granule relative reactivity.

2. Materials and methods

2.1. Materials

Wheat starch was isolated via an adapted protein-digestion scheme (Kim & Huber, 2008) from waxy (IDO630) and normal (Jubilee) soft wheat flours, and fractionated into A- and B-type starch granule populations according to the method outlined by Kim (2009). Fraction purities (determined by particle size analysis) for A- and B-type starch granule fractions ranged from 99.6% to 99.7% and from 94.1% to 94.5%, respectively (volume or weight basis), across the two genotypes (Kim, 2009). Additionally, purified A- and B-type granule fractions of waxy and normal wheat starch were reconstituted according to pre-determined mixing ratios (A/B-type granule ratios = 100:0, 75:25, 50:50, 25:75, and 0:100 by weight) to create wheat starches with defined A- and B-type granule contents. Sodium 3-chloro-2-hydroxy-1-propanesulfonate (propylene oxide analog, POA) and propylene oxide (PO) were obtained from Sigma–Aldrich Chemical Corp. (Milwaukee, WI). Other reagents and chemicals used were at minimum of analytical grade.

2.2. Derivatization of starch with a propylene oxide analog (POA)

Purified A- and B-type granule fractions of waxy and normal wheat starch were derivatized with POA using an aqueous-ethanol reaction medium outlined by Huber and BeMiller (2001). The appropriate level of POA reagent was dissolved in a mixture of 0.125 M NaOH, deionized water, and absolute ethanol (Table 1), followed by addition of starch (5.0 g, dry weight basis or d.b.) with rapid stirring. The reaction system was supplemented with an appropriate amount of 2.0 M NaOH based on the amount of incorporated reagent (1 mol POA generates 1 mol HCl) needed to maintain the pH of the reaction medium at 11.5 (Table 1). The reaction mixture was tightly sealed and incubated at 45 °C for 24 h under continuous stirring, after which it was neutralized to pH 6.5 with 1.0 M HCl. After neutralization, POA starch derivatives (including reaction controls) were recovered by centrifugation (3000g, 20 min), and the resulting supernatants were set aside for subsequent determination of leached starch amounts (Section 2.4). Recovered POA starch derivatives were suspended in aqueous ethanol (50%, v/v) (Han & BeMiller, 2006), and shaken on a Wrist Action Shaker (Model 75, Burrell Co., Pittsburgh, PA) for 2 h to extract unbound reagent from granules (while minimizing leaching of POA-derivatized starch molecules from granules). Derivatized starch granules were again recovered by centrifugation (3000g, 20 min). This washing procedure (beginning with the re-suspension of POA derivatives in aqueous ethanol) was repeated a total of three times. Washed POA starch derivatives were suspended in absolute ethanol, recovered on a Büchner funnel, and allowed to air-dry. To determine molar substitution (MS) levels, POA derivatives and reaction controls were assayed for sulfur content via inductively coupled plasma-atomic emission spectroscopy (Anderson, 1996). POA-derivatized starch MS values were calculated based on net sulfur levels (sulfur contents of the modified derivatives minus those of the respective reaction controls).

Table 1
Reaction system parameters for substitution of waxy and normal starch A- and B-type granule fractions with sodium 3-chloro-2-hydroxy-1-propanesulfonate (propylene oxide analog, POA).

Reagent (%, s.b.[a])	Reaction medium composition (pH 11.5)			
	0.125 M NaOH (ml)	2.0 M NaOH (ml)	Deionized water (ml)	Absolute ethanol (ml)
0.0	10.4	0.32	1.28	22.3[b]
2.0	10.4	0.58	1.02	22.3[b]
6.0	10.4	1.10	0.50	22.3[b]
10.0	10.4	1.60	–	22.3[b]

[a] Dry starch weight basis.

[b] Final ethanol concentration in reaction medium: 65% (v/v) (Huber & BeMiller, 2001).

2.3. Derivatization of reconstituted starch with propylene oxide (PO)

Reconstituted starch granule mixtures (5.0 g, d.b.; Section 2.1) were suspended in an aqueous-ethanol reaction medium, corresponding to the 0% POA addition level (Table 1), within a 50-ml round bottom flask with rapid stirring. The reaction vessel was sealed tightly with a septum. PO (20%, dry starch weight basis or s.b.) was added dropwise to the reaction mixture using a syringe. Reaction proceeded at 45 °C for 24 h with continuous stirring, after which the reaction mixture was neutralized to pH 6.5 with 1.0 M HCl. Reaction controls also were prepared in the same fashion, except that they received no added PO. Hydroxypropylated starches (including reaction controls) were recovered by centrifugation (3000g, 20 min), and the resulting supernatants were set aside for subsequent determination of leached starch amounts (Section 2.4). The resulting hydroxypropylated starches were subjected to the same washing procedure described for POA starch derivatives (Section 2.2). Upon completion of washing, hydroxypropylated starches were re-suspended in absolute ethanol, recovered on a Büchner funnel, and allowed to air-dry. For hydroxypropylated starch MS values, hydroxypropyl contents were determined by the spectrophotometric method of Johnson (1969). MS values were calculated as the mole ratio of hydroxypropyl groups to that of starch within the modified starches.

2.4. Determination of leached starch amounts

To determine the amounts of starch leached from granules during POA or PO reactions, total carbohydrate contents of reaction medium supernatants, retained following derivatization, were determined via the phenol–sulfuric acid colorimetric method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956). Leached starch amounts were quantified as the percent ratio (%) of the total carbohydrate content of the reaction medium supernatant (following reaction) to that of the initial starch content added to the reaction medium.

2.5. Swelling, gelatinization, and pasting properties

Starch swelling properties for POA- and PO-derivatized starches were assessed at 60 and 50 °C, respectively, using a blue dextran exclusion method (Tester & Morrison, 1990). Starch gelatinization properties were analyzed using a DSC 2920 Thermal Analyzer (TA Instruments, Newcastle, DE) as described by Geera et al. (2006), while starch pasting properties were determined as outlined by Batey, Curtin, and Moore (1997) using the Rapid Visco Analyzer (RVA) (Newport Scientific, NSW, Australia).

2.6. Experimental design and statistical analysis

POA and PO reactions were replicated twice for each genotype/granule type/reagent addition level combination and for each genotype/A:B-type granule ratio combination, respectively. MS values and all measured starch properties were determined at least once for each experimental replicate (including reaction controls). Experimental data were analyzed using Analysis of Variance (ANOVA), and expressed as mean values ± standard deviations. A least square difference (LSD) test was used to identify significant differences among experimental mean values ($\alpha < 0.05$). Relative reactivities (B/A-type granule MS ratios) of POA-derivatized A- and B-type starch granules were analyzed by genotype (across reagent levels) and by reagent level (across genotypes) using a two-tailed *t*-test as conducted by Bertolini et al. (2003): where H_0: B/A-type granule MS ratio = 1 (denotes equal modification of A- and B-type granules) and H_a: B/A-type granule MS ratio ≠ 1 (denotes unequal modification of A- and B-type granules). All statistical computations and analyses were conducted using SAS version 9.1 for Windows (SAS Institute, Cary, NC).

3. Results and discussion

3.1. Substitution of wheat starch A- and B-type granules with a propylene oxide analog (POA)

A propylene oxide analog (POA, sodium 3-chloro-2-hydroxy-1-propanesulfonate) was employed to investigate A- and B-type starch granule reactivity, because it: (1) reacts with starch molecules in a manner similar to PO, (2) facilitates straightforward determination of modified starch MS levels (based on the amount of incorporated sulfur), and (3) possesses an anionic group that aids investigation of the locale of reaction sites within granules, accommodating future analysis of granular reaction patterns (Gray & BeMiller, 2004, 2005; Huber & BeMiller, 2001). To minimize starch leaching from granules during derivatization, an aqueous-ethanol reaction system was used for POA reactions, as reported by Han and Sosulski (1998), who revealed 5–7 times lesser amounts of starch leachate for an aqueous-ethanol starch cationization process relative to that conducted in an aqueous medium. In the present study, minimal variation in starch leachate amounts was observed between reagent levels, granule types, and/or genotypes (Table 2; values in parentheses). Han and BeMiller (2005) reported considerable leaching (0.31–0.38% vs. 0.01–0.07% in the present study) of highly-derivatized starch molecules from granules during hydroxypropylation reactions, which leaching might alter true MS values of hydroxypropylated starches. Thus, the aqueous-ethanol reaction system appeared to be least confounded for elucidating the relative reactivities of A- and B-type granules in POA reactions. Moreover, MS values for all POA derivatives (Table 2) were much lower than those typically encountered in commercial hydroxypropylated starches (MS ≈ 0.1). For POA reactions, commercial MS values could not be achieved due to granule destabilization, which resulted from electrostatic repulsion among POA-derivatized starch molecules within granules (POA possesses an anionic group), as previously reported by Bertolini et al. (2003). Nevertheless, MS values for all POA derivatives increased as reagent levels increased from 2% to 10% (Table 2).

3.1.1. Relative reactivities of A- and B-type granule fractions in POA reactions

The ratio of B-type to A-type granule MS values (B/A MS ratio) was calculated for a given genotype and POA addition level to investigate the relative reactivities of A- and B-type granules. The statistical hypothesis (H_0: B/A MS ratio = 1; H_a: B/A MS ratio ≠ 1) was used to assess granule fraction relative reactivities. Where the B/A MS ratio is equal to 1, A- and B-type starch granule relative reactivities are not presumed to differ, while a B/A MS ratio greater or lower than 1 implies a greater reactivity for either B-type or A-type starch granules, respectively. Mean B/A MS ratios, pooled either across genotype (within a given reagent level) or across reagent levels (within a given genotype), were not significantly different from 1 (Table 2), indicating approximately equal derivatization of A- and B-type granules in POA reactions. These results are

Table 2
Mean[a] values for molar substitution (MS), leached starch amounts, and B/A MS ratios[b] for waxy and normal wheat starch A- and B-type granule fractions substituted with sodium 3-chloro-2-hydroxy-1-propanesulfonate (POA).

Genotype/granule type	Molar substitution (leached starch, %)[c]			Mean B/A MS ratio[b] (across reagent levels)
	2% POA	6% POA	10% POA	
Waxy				
A-type	0.0030^{C} (0.01)	0.0124^{B} (0.02)	0.0235^{A} (0.01)	
B-type	0.0029^{C} (0.01)	0.0126^{B} (0.01)	0.0230^{A} (0.02)	
B/A MS ratio[b]	0.97	1.02	0.98	0.99ns[d]
Normal				
A-type	0.0028^{C} (0.02)	0.0119^{B} (0.03)	0.0230^{A} (0.03)	
B-type	0.0028^{C} (0.06)	0.0119^{B} (0.07)	0.0222^{A} (0.06)	
B/A MS ratio[b]	0.99	1.00	0.97	0.99ns[d]
Mean B/A MS ratio[b] (across genotype)	0.97ns[d]	1.01ns[d]	0.97ns[d]	

[a] Mean value of two replicate reactions; values sharing a common upper-case letter within the same row are not significantly different ($p < 0.05$).

[b] Defined as the ratio of MS values of B-type to A-type granules.

[c] Amount of starch leached from granules during reaction is shown in parentheses adjacent to MS mean values; defined as the percent ratio (%) of the total carbohydrate content (g) within the reaction supernatant to the starch weight (g) initially added to the reaction medium.

[d] Mean B/A MS ratio is not significantly different from 1 ($p < 0.05$).

consistent with the report of Bertolini et al. (2003), who observed no significant differences in the relative reactivities of A- and B-type granules (though granule fractions were separated after derivatization) in their POA reactions. Stapley and BeMiller (2003) reported only subtle or no differences between the MS values of small and large wheat starch granule fractions hydroxypropylated at low (MS $\approx$ 0.123) and high (MS $\approx$ 0.206) PO levels, respectively (granules were fractionated following reaction). However, even in the case where subtle MS differences were noted between the two granule fractions, they were not considered to be of practical significance. In contrast, Van Hung and Morita (2005) reported 24% higher reactivity for wheat starch A-type (relative to B-type) granules, which were hydroxypropylated independently as purified granule fractions. However, in this latter finding, results were based on a single hydroxypropylation reaction without experimental replication. The authors further attributed differences between their findings and those of the two former studies (Bertolini et al., 2003; Stapley & BeMiller, 2003) to different fractionation/derivatization sequences (both previous studies fractionated A- and B-type granules from wheat starch after derivatization). However, though identical schemes (i.e., derivatization after fractionation) were utilized in the Van Hung and Morita (2005) and the present study, the experimental findings still conflict. Further, the relative A- and B-type granule reactivities (Table 2) obtained within the present study were identical to those of Bertolini et al. (2003), even though reverse fractionation/derivatization sequences were used in the two studies. More recently, Huang, Schols, Jin, Sulmann, and Voragen (2007) demonstrated that in acetylation reactions with slow-reacting vinyl acetate (similar to PO), very similar degree of substitution values were observed between small and large granule fractions of yellow pea starch, regardless of the fractionation/derivatization sequence. Thus, the specific fractionation/derivatization sequence did not appear to impact A- and B-type granule relative reactivity in POA reactions conducted in an aqueous-ethanol medium. Despite the unresolved differences in the relative reactivities of wheat starch A- and B-type granules in PO/POA reactions, the findings of the present study are validated by documented granule fraction purities, minimal leaching of modified starch molecules, and replicated reactions.

3.1.2. Swelling and gelatinization properties (POA-derivatized A- and B-type granule fractions)

Swelling properties of POA starch derivatives and their reaction controls were assessed at 60 °C, because granules of all POA starch derivatives became fully gelatinized at test conditions above this temperature. However, even at 60 °C, swelling factors could not be effectively determined for the 10% POA addition level (Table 3), due to gelatinization/disintegration of POA-derivatized starch granules (i.e., blue dextran solution obtained from swollen granules was cloudy). POA derivatization introduces molecular repulsion between derivatized starch chains within granules, and thus enhances water uptake and swelling of starch granules. With increasing reagent addition levels, swelling factors increased, regardless of genotype and/or granule type (Table 3), as has been generally observed for hydroxypropylated and cationized starches (Kweon, Sosulski, & Bhirud, 1997; Lawal, 2009; Villwock & BeMiller, 2005). For a given granule type, waxy starch derivatives generally exhibited greater swelling factors relative to their respective normal starch derivatives. Swelling differences noted between like-granules of waxy and normal native starches (for both reaction controls and derivatives) are most likely explained by their large inherent differential in amylose and lipid-complexed amylose contents (higher for normal starch) (Geera et al., 2006; Kim, 2009), which adversely impact native starch swelling behavior (Tester & Morrison, 1990). For equivalent reagent levels within a given genotype, A-type granule derivatives swelled less than B-type granule derivatives. The swelling patterns observed between POA-derivatized A- and B-type granules of a common genotype were comparable with those of their native (unmodified) wheat starch A- and B-type granule reaction controls (Table 3). The greater swelling capacity of native wheat starch B-type (relative to A-type) granules is likely due to their greater proportion of amylopectin short branch chains (DP < 13) (Kim, 2009; Salman et al., 2009) and greater granule surface area (Fortuna et al., 2000; Kim, 2009; Soulaka & Morrison, 1985). Consequently, the findings in the present study suggest that POA derivatization did not disproportionately alter the native granular/molecular characteristics of the two granule types, as substitution did not override the traditional swelling property differential observed between native starch A- and B-type granules.

Gelatinization properties of POA derivatives and their reaction controls are depicted in Table 3. Regardless of granule type and/or genotype, there was a general trend for gelatinization onset (T_o), peak (T_p), and completion (T_c) temperatures to be reduced with increasing reagent addition levels, which result is in agreement with previous reports (Chuenkamol, Puttanlek, Rungsardthong, & Uttapap, 2007; Kuo & Lai, 2007; Lawal, 2009; Liu, Ramsden, & Corke, 1999). The reduction in gelatinization temperature in response to POA derivatization is likely attributable to the disruption of the granule ordered structure, due to the presence of charged (derivatized) starch substituents (Chuenkamol et al., 2007; Perera & Hoover, 1999). However, gelatinization enthalpies (ΔH) differed only slightly for POA derivatives of a given granule type across reagent addition levels, though an apparent downward trend in enthalpy was generally observed with increasing levels of derivatization (a statistical difference was noted only for normal A-type granule derivatives). Previous studies have also reported an inability to detect significant gelatinization enthalpy differences between reaction controls (or native starch) and substituted starch derivatives of low MS (<0.05) (Chuenkamol et al., 2007; Lawal, 2009). In general, gelatinization temperatures and enthalpies for waxy wheat derivatives of a given granule type were generally higher than those of equivalently derivatized normal wheat starch. Within a genotype, higher gelatinization onset temperatures and enthalpies were observed for A-type (relative to B-type) granules given equivalent levels of derivatization, while the reverse was generally true for gelatinization peak and completion temperatures. These noted differentials in gelatinization properties were very similar to those observed for A- and B-type granules of native waxy and normal wheat starches (Geera et al., 2006; Kim, 2009), though gelatinization temperatures and enthalpies of modified starch granule fractions gradually became reduced by POA derivatization. Reduced gelatinization onset temperatures for B-type (relative to A-type) granules within a genotype could be attributable to their greater content of amylopectin short branch chains, while increased gelatinization completion temperatures (for B-type granules) have been potentially ascribed to a population of more perfect crystallites (Chiotelli & Le Meste, 2002). In summary, POA derivatization did not completely overcome relative differences in gelatinization properties noted between A- and B-type granules of native waxy and normal wheat starch.

3.1.3. Starch pasting properties (POA-derivatized A- and B-type granule fractions)

Pasting profiles of POA derivatives and their reaction controls are shown in Fig. 1. As the degree of POA derivatization increased, peak viscosities progressively increased and the time to achieve peak viscosity decreased for a given granule fraction of a genotype, paralleling similar observations for modified granule fraction swelling properties (Table 3). These tendencies are comparable with pasting viscosity patterns previously reported for hydroxypropylated and cationized starches (Chuenkamol et al., 2007;

Table 3
Mean[a] swelling, gelatinization, and pasting properties of waxy and normal wheat starch A- and B-type granule fractions substituted with sodium 3-chloro-2-hydroxy-1-propanesulfonate (POA).

Properties	POA (%, s.b.[b])	Waxy (IDO630)		Normal (Jubilee)	
		A-type	B-type	A-type	B-type
Swelling factors[c]					
	0.0	$4.5 \pm 0.0^{c/C}$	$8.5 \pm 0.1^{a/C}$	$4.2 \pm 0.1^{d/C}$	$5.5 \pm 0.0^{b/C}$
	2.0	$9.3 \pm 0.5^{b/B}$	$13.7 \pm 0.1^{a/B}$	$5.5 \pm 0.1^{d/B}$	$7.9 \pm 0.0^{c/B}$
	6.0	$18.0 \pm 3.3^{c/A}$	$33.5 \pm 0.2^{a/A}$	$21.2 \pm 0.4^{c/A}$	$27.9 \pm 1.1^{b/A}$
	10.0	N/D[d]	N/D[d]	N/D[d]	N/D[d]
Gelatinization[e]					
T_o	0.0	$58.1 \pm 0.1^{a/A}$	$55.5 \pm 0.1^{c/A}$	$56.3 \pm 0.2^{b/A}$	$53.7 \pm 0.4^{d/A}$
	2.0	$57.9 \pm 0.1^{a/A}$	$56.1 \pm 0.6^{b/A}$	$56.8 \pm 0.7^{ab/A}$	$53.5 \pm 0.1^{b/A}$
	6.0	$55.0 \pm 0.3^{a/B}$	$53.6 \pm 0.1^{ab/B}$	$53.8 \pm 1.1^{a/B}$	$52.1 \pm 0.1^{b/B}$
	10.0	$51.2 \pm 0.0^{a/C}$	$50.8 \pm 0.2^{b/C}$	$50.3 \pm 0.1^{c/C}$	$49.3 \pm 0.0^{d/C}$
T_p	0.0	$66.3 \pm 0.3^{a/A}$	$66.7 \pm 0.1^{a/A}$	$62.1 \pm 0.3^{b/A}$	$62.3 \pm 0.0^{b/A}$
	2.0	$66.6 \pm 0.1^{b/A}$	$67.0 \pm 0.3^{a/A}$	$61.9 \pm 0.1^{b/B}$	62.0 ± 0.1^{WA}
	6.0	$64.7 \pm 0.1^{b/B}$	$65.6 \pm 0.1^{a/B}$	$59.2 \pm 0.3^{d/B}$	$59.9 \pm 0.1^{c/B}$
	10.0	$61.4 \pm 0.1^{b/C}$	$62.8 \pm 0.0^{a/C}$	$55.6 \pm 0.1^{c/C}$	$56.2 \pm 0.6^{c/C}$
T_c	0.0	$76.9 \pm 0.3^{b/AB}$	$78.5 \pm 0.2^{a/A}$	$72.6 \pm 0.5^{c/}_{A}$	$78.1 \pm 0.6^{ab/A}$
	2.0	$77.0 \pm 0.3^{a/A}$	$78.3 \pm 0.0^{a/A}$	$71.9 \pm 0.5^{b/A}$	$77.7 \pm 0.8^{a/A}$
	6.0	$76.4 \pm 0.1^{a/C}$	$76.6 \pm 0.2^{a/B}$	$68.5 \pm 0.1^{c/B}$	$73.7 \pm 1.3^{b/B}$
	10.0	$75.0 \pm 0.1^{a/C}$	$75.9 \pm 1.2^{a/B}$	$68.3 \pm 0.4^{c/B}$	$72.9 \pm 0.8^{b/B}$
ΔH	0.0	$11.2 \pm 0.3^{a/A}$	$9.6 \pm 0.6^{ab/A}$	$8.8 \pm 0.0^{ab/A}$	$8.0 \pm 1.8^{b/A}$
	2.0	$11.3 \pm 0.4^{a/A}$	$9.1 \pm 1.1^{b/A}$	$8.5 \pm 0.1^{b/A}$	$7.8 \pm 1.1^{b/A}$
	6.0	$11.5 \pm 0.5^{a/A}$	$10.2 \pm 0.1^{b/A}$	$8.6 \pm 0.2^{c/A}$	$7.3 \pm 0.2^{d/A}$
	10.0	$10.8 \pm 0.4^{a/A}$	$8.9 \pm 0.4^{b/A}$	$7.3 \pm 0.8^{c/B}$	$7.0 \pm 0.2^{c/A}$
Pasting characteristics (RVU)					
Peak	0.0	$453.6 \pm 2\ 2^{a/D}$	$221.1 \pm 2\ 1^{c/C}$	$339.0 \pm 2.1^{b/D}$	$209.7 \pm 2.1^{d/D}$
	2.0	$468.4 \pm 1.5^{b/C}$	$233.6 \pm 1.1^{d/C}$	$481.5 \pm 1.8^{a/C}$	$330.9 \pm 3.6^{c/C}$
	6.0	$583.1 \pm 1.3^{b/B}$	$381.1 \pm 20.8^{c/B}$	$679.0 \pm 23.9^{a/B}$	$645.8 \pm 1.5^{a/B}$
	10.0	$686.2 \pm 91^{b/A}$	$462.9 \pm 8.6^{c/A}$	$858.7 \pm 79.9^{a/A}$	$773.3 \pm 80.4^{ab/A}$
Trough	0.0	$106.9 \pm 1.3^{b/B}$	$76.1 \pm 2.1^{c/B}$	$139.8 \pm 2.1^{a/A}$	$105.1 \pm 2.1^{b/A}$
	2.0	$112.9 \pm 1.5^{b/AB}$	$78.3 \pm 0.7^{d/B}$	$117.5 \pm 1.8^{a/B}$	$95.6 \pm 1.1^{c/B}$
	6.0	$123.1 \pm 19\ 4^{a/AB}$	$113.0 \pm 14.4^{ab/A}$	$102.6 \pm 0.3^{ab/C}$	$82.5 \pm 0.3^{b/C}$
	10.0	$137.2 \pm 5.9^{a/A}$	$117.1 \pm 1.1^{b/A}$	$97.2 \pm 3.4^{c/C}$	$80.8 \pm 1.3^{d/C}$
Breakdown	0.0	$346.7 \pm 3.5^{a/C}$	$146.5 \pm 2.1^{c/C}$	$200.8 \pm 2.1^{b/D}$	$106.1 \pm 2.1^{d/D}$
	2.0	$357.7 \pm 2.9^{a/C}$	$155.2 \pm 1.8^{c/C}$	$364.1 \pm 0.1^{a/C}$	$235.4 \pm 4.6^{b/C}$
	6.0	$460.0 \pm 20.7^{b/B}$	$268.2 \pm 6.4^{c/B}$	$576.4 \pm 24.2^{a/B}$	$563.3 \pm 1.8^{a/B}$
	10.0	$549.1 \pm 3.2^{b/A}$	$345.8 \pm 9.7^{c/A}$	$761.5 \pm 76.6^{a/A}$	$692.5 \pm 81.6^{ab/A}$
Final	0.0	$174.8 \pm 2.9^{c/C}$	$109.7 \pm 2.1^{d/B}$	$370.8 \pm 2.1^{a/A}$	$224.3 \pm 2.1^{b/A}$
	2.0	$184.9 \pm 1.4^{c/AB}$	$119.1 \pm 0.0^{d/B}$	$318.3 \pm 5.0^{a/B}$	$226.5 \pm 3.5^{b/A}$
	6.0	$199.4 \pm 9.1^{b/AB}$	$160.2 \pm 17.6^{c/A}$	$238.0 \pm 2.3^{a/C}$	$209.3 \pm 0.1^{b/B}$
	10.0	$213.9 \pm 6.4^{ab/A}$	$167.4 \pm 0.1^{c/A}$	$223.3 \pm 1.8^{a/D}$	$204.6 \pm 9.8^{b/B}$
Setback	0.0	$67.9 \pm 1.6^{c/A}$	$35.1 \pm 2.1^{d/B}$	$232.6 \pm 2.1^{a/A}$	$120.7 \pm 2.1^{b/A}$
	2.0	$74.4 \pm 3.0^{c/A}$	$40.8 \pm 0.7^{d/B}$	$200.9 \pm 3.3^{a/B}$	$131.0 \pm 2.5^{b/A}$
	6.0	$76.4 \pm 10.3^{b/A}$	$47.2 \pm 3.3^{c/A}$	$135.4 \pm 2.1^{a/C}$	$126.8 \pm 0.1^{a/A}$
	10.0	$76.8 \pm 0.5^{b/A}$	$50.4 \pm 0.9^{c/A}$	$126.1 \pm 5.2^{a/C}$	$123.8 \pm 11.0^{a/A}$

[a] Mean value of two measurements; values sharing a common lower-case letter within a row are not significantly different ($p < 0.05$); values sharing a common upper-case letter within a column (for a particular measurement) are not significantly different ($p < 0.05$).

[b] Dry starch weight basis.

[c] Assessed at 60 °C.

[d] Not determined.

[e] T_o, T_p, and T_c refer to gelatinization onset, peak, and completion temperatures (°C), respectively; AH denotes gelatinization enthalpy (J/g).

Han & Sosulski, 1998; Kuo & Lai, 2007; Lawal, 2009; Liu et al., 1999). For reaction controls within a genotype, A-type (relative to B-type) granules exhibited higher viscosity values at virtually all points of the pasting profile (Fig. 1A and B), similar to pasting viscosity patterns observed for native (unmodified) waxy and normal wheat starch A- and B-type granules (Geera et al., 2006; Kim, 2009).

Pasting characteristics of POA derivatives and their reaction controls depicted in Fig. 1 are further described in Table 3. As POA reagent levels increased, peak and breakdown viscosities increased regardless of granule type or genotype. POA derivatization likely accelerated granule swelling and water uptake due to repulsion among charged POA-derivatized starch molecules within granules, resulting in greater peak viscosities (Liu et al., 1999). Subsequently, highly swollen granules rapidly lose integrity under conditions of shear stress, and thus experience a high degree of breakdown, leading to relatively lower trough viscosities with increasing levels of POA derivatization (Kuo & Lai, 2007). For a given level of POA reagent addition, waxy A-type granule derivatives consistently exhibited greater peak and breakdown viscosities than their respective B-type counterparts. For normal starch derivatives, however, peak and breakdown viscosities for modified A- and B-type granules were no longer significantly different at reagent addition levels of 6% and 10%. In comparing like-granule fractions of the two genotypes, higher peak and breakdown viscosities were observed for reaction controls of waxy wheat starch

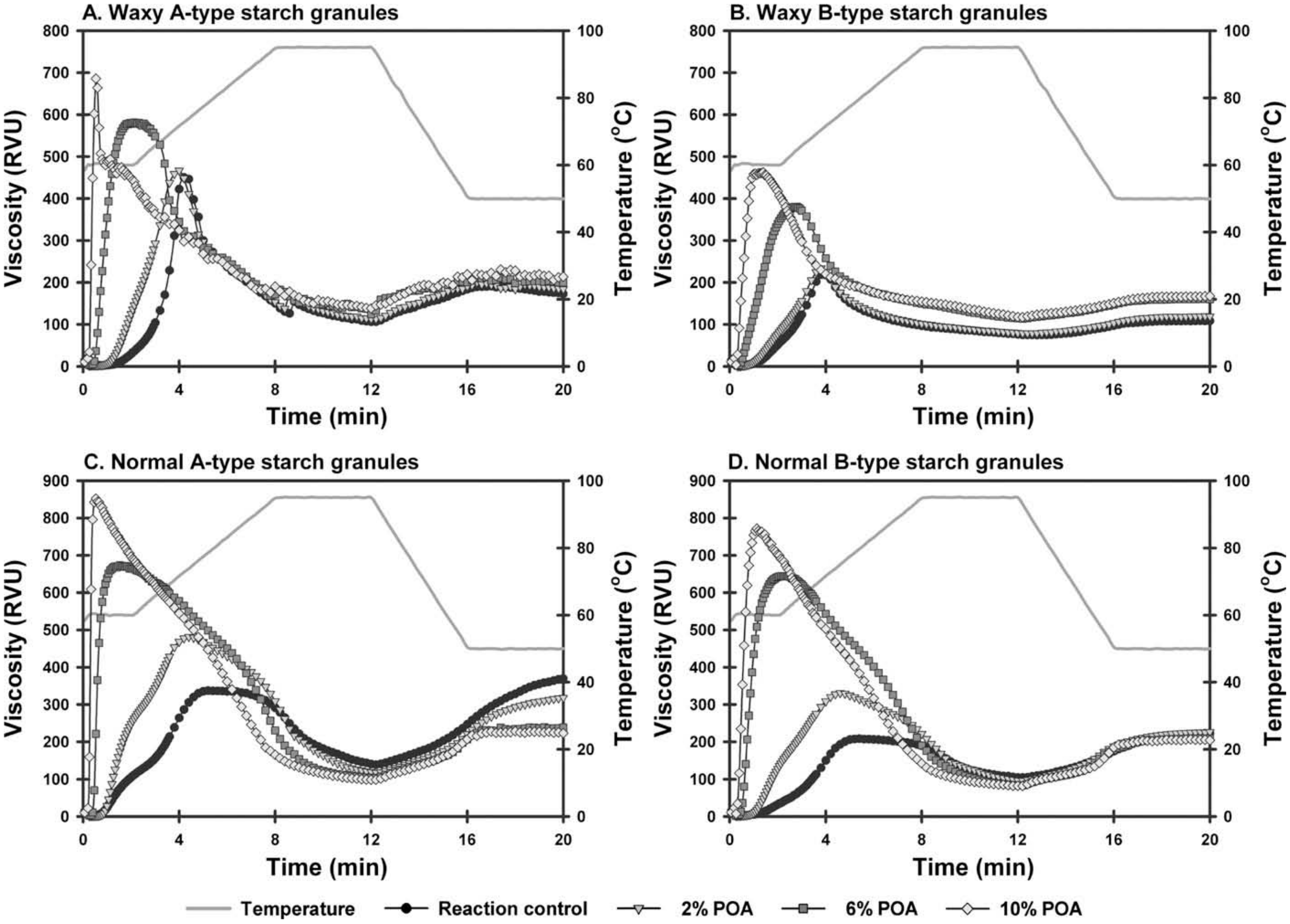

Fig. 1. Pasting viscosity profiles of waxy and normal wheat starch A-type and B-type granules substituted with POA.

granule fractions relative to their respective normal starch granule fractions, in agreement with trends observed for native (unmodified) wheat starch granules (Geera et al., 2006; Kim, 2009). However, for all modified starch derivatives (2–10% POA addition), this trend was reversed (normal starch A- and B-type granule derivatives possessed higher peak and breakdown viscosities than their respective waxy starch granule fraction derivatives). In short, POA derivatization further destabilized waxy starch granules (relative to normal starch granules) to the extent that the rate of granule swelling and disintegration (i.e., breakdown) was accelerated, ultimately resulting in decreased net peak viscosities (the high rate of granule disintegration during initial heating prevented full peak viscosity from being achieved).

Final and setback viscosities for waxy A- and B-type granule derivatives increased with increasing reagent levels (exception: waxy A-type granule setback did not significantly change upon modification), most likely due to increases in the hydrodynamic volumes of POA-derivatized starch molecules (Whistler & BeMiller, 1997). In general, charged (relative to uncharged) polymers exhibit greater molecular extension and rigidity in solution, and thus possess larger hydrodynamic volumes, resulting in greater viscosities (Whistler & BeMiller, 1997). In contrast, final and setback viscosities of both normal A- and B-type granule derivatives either decreased or remained unchanged as reagent addition levels increased. This phenomenon was attributable to steric hindrance between bulky, charged substituent groups bound to starch molecules, preventing intermolecular associations between amylose chains that otherwise promote gel formation (Liu et al., 1999). Within a given genotype, A-type granule derivatives exhibited higher final viscosities relative to B-type granule derivatives. Moreover, waxy starch derivatives of a given granule type generally exhibited lower final and setback viscosities than their respective normal starch derivatives. These final and setback viscosity differences between the modified starches of the two granule types (within a genotype) or between like-granule types (across genotypes) likely resulted primarily from differences in amylose content within the native granules.

For waxy wheat starch, statistical differences in pasting viscosity attributes observed between unmodified A- and B-type granule fractions were almost exclusively maintained at all levels of POA derivatization (comparing A- and B-type granule pasting attributes at equivalent levels of derivatization) (Fig. 1A and B and Table 3). Nevertheless, pasting attribute differentials between A- and B-type granule fractions did decrease in magnitude with increasing levels of derivatization. For POA-derivatized normal starch granules, pasting viscosities of B-type granules more closely approached those of A-type granules (comparing granules of equivalent MS levels), as reagent levels increased from 2% to 10% (Fig. 1C and D and Table 3). At the two highest levels of POA derivatization, statistical differences in A- and B-type granule pasting attributes (i.e., peak, trough, breakdown, and setback viscosities) were generally no longer apparent. However, in further analyzing these phenomena, it was noted that the magnitude differences in pasting attributes observed between A- and B-type granules of each genotype appeared to decline at similar rates with increasing levels of POA modification. Thus, the observation that pasting attributes of normal starch A- and B-type granules became more closely aligned (relative to those of waxy A- and B-type starch granules) at the highest levels of POA derivatization was simply because native normal starch A- and B-type granule fractions exhibited smaller magnitude pasting differences in the first place. The greatest gains in peak/breakdown viscosities for B-type granules (in becoming more similar to those of A-type granules of the same genotype) occurred between the 2% and 6% POA addition levels. However, no

Table 4

Mean[a] values for molar substitution (MS), leached starch (LS) amounts, and swelling factors (SF) of hydroxypropylated reconstituted wheat starch granule mixtures.

Genotype	A-type granule[b] (%, w/w)	MS		LS[c]		SF_{50}[d]	
		Control	HP	Control	HP	Control	HP
Waxy	5.5	–	0.103 ± 0.005^{a}	$0.02 \pm 0.01^{c/B}$	$0.35 \pm 0.02^{bc/A}$	$3.5 \pm 0.0^{abc/B}$	$18.4 \pm 0.8^{a/A}$
	25.0	–	0.102 ± 0.006^{a}	$0.03 \pm 0.01^{c/B}$	$0.30 \pm 0.00^{c/A}$	$3.5 \pm 0.1^{bc/B}$	$15.2 \pm 0.1^{b/A}$
	50.0	–	0.100 ± 0.010^{a}	$0.02 \pm 0.00^{c/B}$	$0.33 \pm 0.00^{c/A}$	$3.3 \pm 0.1^{c/B}$	$15.2 \pm 1.6^{b/A}$
	75.0	–	0.105 ± 0.001^{a}	$0.03 \pm 0.01^{c/B}$	$0.33 \pm 0.02^{c/A}$	$2.9 \pm 0.0^{d/B}$	$14.9 \pm 0.5^{b/A}$
	99.6	–	0.104 ± 0.001^{a}	$0.02 \pm 0.01^{c/B}$	$0.30 \pm 0.05^{c/A}$	$2.1 \pm 0.0^{e/B}$	$13.7 \pm 0.4^{b/A}$
Normal	5.9	–	0.099 ± 0.005^{a}	$0.08 \pm 0.03^{b/A}$	$0.68 \pm 0.21^{a/A}$	$3.8 \pm 0.1^{a/B}$	$11.2 \pm 0.7^{c/A}$
	25.0	–	0.095 ± 0.001^{a}	$0.11 \pm 0.00^{a/A}$	$0.57 \pm 0.19^{ab/A}$	$3.7 \pm 0.1^{ab/B}$	$10.1 \pm 0.7^{dc/A}$
	50.0	–	0.097 ± 0.002^{a}	$0.08 \pm 0.01^{b/B}$	$0.48 \pm 0.11^{abc/A}$	$3.3 \pm 0.0^{c/B}$	$9.9 \pm 0.4^{dc/A}$
	75.0	–	0.096 ± 0.006^{a}	$0.06 \pm 0.00^{b/B}$	$0.34 \pm 0.08^{c/A}$	$3.3 \pm 0.4^{c/B}$	$9.2 \pm 0.4^{de/A}$
	99.7	–	0.097 ± 0.005^{a}	$0.03 \pm 0.00^{c/B}$	$0.35 \pm 0.04^{bc/A}$	$2.2 \pm 0.1^{e/B}$	$7.6 \pm 0.8^{e/A}$

[a] Mean value of two replicate reactions (or measurements); values sharing the same lower-case letter within a column are not significantly different ($p < 0.05$); values sharing the same upper-case letter within a row for a given each characteristic are not significantly different ($p < 0.05$).

[b] A-type granule content (by weight) within reconstituted wheat starch mixtures.

[c] Amount of starch leached from granules during reaction; defined as the percent ratio (%) of the total carbohydrate content (g) within the reaction supernatant to the starch weight (g) initially added to the reaction medium.

[d] Determined at 50 °C.

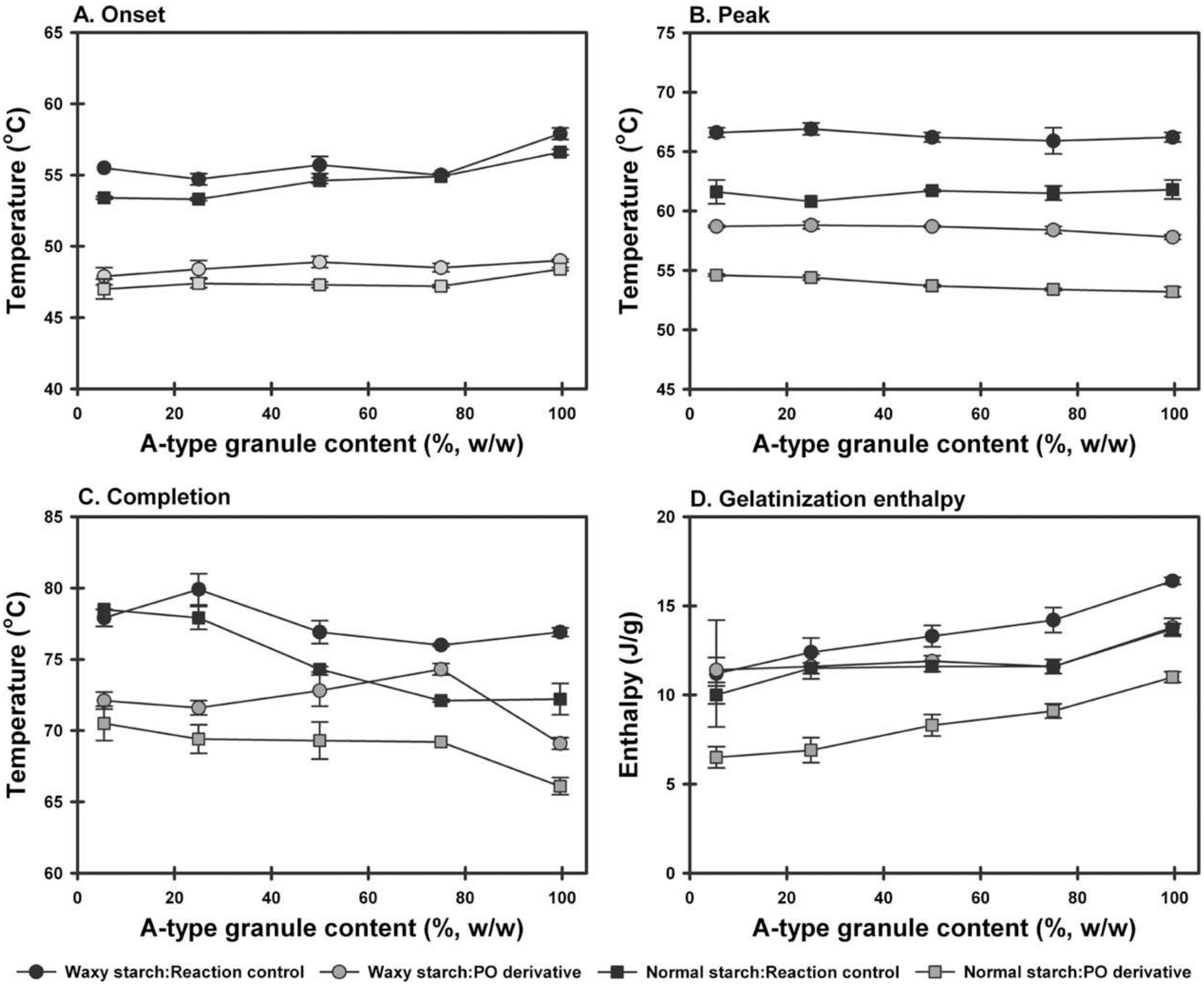

Fig. 2. Effects of A-type granule contents on gelatinization onset, peak, and completion temperatures and enthalpies of unmodified and hydroxypropylated starch granule mixtures (reconstituted according to differing A- and B-type granule mixing ratios) for waxy and normal wheat genotypes.

similar gains were observed in regard to swelling behavior, which involved static heating of starch in the absence of shear (Table 3). As the peak viscosity measurement represents the net balance of opposing phenomena (granule swelling vs. granule disintegration), it is presumed that the relative stability of swollen granules during pasting was greater for B-type (compared to A-type granules of the same genotype) modified at the 6% POA addition level (allowing more similar peak and breakdown viscosities for the two granule types). However, there is likely an upper limit regarding the extent to which peak/breakdown viscosities may be increased with increasing levels of POA modification (rate of granule disintegration, due to excessive swelling imparted by modification, will at some point limit the degree of viscosity buildup at the peak). Nevertheless, it is not known whether it might be theoretically possible for B-type granules to attain pasting viscosities even more similar to those A-type granules, should they be derivatized to relatively greater degrees than A-type granules. In short, inherent differences in pasting characteristics between native (unmodified) A- and B-type granules were partially, but not completely, overcome by POA derivatization at reagent addition levels of 2–10%.

3.2. Substitution of reconstituted wheat starches with propylene oxide (PO)

In substitution reactions with POA (Section 3.1), purified A- and B-type granule fractions of both waxy and normal wheat starch exhibited similar reactivities for equivalent levels of reagent addition. With increasing reagent addition levels, POA derivatization (MS ≈ 0.0028–0.0235) somewhat reduced inherent differences in gelatinization and pasting properties noted between native (unmodified) A- and B-type starch granules. These findings led to a hypothesis that both reactivities and properties of hydroxypropylated wheat starch modified at commercial derivatization levels (MS ≈ 0.1) may no longer be influenced by the proportion of A- and B-type granules within wheat starch. To test this hypothesis, purified waxy and normal wheat starch A- and B-type granule fractions were reconstituted to create wheat starches possessing defined A/B-type granule ratios (Section 2.1), followed by derivatization in an aqueous-ethanol reaction medium to commercial MS levels. The resulting hydroxypropylated starches were assessed with respect to MS, as well as swelling, gelatinization and pasting properties.

3.2.1. Relative reactivities of reconstituted wheat starches in PO reactions

Leached starch amounts and MS values for hydroxypropylated reconstituted starches are depicted in Table 4. Hydroxypropylation (relative to reaction controls) enhanced leaching of starch molecules from granules during derivatization (Table 4), comparable with the results of Han and BeMiller (2005). For waxy starch, degrees of leached starch generated during reaction did not differ among any of the reconstituted A/B-type granule mixtures for

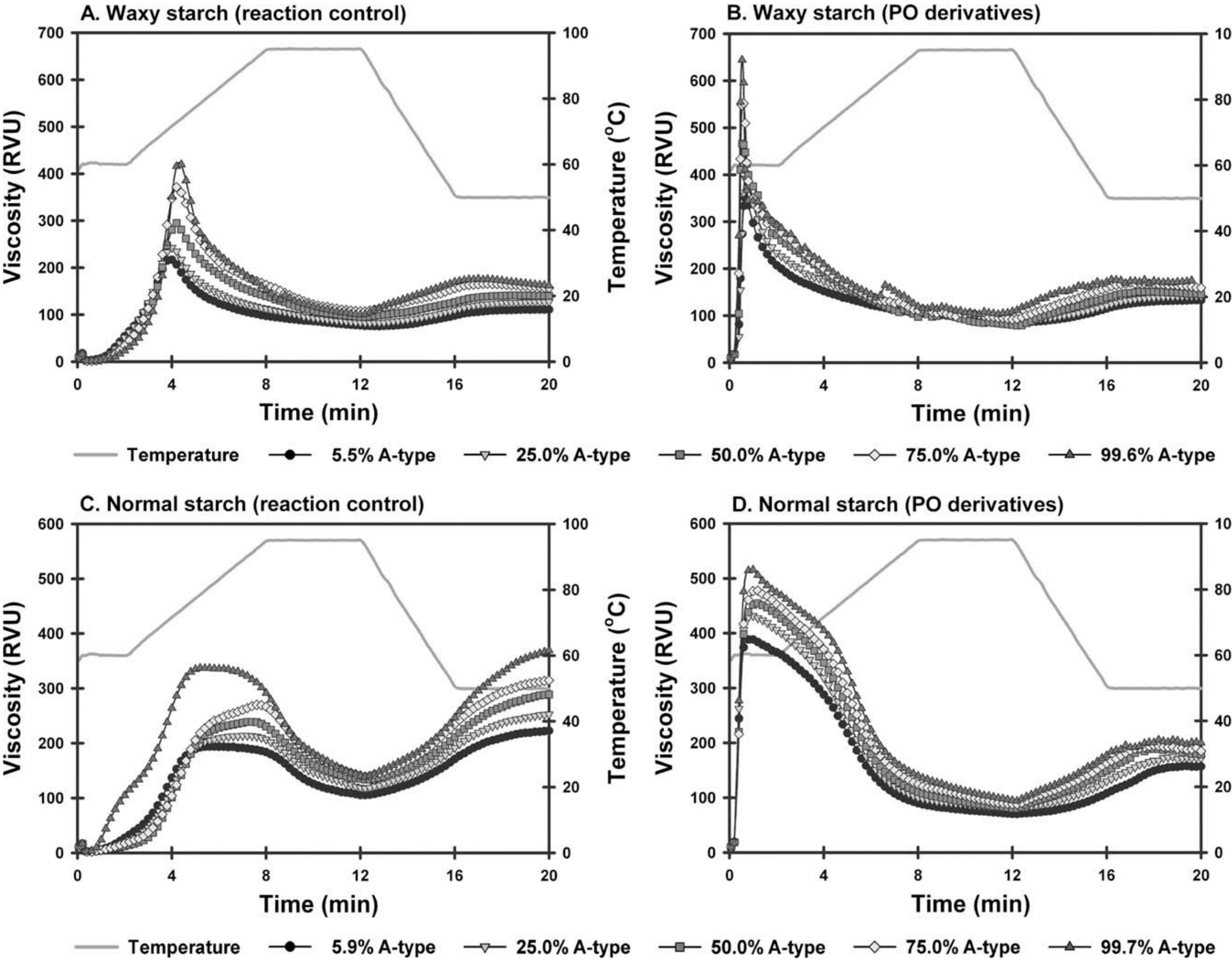

Fig. 3. Pasting viscosity profiles of unmodified and hydroxypropylated starch granule mixtures (reconstituted according to differing A- and B-type granule mixing ratios) for waxy and normal wheat genotypes.

either the hydroxylpropyl derivatives or reaction controls (Table 4). For normal starch, subtle trends (though not all reconstituted fractions were distinguished by statistical significance) in leached starch amounts were commonly observed across reconstituted A/B-type granule mixtures for both starch derivatives and reaction controls (Table 4), with a general trend toward decreased starch leachate as A-type granule content increased. Consequently, these minimal variations in leached starch amounts did not likely confound comparison of MS values of reconstituted hydroxypropylated starch fractions (only a small degree of starch leaching occurred during derivatization).

Regarding reactivity, no significant MS value differences were observed between genotypes or reconstituted starch fractions of variable A/B-type granule content (Table 4), mirroring the results obtained from POA reactions of isolated A- and B-type granules. The lack of MS differences among starch genotypes/fractions is likely explained by the slow-reacting nature of the PO reagent, which is able to diffuse throughout the granule matrix prior to reaction (Gray & BeMiller, 2004; Huber & BeMiller, 2001). Consequently, substitution reactions with PO reagent are less influenced by differences in starch structural characteristics (e.g., granule size, relative crystallinity, amylopectin structure) that exist between

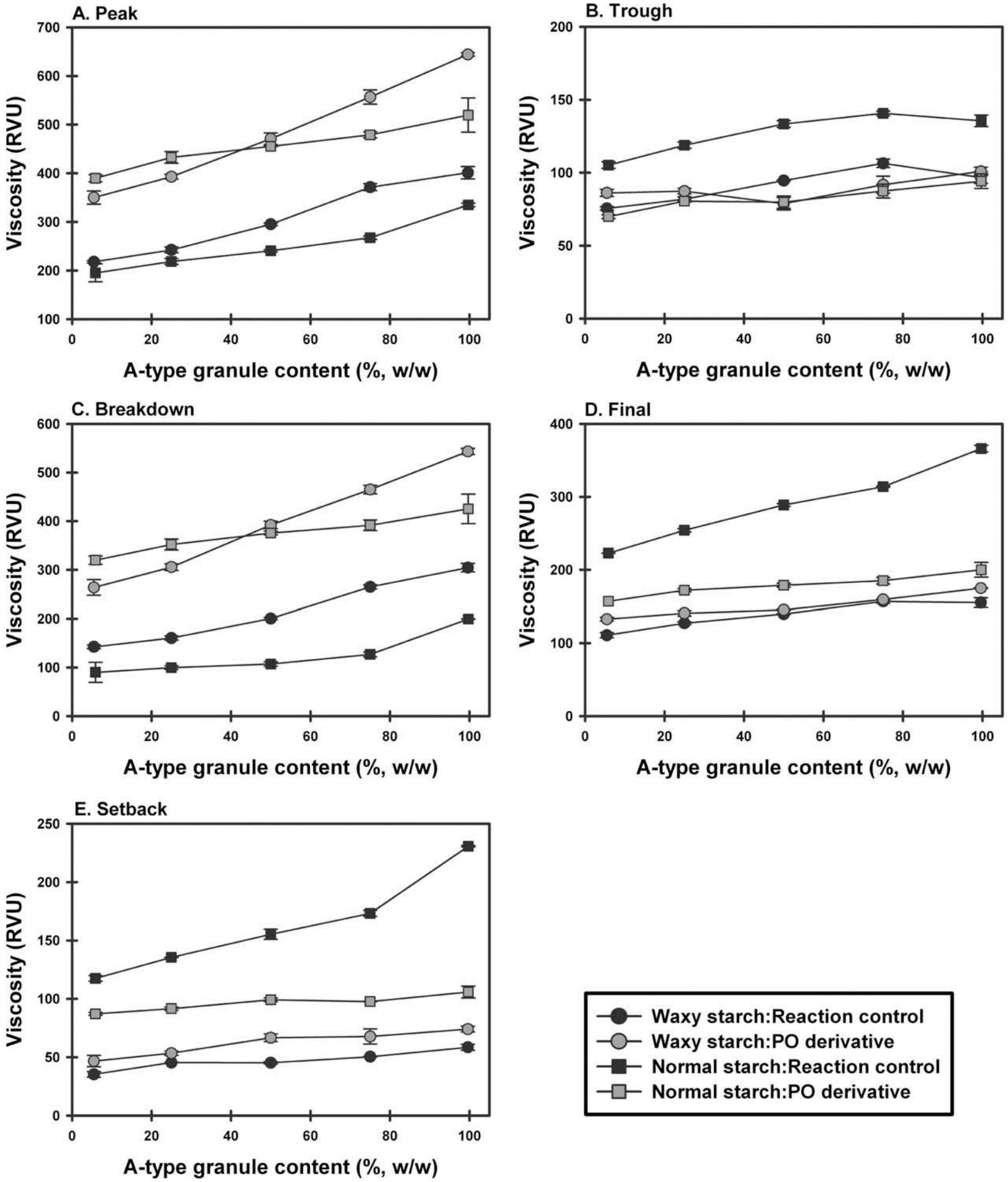

Fig. 4. Effects of A-type granule contents on pasting viscosity characteristics of unmodified and hydroxypropylated starch granule mixtures (reconstituted according to differing A- and B-type granule mixing ratios) for waxy and normal wheat genotypes.

native wheat starch A- and B-type granules. Consequently, wheat starch reactivity in hydroxypropylation reactions was not directly impacted by the proportion of A- and B-type granules within a starch population.

3.2.2. Swelling, gelatinization, and pasting properties (PO-derivatized reconstituted wheat starches)

Swelling properties of hydroxypropylated starch derivatives and their reaction controls were assessed at 50 °C (Table 4), due to gelatinization/disintegration of hydroxypropylated starch granules at test temperatures above 55 °C. Similar to POA derivatization (Section 3.1.2), incorporation of bulky hydroxypropyl groups onto starch molecules facilitated penetration and uptake of water into granules, enhancing hydration and swelling of starch granules (Chuenkamol et al., 2007). Within a genotype, hydroxypropylation greatly enhanced swelling of reconstituted starches compared to that of their respective reaction controls. An increase in A-type granule content within reconstituted hydroxypropylated starches generally led to decreased swelling factors, mirroring the same subtle swelling factor trends detected in the reaction controls. Thus, hydroxypropylation, even at commercial derivatization levels, did not appear to overcome or override inherent A/B-type granule ratio effects on wheat starch swelling properties.

Gelatinization properties of hydroxypropylated starch derivatives and their reaction controls are depicted in Fig. 2. As is commonly observed for hydroxypropylated starches (Chuenkamol et al., 2007; Lawal, 2009; Liu et al., 1999), hydroxypropylation reduced gelatinization temperatures and enthalpies of reconstituted starches relative to those of their reaction controls (Fig. 2). Within a genotype, significant differences in gelatinization onset and peak temperatures (Fig. 2A and B) were not observed across A-type granule contents of hydroxypropylated starch derivatives or their reaction controls (except for gelatinization onset temperatures of pure A-type starch granule fractions of unmodified reaction controls). While a trend toward decreased gelatinization completion temperatures was observed for reaction controls with increasing A-type granule content, the trend was slightly less evident and consistent for hydroxypropylated starch derivatives (Fig. 2C). However, an increase in A-type granule content within hydroxypropylated starch derivatives and their reaction controls enhanced gelatinization enthalpies (Fig. 2D). In short, hydroxypropylation did not appear to greatly alter gelatinization patterns observed between differing A/B-type granule mixtures of the reaction controls.

Pasting profiles of hydroxypropylated starch derivatives and reaction controls are shown in Fig. 3. Hydroxypropylation enhanced pasting viscosities of reconstituted starches relative to those of their reaction controls, as commonly reported by others (Chuenkamol et al., 2007; Lawal, 2009; Liu et al., 1999) and previously observed in POA reactions (Fig. 1). As A-type granule content increased within the reaction controls of a given genotype, pasting viscosities increased at all points of the pasting profile (Fig. 3A and C). Despite statistically-equivalent MS values among reconstituted starches (Table 4), hydroxypropylated starch derivatives still tended to exhibit distinct pasting viscosity profile patterns (Fig. 3B and D), as was observed for the reaction controls (Fig. 3A and C). Within a genotype, pasting viscosity characteristics (e.g., peak, trough, final, breakdown, setback) of hydroxypropylated starch derivatives and their reaction controls generally increased with an increase in A-type granule content (Fig. 4). For equivalent A-type granule contents of a given genotype, deviations in pasting viscosity characteristics between hydroxypropylated starch derivatives and their respective reaction controls were largely maintained. Thus, the influence of differing A/B-type granule ratios on wheat starch pasting properties did not appear to be alleviated by hydroxypropylation.

4. Conclusions

This work investigated the effect of granule size distribution on the reactivity and swelling, gelatinization and pasting properties of waxy and normal wheat starch derivatized with either PO or POA. For highly-purified A- and B-type starch granule fractions reacted with POA at low substitution levels, no significant MS value differences were observed between the two granule types and/or between waxy and normal genotypes. This same result was also observed in reactions with PO at commercial MS levels, as wheat starches reconstituted to possess differing A/B-type granule ratios also exhibited indistinguishable reactivities. Thus, reactions involving slow-reacting reagents (i.e., PO, POA), may reduce the significance of starch intrinsic characteristic differences (e.g., granule size/surface area, relative crystallinity, amylopectin structure) in chemical modification reactions involving wheat starch A- and B-type granules. Despite indistinguishable MS values observed between hydroxypropylated reconstituted wheat starches possessing varied A/B-type granule ratios, including pure A- and B-type granule fractions, general trends in swelling, gelatinization, and pasting properties observed across the hydroxypropylated starch granule fractions closely followed those of their respective reaction controls (though in some cases property differences between reconstituted A- and B-type granule mixtures were slightly lessened by hydroxypropylation). POA derivatization appeared to have a more profound impact on minimizing pasting attribute differences between A- and B-type granules of a given genotype than did hydroxypropylation, despite the fact that the highest POA MS levels ($MS \approx 0.022$–0.0235) were approximately fourfold lower than those of PO ($MS \approx 0.095$–0.105). It is likely that the charged nature of the POA reagent induced more significant changes to starch molecules and/or granules; thus, a charged reagent may be more likely to mitigate inherent differences in native A- and B-type granule physical properties than an uncharged one. These results suggest that while substitution reactions with PO (or POA) may not completely override inherent differences in native wheat starch properties (due to variable A/B-type granule ratios), substitution has potential to minimize or normalize wheat starch properties across slight fluctuations in A/B-type granule ratios.

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