Available online at www.sciencedirect.com
ScienceDirect
Food Chemistry 108 (2008) 14–22
Food Chemistry
www.elsevier.com/locate/foodchem

Effect of hydroxypropyl β-cyclodextrin on physical properties and transition parameters of amylose–lipid complexes of native and acetylated starches

Anil Gunaratne, Harold Corke *

The School of Biological Sciences, The University of Hong Kong, Pokfulam Road, Hong Kong

Received 24 September 2006; received in revised form 4 July 2007; accepted 4 July 2007

Abstract

The effect of hydroxpropyl β-cyclodextrin (HPβ-CD) on physical properties and digestibility of wheat, potato, waxy maize and high-amylose maize starches before and after acetylation was studied. Effect of HPβ-CD on amylose–lipid complexes in native and acetylated potato starches synthesized using α-lysophosphatidylcholine was also studied. Acetylation increased swelling factor, amylose leaching, peak viscosity and susceptibility to α-amylase hydrolysis, but decreased gelatinization temperature and enthalpy and gel hardness in all starches. HPβ-CD markedly increased swelling factor and amylose leaching in native and acetylated wheat starches but had little or no impact on other starches. Wheat starch gelatinization enthalpy decreased in the presence of HPβ-CD but gelatinization temperature of all the starches was slightly increased. HPβ-CD had no influence on enzymatic hydrolysis. Melting enthalpy of amylose–lipid complex in both native and acetylated wheat starches was decreased by HPβ-CD. Acetylation also decreased the melting enthalpy of amylose–lipid complex in wheat starch. Similar trend of thermal transitions was observed in the presence of HPβ-CD for the amylose–lipid complexes synthesized in potato starch. Acetylation reduces the complex formation ability of the amylose polymer. Similar to gelatinization, acetylation widened the melting temperature range of amylose–lipid complexes while shifting it to a lower temperature. Higher swelling and amylose leaching, and decreased gelatinization temperature and enthalpy resulting from acetylation of wheat starch is consistent with its influence on starch hydration. Similar effects resulting from the inclusion of HPβ-CD were consistent with the disruption of amylose–lipid complex by HPβ-CD which promotes granular hydration.

Keywords: Hydroxypropyl β-cyclodextrin; Amylose–lipid complex; Acetylation

1. Introduction

Cycloheptaamylose (β-cyclodextrin; β-CD) is a cyclic oligosaccharide composed of seven glucose units arranged in a donut-shaped ring. β-CD is widely applied in food, pharmaceutical and cosmetic industries. Its hydrophobic core can complex with a variety of guest organic molecules such as fatty acids and flavour compounds, and has been applied to remove cholesterol from lard (Yen & Tsui, 1995), egg yolk (Smith, Awad, Bennink, & Gill, 1995) and cream (Ahn & Kwak, 1999), and also used as a flavour carrier for some products (Kant, Linforth, Hort, & Taylor, 2004). When β-CD is complexed with guest molecules it is less soluble and more stable. Kim and Hill (1984a, 1984b) investigated the effect of β-CD on wheat starch dough properties and wheat starch gelatinization. They reported that β-CD in dilute solution can disrupt the amylose–lipid complex by complexing with starch lipids which increases swelling, amylose leaching and solubility. Hydroxypropyl β-cyclodextrin (HPβ-CD) is produced by substituting hydroxypropyl groups to the hydroxyl groups of cycloheptaamylose (β-cyclodextrin).

Very little investigation has been carried out to test β-CD–starch interaction and its effect on starch functional

* Corresponding author. Tel.: +852 2299 0314; fax: +852 2858 3477.
E-mail addresses: hcorke@yahoo.com, Harold@hku.hk (H. Corke).

0308-8146/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2007.07.010

properties and no information reported on the effect of readily more water soluble HPβ-CD on starch properties. In food systems, behaviour of the amylose–lipid complex is of technological interest because it can affect the quality of starch-based food products. For example decreased swelling, solubilization and thickening power of starch (Galliard & Bowler, 1987), retardation of starch retrogradation and bread firming (Biliaderis & Tonogai, 1991; Krog, 1971), prevention of stickiness of dried potato (Hoover & Hadziyev, 1981), and improvement of structural integrity of cereal kernels during cooking (e.g., parboiled rice) (Biliaderis, Tonogai, Pereze, & Juliano, 1993) have been reported in the presence or because of the formation of the amylose–lipid complex. Studies have shown that in enzymatic hydrolysis of wheat starch to glucose, the presence of amylose–lipid complexes decreased swelling and dissolving capacity and the water binding capacity of starch, thereby delaying the access of amylolytic enzymes into the starch granules (Nebesnky, Rosicka, & Tkaczyk, 2002, 2004). Furthermore, the complexes negatively influence the colour, transparency and aroma of starch hydrolysates as well as their filtration rate (Master & Steeneken, 1998a, 1998b). The resistance towards α-amylase hydrolysis increased when amylose complexed with lipids. This could reduce the effectiveness of starch hydrolysis, thus requiring more enzyme or longer treatment. Acetylation is a commonly used technique for making modified starch. Substituting acetyl groups onto starch chains loosens the starch structure by preventing interchain association of adjacent starch chains facilitating starch granule hydration (Liu, Ramsden, & Corke, 1997, 1999). Extensively hydrated starch granules require less energy to reach gelatinization. By preventing interchain association, acetylation decreases retrogradation providing greater freeze–thaw stability (Liu et al., 1997, Liu, Ramsden, & Corke, 1999). It can be expected that after substituting more bulky acetyl groups onto starch chains, there could be some specific interaction with larger HPβ-CD molecules creating some novel starch functional properties. Acetylation could also affect the amylose–lipid complex and the complex forming ability of amylose chains. This study therefore aimed to characterize the interaction between HPβ-CD and acetylated starches and its effect on some structural and functional properties of starch.

2. Materials and methods

2.1. Materials

Potato and wheat starches, hydroxypropyl β-cyclodextrin (MS = 0.8), α-lysophosphatidylcholine and fungal α-amylase were from Sigma Chemical Co., (St. Louis, MO, USA). Waxy maize and high-amylose maize starches were obtained from Starch Australasia Limited. Acetic anhydride was from Merck Co., Germany.

2.2. Methods

2.2.1. Total amylose content

An amylose/amylopectin assay kit from Megazyme International Co., Wicklow, Ireland, was used to estimate the total amylose content of all the starches. This assay is based on the principle of specific formation of amylopectin complex with Concanavalin-A (Con A), after a pre-treatment to remove lipids.

2.2.2. Total lipids

Total lipids in starches were extracted with 2:1 (v/v) chloroform/methanol solvent for 5 h using an extraction/desolventizing unit (Soxtec System HT6, Tecator, Sweden).

2.2.3. 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), when starch (50 mg, db) was heated at 85 °C in 5 ml of water.

2.2.4. 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).

2.2.5. 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). Starch (3 mg, db) was directly weighed into the aluminum DSC pan and then distilled water (3 μl) was added by a microsyringe. 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 5 °C/min, respectively. An empty pan was used as reference for all measurements.

2.2.6. Differential scanning calorimetry of synthesized amylose–lipid complex in native and acetylated potato starches using α-lysophosphatidylcholine

Alpha-lysophosphatidylcholine potato starch (native and acetylated) amylose–lipid complex was synthesized in the DSC pan. Starch (3 mg, db) was directly weighed into the DSC pan and α-lysophosphatidylcholine (0.6 mg dissolved in water) was added to make 5:1 starch to α-lysophosphatidylcholine ratio an then distilled water (3 μl) was directly added into the pan. Pans were sealed, and heated at 90 °C for 1.5 h in an incubator. After cooling to room temperature pans were scanned. The scanning temperature and the heating rates were 30–140 °C and 10 °C/min, respectively.

2.2.7. Pasting properties

Pasting properties of starches were determined using a Rapid Visco-Analyser (RVA) model 3 D (Newport Scientific, Warriewood, Australia). Distilled water (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.

2.2.8. 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 4 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.

2.2.9. Enzymatic hydrolysis

Enzymatic hydrolysis was measured using a viscoamylographic (RVA) method as described by Li, Huang, and Corke (2000) with slight modifications. Development of peak viscosity was measured before and after adding 100 units of fungal α-amylase (enzyme was directly added to the canister) and percent decrease of peak viscosity was calculated to detect the extent of enzyme hydrolysis. Same heating–cooling program, and starch concentration were used as in the measurement of pasting properties.

2.2.10. Acetylation

Acetylation was carried out as described by Wang and Wang (2002) with slight modifications. Starch (100 g db) was dissolved in distilled water (185 ml) to make 35% slurry. The pH of the slurry was adjusted to 8.0–8.5 with 1 M NaOH and then mechanically stirred for 30 min. Acetic anhydride (8 g) was slowly (dropwise) added while maintaining pH 8.0-8.5. The reaction was continued for 90 min before acidifying to pH 5.5 with 1 M HCl. The slurry was then washed with three-fold distilled water three times and dried at 35 °C.

Note: Hydroxypropyl β-cyclodextrin (MS = 0.8) 0.01 M was added instead of water in all the above experiments where appropriate.

3. Results and discussion

3.1. Swelling factor and amylose leaching

Swelling factor of native starches at 85 °C followed the order: potato > waxy maize > wheat > high-amylose maize starch (Table 1). As commonly observed, acetylation increased swelling ability of all the starches by promoting granule hydration. HPβ-CD markedly increased the swelling factor of wheat starch, but had little or no impact on low-lipid starches (potato and waxy maize) (Table 1). Although high-amylose maize starch had comparatively high lipid content, swelling factor was low and unaffected by HPβ-CD. Acetylation substantially increased amylose leaching of all the starches, whereas, HPβ-CD increased amylose leaching only in wheat starch (Table 2). Similar to native starch, swelling factor and amylose leaching of acetylated wheat starch was increased in the presence of HPβ-CD. HPβ-CD had little or no impact on the swelling factor and amylose leaching of other acetylated starches.

Table 1
Swelling factor (SF) at 85 °C, gel hardness (GH), retrogradation enthalpy (ΔH_R), total lipid, and total amylose content of starches

Starch	Treatment[a]	SF	GH (g)	ΔH_R (J/g)	Total lipid (%)	Total amylose (%)
Wheat	Native	13.2 ± 0.2	74 ± 1.7	4.2 ± 0.1	1.1 ± 0.2	24.3 ± 0.3
	Native + CD	48.1 ± 0.4	42 ± 0.6	4.4 ± 0.2		
	AC	21.1 ± 0.3	–	1.8 ± 0.1		
	AC + CD	35.2 ± 0.2	–	1.8 ± 0.4		
Potato	Native	49.6 ± 0.5	31 ± 0.8	8.2 ± 0.3	0.1 ± 0.2	24.5 ± 0.2
	Native + CD	49.9 ± 0.1	23 ± 0.7	8.1 ± 0.2		
	AC	58.1 ± 0.3	15 ± 0.2	5.7 ± .0.3		
	AC + CD	57.9 ± 0.2	14 ± 0.6	5.5 ± 0.5		
Waxy maize	Native	38.7 ± 0.1	7.5 ± 0.9	9.1 ± 0.2	0.15 ± 0.1	3.8 ± 0.1
	Native + CD	40.1 ± 0.6	–	9.0 ± 0.3		
	AC	44.1 ± 0.4	–	3.3 ± 0.1		
	AC + CD	44.6 ± 0.2	–	3.4 ± 0.1		
High-amylose maize	Native	3.2 ± 0.3	–	2.3 ± 0.2	0.7 ± 0.1	65.4 ± 0.2
	Native + CD	3.5 ± 0.1	–	2.5 ± 0.2		
	AC	9.1 ± 0.2	–	2.5 ± 0.1		
	AC + CD	8.9 ± 0.1	–	2.6 ± 0.2		

Values are mean of triplicate determination ± standard deviation.
[a] A = acetylated, CD = HPβ-CD.

Table 2
Amylose leaching of native and acetylated starches at different temperature in the presence of HPβ-CD

Starch	Treatment[a]	60 (°C)	70 (°C)	80 (°C)	90 (°C)
Wheat	Native	1.2 ± 0.1	4.7 ± 0.3	10.3 ± 0.2	23.1 ± 0.1
	Native + CD	5.2 ± 0.2	20.1 ± 0.4	22.3 ± 0.1	23.8 ± 0.2
	AC	1.2 ± 0.1	7.1 ± 0.1	13.8 ± 0.4	23.2 ± 0.3
	AC + CD	1.6 ± 0.1	19.2 ± 0.5	21.2 ± 0.2	22.6 ± 0.1
Potato	Native	5.1 ± 0.3	10.2 ± 0.3	14.1 ± 0.5	19.2 ± 0.5
	Native + CD	5.3 ± 0.1	10.8 ± 0.2	14.8 ± 0.2	19.3 ± 0.3
	AC	7.4 ± 0.1	11.9 ± 0.4	16.1 ± 0.1	20.1 ± 0.1
	AC + CD	7.5 ± 0.2	11.3 ± 0.4	15.1 ± 0.3	19.7 ± 0.3
Waxy maize	Native	0.2 ± 0.0	0.6 ± 0..03	1.2 ± 0.0	2.1 ± 0.2
	Native + CD	0.3 ± 0.0	0.5 ± 0.01	1.4 ± 0.1	2.6 ± 0.1
	AC	0.2 ± 0.0	0.6 ± 0.02	1.3 ± 0.2	2.4 ± 0.1
	AC + CD	0.1 ± 0.0	0.6 ± 0.01	1.0 ± 0.0	2.5 ± 0.0
High-amylose maize	Native	0.0	2.1 ± 0.1	3.4 ± 0.2	8.2 ± 0.1
	Native + CD	0.0	2.0 ± 0.1	3.8 ± 0.4	7.9 ± 0.3
	AC	1.2 ± 0.1	4.8 ± 0.3	6.8 ± 0.2	15.8 ± 0.2
	AC + CD	1.2 ± 0.0	4.7 ± 0.4	6.3 ± 0.0	13.1 ± 0.2

Values are mean of triplicate determination ± standard deviation.
[a] AC = Acetylated, CD = HPβ-CD.

This is consistent with disruption of the amylose–lipid complex by HPβ-CD. It was explained that the formation of amylose–lipid complex either *in situ* or naturally reduced the swelling ability and amylose leaching of the starch granules (Becker, Hill, & Mitchell, 2001; Biliaderis, Page, Slade, & Sirett, 1985; Morrison, 1981; Richardson, Langton, Bark, & Hermansson, 2003). Virtually lipid-free potato and waxy maize starches (Table 1) showed lesser interaction with HPβ-CD. In case of high amylose-maize starch, densely packed amylose chains would prevent the penetration of both water and HPβ-CD to the starch granules resulting in low swelling and amylose leaching. Despite the fairly high content of total lipids in high-amylose maize starch (Table 1), DSC curves did not show the presence of amylose–lipid complex (curves not shown). Increased amylose leaching resulted in all the acetylated starches indicating that extensively hydrated starch granules after acetylation promote the mobility of starch chains. Perhaps by preventing interactions between adjacent amylose chains, acetyl groups facilitate the amylose leaching.

3.2. Gelatinization

Decreases were observed for gelatinization temperature and enthalpy of all acetylated starches. HPβ-CD decreased gelatinization enthalpy only in wheat starch but it slightly increased gelatinization temperature of all starches. Gelatinization enthalpy of potato, waxy maize and high-amylose maize starch was unchanged in the presence of HPβ-CD (Table 3 and Fig. 1). Introduction of acetyl groups could prevent the interchain association loosening the starch structure. This facilitates more water penetration into the starch granules with a consequent increase of swelling. Accelerated granular swelling reduces the energy requirement to disrupt the starch structure because gelatinization is a swelling-driven process. Disruption of amylose–lipid complex by HPβ-CD also hydrates the wheat starch granules reducing the energy requirement to reach gelatinization. Melting enthalpy of amylose–lipid complexes in both native and acetylated wheat starches decreased in the presence of HPβ-CD but melting temperature was unaffected. Acetylation also decreased the melting enthalpy of amylose–lipid complex, but melting temperature was shifted to a lower temperature point (Table 2 and Fig. 1). Virtually lipid-free potato starch did not show any amylose–lipid complex, but formation of amylose–lipid complex was evident when α-lysophosphatidylcholine was added (Fig. 2). Interestingly, transition parameters observed for the synthesized potato-α-lysophosphatidylcholine amylose–lipid complexes followed a similar trend as that exhibited for native and acetylated wheat starch amylose–lipid complexes in the presence of HPβ-CD (Table 2 and Fig. 2). Melting enthalpy of amylose–lipid complex synthesized in acetylated potato starch was lower than that of amylose–lipid complex synthesized in native potato starch. This indicates that acetyl groups in amylose chains reduce the complex formation ability of amylose polymer. Acetylation increases the hydrophobicity of amylose chains. This may change the molecular characteristics of amylose chains negatively affecting the complex formation. Perhaps, depending on the degree of acetylation and distribution mode of acetyl groups on amylose chains, actual helix formation may be diminished, thus making unfeasible the development of well-organized amylose structures (V-structure). Similar to gelatinization, acetylation broadens the transition temperature range of amylose–lipid complexes. Reduction of melting temperature and enthalpy of wheat starch amylose–lipid complex after acetylation is most probably due to the greater hydration of starch granules resulting from acetylation. Substitution could also take place in the amylose–lipid complex weakening its bonding forces, and the structurally weaker complex

Table 3
Gelatinization parameters and dissociation parameters of amylose–lipid complexes (native wheat starch amylose–lipid complex and synthesized amylose–lipid complex in native and acetylated potato starches) in the presence of HPβ-CD

Starch	Treatment[c]	Gelatinization parameters[a]				ΔH_G (J/g)	Transition parameters of amylose–lipid complexes[b]				ΔH_A (J/g)
		T_o (°C)	T_p (°C)	T_c (°C)	$T_c - T_o$		T_o (°C)	T_p (°C)	T_c (°C)	$T_c - T_o$	
Wheat	Native	55.3 ± 0.2	59.4 ± 0.3	83.7 ± 0.1	28.4 ± 0.1	11.1 ± 0.2	103.1 ± 0.1	106.3 ± 0.1	112.8 ± 0.4	9.7 ± 0.5	1.7 ± 0.2
	Native + CD	55.9 ± 0.1	59.8 ± 0.5	84.8 ± 0.3	28.9 ± 0.3	9.7 ± 0.1	101.3 ± 0.4	105.6 ± 0.2	113.1 ± 0.6	11.8 ± 0.3	0.8 ± 0.2
	AC	52.2 ± 0.3	56.1 ± 0.2	82.4 ± 0.2	30.2 ± 0.1	9.6 ± 0.2	96.4 ± 0.5	103.7 ± 0.3	109.5 ± 0.2	13.1 ± 0.2	1.2 ± 0.1
	AC + CD	52.2 ± 0.1	56.4 ± 0.1	81.5 ± 0.1	29.3 ± 0.2	8.4 ± 0.1	94.2 ± 0.7	103.1 ± 0.1	109.2 ± 0.3	15.0 ± 0.1	0.7 ± 0.1
Potato	Native	59.8 ± 0.4	64.2 ± 0.3	82.6 ± 0.4	22.8 ± 0.3	15.5 ± 0.2	100.2 ± 0.3	111.1 ± 0.1	120.2 ± 0.1	20.0 ± 0.2	5.8 ± 0.2
	Native + CD	60.7 ± 0.1	65.5 ± 0.1	81.8 ± 0.5	21.1 ± 0.3	15.9 ± 0.2	99.5 ± 0.2	110.2 ± 0.3	119.6 ± 0.2	20.3 ± 0.4	4.9 ± 0.1
	AC	55.3 ± 0.2	60.5 ± 0.2	80.8 ± 0.1	25.5 ± 0.2	14.2 ± 0.3	95.4 ± 0.4	107.1 ± 0.2	118.2 ± 0.1	22.8 ± 0.3	3.5 ± 0.1
	AC + CD	56.4 ± 0.1	61.6 ± 0.3	80.1 ± 0.3	23.7 ± 0.1	14.3 ± 0.1	95.2 ± 0.2	106.4 ± 0.4	118.1 ± 0.3	23.2 ± 0.5	2.8 ± 0.1
Waxy maize	Native	62.8 ± 0.3	68.4 ± 0.1	88.3 ± 0.1	25.5 ± 0.2	15.1 ± 0.3					
	Native + CD	64.2 ± 0.1	70.0 ± 0.3	90.2 ± 0.2	26.0 ± 0.2	14.9 ± 0.4					
	AC	59.2 ± 0.3	65.2 ± 0.3	85.9 ± 0.1	26.7 ± 0.3	12.3 ± 0.4					
	AC + CD	60.3 ± 0.4	66.7 ± 0.4	86.9 ± 0.3	26.6 ± 0.1	12.1 ± 0.2					
High-amylose maize	Native	69.9 ± 0.1	78.3 ± 0.1	111.7 ± 0.4	41.8 ± 0.2	10.5 ± 0.1					
	Native + CD	71.2 ± 0.2	80.4 ± 0.2	111.5 ± 0.3	40.3 ± 0.1	10.4 ± 0.3					
	AC	62.2 ± 0.1	74.6 ± 0.1	105.3 ± 0.2	43.1 ± 0.1	9.5 ± 0.1					
	AC + CD	62.9 ± 0.3	74.8 ± 0.1	105.6 ± 0.2	42.7 ± 0.2	9.8 ± 0.2					

[a] T_o = onset, T_p = peak, T_c = conclusion, ΔH_G = gelatinization enthalpy.
[b] T_o = onset, T_p = peak, T_c = conclusion, ΔH_A = melting enthalpy of amylose–lipid complexes.
[c] AC = acetylated, CD = HPβ-CD. Values are mean of triplicate determination ± standard deviation.

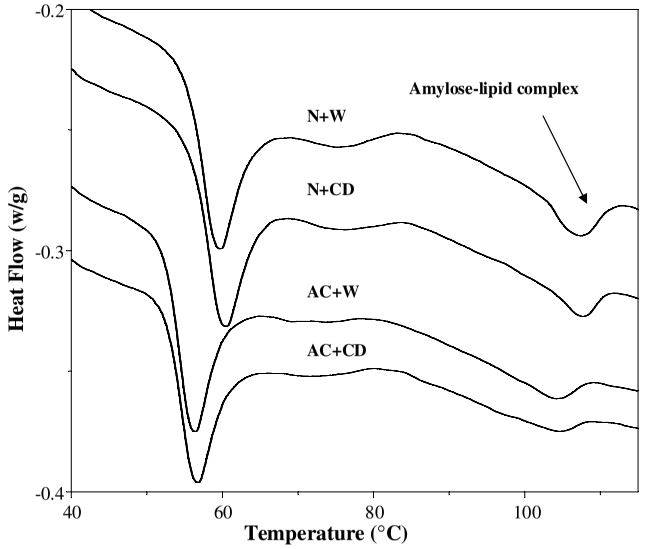

Fig. 1. DSC curves of native and acetylated wheat starches in the presence of HPβ-CD; N = native, W = water, AC = acetylated, CD = HPβ-CD.

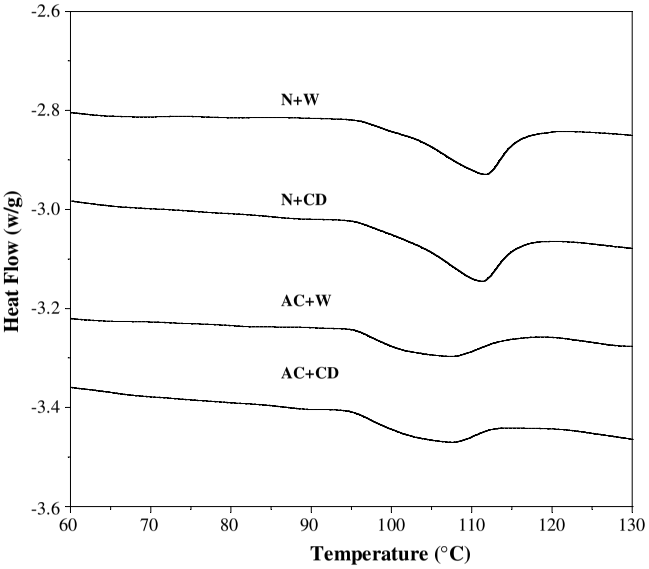

Fig. 2. DSC curves of synthesized amylose–lipid complexes using α-lysophosphatidylcholine in native and acetylated potato starches in the presence of HPβ-CD. N + W = native potato starch amylose–lipid complex with water, AC + CD = native potato starch amylose–lipid complex with HPβ-CD, AC + W = acetylated potato starch amylose–lipid complex with water, AC + CD = acetylated potato starch amylose–lipid complex with HPβ-CD.

may require less energy to complete the thermal transition. In contrast, HPβ-CD reduces melting enthalpy of amylose–lipid complexes by complexing with starch lipids and thereby increases the hydration of the starch granules.

3.3. Pasting properties

All starches showed increased peak viscosity and early onset of pasting after acetylation. Inclusion of HPβ-CD

decreased peak viscosity of wheat and potato starches but it was slightly increased in waxy maize starch, however, high-amylose maize starch remained unaffected (Fig. 3). Early onset of peak viscosity was found for wheat starch in the presence of HPβ-CD but not in other starches (Fig. 3). Addition of HPβ-CD to acetylated wheat starch increased peak viscosity and further reduced the temperature of onset of pasting, but in other acetylated starches, no influence on peak viscosity or pasting onset temperature in the presence of HPβ-CD was found. Viscosity in a dilute system is governed by the volume fraction of swollen granules, but in a concentrated system, it is governed by particle rigidity (Steeneken, 1989). Doublier, Llamas, and Le Meur (1987) suggested that overall viscosity of starch paste is primarily governed by a combination of swollen starch granules and composition of the continuous phase, thus swelling, amylose leaching and rupture of starch granules play a key role in determining the development of viscosity. Early viscosity increase of wheat starch in the presence of HPβ-CD could relate to its greater influence on swelling and amylose leaching. Perhaps addition of HPβ-CD could promote the close packing of swollen starch granules resulting in an early onset of viscosity. Evidence has been reported that polyhydroxy compounds such as sugars accelerate early onset of peak viscosity by promoting the close packing of swollen starch granules (Doublier et al., 1987; Richardson et al., 2003). Disruption of amylose–lipid complex followed by extensive swelling in the presence of HPβ-CD may weaken the structure of swollen wheat starch granules causing more deformation in swollen granules during stirring. This can reduce the peak viscosity. However, addition of HPβ-CD to acetylated wheat starch increased peak viscosity and caused early viscosity development. This indicates that acetylated wheat starch granules have gained some granular rigidity (resistance to deformation during stirring) and tendency to close packing with the inclusion of HPβ-CD. Several studies have shown that polyhydroxy compounds such as sugars can bridge starch chains stabilizing amorphous region (Baek, Yoo, & Lim, 2004; Chiotelli, Rolee, & Meste, 2000; Hoover & Senanayake, 1996; Spies & Hoseney, 1982). This kind of interaction could be promoted by introducing acetyl groups to starch chains in the amorphous region. However, inclusion of HPβ-CD had less impact on peak viscosity of other acetylated starches. This discrepancy may relate to the variation of physical properties of starch polymers, swelling tendency, and close packing ability in the presence of HPβ-CD. Increased cold paste viscosity of acetylated

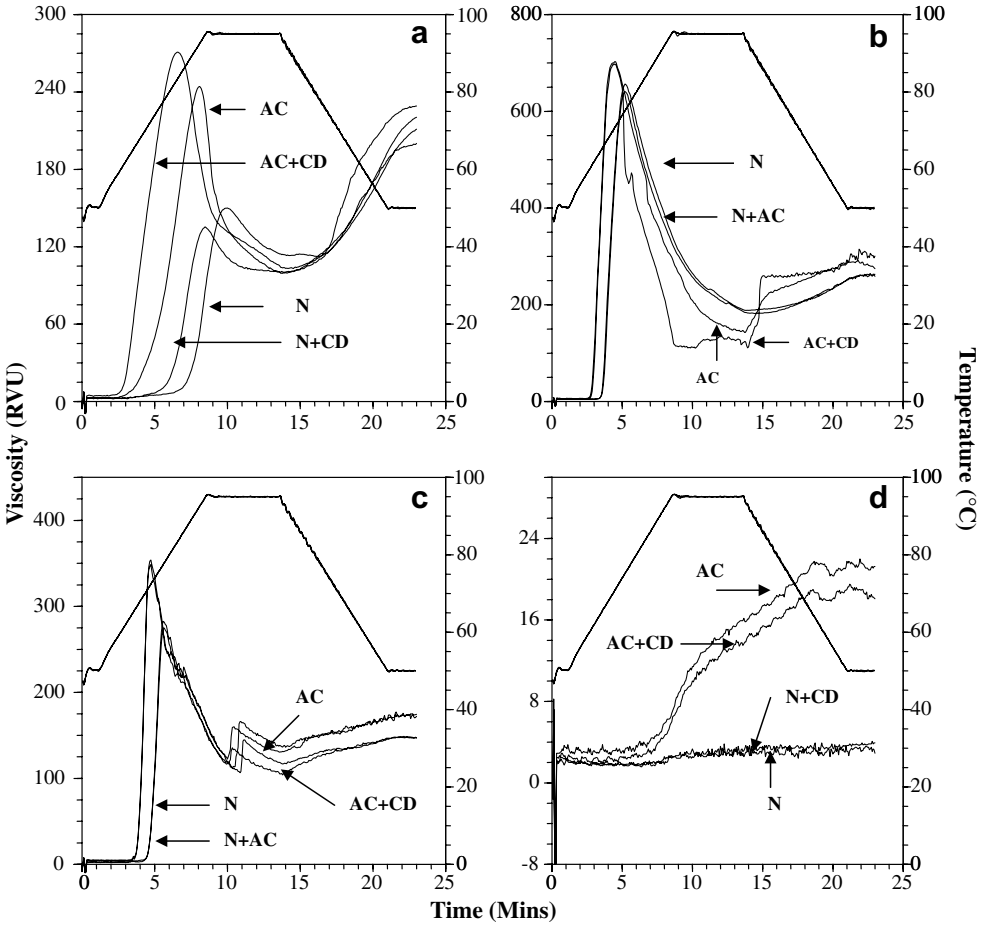

Fig. 3. RVA curves of native and acetylated wheat (a), potato (b), waxy maize (c), and high-amylose maize (d) in the presence of HPβ-CD. N = native, AC = acetylated, CD = HPβ-CD.

starches is consistent with higher amylose leaching resulting from acetylation because in cooling, starch paste gains some viscosity increase primarily due to the realignment of amylose chains. HPβ-CD increased setback (retrogradation) of wheat starch. HPβ-CD facilitates amylose leaching during pasting by the action of defatting the amylose chains. Lipid-free amylose can retrograde to a greater extent than lipid-complexed amylose.

Gel hardness of the native starches followed the order: wheat > potato > waxy maize (Table 1). High-amylose maize starch produced a very soft gel where the gel hardness was not measurable under the experimental conditions. HPβ-CD decreased gel hardness of all starches, but most in wheat starch. Acetylation markedly decreased gel hardness of all starches tested. Except for potato starch, gel hardness was not measurable in the acetylated starches under the conditions used. Although acetylation and HPβ-CD increased amylose leaching, the resulting gels were very soft. According to Ring (1985), the starch gel is a composite in which swollen gelatinized starch granules reinforce an interpenetrating amylose gel matrix. Mechanical properties of a starch gel would depend on the rheological characteristics of the amylose matrix, the volume fraction and the rigidity (deformability) of the gelatinized granules, and interactions between the dispersed and the continuous phases (Eliasson, 1986). Properties of starch gel should be interpreted in relation to the properties of the gel matrix amylose, deformable filler swollen particles, volume fraction of the swollen particles, and filler-matrix interaction (Morris, 1990). The decreased gel hardness of acetylated starch therefore should be due to the interplay among the following factors; less rigid swollen particles resulting from acetylation; substituted hydrophobic acetyl groups in the filler component (swollen starch granules) which could have weakened the interaction between filler component and the gel matrix; acetyl groups which could have reduced the conformation ordering, and intermolecular association of starch polymers by inhibiting the formation of junction zones. Greatly reduced gel hardness of wheat starch in the presence of HPβ-CD could be attributed to the weaker swollen gelatinized granules resulting in the disruption of amylose–lipid complex and the subsequent greater hydration of starch granules.

3.4. Enzymatic hydrolysis

Percent decrease of peak viscosity was used to detect the extent of starch hydrolysis by α-amylase (Table 4). The extent of enzymatic hydrolysis in native starches followed the order: waxy maize > potato > wheat. For high-amylose maize starch, this method cannot be successfully applied since it does not develop a distinguishable peak. Acetylation increased the enzymatic digestibility of all the starches. Loosened starch structure resulting after acetylation due to the disruption of hydrogen bonding between adjacent starch chains could increase the enzyme access to starch granules. Weselake and Hill (1983) reported that β-CD inhibited cereal α-amylase hydrolysis by binding with the non-catalytic site of the enzyme. This inhibits the binding of α-amylase with the substrate (starch). Weselake and Hill (1982) reported that α-amylase has a strong affinity for β-CD. However, in this study we did not see any increase of peak viscosity for both native and acetylated starches with enzyme added in the presence of HPβ-CD, indicating no inhibition of α-amylase. Similarly, no inhibition was reported for wheat starch bacterial α-amylase hydrolysis in the presence of β-CD (Li et al., 2000). This discrepancy however, may be attributed to the variation among types of α-amylases, cyclodextrins and methods used for the analysis.

Table 4
Percentage decrease of peak viscosity (PV) of native and acetylated starches after addition of α-amylase in the presence of HPβ-CD

Starch	Treatment[a]	PV (control)	PV (with α-amylase)	Percentage decrease
Wheat	Native	153 ± 0.4	30 ± 1.2	80 ± 0.7
	Native + CD	128 ± 0.7	17 ± 0.8	86 ± 0.8
	AC	244 ± 0.5	19 ± 0.5	92 ± 0.6
	AC + CD	270 ± 1.2	20 ± 0.4	92 ± 0.4
Potato	Native	655 ± 1.1	73 ± 0.9	88 ± 1.1
	Native + CD	640 ± 0.9	71 ± 0.7	89 ± 1.2
	AC	702 ± 1.3	36 ± 0.8	95 ± 0.6
	AC + CD	697 ± 1.5	41 ± 0.6	95 ± 0.7
Waxy	Native	175 ± 0.4	10 ± 0.3	94 ± 0.8
	Native + CD	282 ± 0.8	9 ± 0.5	94 ± 0.6
	AC	353 ± 1.3	6 ± 0.8	98 ± 0.9
	AC + CD	348 ± 1.6	6 ± 0.5	98 ± 1.2
High-amylose maize	Native	3 ± 0.1	2.5 ± 0.4	16 ± 0.3
	Native + CD	3 ± 0.2	2.5 ± 0.2	16 ± 0.2
	AC	14 ± 0.4	10 ± 0.1	29 ± 0.3
	AC + CD	15 ± 0.3	10 ± 0.5	33 ± 0.6

Values are mean of triplicate determination ± standard deviation.
[a] AC = acetylated, CD = HPβ-CD, En = α-amylase enzyme (100 mg).

4. Conclusions

Both acetylation and addition of hydroxypropyl β-cyclodextrin are capable of increasing swelling and amylose leaching while decreasing gelatinization enthalpy and pasting onset of wheat starch. The common cause for these changes in properties relates to the hydration of the starch granule. Loosened starch structure by acetylation prevents interchain association facilitating more water penetration into the granules. By disrupting the amylose–lipid complex by complexing with starch lipids, hydroxypropyl β-cyclodextin extensively hydrates the starch granules. Acetylation reduces the complex forming ability of amylose and facilitates the dissociation of the amylose–lipid complex. Understanding the transformation and dissociation parameters of amylose–lipid complex within the starch granules is of great fundamental and technological importance, considering the multifunctional role of lipids in starch-based products. This study showed that HPβ-CD is capable of disrupting amylose–lipid complex making significant changes to starch functional properties. Ability to disrupt amylose–lipid complexes by HPβ-CD could potentially be applied to improve process efficiency such as in production of glucose syrup from cereal starches via amylolytic reaction. This is feasible because HPβ-CD has no inhibiting effect on α-amylase hydrolysis and thus, HPβ-CD and α-amylase can be used together. A small quantity of HPβ-CD is sufficient to greatly destabilize the amylose–lipid complex.

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

Ahn, J., & Kwak, H. S. (1999). Optimizing cholesterol removal in cream using β-cyclodextrin and response surface methodology. *Journal of Food Science, 64*, 629–632.

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 Hydrocolloids, 18*, 133–142.

Becker, A., Hill, S. E., & Mitchell, J. R. (2001). Relevance of amylose–lipid complex to the behavior of thermally processed starches. *Starch/Starke, 53*, 121–130.

Biliaderis, C. G., & Tonogai, J. R. (1991). Influence of lipids on the thermal and mechanical properties of concentrated starch gels. *Journal of Agricultural and Food Chemistry, 39*, 833–840.

Biliaderis, C. G., Page, C. M., Slade, L., & Sirett, R. R. (1985). Thermal behavior of amylose–lipid complexes. *Carbohydrate Polymers, 5*, 367–389.

Biliaderis, C. G., Tonogai, J. R., Pereze, C. M., & Juliano, B. O. (1993). Thermophysical properties of milled rice starches as influenced by variety and parboiling method. *Cereal Chemistry, 70*, 512–516.

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.

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. (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.

Galliard, T., & Bowler, P. (1987). Morphology and composition of starch. In T. Galliard (Ed.), *Starch: Properties and potential* (pp. 55–79). Chichester, England: Wiley.

Hoover, R., & Hadziyev, D. (1981). Characterization of potato starch and its monoglyceride complexes. *Starch, 33*, 290–300.

Hoover, R., & Senanayake, N. (1996). Effect of sugars on the thermal and retrogradation properties of oat starches. *Journal of Food Biochemistry, 20*, 65–83.

Krog, N. (1971). Amylose complexing effect of food grade emulsifiers. *Starch, 23*, 206–210.

Kim, H. O., & Hill, R. D. (1984a). Modification of wheat starch flour dough characteristics by cycloheptaamylose. *Cereal Chemistry, 61*, 406–409.

Kim, H. O., & Hill, R. D. (1984b). Physical characteristics of wheat starch granule gelatinization in the presence of cycloheptaamylose. *Cereal Chemistry, 61*, 432–435.

Kant, A., Linforth, R. S. T., Hort, J., & Taylor, A. J. (2004). Effect of β-cyclodextrin on aroma release and flavor perception. *Journal of Agricultural and Food Chemistry, 52*, 2028–2035.

Li, W. D., Huang, J. C., & Corke, H. (2000). Effect of β-cyclodextrin on pasting properties of wheat starch. *Nahrung – Food, 44*, 164–167.

Liu, H. J., Ramsden, L., & Corke, H. (1997). Physical properties and enzymatic digestibility of acetylated ae, wx and normal maize starch. *Carbohydrate Polymers, 34*, 283–289.

Liu, H. J., Ramsden, L., & Corke, H. (1999). Physical properties of cross-linked and acetylated normal and waxy rice starch. *Starch/Starke, 51*, 249–252.

Master, M., & Steeneken, P. A. M. (1998a). Filtration characteristics of maize and wheat starch hydrolysates. *Cereal Chemistry, 75*, 289–293.

Master, M., & Steeneken, P. A. M. (1998b). Origins of the poor filtration characteristics of wheat starch hydrolysates. *Cereal Chemistry, 75*, 289–293.

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

Morrison, W. R. (1981). Starch lipids: A reappraisal. *Starch/Starke, 33*, 408–410.

Nebesnky, E., Rosicka, J., & Tkaczyk, M. (2002). Effect of enzymatic hydrolysis of wheat starch on amylose–lipid complexes stability. *Starch, 54*, 603–608.

Nebesnky, E., Rosicka, J., & Tkaczyk, M. (2004). Influence of conditions of maize starch enzymatic hydrolysis on physicochemical properties of glucose syrup. *Starch, 56*, 132–137.

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. (1985). Some studies on starch gelation. *Starch, 37*, 80–83.

Smith, D. M., Awad, A. C., Bennink, M. R., & Gill, J. L. (1995). Cholesterol reduction in liquid egg-yolk using β-cyclodextrin. *Journal of Food Science, 60*, 669–691.

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.

Wang, Y. J., & Wang, L. (2002). Characterization of acetylated waxy maize starches prepared under catalysis by different alkali and alkaline-earth hydroxides. *Starch, 54*, 25–30.

Weselake, R. J., & Hill, R. D. (1982). Cycloheptaamylose as an affinity ligand of cereal α-amylase. Characteristics and a possible mechanism of the interaction. *Carbohydrate Research, 108*, 153–161.

Weselake, R. J., & Hill, R. D. (1983). Inhibition of alpha-amylase-catalyzed starch granule hydrolysis by cycloheptaamylose. *Cereal Chemistry, 60*, 98–101.

Yen, G. C., & Tsui, L. T. (1995). Cholesterol removal from a lard–water mixture with β-cyclodextrin. *Journal of Food Science, 60*, 561–564.