

# Thermal, pasting, and gelling properties of wheat and potato starches in the presence of sucrose, glucose, glycerol, and hydroxypropyl $\beta$ -cyclodextrin

Anil Gunaratne <sup>a</sup>, Somathilaka Ranaweera <sup>b</sup>, Harold Corke <sup>a,\*</sup>

<sup>a</sup> Cereal Science laboratory, School of Biological Sciences, The University of Hong Kong, Pokfulam Road, Hong Kong

<sup>b</sup> Department of Food Science & Technology, Faculty of Applied Science, University of Sri Jayawardanapura, Gangodawilla, Colombo, Sri Lanka

Received 2 January 2007; received in revised form 28 February 2007; accepted 9 March 2007

Available online 30 March 2007

## Abstract

Thermal, pasting, and gelling properties of wheat and potato starches were studied in the presence of sucrose, glucose, glycerol, and hydroxypropyl  $\beta$ -cyclodextrin (HP $\beta$ -CD). Swelling factor of both starches slightly increased up to 20% sucrose and glucose but decreased at 40% concentration (sucrose > glucose). Glycerol did not affect swelling factor of wheat starch even at 40% concentration but decreased it in potato starch. Amylose leaching of wheat and potato starches tends to decline above 5% and 1% concentration of sucrose and glucose, respectively. However, similar to swelling factor the extent of amylose leaching in wheat starch was unaffected in the presence of glycerol. Gelatinization temperature and enthalpy of both starches were increased by sucrose, glucose and glycerol in the order of sucrose > glucose > glycerol. Glucose increased peak viscosity of the two starches more than other polyols. Cold paste viscosity increased in wheat starch following the order: glucose > sucrose > glycerol but sucrose was most effective in potato starch. Gel hardness of wheat starch was increased following the order glucose > sucrose > glycerol but sucrose was more effective in potato starch. All above results indicate the occurrence of starch–polyhydroxy interaction which reinforces the starch granules depending on the botanical source of starch and the type and concentration of polyhydroxy compound. The influence of HP $\beta$ -CD on the swelling factor, amylose leaching, and dissociation parameters of amylose–lipid complex in wheat starch is consistent with the disruption of amylose–lipid complex. This greatly affects the gelatinizing, pasting, and gelling properties of wheat starch.

© 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Polyhydroxy compounds; Starch properties; Amylose–lipid complex

## 1. Introduction

Gelatinization, pasting, and subsequent gel properties of starch are key functional properties that determine many applications of starch in the food industry. Usually these properties are not optimal in native starch, and thus need to be modified by various techniques to suit the relevant end product.

Additives such as sugars are commonly used in starch-based foods in order to optimize the process operation and cause some textural modification in addition to its role as a

sweetening agent. Employing various techniques, many researchers have reported that sugar and other related polyhydroxy compounds can delay the gelatinization process. Suggestions proposed for the mechanism of this delay are (1) that sugars reduce the water activity in the system due to competition for water with starch molecules which always favors sugars (D'Appolonia, 1972; Spies & Hoseney, 1982), (2) that there is a sugar–starch interaction (Baek, Yoo, & Lim, 2004; Chiotelli, Rolee, & Meste, 2000; Hoover & Senanayake, 1996; Spies & Hoseney, 1982), (3) that there is less plasticizing effect of sugar than water (Levine & Slade, 1988; Perry & Donald, 2002). Different sugars, however, substantially differ in the magnitude that they can increase the gelatinization temperature. Disaccharides increase

\* Corresponding author. Tel.: +852 2859 0314; fax: +852 3015 6473.

E-mail addresses: [Harold@hku.hk](mailto:Harold@hku.hk), [hcorke@yahoo.com](mailto:hcorke@yahoo.com) (H. Corke).

gelatinization temperature more than monosaccharides (Ahmad & Williams, 1999; Baek et al., 2004; Savage & Osman, 1978). Sugars restrict the swelling and amylose leaching of starch depending on the type of sugar and the concentration (Ahmad & Williams, 1999; Hoover & Senanayake, 1996; Richardson, Langton, Bark, & Hermansson, 2003; Savage & Osman, 1978).

Influence of sugars on rheological properties of starch has also been discussed by several researchers. With increase of sugar concentration, peak viscosity and pasting temperature of wheat starch increase substantially (Bean & Yamazaki, 1978; D'Appolonia, 1972; Richardson et al., 2003). By promoting polymer–polymer association, sugars can markedly change the conformational ordering and intermolecular association of starch polymers. This greatly affects the physical and mechanical properties of starch gel. The effectiveness of promoting conformational ordering and intermolecular association depends on the type of sugar molecule (Evageliou, Richardson, & Morris, 2000).

Although there have been many reports on the effect of sugars on starch gelatinization, pasting, and gelling properties, little or no information is available for the detailed analysis of these properties involving non-sugar polyols such as glycerol and hydroxypropyl  $\beta$ -cyclodextrin (HP $\beta$ -CD). HP $\beta$ -CD is produced from  $\beta$ -cyclodextrin by hydroxypropylation of the hydroxyl groups which enhances water solubility. HP $\beta$ -CD is a permitted food additive in some countries and usually used as a flavor carrier, extraction of cholesterol from egg yolk, and processing aid. Previous investigations on  $\beta$ -CD and starch interaction showed that the structural configuration  $\beta$ -cyclodextrin can complex with starch lipids causing disruption of amylose–lipid complex (Kim & Hill, 1984). But not much detailed information is available on modified  $\beta$ -CD–starch interaction. In addition to new information of HP $\beta$ -CD–starch interaction and its influence on starch functional properties, this study will lead to deeper insight into sugar–starch interaction by comparing the HP $\beta$ -CD–starch interaction with other polyol–starch interaction.

## 2. Materials and methods

### 2.1. Materials

Wheat and potato starches, hydroxypropyl  $\beta$ -cyclodextrin (HP $\beta$ -CD with 0.8 molecular substitution), D-glucose and sucrose were purchased from Sigma Chemical Co., (St. Louis, MO). Glycerol was from Fluka Chemie. Different concentrations of sucrose, glucose, glycerol, and HP $\beta$ -CD solutions were prepared as w/v (weight per volume) solutions in dw (dry weight).

### 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 deter-

mined by the method of Tester and Morrison (1990a), when starch (50 mg, db) was heated at 85 °C in 5 mL water.

#### 2.2.2. Amylose leaching

Distilled water or solution of polyhydroxy compound (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 2000g 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 of amylose–lipid complex 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 onto the aluminum DSC pan and distilled water or solution of polyhydroxy compound (3  $\mu$ L) 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 liquid. The scanning temperature and heating rates were 30–140 and 5 °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-Analyser (RVA) model 3D (Newport Scientific, Warriewood, Australia). Distilled water or solution of polyhydroxy compound (25.5 g) was added to starch (2.5 g, db) in the RVA canister to obtain a total constant sample weight of 28 g. 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 and adhesiveness were determined on the starch gel made in the RVA testing using a TA-XT2 Texture Analyzer (Stable Micro Systems, Godalming, Surrey, 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, and gel hardness and adhesiveness, chewiness, and gumminess were noted. The maximum force peak in the TPA profile represents the gel hardness while negative area of the curve provides the adhesiveness, when the probe pulls back to the initial position. Gumminess and chewiness were also recorded from the results of TPA profile.

### 3. Results and discussion

#### 3.1. Swelling factor and amylose leaching

Swelling factor and amylose leaching of wheat and potato starches at 85 °C in the presence of sucrose, glucose, glycerol, and HP $\beta$ -CD are presented (Fig. 1). Consistent with previous investigations potato starch showed a higher swelling ability than native wheat starch. Swelling factor of the two starches was slightly increased up to 20% sucrose and glucose concentration but substantially decreased at 40% concentration with sucrose showing more effect than glucose. The reduction of swelling factor at higher concentration was greater in wheat starch. These results are comparable with previous investigations on the effect of sugars on starch swelling (Ahmad & Williams, 1999; Savage & Osman, 1978). Glycerol did not affect swelling factor of wheat starch even at 40% concentration, but its effect was more pronounced in potato starch at 40% concentration.

HP $\beta$ -CD greatly increased swelling factor of wheat starch even at 1% concentration. For potato starch, HP $\beta$ -CD inhibited swelling similar to the higher concentration of sucrose, glucose, and glycerol but required lower concentration to achieve this. Spies and Hoseney (1982) proposed that sugar molecules can restrict the mobility and flexibility of starch chains hence stabilizing the amorphous region of the starch granule, and that longer sugar chains can bridge more starch chains than shorter chains. Formation of a bridge between starch chains and sugar molecules restricts swelling ability depending on the type, concentration, size, and the flexibility of the polyhydroxy compounds and thus the decreasing order of swelling factor (sucrose > glucose > glycerol) shown for wheat starch can be explained based on size of the molecules. This kind

of polyol–starch chain interaction could be the reason for observed amylose leaching reduction (Fig. 1) by tested polyhydroxy compounds because cross-bonded amylose chains are difficult to leach out in contrast to free amylose.

However, HP $\beta$ -CD significantly increased amylose leaching of wheat starch in a manner consistent with the disruption of amylose–lipid complex. This is further supported by higher swelling and decreased transition parameters of amylose–lipid complex of wheat starch in the presence of HP $\beta$ -CD (Table 2). Similar to other tested polyol–starch interactions there could be a HP $\beta$ -CD–starch chain interaction that could negatively affect wheat starch swelling but increased swelling factor of wheat starch suggests that disruption of amylose–lipid complex and subsequent hydration of starch granule by HP $\beta$ -CD can dominate the negative effect of HP $\beta$ -CD–starch chain cross-linking on wheat starch swelling.

#### 3.2. Gelatinization

Gelatinization parameters of potato and wheat starches in the presence of different concentrations of sucrose, glucose, glycerol, and HP $\beta$ -CD are presented (Table 1) and some representative DSC curves are shown (Fig. 2a and b). Starch gelatinization in the presence of sugars has been extensively studied by using different techniques such as DSC (Eliasson, 1992; Kohyama & Nishinari, 1991; Wootton & Bamunuarachchi, 1980), light microscopy (Bean & Yamazaki, 1978), and NMR (Chinachoti, Kim-Shin, Mari, & Lo, 1991). Among the different methods DSC has been the most widely used.

Inclusion of sucrose, glucose, glycerol, and HP $\beta$ -CD increased the gelatinization temperature of both starches as the concentration increased in the order of

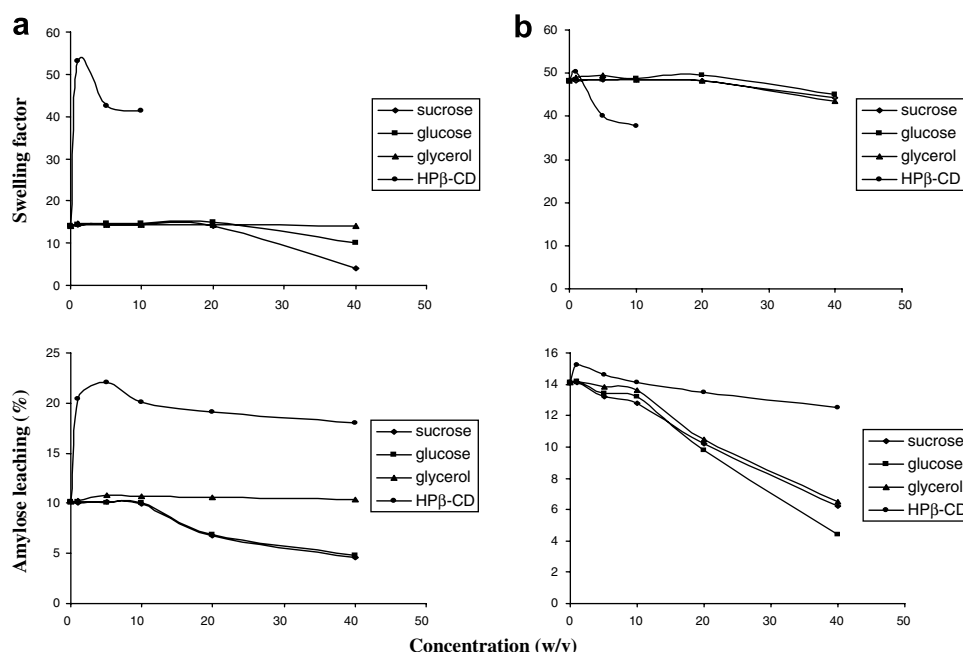


Fig. 1. Swelling factor and amylose leaching of wheat (a) and potato (b) starches at different concentrations of sucrose, glucose, glycerol, and HP $\beta$ -CD.

Table 1

Gelatinization temperature ( $T_p$ ) and enthalpy ( $\Delta H$ ) of wheat and potato starches in the presence of sucrose, glucose, glycerol, and HP $\beta$ -CD

Starch	Concentration (%)	Sucrose		Glucose		Glycerol		HP $\beta$ -CD	
		$T_p$ ( $^{\circ}\text{C}$ )	$\Delta H$ (J/g)	$T_p$ ( $^{\circ}\text{C}$ )	$\Delta H$ (J/g)	$T_p$ ( $^{\circ}\text{C}$ )	$\Delta H$ (J/g)	$T_p$ ( $^{\circ}\text{C}$ )	$\Delta H$ (J/g)
Wheat	0	59.2 $\pm$ 0.2	11.0 $\pm$ 0.4	59.2 $\pm$ 0.5	11.0 $\pm$ 0.2	59.2 $\pm$ 0.2	11.0 $\pm$ 0.5	59.2 $\pm$ 0.2	11.0 $\pm$ 0.2
	1	60.8 $\pm$ 0.1	11.1 $\pm$ 0.2	59.3 $\pm$ 0.1	11.0 $\pm$ 0.2	59.4 $\pm$ 0.1	11.0 $\pm$ 0.1	59.4 $\pm$ 0.3	8.5 $\pm$ 0.3
	5	62.1 $\pm$ 0.3	11.2 $\pm$ 0.1	60.2 $\pm$ 0.3	11.1 $\pm$ 0.1	60.1 $\pm$ 0.1	11.2 $\pm$ 0.3	59.6 $\pm$ 0.1	8.2 $\pm$ 0.4
	10	62.4 $\pm$ 0.4	11.5 $\pm$ 0.3	61.2 $\pm$ 0.2	11.3 $\pm$ 0.3	61.2 $\pm$ 0.2	11.3 $\pm$ 0.4	62.7 $\pm$ 0.1	6.3 $\pm$ 0.2
	20	66.1 $\pm$ 0.1	11.8 $\pm$ 0.5	63.7 $\pm$ 0.3	11.5 $\pm$ 0.4	63.4 $\pm$ 0.6	11.5 $\pm$ 0.4	66.5 $\pm$ 0.3	6.2 $\pm$ 0.3
	40	76.4 $\pm$ 0.3	12.4 $\pm$ 0.2	71.0 $\pm$ 0.1	12.0 $\pm$ 0.5	68.5 $\pm$ 0.3	11.8 $\pm$ 0.3	76.2 $\pm$ 0.5	5.8 $\pm$ 0.1
Potato	0	62.0 $\pm$ 0.4	14.6 $\pm$ 0.1	62.0 $\pm$ 0.4	14.6 $\pm$ 0.2	62.0 $\pm$ 0.4	14.6 $\pm$ 0.6	62.0 $\pm$ 0.1	14.6 $\pm$ 0.3
	1	62.8 $\pm$ 0.5	14.7 $\pm$ 0.2	62.2 $\pm$ 0.4	14.7 $\pm$ 0.1	62.1 $\pm$ 0.1	14.6 $\pm$ 0.5	62.8 $\pm$ 0.1	14.7 $\pm$ 0.3
	5	64.5 $\pm$ 0.1	15.0 $\pm$ 0.1	62.6 $\pm$ 0.3	14.9 $\pm$ 0.3	62.9 $\pm$ 0.4	14.6 $\pm$ 0.3	64.7 $\pm$ 0.4	14.9 $\pm$ 0.1
	10	65.7 $\pm$ 0.4	15.2 $\pm$ 0.4	64.3 $\pm$ 0.2	15.0 $\pm$ 0.4	63.8 $\pm$ 0.5	14.9 $\pm$ 0.2	66.5 $\pm$ 0.1	15.3 $\pm$ 0.4
	20	67.5 $\pm$ 0.6	15.4 $\pm$ 0.1	66.6 $\pm$ 0.1	15.2 $\pm$ 0.3	65.9 $\pm$ 0.3	15.0 $\pm$ 0.1	68.3 $\pm$ 0.1	15.5 $\pm$ 0.1
	40	76.5 $\pm$ 0.3	15.9 $\pm$ 0.3	72.5 $\pm$ 0.3	15.5 $\pm$ 0.2	70.8 $\pm$ 0.2	15.2 $\pm$ 0.2	75.3 $\pm$ 0.3	16.8 $\pm$ 0.3

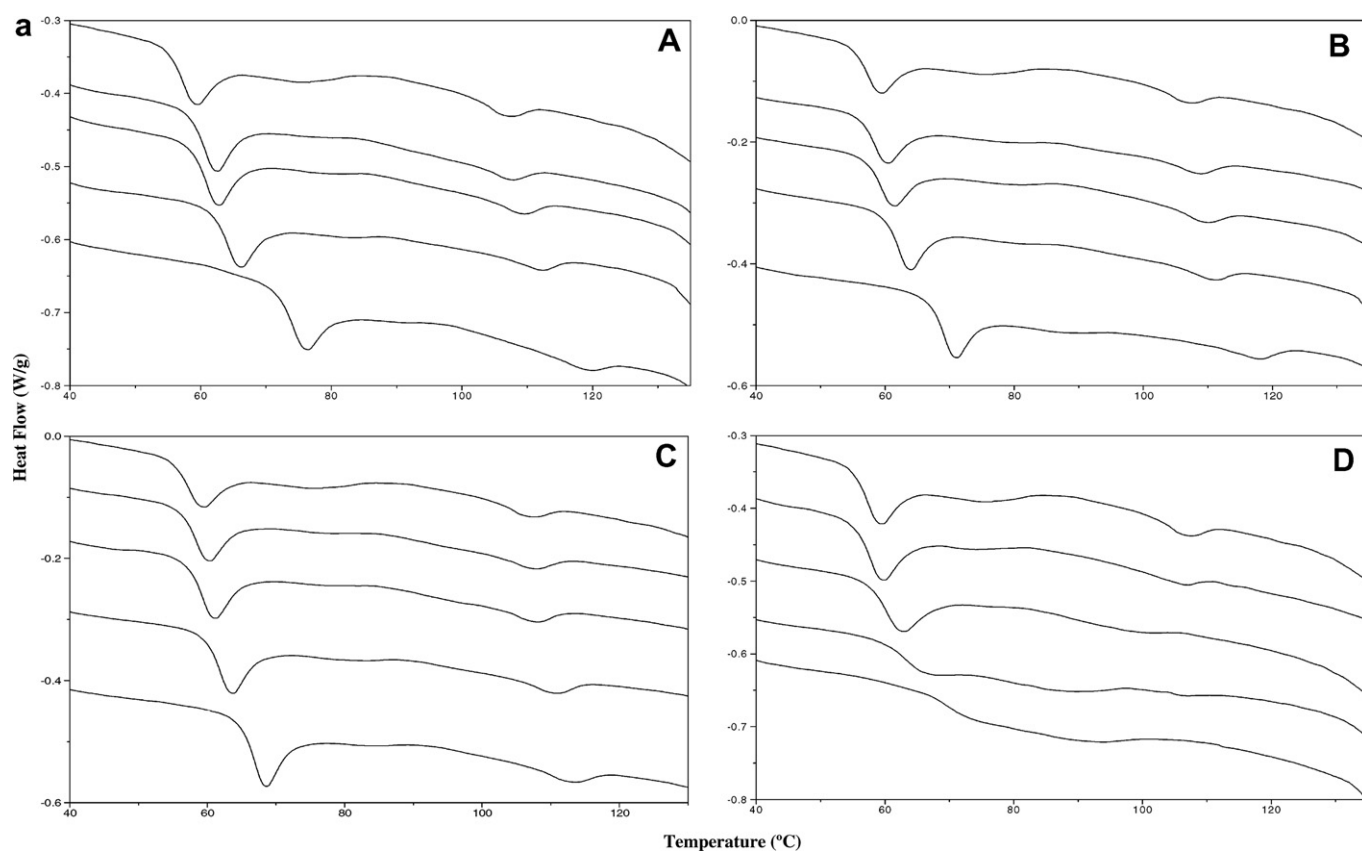
Values are means of triplicate determinations  $\pm$  standard deviation.

Fig. 2. (a) DSC curves of wheat starch in the presence of 0%, 5%, 10%, 20%, and 40% sucrose (A), glucose (B), glycerol (C), and HP $\beta$ -CD (D); curves represent increasing concentration from top to bottom. (b) DSC curves of potato starch in the presence of 0%, 5%, 10%, 20%, and 40% sucrose (A), glucose (B), glycerol (C), and HP $\beta$ -CD (D); curves represent increasing concentration from top to bottom.

HP $\beta$ -CD > sucrose > glucose > glycerol. However, HP $\beta$ -CD slightly affected the gelatinization temperature of wheat starch at lower concentration (up to 5%) compared with other tested polyols and at 40% concentration its effect was lower than that of sucrose but higher than glucose and glycerol.

Recent explanations proposed for the delaying effect on starch gelatinization upon addition of sugars are decreased

water activity, sugar–starch interaction and less plasticization effect of sugar than water. Spies and Hoseney (1982) proposed that in addition to lowering available water content, sugars can stabilize the amorphous region by cross-linking starch chains (as described above). A similar suggestion was made by Baek et al. (2004), Chiotelli et al. (2000) and Hoover and Senanayake (1996). These results also showed that delayed gelatinization in the presence of

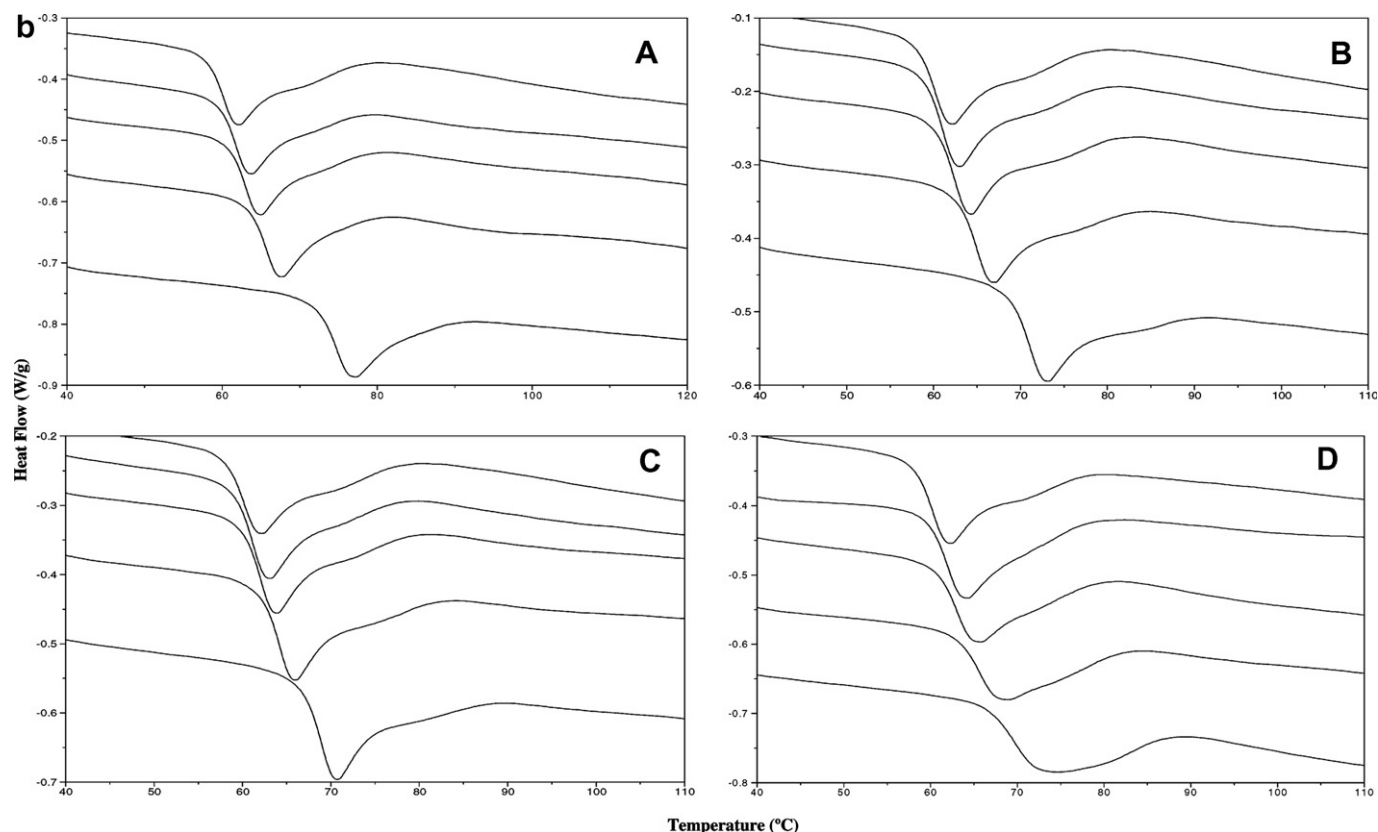


Fig. 2 (continued)

tested polyols except HP $\beta$ -CD could relate to a possible polyol–starch chain interaction which appears to stabilize the amorphous region of the starch granules. Decreased swelling factor, amylose leaching, and granular breakdown, particularly at higher concentration of polyol, indicates the existence polyol–starch chain interaction. The higher the concentration of polyol the greater the gelatinization temperature increased.

After studying different sugars and their alcoholic derivatives, Baek et al. (2004) suggested that the number of hydroxyl groups in a sugar molecule plays a key role in determining the gelatinization temperature. Watase, Kohyama, and Nishinari (1992) reported that the content of equatorial hydroxyl groups of sugar molecules determines the relative effectiveness of different sugars in stabilizing the intermolecular association of biopolymers. Ahmad and Williams (1999) also reported the importance of axial or equatorial hydroxyl groups in the effectiveness of sugar–starch interaction. Hoover and Senanayake (1996) have shown that sucrose has more interactions with starch chains than glucose and fructose as it contains more binding sites. The above investigations could explain the observed differences in the extent of the increased gelatinization temperature in the presence of sucrose and glucose (sucrose > glucose). Perhaps similar explanations could be valid for glycerol and HP $\beta$ -CD, where the smaller molecule of glycerol that has fewer binding sites showed the lowest impact on starch gelatinization temperature and the larger

molecule of HP $\beta$ -CD with more hydroxyl groups showed the highest gelatinization temperature increase. However, at 40% the effect of HP $\beta$ -CD was less than sucrose. This may be due to the problems associated with preparation of 40% HP $\beta$ -CD where the real concentration may be less than the expected. Previous investigations have generally shown that disaccharides increase gelatinization temperature more than monosaccharides. This is in agreement with observed results for both wheat and potato starches.

In case of HP $\beta$ -CD reduction of gelatinization temperature of wheat starch was not very obvious at lower concentrations compared with other tested polyols but at higher concentration it delayed the gelatinization more than other polyols. As we have discussed before (Gunaratne & Corke, 2007) extensive hydration of wheat starch granules due to the disruption of amylose–lipid complex could require less energy for gelatinization. The way that HP $\beta$ -CD affects swelling factor, amylose leaching, and gelatinization of potato starch was similar to that for other polyols. This indicates that HP $\beta$ -CD has weaker interaction with potato starch. Conflicting results were reported for the changes of gelatinization enthalpy in the presence of sugars and other polyols.

Decreased (Chungcharoen & Lund, 1987; Wootton & Bamunuarachchi, 1980), unchanged (Eliasson, 1992; Evans & Haisman, 1982; Maauf, Che Man, Asbi, Junainah, & Kennedy, 2001) or increased (Ahmad & Williams, 1999; Baek et al., 2004; Chiotelli et al., 2000; Sopade, Halley, &



Junming, 2004) gelatinization enthalpies were reported in the presence of sugars. In this study increased gelatinization enthalpy of wheat starch followed the order: sucrose > glucose > glycerol > control > HP $\beta$ -CD, whereas for potato starch, the order was HP $\beta$ -CD > sucrose > glucose > glycerol. An increased enthalpy indicates more energy requirement to disrupt the starch structure. Gelatinization is a swelling-driven process in which expansion of the amorphous region disrupts the crystalline domain due to the stress applied on it (Donovan, 1979). Thus restricted granular swelling caused by sugars and polyols may require more energy to pull the crystals apart during gelatinization. Similarly increased swelling due to the disruption of amylose–lipid complex by HP $\beta$ -CD may need less energy to destabilize the starch crystalline domain. However, increased gelatinization temperature cannot be explained solely on the polyols–starch interaction and its relation to low swelling. For example with up to 20% concentration of sucrose, glucose, and glycerol swelling factor was increased but gelatinization temperature was not decreased (Table 1). Furthermore gelatinization of wheat starch was delayed at higher concentration of HP $\beta$ -CD while increasing the swelling. Thus it is difficult to explain the delayed gelatinization by sugars and other polyols considering a one factor alone, so that other factors should be considered too. Thus increased gelatinization temperature and enthalpy by sugar and other polyols could be due to the interplay of decreased water activity, sugar–starch interaction, change of water structure, and reduced plasticizing effect of solvent due to sugar–starch interaction. However, the magnitude of each factor in delaying the gelatinization temperature may substantially vary depending on the botanical source of starch, types of polyols, and the sugar–starch–water system.

It has been reported that when sugar concentration is increased in low water content starch gelatinization systems (1:1, starch:water ratio), the double endotherm shifts to a single endotherm (Eliasson, 1992; Maaurf et al., 2001) but in this study the existence of double endotherm or biphasic character at higher concentration of all tested polyols in 1:1 starch:water ratio was observed (Fig. 2a and b). Similar results were reported for the presence of a double endotherm at higher concentration of sugars in low water content starch gelatinization systems (Ahmad & Williams, 1999; Sopade et al., 2004). This discrepancy could be due to differences in the heating rate, type of starch or the way that the sugar–starch–water system prepared. An uneven shape of gelatinization endotherm shown particularly in wheat starch at higher concentration of HP $\beta$ -CD could be due to incomplete gelatinization. Substitution of the hydroxyl groups of  $\beta$ -cyclodextrin by hydroxypropyl groups disrupts the network of hydrogen bonding around the rim of the  $\beta$ -CD which increases the interaction of hydroxyl groups with water. Thus at higher concentration of HP $\beta$ -CD it could bind more water molecules limiting the available water for gelatinization leading to an incomplete gelatinization.

For the amylose–lipid complex of wheat starch in the presence of polyols, the melting temperature was shifted to higher temperature as the concentration of sucrose, glucose and glycerol increased (sucrose > glucose > glycerol) but corresponding melting enthalpies seemed slightly decreased with increased concentration (Fig. 2a and Table 2). This is in agreement with the finding of Eliasson (1992) for the transition parameters of normal maize amylose–lipid complex in the presence of sucrose. In contrast, HP $\beta$ -CD dramatically decreases both melting temperature and enthalpy of amylose–lipid complex with increased concentration. Even at 1% HP $\beta$ -CD, the melting enthalpy of amylose–lipid complex was substantially decreased indicating its capability to destabilize the amylose–lipid complex (Table 2).

### 3.3. Pasting and gel textural properties

Pasting curves of wheat and potato starches at different concentrations of sucrose, glucose, glycerol, and HP $\beta$ -CD are presented (Fig. 3a and b) and results summarized (Table 3). Peak viscosity of wheat and potato starches increased as the concentration of sucrose, glucose, and glycerol increased. However, addition of HP $\beta$ -CD reduced peak viscosity in both starches. For both starches, peak viscosity increased in the following order: glucose > sucrose > glycerol. When the concentration of sucrose, glucose, glycerol, and HP $\beta$ -CD was increased the early onset of viscosity development was observed in wheat starch but generally potato starch showed delayed first

Table 2  
Melting temperature ( $T_m$ ) and enthalpy ( $\Delta H$ ) of amylose–lipid complex of wheat starch in the presence of sucrose, glucose, glycerol, and HP $\beta$ -CD

Treatment	Concentration (%)	$T_m$ (°C)	$\Delta H$ (J/g)
Sucrose	Control	107.6 $\pm$ 0.8	1.6 $\pm$ 0.1
	1	107.7 $\pm$ 0.2	1.6 $\pm$ 0.2
	5	107.9 $\pm$ 0.5	1.6 $\pm$ 0.1
	10	109.2 $\pm$ 0.3	1.4 $\pm$ 0.3
	20	112.2 $\pm$ 0.7	1.4 $\pm$ 0.1
	40	121.7 $\pm$ 0.2	1.3 $\pm$ 0.1
Glucose	1	107.7 $\pm$ 0.2	1.6 $\pm$ 0.2
	5	108.1 $\pm$ 0.1	1.6 $\pm$ 0.1
	10	109.1 $\pm$ 0.3	1.5 $\pm$ 0.2
	20	111.2 $\pm$ 0.1	1.5 $\pm$ 0.1
	40	118.1 $\pm$ 0.1	1.3 $\pm$ 0.1
Glycerol	1	107.5 $\pm$ 0.4	1.6 $\pm$ 0.1
	5	107.9 $\pm$ 0.5	1.6 $\pm$ 0.3
	10	108.3 $\pm$ 0.2	1.6 $\pm$ 0.3
	20	110.5 $\pm$ 0.3	1.4 $\pm$ 0.2
	40	112.8 $\pm$ 0.4	1.4 $\pm$ 0.1
HP $\beta$ -CD	1	106.7 $\pm$ 0.2	0.9 $\pm$ 0.2
	5	105.8 $\pm$ 0.1	0.6 $\pm$ 0.3
	10	100.6 $\pm$ 0.3	0.3 $\pm$ 0.4
	20	ND	ND
	40	ND	ND

ND, not determined.

Values are means of triplicate determinations  $\pm$  standard deviation.

viscosity increase as the concentration of all tested polyols increased, particularly after 5% concentration sucrose, glucose, and glycerol and 1% HP $\beta$ -CD. Pasting properties of starch are primarily related to the swelling and rupture of the starch granules. Richardson et al. (2003) demonstrated by microscopic analysis that starch granules can keep together better in sucrose solution than in water. They further explained that early viscosity increase with the addition of sugar could be attributed to the influence of sugar on the close packing concentration of swollen starch granule as described by Doublier, Llamas, and Le Meur (1987). However, onset of viscosity increase in potato starch was slightly affected up to 5% concentration after that it was increased significantly by all tested polyols (Fig. 3b). This might be attributed to the differences in the influence of tested polyols on close packing of potato and wheat starch granules due to their differences in swelling properties. After testing influence of sucrose on wheat starch gelatinization and pasting properties D'Appolonia (1972) reported that the increased onset pasting, gelatinization temperatures and higher peak viscosity were related to the inhibition of starch granule hydration by sucrose molecules. Steeneken (1989) proposed that in dilute paste (8.9%), viscosity is governed by the volume fraction of starch granules, and as the paste becomes more concentrated it is

controlled by particle rigidity. Interaction of sugar molecules with starch chains as reported by Spies and Hosney (1982) could increase the rigidity of starch granules. This could permit granules to swell for a longer time achieving higher peak viscosity before some granular breakdown occurs. Monosaccharides have been reported to increase peak viscosity more than disaccharides (Bean & Osman, 1958). This was consistent with the results of this study for both starches. HP $\beta$ -CD reduced peak viscosity of wheat starch. Disruption of amylose–lipid complex and subsequent extensive hydration of wheat starch granules in the presence of HP $\beta$ -CD could weaken the starch structure. Thus weaker granules can undergo greater shear thinning at higher temperature. Potato is a higher swelling starch thus little increase of swelling was caused by HP $\beta$ -CD at 1% concentration, which may influence on the shear thinning at higher temperature. The two starches showed an increased cold paste viscosity (CPV) in the presence of all polyols but to a different extent. Sugars can create junction zones on amylose chains facilitating realignment of amylose in cold paste. For wheat starch the increase of CPV followed the order: glucose > sucrose > glycerol but sucrose was more effective on potato starch followed by glucose and glycerol. This implies that the conformational ordering and intermolecular association of starch polymers

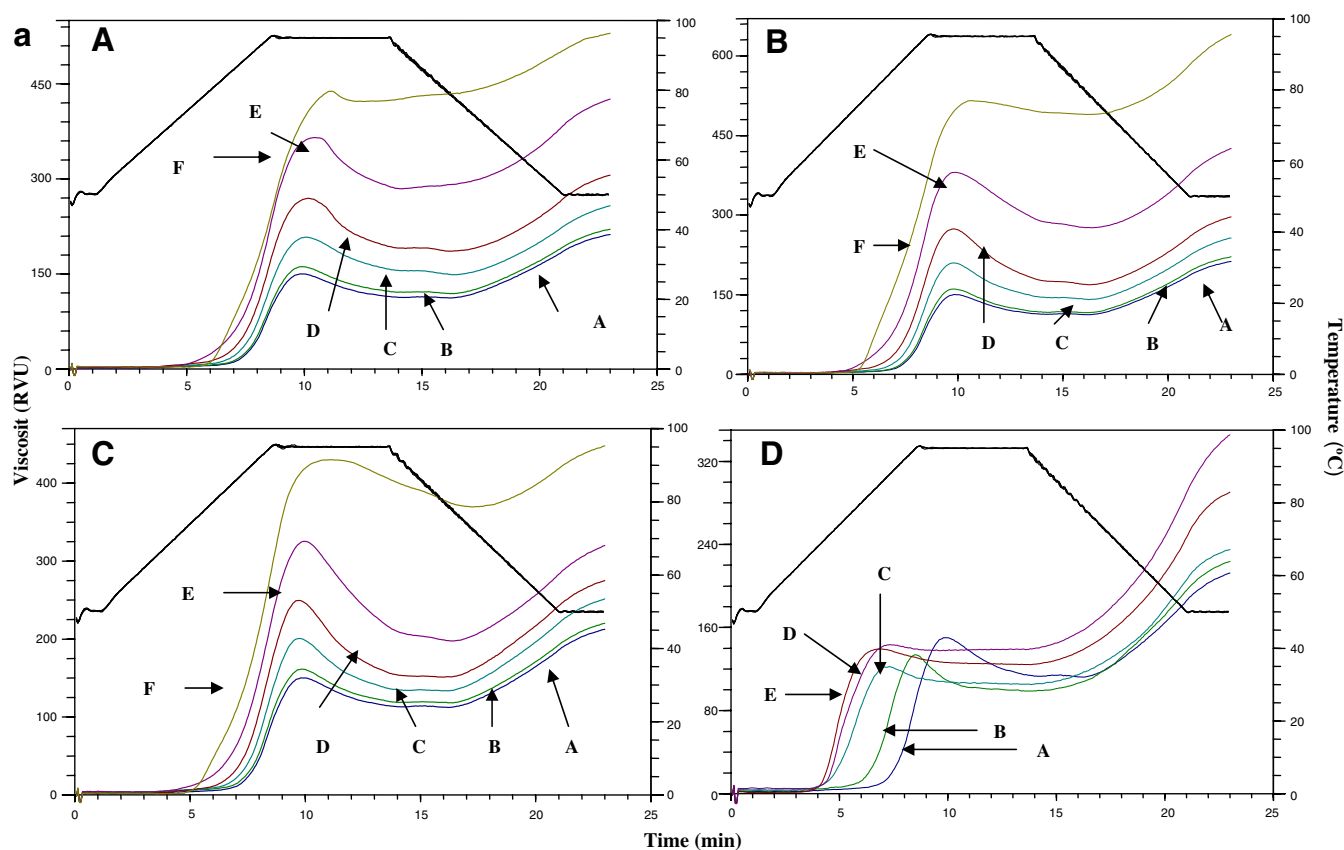


Fig. 3. (a) RVA curves of wheat starch in different concentrations of sucrose (A), glucose (B), glycerol (C), and HP $\beta$ -CD (D). A, native; B, 1%; C, 5%; D, 10%; E, 20%; and F, 40%. (b) RVA curves of potato starch in different concentrations of sucrose (A), glucose (B), glycerol (C), and HP $\beta$ -CD (D). A, native; B, 1%; C, 5%; D, 10%; E, 20%; and F, 40%.

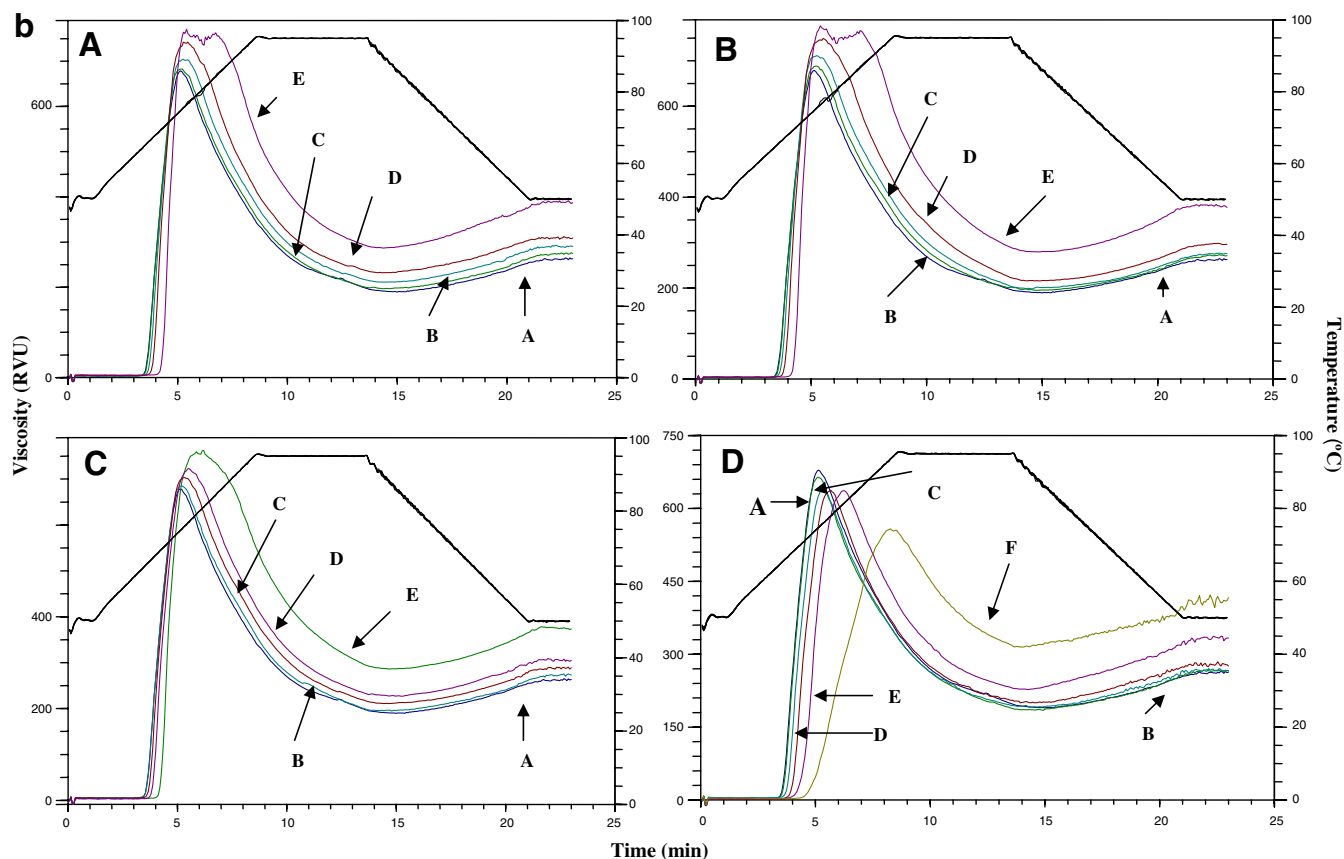


Fig. 3 (continued)

depend on type of polyol as well as botanical source of the starch.

The observed increased gel hardness in wheat and potato starch in the presence of sucrose, glucose, and glycerol is consistent with the increased CPV. Textural properties of wheat and potato starch gel (Table 4) were determined after 24 h at 4 °C. Thus textural properties should be predominantly affected by the short-term amylose gelation as this time is generally not enough for longer term amylopectin association. Starch gels are metastable and non-equilibrium systems and therefore undergo structural changes during storage (Ferrero, Martin, & Zantzy, 1994). Miles, Morris, Orford, and Ring (1985) and Ring et al. (1987) attributed the initial gel firmness during retrogradation to the formation of an amylose matrix gel and the subsequent slow increase in gel firmness to reversible crystallization of amylopectin. Morris (1990) explained that starch gel properties relate to the characteristics of gel matrix, the amylose, the deformable fillers (swollen granules) that are embedded on the continuous amylose matrix, volume fraction of the filler, and the filler–matrix interaction. Doublier et al. (1987) suggested the main structural parameters of a starch gel involved are the deformability of swollen starch particles and the amylose concentration in the continuous network. Increased gel hardness of wheat and potato starch by sucrose, glucose, and glycerol could therefore be attributed to the formation

of a strong amylose gel matrix network via changes of conformational ordering and intermolecular association of amylose chains probably by creating more junction zones on amylose chains. Influence of polyols on the deformability (rigidity) of swollen particles due to starch chain–polyol interaction could also affect the gel hardness. Decreased gel hardness at higher concentration (40%) of sucrose and glucose in wheat starch could therefore be attributed to the greater reduction of amylose leaching that reduces the amylose concentration in the continuous network. However, recent evidence in the literature argues that another mechanism may be at play. Polysaccharides (agarose, κ-carrageenan, deacylated gellan) forming gels on the basis of a double helix arrangement, as for amylose, are increasingly unable to support intermolecular order in the presence of sugars at levels of 40% or beyond (Kasapis & Al-Marhoobi, 2003). According to this argument, decreased gel hardness could be due to reduced amylose order as opposed to reduced amylose concentration. Even at 40% concentration, glycerol did not decrease the gel hardness of wheat starch because it did not reduce the amylose leaching and probably it has no effect on the amylose order even at 40% concentration. However, gel hardness of potato starch was not reduced despite amylose leaching was decreased at higher concentration of sucrose, glucose, and glycerol indicating that creation of more junction zones and the granular deformability (rigidity) of potato



Table 3

Pasting properties of wheat and potato starches in the presence of sucrose, glucose, glycerol, and HP $\beta$ -CD

Starch	Treatment	Concentration (%)	PV	HPV	BD	CPV	SB
Wheat	Control	0	150	112	38	212	100
		1	160	118	41	219	101
		5	209	147	60	258	110
		10	268	183	85	305	120
		20	365	284	78	425	140
		40	438	422	16	530	112
	Glucose	1	160	116	43	221	103
		5	210	140	70	256	116
		10	273	168	105	297	128
		20	380	276	104	428	150
		40	526	502	24	655	153
	Glycerol	1	162	117	45	221	102
		5	200	133	67	250	116
		10	249	151	98	275	124
		20	325	197	127	319	122
		40	430	369	60	450	75
	HP $\beta$ -CD	1	134	98	35	220	125
		5	120	104	17	235	130
		10	132	119	12	275	158
		20	138	134	4	340	206
		40	ND	ND	ND	ND	ND
Potato	Control	0	678	190	489	270	74
		1	680	193	484	275	79
		5	704	211	490	287	75
		10	740	230	506	310	80
		20	773	284	488	389	100
		40	ND	ND	ND	ND	ND
	Glucose	1	685	194	490	269	73
		5	707	198	509	275	76
		10	749	215	533	296	80
		20	780	279	499	376	98
		40	ND	ND	ND	ND	ND
	Glycerol	1	680	194	488	270	75
		5	703	210	492	285	76
		10	722	230	494	305	78
		20	760	286	475	372	84
		40	ND	ND	ND	ND	ND
	HP $\beta$ -CD	1	669	185	480	266	91
		5	637	191	446	267	75
		10	636	199	437	275	76
		20	634	227	409	333	106
		40	558	314	243	416	102

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

ND, not determined as the consistent of the profile was not constant.

Values are means of at least duplicate determination.

starch at higher concentrations could override the negative effect of decreased amylose leaching to form a harder gel structure. In the gelation of oxidized starch, [Evageliou et al. \(2000\)](#) found that addition of sucrose, glucose, and fructose increases the rate of conformational ordering of oxidized starch polymers during cooling in the order of

Table 4  
Textural properties of wheat and potato starch gel prepared with sucrose, glucose, glycerol, and HP $\beta$ -CD

Starch	Concentration (w/v)	Sucrose						Glucose						Glycerol						HP $\beta$ -CD					
		Concentration			Sucrose			Glucose			Glucose			Glycerol			Glycerol			HP $\beta$ -CD			HP $\beta$ -CD		
		HD	AD	CH	HD	AD	CH	HD	AD	CH	HD	AD	CH	HD	AD	CH	HD	AD	CH	HD	AD	CH	HD	AD	CH
Wheat	0	77	197	30	77	197	30	77	197	30	77	197	30	77	197	30	77	197	30	77	197	30	77	197	30
	1	80	200	34	80	200	34	80	200	34	80	200	34	80	200	34	80	200	34	80	200	34	80	200	34
	5	82	113	40	82	113	40	82	113	40	82	113	40	82	113	40	82	113	40	82	113	40	82	113	40
	10	118	182	43	118	182	43	118	182	43	118	182	43	118	182	43	118	182	43	118	182	43	118	182	43
	20	146	280	58	146	280	58	146	280	58	146	280	58	146	280	58	146	280	58	146	280	58	146	280	58
	40	78	150	35	78	150	35	78	150	35	78	150	35	78	150	35	78	150	35	78	150	35	78	150	35
Potato	0	38	1	19	38	1	19	38	1	19	38	1	19	38	1	19	38	1	19	38	1	19	38	1	19
	1	38	5	20	38	5	20	38	5	20	38	5	20	38	5	20	38	5	20	38	5	20	38	5	20
	5	39	5	20	39	5	20	39	5	20	39	5	20	39	5	20	39	5	20	39	5	20	39	5	20
	10	53	6	25	53	6	25	53	6	25	53	6	25	53	6	25	53	6	25	53	6	25	53	6	25
	20	67	8	31	67	8	31	67	8	31	67	8	31	67	8	31	67	8	31	67	8	31	67	8	31
	40	86	12	48	86	12	48	86	12	48	86	12	48	86	12	48	86	12	48	86	12	48	86	12	48

HD, hardness; AD, adhesiveness; GU, gumminess; CH, chewiness ND, not determined.

Values are means of at least duplicate determination.

sucrose > glucose > fructose but in subsequent holding at 5 °C the increase of storage module was least in the presence of sucrose followed by glucose and fructose, indicating fructose caused rapid gelation and sucrose had least effect. Accordingly, they suggested that sucrose is very effective in the rate of ordering but less effective in network formation that required aggregation of polymers. This might be one of the reasons for the observed order of gel hardness (glucose > sucrose > glycerol) in wheat starch but this reasoning can not be applied for the outcome for potato starch. However, these results suggest that the conformational ordering and intermolecular association of starch chains not only depend on the types of sugar molecules but also on the botanical source of the starch.

Although both amylose leaching and cold paste viscosity were dramatically increased by HP $\beta$ -CD in wheat starch, the resulting gel was soft. Disruption of amylose–lipid complex accompanied by the extensive swelling of starch granules may alter the rigidity (the deformability) and close packing of the swollen particles that are embedded in the amylose matrix. However, increased gel hardness of potato starch at higher concentration of HP $\beta$ -CD implies that more interaction between HP $\beta$ -CD and starch chains would preserve more granules from disintegration (Table 3) affecting the shape and the deformability (rigidity) of the starch granules. Table 4 shows that the other textural properties, especially in wheat starch, the adhesiveness, chewiness, and gumminess also followed a similar trend as exhibited for gel hardness in the presence of tested polyols. Except HP $\beta$ -CD all other tested polyols increased the chewiness and formed more adhesive gel.

#### 4. Conclusions

Polyhydroxy compounds could interact with starch molecules depending on size of the molecule and the type of starch, altering thermal, pasting, and gelling properties. However, it seems that polyol–starch interaction is not the sole factor that determines the gelatinization properties of starch in the presence of polyhydroxy compounds. Gel hardness and other textural properties of starch paste, particularly in wheat starch consistently increased up to 20% of sucrose and glucose despite decreasing amylose leaching. This would suggest that in addition to the amylose concentration in the continuous medium other factors such as rigidity of swollen granules, effectiveness of the conformational ordering, and intermolecular association of starch polymers affect the textural properties of starch gel. Significant increase of amylose leaching, and swelling factor and greater reduction of melting parameters of amylose–lipid complex were apparent only in wheat starch in the presence of HP $\beta$ -CD, suggesting the disruption of amylose–lipid complex and its influence on the thermal and pasting properties were very significant. Further useful results would be provided by a comparative study of different sugars with HP $\beta$ -CD of different degree of modification on thermal and pasting properties of starch.

#### Acknowledgments

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

- Ahmad, F. B., & Williams, P. A. (1999). Effect of sugars on the thermal and rheological properties of sago starch. *Biopolymers*, 50, 401–412.
- Baek, M. H., Yoo, B., & Lim, S.-T. (2004). Effects of sugars and sugar alcohols on the thermal transition and cold stability of corn starch gel. *Food Hydrocolloid*, 18, 133–142.
- Bean, M. L., & Osman, E. M. (1958). Behavior of starch during food preparation. II. Effects of different sugars on the viscosity and gel strength of starch pastes. *Food Research*, 24, 665–671.
- Bean, M. M., & Yamazaki, T. Y. (1978). Wheat starch gelatinization in sugar solutions I. Sucrose: Microscopy and viscosity effects. *Cereal Chemistry*, 55, 936–944.
- Chinachoti, P., Kim-Shin, M. S., Mari, F., & Lo, L. (1991). Gelatinization of wheat starch in the presence of sucrose and sodium chloride: correlation between gelatinization temperature and water mobility as determined by oxygen-17 nuclear magnetic resonance. *Cereal Chemistry*, 68, 245–248.
- Chiotelli, E., Rolee, A., & Meste, M. L. (2000). Effect of sucrose on the thermomechanical behavior of concentrated wheat and waxy corn starch–water preparations. *Journal of Agricultural and Food Chemistry*, 48, 1327–1339.
- Chrastil, J. (1987). Improved colorimetric determination of amylose in starches or flours. *Carbohydrate Research*, 159, 367–389.
- Chungcharoen, A., & Lund, D. B. (1987). Influence of solutes and water on rice starch gelatinization. *Cereal Chemistry*, 64, 240–243.
- D'Appolonia, B. L. (1972). Effect of bread ingredients on starch gelatinization properties as measured by the Amylograph. *Cereal Chemistry*, 49, 532–543.
- Donovan, A. M. (1979). Phase transitions of the starch water system. *Biopolymers*, 18, 263–275.
- 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.
- Eliasson, A.-C. (1992). A calorimetric investigation of the influence of sucrose on the gelatinization of starch. *Carbohydrate Polymers*, 18, 131–138.
- Evageliou, V., Richardson, R. K., & Morris, E. R. (2000). Effect of sucrose, glucose, and fructose on gelation of oxidized starch. *Carbohydrate Polymers*, 42, 261–272.
- Evans, I. D., & Haisman, D. R. (1982). The effect of solutes on the gelatinization temperature range of potato starch. *Starch*, 7, 224–231.
- Ferrero, C., Martin, M. N., & Zantzy, N. E. (1994). Cornstarch–xanthan gum interaction and its effect on the stability during storage of frozen gelatinized suspension. *Starch*, 46, 300–305.
- Gunaratne, A., & Corke, H. (2007). Influence of unmodified and modified cycloheptaamylose ( $\beta$ -cyclodextrin) on transition parameters of amylose–lipid complex and functional properties of starch. *Carbohydrate Polymers*, 68, 226–234.
- Hoover, R., & Senanayake, N. (1996). Effect of sugars on the thermal and retrogradation properties of oat starches. *Journal of Food Biochemistry*, 20, 65–83.
- Kasapis, S., & Al-Marhoobi, I. M. (2003). Gelatin vs polysaccharide in mixture with sugar. *Biomacromolecules*, 4, 1142–1149.
- Kohyama, K., & Nishinari, K. (1991). Effect of soluble sugars on gelatinization and retrogradation of sweet potato starch. *Journal of Agricultural and Food Chemistry*, 39, 1406–1410.
- Kim, H. O., & Hill, D. (1984). Physical characteristics of wheat starch granule gelatinization in the presence of cycloheptaamylose. *Cereal Chemistry*, 61, 432–435.

- Levine, H., & Slade, L. (1988). Non-equilibrium behavior of small carbohydrate water system. *Pure and Applied Chemistry*, 60, 1841–1847.
- Maauf, A. G., Che Man, Y. B., Asbi, B. A., Junainah, A. H., & Kennedy, J. F. (2001). Gelatinization of sago starch in the presence of sucrose and sodium chloride as assessed by differential scanning calorimetry. *Carbohydrate Polymers*, 45, 335–345.
- Miles, M. J., Morris, V. J., Orford, P. D., & Ring, S. G. (1985). The roles of amylose and amylopectin in the gelation and retrogradation of starch. *Carbohydrate Research*, 135, 271–281.
- Morris, M. J. (1990). Starch gelation and retrogradation. *Trends in Food Science & Technology*, 1, 2–6.
- Perry, P. A., & Donald, A. M. (2002). The effect of sugars on the gelatinization of starch. *Carbohydrate Polymers*, 49, 155–165.
- Richardson, G., Langton, M., Bark, A., & Hermansson, A.-M. (2003). Wheat starch gelatinization – the effect of sucrose, emulsifiers and the physical state of the emulsifier. *Starch*, 55, 150–161.
- Ring, S. G., Colonna, P., I'anson, K. J., Kalichevsk, M. T., Miles, M. J., Morris, V. J., et al. (1987). The gelation and crystallization of amylopectin. *Carbohydrate Research*, 162, 277–293.
- Savage, H. L., & Osman, E. M. (1978). Effects of sugars and sugar alcohols on the swelling of corn starch granules. *Cereal Chemistry*, 55, 447–454.
- Sopade, P. A., Halley, P. J., & Junming, L. L. (2004). Gelatinization of starch in mixtures of sugars. II. Application of differential scanning calorimetry. *Carbohydrate Polymers*, 58, 311–321.
- Spies, R. D., & Hoseney, R. C. (1982). Effect of sugar on starch gelatinization. *Cereal Chemistry*, 59, 128–131.
- Steeneken, P. A. M. (1989). Rheological properties of aqueous suspensions of swollen starch granules. *Carbohydrate Polymers*, 11, 23–42.
- Tester, R., & Morrison, W. R. (1990a). Swelling and gelatinization of cereal starches: I. Effects of amylopectin, amylose, and lipids. *Cereal Chemistry*, 67, 551–557.
- Watase, M., Kohyama, K., & Nishinari, K. (1992). Effects of sugars and polyols on the gel–sol transition of agarose by differential scanning calorimetry. *Thermochemica Acta*, 206, 163–173.
- Wootton, M., & Bamunuarachchi, A. (1980). Application of differential scanning calorimetry to starch gelatinization III. Effects of sucrose and sodium chloride. *Starch*, 32, 126–129.