Available online at www.sciencedirect.com

ScienceDirect

Carbohydrate Polymers 68 (2007) 305–313

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Effect of hydroxypropylation and alkaline treatment in hydroxypropylation on some structural and physicochemical properties of heat-moisture treated wheat, potato and waxy maize starches

Anil Gunaratne, Harold Corke *

Cereal Science Laboratory, Department of Botany, The University of Hong Kong, Pokfulam Road, Hong Kong

Received 26 September 2006; received in revised form 5 December 2006; accepted 7 December 2006
Available online 24 January 2007

Abstract

Hydroxypropylation was carried out on heat-moisture treated (HMT) wheat, potato and waxy maize starches. Hydroxypropylation increased swelling factor and amylose leaching of both native and HMT starches. Hydroxypropylation of HMT starches reduced enthalpies of gelatinization and amylopectin retrogradation more than for the corresponding non-HMT hydroxypropylated starches. This indicates that heat-moisture treatment increases the derivatization of amylopectin. Disruption and reorientation of amylopectin double helices during heat-moisture treatment could facilitate the access of reaction reagent to the highly ordered crystalline regions resulting in greater derivatization. Cold paste viscosity was greatly increased with high pasting stability when hydroxypropyl groups were introduced to HMT wheat and potato starches. Alkaline treatment increased gelatinization temperature of all the starches but enthalpy was unaffected. Amylose leaching and swelling factor greatly increased in wheat but decreased in potato and waxy maize starches with alkaline treatment. This increased amylose leaching and swelling factor along with greater reduction of amylose–lipid complex endotherm of wheat starch by alkaline treatment is consistent with the disruption of amylose–lipid complex. The amylose–lipid complex is susceptible to hydrolysis in alkaline conditions. Heat-moisture treatment had no influence on transition parameters of amylose–lipid complex.

Keywords: Heat-moisture treatment; Hydroxypropylation; Physicochemical properties

1. Introduction

Modified starches are important functional ingredients in processed foods. Hydroxypropylation is commonly used for making modified starch for the food industry. Hydroxypropyl groups are hydrophilic in nature and when introduced into starch granules weaken the internal bond structure holding granules together. The substituent disturbs the association of the polysaccharide chains preventing retrogradation due to the hydrogen bonds. Improved functional properties of hydroxypropylated starches such as extended shelf life of cold storage products (freeze–thaw stability), higher peak viscosity and paste clarity, and decreased gelatinization temperatures are well documented (Hoover, Hannouz, & Sosulski, 1988; Kim & Eliasson, 1993; Liu, Ramsden, & Corke, 1999; Pal, Singhal, & Kulkarni, 2002; Perera, Hoover, & Martin, 1997). By light microscopic studies Kim, Hermansson, and Eriksson (1992) claimed that hydroxypropylation mainly takes place in the central region of the potato starch granule. Biliaderis (1982) reported that modification occurs throughout the granules. Gray and BeMiller (2005) believed that derivatization first occurs in the most accessible amorphous region and proceeds through various regions until it reaches the highly organized crystalline region. Shi and BeMiller (2000, 2002) for normal maize starch, and Kavitha and

---

* Corresponding author. Tel.: +852 2859 0314; fax: +852 3015 6473.
E-mail addresses: Harold@hku.hk, hcorke@yahoo.com (H. Corke).

0144-8617/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2006.12.004

BeMiller (1998) for potato starch showed that derivatization occurs more in the amylose chains than in amylopectin. According to Shi and BeMiller (2002) derivatization facilitates amylose leaching; preferential leaching of derivatized amylose decreased as the MS of the whole granule increased.

Perera et al. (1997) showed that alkaline treatment (NaOH and Na_2SO_4) during hydroxypropylation disrupts the double helices within the amorphous region altering crystalline orientation of the starch granule. It has been reported that granule swelling is essential in order for the substitution reaction to take place in granular starch (Hauber, BeMiller, & Fannon, 1992). Alkaline treatment could induce swelling by ionizing starch hydroxyl groups at higher pH (Gray & BeMiller, 2005). In a study on hydroxypropylation of heat-moisture treated potato starch Perera et al. (1997) reported that heat-moisture treatment enhanced the access of hydroxyl groups to the amorphous region. However, systematic studies to characterize the influence of physical modification (e.g., heat-moisture treatment) on the derivatization process have not been reported. Comparative study of the derivatization of native starch with heat-moisture treated starch may reveal more information on the effect of derivatization on the structural and functional properties.

Structural changes within the amorphous region and crystalline region of starch granules such as starch chain interaction within the amorphous region and disruption and reorientation of starch crystallites caused by heat-moisture treatment has been discussed (Gunaratne & Hoover, 2002; Hoover, Vasanthan, Senanayake, & Martin, 1994; Hoover & Vasanthan, 1994). Derivatization of structurally altered starch granules may require less chemical to achieve desirable chemical bonding and target functionalities probably by affecting the accessibility to reaction reagents and the reaction site. For example, destabilization and reorientation of amylopectin double helices could allow more derivatization to take place within the crystalline region by facilitating access of reaction reagents to the crystalline region. BeMiller (1997) reported that one avenue for the development of novel starch products is the control of the location of the reaction within the starch granules. The objective of this study was therefore to characterize some structural and functional properties when hydroxypropyl groups are introduced to heat-moisture treated starches and to investigate the influence of the alkaline treatment (reaction conditions used during hydroxypropylation) on some structural and functional properties.

2. Materials and methods

2.1. Materials

Potato starch, wheat starch, waxy maize starch and propylene oxide were from Sigma Chemical Co., (St. Louis, MO, USA).

2.2. Methods

2.2.1. Swelling factor

Swelling factor, the ratio of the volume of swollen starch granules to the volume of dry starch was determined by the method of Tester and Morrison (1990a), where starch (50 mg, db) was heated at 85 °C for 30 min in 5 mL water.

2.2.2. Amylose leaching

Distilled water or solution (10 mL) was added to starch (20 mg, db) in a screw cap tube. Tubes were then heated at 85 °C for 30 min. After cooling to ambient temperature, samples were centrifuged at 2000*g* for 10 min. Amylose content of supernatant (0.1 mL) was estimated as described by Chrastil (1987).

2.2.3. Differential scanning calorimetry

Gelatinization and dissociation parameters were measured using a TA 2920 Modulated DSC Thermal Analyzer differential scanning calorimeter equipped with a thermal analysis data station (TA Instruments, Newcastle, DE). Starch (3 mg) was directly measured on to the aluminum DSC pan and distilled water (9 μL) was added with a microsyringe and mixed for homogenization. Pans were sealed, and allowed to stand for 1 h at room temperature for even distribution of water. The scanning temperature and the heating rates were 30–120 °C and 10 °C/min, respectively. An empty pan was used as reference for all measurements.

2.2.4. Pasting properties

Pasting properties of starches were determined using a Rapid Visco-Analyzer (RVA) model 3D (Newport Scientific, Warriewood, Australia). Distilled water or hydrochloric acid solution (25.5 g) was added to starch (2.3 g, db) in the RVA canister to obtain a total constant sample weight of 27.8 g (8.2% starch concentration). The slurry was then manually homogenized using the plastic paddle to avoid lump formation before the RVA run. A programmed heating and cooling cycle was set for 22 min, where it was first held at 50 °C for 1.0 min, heated to 95 °C in 7.5 min, further held at 95 °C for 5 min, cooled to 50 °C within 7.5 min and held at 50 °C for 1 min.

2.2.5. Gel textural analysis

Gel hardness was determined on the starch gel made in the RVA testing using a TA-XT2 Texture Analyzer (Stable Micro Systems, Godalming, England). After RVA testing, the paddle was removed and the starch paste in the canister was covered by Parafilm and stored at 4 °C for 7 h. The gel was compressed at a speed of 0.5 mm/s to a distance of 10 mm with a 6 mm cylindrical probe. The maximum force peak in the TPA profile represents the gel hardness.

2.2.6. Hydroxypropylation

Hydroxypropylation of starches was performed according to the method of Choi and Kerr (2004) with some slight modifications. Starch sample (50 g db) was suspended in distilled water (110 mL) containing 10 g Na_2SO_4 in a centrifuge bottle. After adjusting pH to 11.3 with 1 M NaOH, 1.5, 3.0, 4.5 mL of propylene oxide was added and the bottle was immediately capped and shaken vigorously. Sample was then placed at 35 °C in shaking water bath with continuous shaking for 24 h. The reaction was terminated by adjusting pH to 5.3 with 1 M HCl. Slurry was then centrifuged at 3000*g* for 10 min and recovered starch cake was washed with distilled water and dried at 35 °C. Degree of modification was determined by the method of Johnson (1969).

2.2.7. Retrogradation

Starch gel was prepared in the DSC pan using 1:1 starch to water ratio scanning the sample to 120 °C. Samples were then stored at 4 °C for 24 h to initiate nucleation. After that samples were kept at 40 °C for 7 days before rescanning by DSC. Temperature range and heating rate were 30–120 °C and 10 °C/min, respectively.

3. Results and discussion

3.1. Swelling factor and amylose leaching

As commonly observed, heat-moisture treatment decreased swelling ability of all tested starches while hydroxypropylation increased it (Table 1). Additional chain interaction and loss of some of the double helices during heat-moisture treatment could restrict the swelling capacity (Gunaratne & Hoover, 2002; Hoover & Vasanthan, 1994). Increased granular swelling after hydroxypropylation is expected result because loosened starch structure resulting from hydroxypropylation could increase the swelling factor by promoting water penetration into the granule.

Alkaline treatment (under the conditions prevailing during hydroxypropylation, but in the absence of propylene oxide) [NaOH and Na_2SO_4, heating at 40 °C for 24 h] increased the swelling factor of wheat starch but slightly decreased it in potato and waxy maize starches. In the hydroxypropylation reaction medium, many factors could

Table 1
Swelling factor (SF), amylose leaching (AMYL), gel hardness (GH), retrogradation enthalpy (ΔH_R), and degree of modification (DS) of hydroxypropylated native and heat-moisture treated hydroxypropylated wheat, potato and waxy maize starches

Starch	Treatment[a]	SF at 85 °C	AMYL(%) at 85 °C	GH (g)	ΔH_R (J/g)	DS
Wheat	Native	15.0 ± 0.2[b]	9.5 ± 0.1	76 ± 0.4	4.4 ± 0.1	–
	Control	19.2 ± 0.1	16.7 ± 0.2	73 ± 0.6	4.5 ± 0.2	–
	HP1.5	21.1 ± 0.1	19.3 ± 0.3	38 ± 0.2	2.8 ± 0.1	0.023
	HP3.0	27.5 ± 0.2	20.6 ± 0.1	28 ± 0.4	1.9 ± 0.2	0.042
	HP4.5	29.0 ± 0.3	21.8 ± 0.2	20 ± 0.1	1.5 ± 0.1	0.127
	HMT	10.8 ± 0.1	6.4 ± 0.1	100 ± 0.4	4.2 ± 0.3	–
	Control	12.1 ± 0.1	13.1 ± 0.4	104 ± 0.3	4.2 ± 0.1	–
	HMT-HP1.5	17.8 ± 0.3	14.7 ± 0.3	55 ± 0.5	2.2 ± 0.1	0.024
	HMT-HP3.0	19.4 ± 0.2	16.5 ± 0.1	23 ± 0.1	1.1 ± 0.2	0.049
	HMT-HP4.5	22.1 ± 0.4	18.2 ± 0.1	23 ± 0.2	0.8 ± 0.1	0.139
Potato	Native	49.1 ± 0.2	15.0 ± 0.3	40 ± 0.1	8.5 ± 0.0	–
	Control	47.2 ± 0.1	12.2 ± 0.1	45 ± 0.3	8.4 ± 0.1	–
	HP1.5	56.6 ± 0.4	12.8 ± 0.2	24 ± 0.4	6.7 ± 0.3	0.027
	HP3.0	59.3 ± 0.1	13.7 ± 0.3	–	5.0 ± 0.1	0.047
	HP4.5	64.0 ± 0.2	13.8 ± 0.1	–	4.2 ± 0.2	0.139
	HMT	11.3 ± 0.2	3.8 ± 0.1	45 ± 0.6	7.2 ± 0.1	–
	Control	8.4 ± 0.1	3.4 ± 0.0	52 ± 0.2	7.3 ± 0.2	–
	HMT-HP1.5	14.6 ± 0.1	3.7 ± 0.1	16 ± 0.2	5.0 ± 0.2	0.029
	HMT-HP3.0	17.0 ± 0.3	3.7 ± 0.1	12 ± 0.5	4.2 ± 0.1	0.055
	HMT-HP4.5	18.1 ± 0.1	3.6 ± 0.1	10 ± 0.1	3.0 ± 0.2	0.154
Waxy maize	Native	38.0 ± 0.3	2.1 ± 0.0	8 ± 0.4	8.7 ± 0.3	–
	Control	34.1 ± 0.1	2.0 ± 0.2	9 ± 0.3	8.6 ± 0.1	–
	HP1.5	37.7 ± 0.3	1.9 ± 0.1	–	7.6 ± 0.2	0.019
	HP3.0	39.1 ± 0.2	1.4 ± 0.1	–	6.9 ± 0.1	0.038
	HP4.5	39.8 ± 0.5	1.2 ± 0.2	–	3.1 ± 0.2	0.098
	HMT	34.0 ± 0.1	1.7 ± 0.1	9 ± 0.3	8.8 ± 0.3	–
	Control	28.3 ± 0.1	1.8 ± 0.0	9 ± 0.7	8.7 ± 0.3	–
	HMT-HP1.5	34.1 ± 0.3	1.2 ± 0.1	–	7.2 ± 0.2	0.024
	HMT-HP3.0	34.4 ± 0.1	1.3 ± 0.1	–	5.8 ± 0.1	0.043
	HMT-HP4.5	36.7 ± 0.2	1.2 ± 0.0	–	2.2 ± 0.1	0.109

[a] HMT, heat-moisture treated; HP, hydroxypropylated; HMT-HP, heat-moisture treated hydroxypropylated; 1.5, 3.0, and 4.5, volume (mL) of propylene oxide.

[b] Values are means of triplicate determinations ± standard deviations.

affect granular swelling such as pH, swelling inhibiting salt types and their concentration and starch concentration. By ionizing hydroxyl groups of starch chains, increased pH could disrupt the hydrogen bonds and thereby increase the granular swelling (Gray & BeMiller, 2005). It has been reported that swelling must first occur in the granular starch in order for the derivatization process to proceed (Hauber et al., 1992). Confirming this claim, Shi and BeMiller (2000) reported that replacing of Na_2SO_4 by the more powerful swelling inhibitor potassium citrate requires 1.8 times more propylene oxide to achieve the same degree of modification. Alkaline treatment greatly increased the amylose leaching of wheat starch but slightly decreased it in potato and waxy maize starches. DSC curves of alkaline-treated wheat starch showed loss of amylose–lipid complex to a greater extent (Fig. 1). It is well known that the existence of amylose–lipid complex reduces the amylose leaching and swelling ability of starch granules, thus the cleavage of amylose–lipid complex at higher alkalinity could be the reason for resulting higher amylose leaching and swelling ability of alkaline-treated wheat starch. For potato and waxy maize starches amylose leaching was decreased by alkaline treatment. Hydroxypropylation increased the amylose leaching of all the starches. Hydroxypropyl groups disrupt the hydrogen bonding of adjacent starch chains promoting their flexibility. This could facilitate the mobility of amylose chains.

3.2. Gelatinization

Decreases were observed for gelatinization temperature and enthalpy of all native and heat-moisture treated starches after hydroxypropylation. As commonly observed, heat-moisture treatment increased gelatinization temperature while decreasing the enthalpy. Alkaline treatment increased gelatinization temperature of all the starches but enthalpy was unaffected (Table 2). Delayed gelatinization after alkaline treatment could be due to the influence of a swelling inhibiting salt (Na_2SO_4). Salts like Na_2SO_4 have been shown to increase the gelatinization temperature and to decrease the leaching of starch polysaccharide chains (Oosten, 1990). Consistent with previous studies, increased granular swelling after hydroxypropylation reduces energy requirement for gelatinization. Introduction of hydroxypropyl groups to heat-moisture treated starches decreased gelatinization enthalpy to a higher extent compared with corresponding hydroxypropylated native starches. Gray and BeMiller (2005) reported that in the derivatization process, reagent solution enters most readily to the less ordered amorphous region derivatizing it first, and that derivatization could further swell granules by opening the crystalline region permitting access of the reagent solution. It seems that disruption of starch crystallites and reorientation of amylopectin double helices by heat-moisture treatment allowed more reaction reagents to access the crystalline region increasing derivatization in that region. More derivatization could disrupt more hydrogen bonds in the crystalline region, subsequently it would require less energy to disrupt the crystalline region during gelatinization.

Heat-moisture treatment increased the degree of substitution (Table 1). Similar results were reported for the hydroxypropylation of heat-moisture treated potato starch (Perera et al., 1997). According to them, heat-moisture treatment increased the amount of amorphous region within the granular interior facilitating the derivatization. In this study, as described above heat-moisture treatment facilitates more derivatization to take place in the crystalline region. This may also contribute to increase the degree of modification.

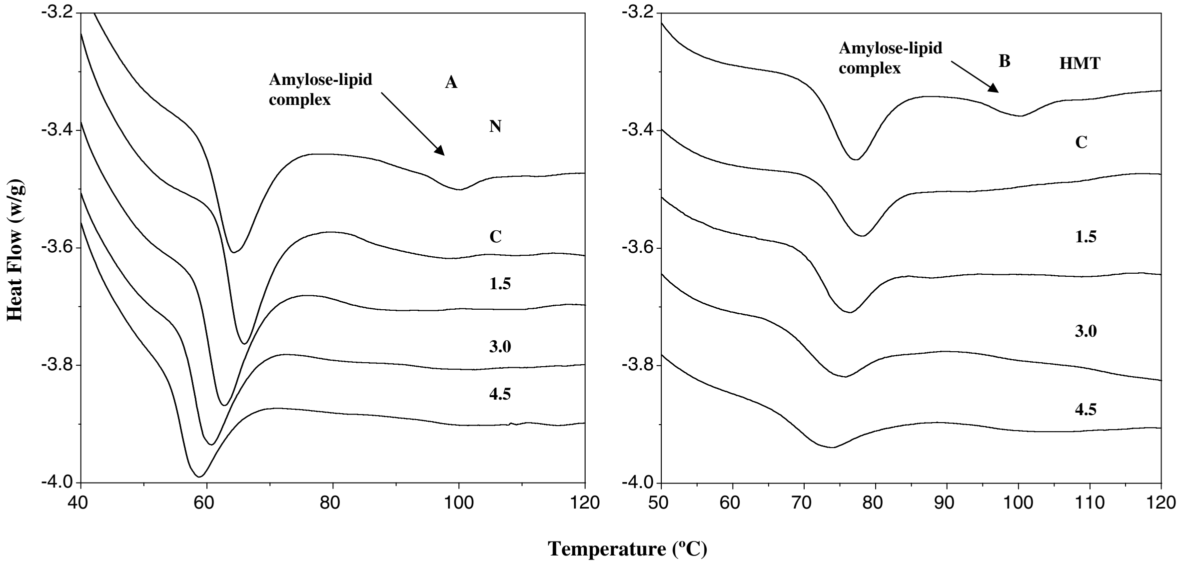


Fig. 1. DSC curves obtained from gelatinization of hydroxypropylated native wheat starch (A); heat-moisture treated hydroxypropylated wheat starch (B). N, native; HMT, heat-moisture treated; C, control; 1.5, 3.0, and 4.5, volume (mL) of propylene oxide used for hydroxypropylation.

Table 2
Gelatinization parameters[a] of hydroxypropylated native and heat-moisture treated hydroxypropylated wheat, potato and waxy maize starches

Starch	Treatment[b]	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Wheat	Native	58.9 ± 0.1[c]	64.3 ± 0.1	76.8 ± 0.5	10.4 ± 0.1
	Control	61.5 ± 0.2	65.7 ± 0.1	79.0 ± 0.1	10.3 ± 0.3
	HP1.5	58.0 ± 0.2	62.6 ± 0.3	75.5 ± 0.3	9.7 ± 0.2
	HP3.0	56.7 ± 0.3	60.6 ± 0.2	71.2 ± 0.1	8.5 ± 0.2
	HP4.5	53.6 ± 0.1	58.5 ± 0.4	69.8 ± 0.3	7.4 ± 0.3
	HMT	71.1 ± 0.1	76.8 ± 0.5	86.0 ± 0.1	5.8 ± 0.2
	Control	71.8 ± 0.4	77.9 ± 0.2	89.2 ± 0.3	5.4 ± 0.1
	HMT-HP1.5	70.2 ± 0.3	75.7 ± 0.1	85.1 ± 0.4	4.1 ± 0.5
	HMT-HP3.0	66.5 ± 0.2	74.9 ± 0.2	84.1 ± 0.1	3.8 ± 0.1
	HMT-HP4.5	64.6 ± 0.2	73.1 ± 0.1	84.8 ± 0.1	3.3 ± 0.4
Amylose–lipid complex	Native	92.9 ± 0.3	100.1 ± 0.4	107.4 ± 0.2	1.6 ± 0.1
	HMT	93.1 ± 0.6	100.3 ± 0.2	107.2 ± 0.5	1.7 ± 0.3
Potato	Native	61.3 ± 0.1	67.0 ± 0.3	82.6 ± 0.5	15.6 ± 0.3
	Control	62.3 ± 0.4	68.2 ± 0.1	81.3 ± 0.1	15.4 ± 0.2
	HP1.5	60.1 ± 0.1	65.2 ± 0.3	78.1 ± 0.1	14.3 ± 0.2
	HP3.0	59.6 ± 0.3	64.5 ± 0.2	76.0 ± 0.3	13.8 ± 0.1
	HP4.5	55.9 ± 0.1	61.1 ± 0.1	73.0 ± 0.2	13.2 ± 0.4
	HMT	73.5 ± 0.2	81.6 ± 0.3	93.1 ± 0.4	6.8 ± 0.3
	Control	74.2 ± 0.4	81.9 ± 0.5	93.4 ± 0.3	6.5 ± 0.1
	HMT-HP1.5	72.2 ± 0.2	80.6 ± 0.3	91.9 ± 0.1	5.6 ± 0.2
	HMT-HP3.0	70.7 ± 0.1	79.8 ± 0.2	89.4 ± 0.3	4.6 ± 0.1
	HMT-HP4.5	68.5 ± 0.1	77.9 ± 0.1	88.1 ± 0.4	4.5 ± 0.1
Waxy maize	Native	68.4 ± 0.3	74.1 ± 0.4	85.3 ± 0.2	14.5 ± 0.3
	Control	68.6 ± 0.1	74.9 ± 0.2	86.9 ± 0.5	14.2 ± 0.3
	HP1.5	67.4 ± 0.1	72.2 ± 0.1	84.8 ± 0.1	13.9 ± 0.4
	HP3.0	66.1 ± 0.3	71.4 ± 0.1	82.3 ± 0.3	13.5 ± 0.1
	HP4.5	64.8 ± 0.2	70.3 ± 0.2	82.1 ± 0.2	13.1 ± 0.2
	HMT	77.6 ± 0.3	83.2 ± 0.3	95.8 ± 0.3	11.8 ± 0.3
	Control	77.9 ± 0.4	83.8 ± 0.2	95.9 ± 0.1	11.7 ± 0.1
	HMT-HP1.5	77.2 ± 0.1	83.1 ± 0.2	93.8 ± 0.6	9.7 ± 0.2
	HMT-HP3.0	75.8 ± 0.2	81.2 ± 0.1	91.2 ± 0.3	9.4 ± 0.2
	HMT-HP4.5	74.1 ± 0.1	80.0 ± 0.5	90.3 ± 0.4	8.8 ± 0.1

[a] T_o, onset; T_p, peak; T_c, conclusion.

[b] HP, hydroxypropylated; HMT, heat-moisture treated; HMT-HP, heat-moisture treated hydroxypropylated; 1.5, 3.0, and 4.5, volume (mL) of propylene oxide.

[c] Values are means of triplicate determination ± standard deviation.

3.3. Pasting properties and gel hardness

As expected, hydroxypropylation decreased pasting temperature but increased peak viscosity in all the native starches (Table 3 and Fig. 2a, b and c). Heat-moisture treatment increased pasting temperature and pasting stability to a greater extent whereas hydroxypropylation decreased pasting stability of all native starches. These are expected pasting characteristics of hydroxypropylated starches because higher swelling and amylose leaching from the loosened hydroxypropylated granule will allow granules to reach higher peak viscosity, but structurally weaker granules will disintegrate rapidly at higher temperature resulting in rapid loss of viscosity. By restricting swelling and amylose leaching, heat-moisture treatment could increase the pasting temperature while decreasing peak viscosity. Higher pasting stability of heat-moisture treated starches is consistent with greatly reduced granule breakdown during the pasting process. Similar to native starches, introduction of hydroxypropyl groups decreased the pasting onset temperature of heat-moisture treated starches. The most interesting pasting characteristic observed for the hydroxypropylated heat-moisture treated wheat and potato starches is the increase of cold paste viscosity (CPV) and setback (SB) to a greater extent while maintaining higher pasting stability (Table 3 and Fig. 2a and b). Thus the introduction of hydroxypropyl groups to heat-moisture treated starches could be applied for products which require higher end viscosity. It is well known that when gelatinized starch paste is subjected to cooling the extent of viscosity increase is mainly governed by the rapid reassociation of linear amylose chains via formation of gel matrix. In case of potato starch, heat-moisture treatment decreased amylose leaching to a greater extent. Alkaline treatment or hydroxypropylation also did not much affect the magnitude of the amylose leaching of heat-moisture treated potato starch (Table 1) but still cold paste viscosity and setback were greatly increased in hydroxypropylated heat-moisture treated potato starch. This indicates that the concentration of amylose in the continuous media does not play a key role in the increase of final viscosity. Therefore, it appears that greater extent of derivatization in amy-

Table 3
Pasting properties[a] of hydroxypropylated native and heat-moisture treated hydroxypropylated wheat, potato and waxy maize starches

Starch	Treatment[b]	PV	HPV	BD	CPV	SB
Wheat	Native	150 ± 0.8[c]	112 ± 0.6	38 ± 0.7	212 ± 0.9	100 ± 0.5
	Control	164 ± 1.3	93 ± 0.9	71 ± 0.4	241 ± 0.7	145 ± 0.8
	HP1.5	223 ± 2.1	74 ± 1.8	148 ± 0.9	196 ± 0.6	122 ± 1.3
	HP3.0	240 ± 0.9	69 ± 1.1	171 ± 0.8	182 ± 0.9	112 ± 1.1
	HP4.5	258 ± 0.8	68 ± 0.8	190 ± 0.6	178 ± 1.2	109 ± 0.6
	HMT	100 ± 1.6	85 ± 0.7	15 ± 0.4	130 ± 1.5	46 ± 0.5
	Control	74 ± 1.5	73 ± 1.5	0.0	173 ± 0.9	99 ± 0.7
	HMT-HP1.5	83 ± 1.1	83 ± 1.1	0.0	240 ± 0.8	157 ± 0.9
	HMT-HP3.0	88 ± 0.3	88 ± 0.3	0.0	288 ± 0.5	200 ± 1.2
	HMT-HP4.5	108 ± 0.6	102 ± 1.8	6.0 ± 0.4	333 ± 1.3	232 ± 0.7
Potato	Native	665 ± 0.7	174 ± 0.7	491 ± 1.5	256 ± 1.6	81 ± 0.8
	Control	705 ± 1.6	197 ± 1.2	512 ± 1.6	289 ± 0.9	92 ± 0.6
	HP1.5	726 ± 1.8	174 ± 1.5	552 ± 1.2	228 ± 1.1	54 ± 1.3
	HP3.0	745 ± 1.2	175 ± 0.9	570 ± 2.1	234 ± 0.8	58 ± 0.6
	HP4.5	775 ± 2.1	165 ± 1.2	610 ± 1.6	234 ± 1.3	68 ± 1.4
	HMT	162 ± 1.3	162 ± 1.3	0.0	253 ± 0.9	91 ± 1.2
	Control	180 ± 1.8	180 ± 1.8	0.0	290 ± 1.2	109 ± 0.9
	HMT-HP1.5	174 ± 0.9	174 ± 0.9	0.0	298 ± 1.4	123 ± 1.3
	HMT-HP3.0	208 ± 1.1	208 ± 1.1	0.0	390 ± 0.9	181 ± 0.6
	HMT-HP4.5	217 ± 0.7	217 ± 0.7	0.0	445 ± 1.3	230 ± 0.5
Waxy maize	Native	278 ± 2.2	117 ± 1.5	160 ± 1.2	147 ± 0.5	43 ± 0.6
	Control	271 ± 1.5	104 ± 1.4	168 ± 0.9	138 ± 0.8	35 ± 1.1
	HP1.5	280 ± 1.6	98 ± 0.5	182 ± 0.8	138 ± 0.7	43 ± 0.7
	HP3.0	284 ± 0.9	104 ± 0.7	180 ± 1.2	141 ± 0.5	37 ± 0.7
	HP4.5	304 ± 1.9	111 ± 0.4	193 ± 1.1	148 ± 1.4	37 ± 1.1
	HMT	144 ± 0.8	69 ± 1.2	75 ± 1.5	82 ± 0.7	13 ± 0.5
	Control	146 ± 0.7	62 ± 1.3	83 ± 0.5	77 ± 0.6	14 ± 0.8
	HMT-HP1.5	162 ± 1.6	77 ± 1.1	85 ± 0.6	94 ± 0.4	17 ± 0.5
	HMT-HP3.0	169 ± 2.9	78 ± 2.1	90 ± 0.8	96 ± 0.7	18 ± 0.8
	HMT-HP4.5	167 ± 1.7	80 ± 0.8	87 ± 1.5	98 ± 1.1	17 ± 1.2

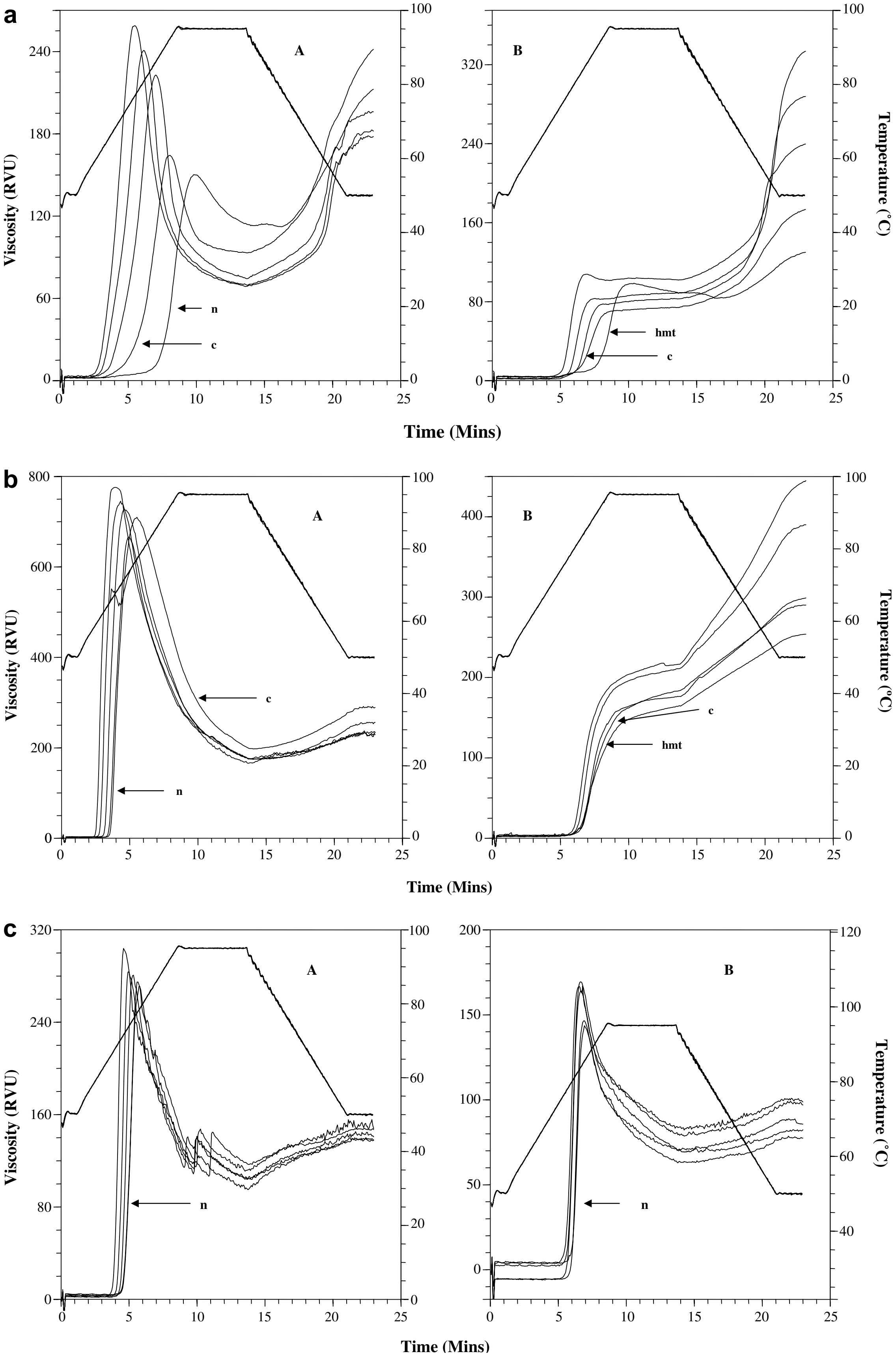
[a] PV, peak viscosity; HPV, hot paste viscosity; BD, breakdown; CPV, cold paste viscosity; SB, setback.

[b] HMT, heat-moisture treatment; HP, hydroxypropylation; HMT-HP, heat-moisture treated hydroxypropylated; 1.5, 3.0 and 4.5, volume (mL) of propylene oxide.

[c] Values are means of triplicate determinations ± standard deviation.

lopectin polymers in heat-moisture treated starch as concluded before could promote more interactions between amylopectin rich filler component and continuous gel matrix. This could increase the CPV. Control samples of wheat and potato starches also showed a substantial increase of cold paste viscosity. This was probably due to the influence of swelling inhibiting salt (Na_2SO_4) in the formation of gel matrix. The nearly unchanged CPV and SB of hydroxypropylated heat-moisture treated waxy maize starch were expected as it is virtually amylose-free. While hydroxypropylation resulted in soft gels, heat-moisture treatment increased gel hardness. Alkaline treatment slightly increased the gel hardness of potato and waxy maize starches but decreased it in wheat starch, indicating that weaker wheat starch granules resulted due to the disruption of amylose–lipid complex during alkaline treatment, and the subsequent hydration reduced the stiffness of the gel. Hydroxypropylation caused decreased gel hardness of heat-moisture treated wheat and potato starch. At higher degree of modification both native and heat-moisture treated waxy maize and potato native starch produced very soft gel which was not measurable under the experimental conditions (Table 1). In the starch gel, interchain association of exuded amylose chains from the swollen granules surround the gelatinized starch granules, and thus a starch gel can be regarded as a hydrated polymer composite where swollen amylopectin-rich granules are embedded in and reinforce a continuous matrix of entangled amylose molecules

Fig. 2. (a) RVA curves of hydroxypropylated wheat native (A) and heat-moisture treated hydroxypropylated wheat (B) starches; n, native; HMT, heat-moisture treated; c, control; other curves represented in both (A) and (B) from right to left are native or HMT hydroxypropylated with 1.5, 3.0 and 4.5 mL propylene oxide. (b) RVA curves of hydroxypropylated potato native (A), and heat-moisture treated hydroxypropylated potato (B) starches; *n*, native; HMT, heat-moisture treated; c, control; other curves represented in both (A) and (B) from right to left are native or HMT hydroxypropylated with 1.5, 3.0 and 4.5 mL of propylene oxide. (c) RVA curves of hydroxypropylated waxy maize native (A) and heat-moisture treated hydroxypropylated waxy maize (B) starches; c, control; other curves represented in both (A) and (B) from right to left are native or HMT, hydroxypropylated with 1.5, 3.0 and 4.5 mL of propylene oxide.


a
A
B
Viscosity (RVU)
Temperature (°C)
n
c
hmt
Time (Mins)
0
60
120
180
240
80
160
240
320
0
20
40
60
80
100
0
5
10
15
20
25
b
A
B
Viscosity (RVU)
Temperature (°C)
c
n
c
hmt
0
200
400
600
800
0
100
200
300
400
Time (Mins)
c
A
B
Viscosity (RVU)
Temperature (°C)
n
n
0
80
160
240
320
0
50
100
150
200
40
60
80
100
120
Time (Mins)

(Ring, 1985). The textural and mechanical properties of starch gel where swollen gelatinized amylopectin-rich granules are embedded in the continuous amylose gel matrix would depend on the amylose concentration and rheological characteristics of the amylose gel matrix, rigidity (deformability) of the swollen starch particles, volume fraction of the swollen granules, and interaction between swollen particles and amylose matrix (Doublier, Llamas, & Le Meur, 1987; Eliasson, 1986; Morris, 1990). Weaker, fragile less rigid swollen granules resulting from hydroxypropylation could produce soft gel. Eerlingen, Jacobs, Block, and Delcour (1997) found that increased or decreased gel storage moduli could result based on the heat-moisture treatment conditions and the concentration of the starch gel, as these affect the extent of swelling, solubility and close packing concentration. Hoover et al. (1994) reported that restriction of swelling by HMT favors amylose aggregation in the formation of the gel matrix leading to firmer gels after HMT.

3.4. Retrogradation

Hydroxypropylation decreased amylopectin retrogradation, as expected, in all the starches. The greater the degree of modification, the more the retrogradation decreased. By inhibiting interchain association, hydroxypropyl groups substituted to amylopectin chains could decrease the extent of reassociation or retrogradation. Inclusion of the same propylene oxide volume in the derivatization reaction resulted in more inhibition of amylopectin retrogradation in heat-moisture treated starch compared to the corresponding non-HMT starches (Table 1 and Fig. 3). As stated above, disruption and reorientation of amylopectin double helices during heat-moisture treatment facilitates more reaction reagent to access the crystalline region causing greater modification of amylopectin. More derivatized amylopectin could reduce the interchain association of amylopectin to a greater extent compared with native starch decreasing amylopectin retrogradation. Alkaline treatment showed no influence on amylopectin retrogradation in all the starches, but heat-moisture treatment resulted in amylopectin retrogradation of potato starch while other starches were unaffected. Longer amylopectin chains of potato starch (B-type starch) could be more susceptible to the degradation during heat-moisture treatment reducing the average unit chain length. This may weaken the lateral association of amylopectin in the retrogradation process.

4. Conclusions

In the derivatization reaction, alkaline treatment greatly influenced on properties of wheat starch such as higher amylose leaching, swelling, and early onset of peak viscosity. This seems highly related to the disruption of amylose–lipid complex at higher pH (11.4). Destabilization and reorientation of amylopectin double helices during heat-moisture treatment facilitates more modification in the crystalline region. Thus heat-moisture treatment could be employed to alter the location of the derivatization reaction while achieving novel starch properties such as higher final paste viscosity with greater pasting stability. Increased degree of modification after heat-moisture treatment indicates increased reaction efficiency. Thus, it would require less concentration of reaction reagents to achieve the desired degree of chemical bonding and improved functional characteristics. Characterization of hydroxypropylation of heat-moisture treated starches which are treated with different heat and moisture combinations, and determina-

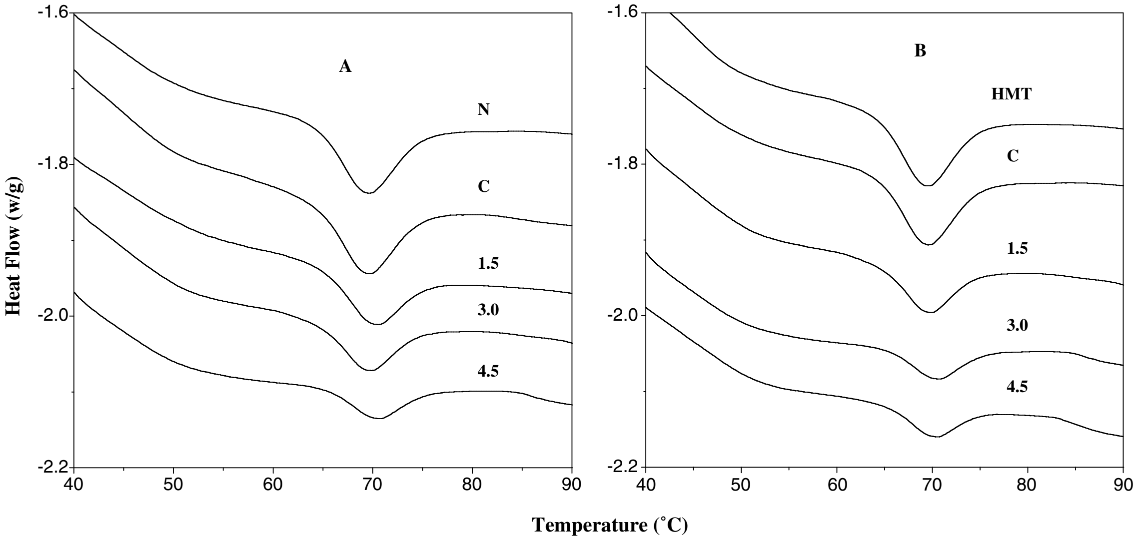


Fig. 3. DSC curves obtained from retrogradation of hydroxypropylated wheat native (A) and heat-moisture treated hydroxypropylated wheat (B) starches. N, native; HMT, heat-moisture treated; C, control; 1.5, 3.0 and 4.5, volume (mL) of propylene oxide used for hydroxypropylation.

tion of the best combination that best mimics the desired behavior with minimum chemical bonding, is important.

Acknowledgements

This work was supported by grants from the University of Hong Kong Committee on Research and Conference Grants, and the Hong Kong Research Grant Council.

References

BeMiller, J. N. (1997). Starch modification: challenges and prospects. *Starch/Starke, 49*, 127–131.

Biliaderis, C. G. (1982). Physical characteristics, enzymatic digestibility, and structure of chemically modified smooth pea and waxy maize starches. *Journal of Agricultural and Food Chemistry, 30*, 925–930.

Choi, S. G., & Kerr, W. L. (2004). Swelling characteristics of native and chemically modified wheat starches as a function of heating temperature and time. *Starch/Starke, 56*, 181–189.

Chrastil, J. (1987). Improved colorimetric determination of amylose in starches or flours. *Carbohydrate Research, 159*, 154–158.

Doublier, J. L., Llamas, G., & Le Meur, M. (1987). A rheological investigation of cereal starch pastes and gels. Effects of pasting procedures. *Carbohydrate Polymers, 7*, 251–275.

Eerlingen, R. C., Jacobs, H., Block, K., & Delcour, J. A. (1997). Effects of hydrothermal treatments on the rheological properties of potato starch. *Carbohydrate Research, 297*, 247–356.

Eliasson, A. C. (1986). Viscoelastic behavior during the gelatinization of starch. I. Comparison of wheat, maize, potato, and waxy barley starches. *Journal of Textural Studies, 17*, 253–265.

Gray, J. A., & BeMiller, J. N. (2005). Influence of reaction conditions on the location of reactions in waxy maize starch granules reacted with a propylene oxide analog at low substitution levels. *Carbohydrate Polymers, 60*, 147–162.

Gunaratne, A., & Hoover, R. (2002). Effect of heat-moisture treatment on the structure and physicochemical properties of tuber and root starches. *Carbohydrate Polymers, 49*, 425–437.

Hauber, R., BeMiller, J. N., & Fannon, J. E. (1992). Swelling and reactivity of maize starch granules. *Starch/Starke, 44*, 323–327.

Hoover, R., Hannouz, D., & Sosulski, F. W. (1988). Effect of hydroxypropylation on thermal properties, starch digestibility and freeze–thaw stability of field pea (*Pisum sativum* cv Trapper) starch. *Starch/Starke, 40*, 383–387.

Hoover, R., Vasanthan, T., Senanayake, N. J., & Martin, A. M. (1994). The effect of defatting and heat-moisture treatment on the retrogradation of starch gels from wheat, oat, potato, and lentil. *Carbohydrate Research, 261*, 13–24.

Hoover, R., & Vasanthan, T. (1994). Effect of heat-moisture treatment on the structure and physicochemical properties of cereal, legume, and tuber starches. *Carbohydrate Research, 252*, 33–53.

Johnson, D. P. (1969). Spectrophotometric determination of the hydroxypropyl groups in the starch ethers. *Analytical Chemistry, 41*, 859–860.

Kavitha, R., & BeMiller, J. N. (1998). Characterization of hydroxypropylated potato starch. *Carbohydrate Polymers, 37*, 115–121.

Kim, H. R., & Eliasson, A. C. (1993). The influence of molar substitution on thermal transition properties of hydroxypropyl potato starches. *Carbohydrate Polymers, 22*, 331–335.

Kim, H. R., Hermansson, A. M., & Eriksson, C. E. (1992). Structural characteristics of hydroxypropyl potato starch granules depending on their molar substitution. *Starch/Starke, 44*, 111–116.

Liu, H. J., Ramsden, L., & Corke, H. (1999). Physical properties and enzymatic digestibility of hydroxypropylated ae, wx, and normal maize starches. *Carbohydrate Polymers, 40*, 175–182.

Morris, M. J. (1990). Starch gelation and retrogradation. *Trends in Food Science and Technology, 1*, 2–6.

Oosten, B. J. (1990). Interactions between starch and electrolytes. *Starch/Starke, 42*, 327–330.

Pal, J., Singhal, P. S., & Kulkarni, P. R. (2002). Physicochemical properties of hydroxypropyl derivative from corn and amaranth starch. *Carbohydrate Polymers, 48*, 49–53.

Perera, C., Hoover, R., & Martin, A. M. (1997). The effect of hydroxypropylation on the structure and physicochemical properties of native, defatted and heat-moisture treated potato starches. *Food Research International, 30*, 235–247.

Ring, S. G. (1985). Some studies on starch gelation. *Starch/Starke, 37*, 80–83.

Shi, X., & BeMiller, J. N. (2000). Effect of sulfate and citrate salts on derivatization of amylose and amylopectin during hydroxypropylation of corn starch. *Carbohydrate Polymers, 43*, 333–336.

Shi, X., & BeMiller, J. N. (2002). Aqueous leaching of derivatized amylose from hydroxypropylated common corn starch granules. *Starch/Stark, 54*, 16–19.

Tester, R. F., & Morrison, W. R. (1990a). Swelling and gelatinization of cereal starches. 1. Effects of amylopectin, amylose, and lipids. *Cereal Chemistry, 67*, 551–557.