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Carbohydrate Polymers 68 (2007) 226–234
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Influence of unmodified and modified cycloheptaamylose (β-cyclodextrin) on transition parameters of amylose–lipid complex and functional properties of starch

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Received 26 September 2006; received in revised form 14 December 2006; accepted 15 December 2006
Available online 23 December 2006

Abstract

Functional characteristics of starches from cereal, tuber, and root were studied in the presence of β-cyclodextrin and hydroxypropyl β-cyclodextrin. Both cyclodextrin compounds significantly increased swelling factor, amylose leaching, and solubility of cereal starches while tuber and root starches were less affected. Gelatinization enthalpy in cereal starches was slightly decreased in the presence of β-CD and HPβ-CD but in tuber and root starches was not affected. Both β-CD and HPβ-CD decreased dissociation energy of native (wheat, maize, and rice) and synthesized (amylose–lysophosphatidylcholine and amylose–stearic acid) amylose–lipid complex. Reformation of native amylose–lipid complex in cereal starches was decreased by both β-CD and HPβ-CD. Only in cereal starches the presence of β-CD and HPβ-CD during starch pasting result in early swelling and decreased pasting temperature. Both cyclodextrins did not inhibit α-amylase. The results were consistent with the disruption of amylose–lipid complex within the starch granules by both cyclodextrins by complexing with starch lipids, affecting a range of functional properties of starch.
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Keywords: β-Cyclodextrin; Hydroxypropyl β-cyclodextrin; Amylose–lipid complex

1. Introduction

Cycloheptaamylose (β-CD) is a cyclic oligosaccharide composed of seven glucose units arranged in a donut-shaped ring. Its hydrophobic core can complex with a variety of guest organic and inorganic molecules. β-CD is widely applied in food, pharmaceutical, and cosmetic industries. In food industry β-CD 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 a flavor carrier for some products (Kant, Linforth, Hort, & Taylor, 2004). Hydroxypropyl β-cyclodextrin (HPβ-CD) is prepared by substituting hydroxypropyl groups to the hydroxyl groups of the seven glucose molecules that are oriented to form a hydrophobic core in the center of the molecule. Substitution thus may have an effect on complex-forming ability because of greater hydrophilicity and larger molecular size. In a study of wheat starch gelatinization in the presence of β-cyclodextrin, it has been shown that β-cyclodextrin increases amylose leaching, swelling power, and solubility of wheat starch in a manner consistent with the disruption of amylose–lipid complex within the starch granules (Kim & Hill, 1984b) These authors further reported that the effect is more pronounced at the second stage of gelatinization. In food systems, behavior of the amylose–lipid complex is of technological interest because it can affect the quality of starch-based food products. For example, retardation of starch retrogradation and bread firming (Biliaderis & Tonogai, 1991), prevention of stickiness of dried potato (Hoover & Hadziyev, 1981), and improvement of structural integrity of cereal kernels during cooking (e.g.,

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0144-8617/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.carbpol.2006.12.017

parboiled rice) (Biliaderis, Tonogai, & Perez, 1993) have been reported in the presence or formation of the amylose–lipid complex. Understanding of complex formation and dissociation and their role in determining functional properties of starch is technologically important for the quality of starch-related food products. It has been reported that β-CD can inhibit hydrolysis by α-amylase with a slight increase of peak viscosity in wheat starch with α-amylase when β-CD is present (Kim & Hill, 1984a). However, Li, Huang, and Corke (2000) reported decreased viscosity for wheat starch with added bacterial α-amylase in the presence of β-CD, but increased peak viscosity for wheat flour under the same conditions, suggesting that β-CD has strongly inhibited wheat endosperm α-amylase. Very little literature is available on starch–cyclodextrin interaction. So far all previous studies carried out to investigate cyclodextrin–starch interaction have been on unmodified β-CD. However, the effect of hydroxypropyl β-cyclodextrin, a modified β-CD which has greater solubility in water, may interact differently with starch. This study aimed to compare the influence of β-CD with its modified counterpart, HPβ-CD on starch properties, mainly focusing their influence on amylose–lipid complex.

2. Materials and methods

2.1. Materials

Wheat, potato, and rice starch, β-cyclodextrin (β-CD), hydroxypropyl β-cyclodextrin (HPβ-CD), bacterial α-amylase from *Bacillus species*, fungal α-amylase from *Aspergillus oriyzae*, β-amylase from Barley, L-α-lysophosphatidylcholine, and stearic acid were purchased from Sigma Chemical Co., (St. Louis, MO). Normal maize starch was obtained from Starch Australasia Limited (Lane Cove, Australia). Sweet potato and yam starches were processed from local market samples.

2.2. Methods

2.2.1. Amylose leaching

Distilled water (10 mL) was added to starch (20 mg, db) in a screw cap tube. Tubes were then heated at different temperatures (50–100 °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).

2.2.2. 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 different temperatures (50–100 °C) in 5 mL of water.

2.2.3. Solubility

The method of Subramanian, Hoseney, and Bramel-Cox (1994) with minor modification was used to determine the solubility of starch. Starch (0.5 g) was heated at 80 °C temperature in water (15 mL) with continuous stirring to prevent lump formation. The slurry was then centrifuged at 3000*g* for 10 min. A known aliquot of supernatant was dried at 130 °C overnight. The weight of oven-dried supernatant was back-calculated to the volume of supernatant and the initial weight of dry starch and expressed as percent soluble starch.

2.2.4. Synthesis of amylose–lipid complex

The method described by Biliaderis (1985) with slight modifications was employed to synthesize the amylose–lipid complex. Potato amylose (400 mg) was dissolved in DMSO (5 mL). The mixture was then diluted with distilled water at 100 °C to 0.8% (w/v) concentration. To maintain the weight ratio of 5:1 amylose to lipid, 80 mg of α-lysophosphatidylcholine and stearic acid dissolved in water and 4 mL at 60 °C was added to the amylose solution. In case of stearic acid, 80 mg of fatty acid was dissolved in DMSO 4 mL. The mixture was then heated at 90 °C in a water bath with occasional stirring for 3 h. After slowly cooling to room temperature, the suspension was allowed to stand for 3 days. Complex recovered by centrifugation at 8000*g* was then washed with water and freeze-dried at −55 °C for two days.

2.2.5. 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 (3 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 30–140 °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

Distilled water (6 μL) was added to synthesized amylose–lipid complex (1 mg) directly into the aluminum DSC pan and mixed for homogenization. Pans were sealed and allowed to stand for 1 h for uniform distribution of water. The scanning temperature and heating rate were 30–140 °C and 5 °C/min, respectively.

2.2.7. Pasting properties

Pasting properties of starches were determined using a Rapid Visco-Analyser (RVA) model 3D (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. Enzymatic hydrolysis

In order to examine the effect of β-cyclodextrin and hydroxypropyl β-cyclodextrin on enzymatic hydrolysis of starch, a viscoamylometric method was used as described by Li et al. (2000) with slight modifications. One hundred units of different types of amylases (bacterial and fungal α-amylases and β-amylase) were added to starch slurry in the canister containing β-cyclodextrin and hydroxypropyl β-cyclodextrin just before the RVA testing. The development of peak viscosity was then noted.

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

3. Results and discussion

3.1. Swelling factor and solubility

All the starches tested showed increased swelling factor with increasing temperature with or without added cyclodextrins (Fig. 1). For native starches, tuber and root starches showed higher swelling compared to cereal starches.

Both β-CD and HPβ-CD significantly increased swelling factor of all cereal starches whereas tuber and root starches showed slightly increased or unchanged swelling (Fig. 1). The effect of β-CD and HPβ-CD on swelling is more pronounced at the second stage of gelatinization indicating that extensive hydration of starch granules occurred at this stage. Tester and Morrison (1990a) have shown that granular swelling is primarily a property of amylopectin and that amylose is a diluent. However, the other factors indicated above could also influence starch granular swelling. Kim and Hill (1984b) showed that β-CD dramatically increases swelling volume of wheat starch in the presence of β-CD, likely by disrupting the amylose–lipid complex. Presence of amylose–lipid complex which can form a rigid structure in cereal starch granules can restrict both swelling and amylose leaching preventing water absorption to the starch granules (Becker, Hill, & Mitchell, 2001). Biliaderis (1998) reported that the amylose–lipid complex in cereal starches limits granular swelling compared to waxy or lipid free starches. Increased swelling factor only in cereal starches in the presence of both cyclodextrins is consistent with disruption of amylose–lipid complex by both cyclodextrins, because other factors responsible for starch swelling that could be affected by both cyclodextrins should be significant in cereal as well as tuber and root starches.

It can be speculated that greater hydrophilicity of HPβ-CD can inhibit starch swelling by binding more water molecules, thus limiting the starch hydration, but HPβ-CD increased granular swelling, only in cereal starches, and to an even greater extent than did β-CD (Fig. 1). This indicates that HPβ-CD also capable of disrupting the amylose–lipid complex as did β-CD, perhaps to a greater extent. This claim is further supported by increased solubility (Table 1), and less energy requirement to dissociate both native and synthesized amylose–lipid complex in the presence of HPβ-CD compared to β-CD (Table 2). For tuber and root starches HPβ-CD slightly increased the swelling of sweet potato and yam but slightly decreased that of potato starch.

3.2. Amylose leaching

Amylose leaching in cereal starches was significantly increased especially above the gelatinization temperature by both β-CD and HPβ-CD while very slight effects were observed in tuber and root starches similar to the situation for swelling and solubility. Differences of amylose leaching of native starches could also be attributed the differences in amount of amylose, location of amylose, lipid complexed with amylose, chain length of amylose, and inter-chain interaction of amylose and amylopectin in the starch granules. It is clear that the significant increase of amylose leaching only in cereal starches

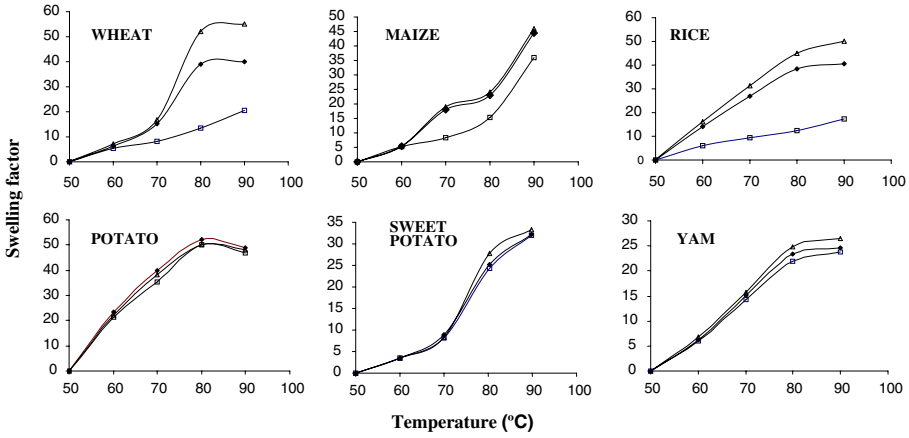

Fig. 1. Swelling factor of starches in the presence of β-CD and HPβ-CD. □, with water; ◆, with β-CD; Δ, with HPβ-CD.

Table 1
Gelatinization parameters[a] and solubility of cereal, tuber, and root starches in the presence of β-CD and HPβ-CD

Starch	Treatment	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)	Solubility (%) at 80 °C
Wheat	Water	54.7 ± 0.1[b]	59.0 ± 0.3	86.7 ± 0.2	10.9 ± 0.6	5.1 ± 0.3
	β-CD	55.3 ± 0.2	59.4 ± 0.2	86.4 ± 0.3	9.1 ± 0.5	16.2 ± 0.2
	HPβ-CD	55.5 ± 0.3	59.6 ± 0.2	86.1 ± 0.3	8.7 ± 0.3	18.8 ± 0.4
Maize	Water	63.9 ± 0.5	68.2 ± 0.1	90.2 ± 0.1	12.1 ± 0.3	6.5 ± 0.2
	β-CD	64.1 ± 0.1	68.4 ± 0.3	90.1 ± 0.4	11.5 ± 0.2	15.2 ± 0.1
	HPβ-CD	64.8 ± 0.4	69.0 ± 0.1	89.5 ± 0.1	11.1 ± 0.3	16.1 ± 0.1
Rice	Water	56.2 ± 0.1	64.7 ± 0.1	89.4 ± 0.3	7.7 ± 0.1	5.5 ± 0.3
	β-CD	57.4 ± 0.6	65.2 ± 0.2	90.3 ± 0.2	6.9 ± 0.1	20.3 ± 0.1
	HPβ-CD	57.4 ± 0.1	65.3 ± 0.3	90.2 ± 0.3	6.7 ± 0.2	22.1 ± 0.3
Potato	Water	57.3 ± 0.3	61.7 ± 0.1	80.5 ± 0.2	14.1 ± 0.4	5.5 ± 0.1
	β-CD	58.5 ± 0.4	62.3 ± 0.4	80.4 ± 0.1	14.3 ± 0.3	7.5 ± 0.1
	HPβ-CD	58.5 ± 0.3	62.5 ± 0.2	80.1 ± 0.2	14.4 ± 0.1	8.1 ± 0.2
Sweet potato	Water	59.6 ± 0.5	65.4 ± 0.3	95.2 ± 0.1	12.0 ± 0.3	3.9 ± 0.1
	β-CD	59.3 ± 0.1	64.9 ± 0.3	95.6 ± 0.1	12.2 ± 0.2	4.8 ± 0.2
	HPβ-CD	60.0 ± 0.2	65.2 ± 0.2	96.1 ± 0.2	12.1 ± 0.1	5.4 ± 0.3
Yam	Water	64.3 ± 0.1	69.3 ± 0.2	81.4 ± 0.2	13.2 ± 0.3	15.1 ± 0.2
	β-CD	63.9 ± 0.2	69.1 ± 0.3	82.6 ± 0.4	13.3 ± 0.1	17.6 ± 0.1
	HPβ-CD	64.1 ± 0.3	69.4 ± 0.1	82.9 ± 0.2	13.5 ± 0.1	18.2 ± 0.3

[a] T_o, onset; T_p, peak; T_c, conclusion; ΔH, enthalpy.
[b] Values are mean of triplicate determination ± standard deviation.

Table 2
Dissociation parameters[a] of amylose–lipid complexes of native cereal starches and amylose–lipid complex synthesized in DSC pan; and reformation of amylose–lipid complex in native starches in the presence of β-CD[b] and HPβ-CD[b]

Source	Treatment	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Wheat	Water	103.3 ± 0.3[d]	107.9 ± 0.2	112.6 ± 0.2	1.5 ± 0.1
	β-CD	100.9 ± 0.2	105.8 ± 0.1	113.2 ± 0.3	0.82 ± 0.1
	HPβ-CD	101.7 ± 0.1	106.5 ± 0.3	113.6 ± 0.2	0.52 ± 0.2
Maize	Water	95.0 ± 0.2	105.2 ± 0.3	112.1 ± 0.3	2.2 ± 0.2
	β-CD	93.5 ± 0.2	105.6 ± 0.2	110.3 ± 0.4	1.8 ± 0.1
	HPβ-CD	93.2 ± 0.3	102.7 ± 0.4	110.1 ± 0.3	1.4 ± 0.2
Rice	Water	96.7 ± 0.4	107.9 ± 0.2	114.5 ± 0.3	2.8 ± 0.3
	β-CD	94.1 ± 0.1	106.2 ± 0.1	114.9 ± 0.5	1.9 ± 0.2
	HPβ-CD	93.3 ± 0.1	105.7 ± 0.4	114.2 ± 0.2	1.3 ± 0.1
Synthesized (lysophospholipid)	Water	98.1 ± 0.3	100.8 ± 0.1	106.8 ± 0.1	13.0 ± 0.1
	β-CD	97.4 ± 0.1	100.5 ± 0.1	107.1 ± 0.3	10.5 ± 0.3
	HPβ-CD	97.9 ± 0.1	101.0 ± 0.2	107.8 ± 0.3	9.4 ± 0.2
Synthesized (stearic acid)	Water	94.2 ± 0.2	97.3 ± 0.3	103.2 ± 0.4	8.3 ± 0.2
	β-CD	90.9 ± 0.5	96.8 ± 0.2	103.1 ± 0.3	7.1 ± 0.1
	HPβ-CD	91.7 ± 0.1	96.8 ± 0.3	103.2 ± 0.3	6.3 ± 0.2
Re-formation of native AML[c]					
Wheat	Water	105.9 ± 0.1	110.3 ± 0.1	113.6 ± 0.5	0.78 ± 0.1
	β-CD	106.9 ± 0.2	111.7 ± 0.1	115.1 ± 0.3	0.61 ± 0.2
	HPβ-CD	104.8 ± 0.3	108.4 ± 0.2	112.3 ± 0.4	0.44 ± 0.2
Maize	Water	123.5 ± 0.1	127.7 ± 0.3	131.2 ± 0.3	0.66 ± 0.3
	β-CD	123.5 ± 0.2	127.5 ± 0.2	133.1 ± 0.4	0.50 ± 0.2
	HPβ-CD	123.5 ± 0.5	128.6 ± 0.3	132.2 ± 0.3	0.36 ± 0.1

[a] T_o, onset; T_p, peak; T_c, conclusion; ΔH, enthalpy.
[b] 0.01 M.
[c] AML, amylose–lipid complex.
[d] Values are mean of triplicate determination ± standard deviation.

should be due to disruption of amylose–lipid complex, because other factors should similarly influence tuber and root starches.

Generally cereal starches are characterized as higher lipid content starch in contrast to tuber and root starches. Many authors have reported that lipid-free

amylose typically leaches out much easier than that of lipid-complexed amylose (Becker et al., 2001; Hoover & Hadziyev, 1981; Tester & Morrison, 1990a). HPβ-CD slightly eased amylose leaching in all cereal starches compared with β-CD except for maize starch (Fig. 2). This result was not consistent with those for swelling factor and solubility because HPβ-CD increased swelling and solubility of all cereal starches more than did β-CD, thus HPβ-CD should increase amylose leaching more than that of β-CD. Quantitative determination of amylose leaching was carried out using an iodometric method. The large HPβ-CD molecule may have interfered in the formation of amylose–iodine complex inhibiting the development of blue colour which to some extent may explain the observed lower amylose leaching with HPβ-CD compared to β-CD.

3.3. DSC parameters

Gelatinization onset temperature and gelatinization peak temperature were slightly increased for all starches upon addition of β-CD and HPβ-CD, although the effect of HPβ-CD was greater (Table 1). Hydrophilic β-CD and HPβ-CD can limit the water availability, forming hydrogen bonding with water molecules resulting in delayed starch gelatinization. However, greater amylose leaching, swelling, solubility, and decreased onset of pasting (Table 3) are not consistent with inhibition of starch hydration. This may suggest that β-CD and HPβ-CD interaction with starch is different from other polyols such as sugars which have been shown to increase the gelatinization temperature while decreasing swelling and amylose leaching (Richardson, Langton, Bark, & Hermansson, 2003; Savage & Osman, 1978). All starches

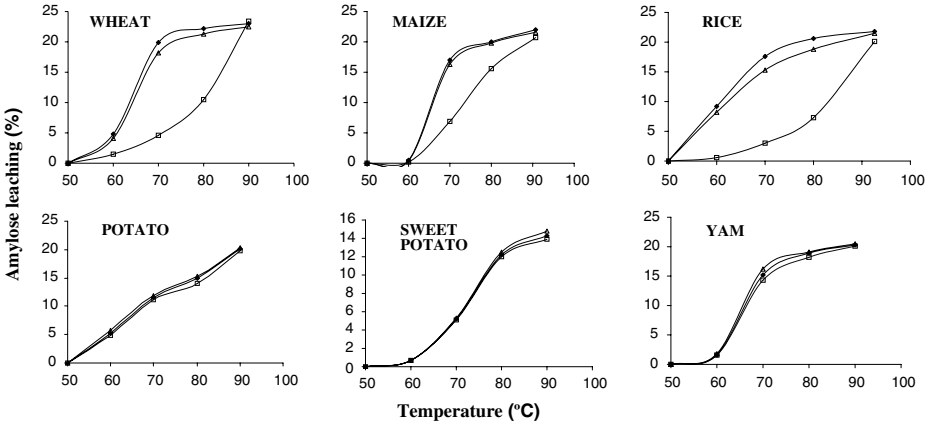

Fig. 2. Amylose leaching of starches in the presence of β-CD and HPβ-CD. □, with water; ◆, with β-CD; Δ, with HPβ-CD.

Table 3
Pasting properties[a] of cereal, tuber, and root starches in the presence of β-CD[b] and HPβ-CD[b]

Starch	Treatment	PV	HPV	BD	CPV	SB	GH
Wheat	Water	148 ± 0.8[c]	112 ± 0.7	35 ± 0.5	204 ± 1.2	93 ± 0.8	64 ± 0.7
	β-CD	135 ± 0.7	99 ± 0.3	36 ± 0.8	221 ± 0.7	121 ± 0.9	53 ± 0.6
	HPβ-CD	128 ± 0.7	98 ± 0.6	29 ± 0.5	216 ± 1.2	118 ± 0.7	46 ± 0.4
Maize	Water	212 ± 0.7	110 ± 1.2	99 ± 1.3	220 ± 0.7	109 ± 0.6	46 ± 0.5
	β-CD	209 ± 0.8	108 ± 0.4	100 ± 0.6	218 ± 0.4	107 ± 0.5	46 ± 0.7
	HPβ-CD	205 ± 0.6	106 ± 0.9	99 ± 0.5	216 ± 0.4	110 ± 0.3	35 ± 0.7
Rice	Water	110 ± 0.7	72 ± 0.6	39 ± 0.8	138 ± 1.1	66 ± 0.8	14 ± 0.4
	β-CD	108 ± 0.6	68 ± 0.4	40 ± 0.7	129 ± 1.2	60 ± 0.6	12 ± 0.4
	HPβ-CD	108 ± 0.9	68 ± 0.4	41 ± 0.8	133 ± 1.1	65 ± 0.5	9 ± 0.6
Potato	Water	659 ± 0.9	187 ± 0.6	475 ± 0.4	274 ± 0.5	80 ± 0.4	39 ± 0.4
	β-CD	665 ± 1.2	180 ± 0.6	486 ± 0.4	254 ± 1.3	73 ± 0.5	38 ± 0.6
	HPβ-CD	640 ± 0.8	639 ± 0.9	459 ± 1.1	255 ± 0.5	75 ± 0.6	35 ± 0.4
Sweet potato	Water	406 ± 0.6	186 ± 0.7	207 ± 0.5	272 ± 0.4	86 ± 0.8	44 ± 0.3
	β-CD	418 ± 0.9	192 ± 0.7	220 ± 1.2	281 ± 1.3	88 ± 0.8	42 ± 0.6
	HPβ-CD	400 ± 1.2	182 ± 0.9	214 ± 0.8	267 ± 0.4	86 ± 0.5	48 ± 0.7
Yam	Water	48 ± 0.6	9 ± 0.2	37 ± 0.9	11 ± 0.7	5 ± 0.3	—
	β-CD	51 ± 0.4	10 ± 0.4	39 ± 0.5	14 ± 0.5	4 ± 0.2	—
	HPβ-CD	44 ± 0.7	8 ± 0.5	35 ± 0.4	13 ± 0.7	4 ± 0.5	—

[a] PV, peak viscosity; HPV, hot paste viscosity; BD, breakdown; CPV, cold paste [b] viscosity; SB, setback; GH, gel hardness (g).
[b] 0.01 M.
[c] Values are mean of triplicate determination ± standard deviation.

showed two transition endotherms during gelatinization and a third, higher temperature endotherm that showed only in cereal starches and is believed to be due to the dissociation of amylose–lipid complex (Fig. 3). The low temperature endotherms represent the melting of starch crystals made by amylopectin. The presence of a double endotherm at moderate moisture content (50% in this study) could be attributed to the uneven moisture distribution or the presence of crystallites differing in thermal stability (Kaletunc & Breslauer, 2003).

Gelatinization enthalpy of all cereal starches was slightly decreased in the presence of β-CD and HPβ-CD. Extensive structural changes in the amorphous region (higher amylose leaching and swelling) due to the dissociation of amylose–lipid complex in the presence of β-CD and HPβ-CD could facilitate the destabilization of amylopectin helices in the crystalline region requiring less energy for the gelatinization process, and could thus explain the slight decrease of ΔH by β-CD and HPβ-CD, perhaps extensive hydration of starch granules could reduce the energy requirement to disrupt the starch structure.

Thermal transition of amylose–lipid complex in native starches in the presence of cyclodextrins showed that both cyclodextrins decreased the dissociation energy requirement (Table 2 and Fig. 3). Starch lipid could be either surface or internal. The internal lipids in the cereals are mostly monoacyl lipids in which lysophospholipids represent the major component (Hargin & Morrison, 1980; Morrison, 1981). According to Meredith, Dengate, and Morrison (1978) wheat starch lipids contain at least 90% lysophospholipids. Monoacyl lipids that occur both on surface and internally can be complexed with amylose (Buleon, Colonna, Planchot, & Ball, 1998), thus an analysis of transition parameters of lysophosphatidyl–amylose complex in the presence of cyclodextrin will provide useful data in understanding the interaction between cyclodextrin and amylose–lipid complex.

Amylose–lipid complex can be crystalline or amorphous depending on the temperature at which they form (Biliaderis, 1992). Amorphous amylose–lipid complexes are believed to be present in native starch granules, next to free amylose and lipids (Morrison, Law, & Snape, 1993). Decreased ΔH in synthesized (amylose–lysophosphatidylcholine and amylose–stearic acid complex) amylose–lipid complexes (Table 2) in the presence of β-CD and HPβ-CD further confirmed the dissociation of amylose–lipid complex by β-CD and HPβ-CD. However, transition temperatures of amylose–lysophosphatidylcholine complex were apparently unchanged in the presence of β-CD and HPβ-CD and also showed only a single endotherm (one endotherm is in agreement with Biliaderis, 1985) while two endotherms were shown in amylose–stearic acid complex (Fig. 4) with decreased onset and peak temperatures. The first endotherm, which dissociates at low temperature, is due to the uncomplexed fatty acids (Serap & Jackson, 2002) and the second endotherm dissociated at higher temperature reflects the crystalline amylose–lipid complex. The magnitude of the decrease of ΔH in both synthesized and native amylose–lipid complex (Table 2) was greater with HPβ-CD than that of β-CD, indicating that HPβ-CD is more capable of disrupting amylose–lipid complex. However, decrease of transition temperatures was not consistent.

Dissociated amylose–lipid complex can be reformed on cooling. This concept was used to examine whether β-CD and HPβ-CD can form new cyclodextrin–starch lipid complex preventing the formation of amylose–lipid complex in native starch. It has been reported that fatty acids can form inclusion complex with cycloheptaamylose (Schlenk & Sand, 1961). Amylose–lipid complex of native starches was dissociated by heating samples in DSC pans at 120 °C in the presence of β-CD and HPβ-CD followed by rescanning after cooling at room temperature for 20 min. In wheat and maize starches, the observed decrease of ΔH in reformed amylose–lipid complex in the presence of β-CD and HPβ-CD compared with control sample indicated that both cyclodextrin molecules are capable of complexing with starch lipids, although HPβ-CD has more effect (Table 2). Dissociation of reformed amylose–lipid complex in both maize and rice starch showed a very small endotherm at around 130 °C (not

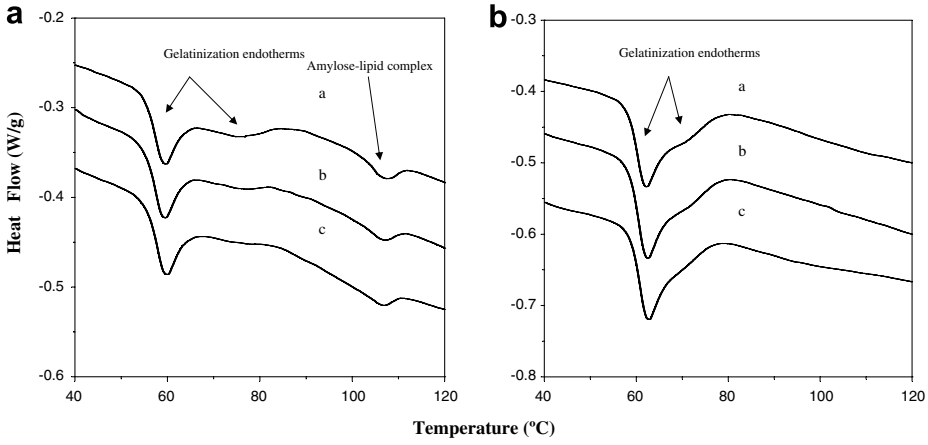

Fig. 3. DSC thermograms of representative (a) cereal (wheat), (b) tuber and root (potato) starches in the presence of β-CD and HPβ-CD. a, with water; b, with β-CD; c, with HPβ-CD.

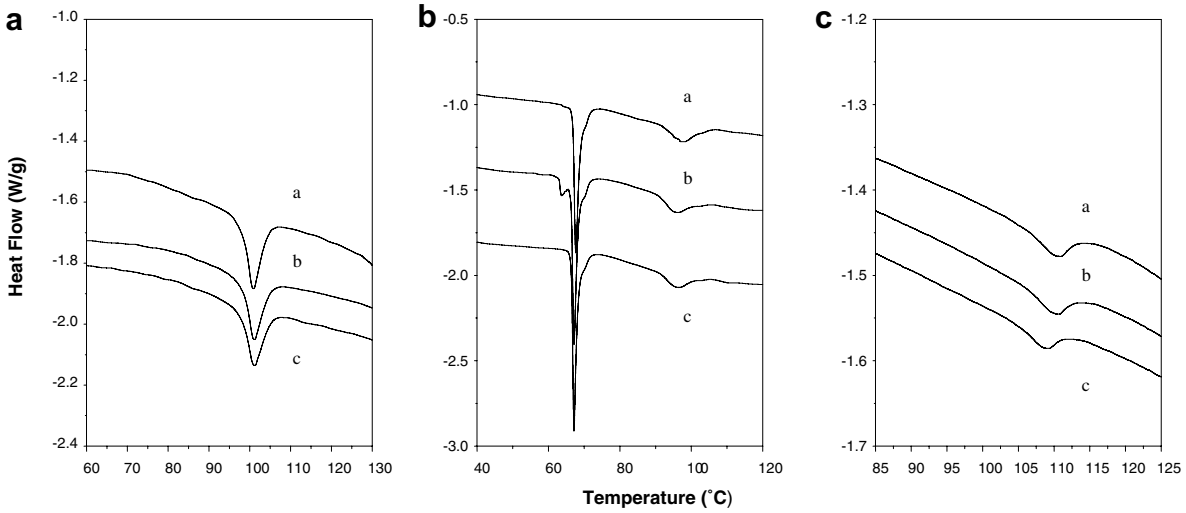

Fig. 4. DSC curves of (a) synthesized amylose–lysophosphatidylcholine, (b) amylose–stearic acid, and (c) reformed amylose–lipid complex in wheat starch in the presence of water (a), β-CD (b), and HPβ-CD (c).

shown in the figure) under the given condition. This could be attributed to either the dissociation of reformed amylose–lipid complex or retrograded amylose polymer formed at cooling.

3.4. Pasting properties

Pasting behavior of all cereal starches in the presence of β-CD and HPβ-CD showed a similar trend, while tuber and root starches as a group also showed similar behavior (Fig. 5). Both β-CD and HPβ-CD caused early swelling, decreased onset of pasting temperature, and decreased peak viscosity in cereal starches while tuber and root starches showed unchanged onset of pasting temperature, and early swelling (Fig. 5). However, β-CD increased the peak viscosity of all tuber and root starches, but HPβ-CD decreased peak viscosity.

Decreased peak viscosity by HPβ-CD compared to β-CD is consistent with granular swelling (Fig. 1) because highly swollen granules are more liable to disintegrate at higher temperature under shear, perhaps severe disruption of amylose–lipid complex may weaken the starch structure causing more disintegration by HPβ-CD. In addition, Fig. 5 shows that HPβ-CD causes early onset of pasting temperature indicating early hydration of starch granules compared to β-CD. The main contributor to the cold paste viscosity and setback is the association of amylose chains leached out from starch granules, thus higher amylose leaching in all cereal starches in the presence of β-CD and HPβ-CD should increase both cold paste viscosity and set back. However, only wheat starch showed substantial increase of cold paste viscosity and setback in the presence of β-CD and HPβ-CD while maize and rice starch showed slight decreases (Table 3). Lipid removal, especially from the amylose by β-CD and HPβ-CD may be the reason for higher setback in wheat starch, since lipid-free amylsoe can associate much easier in contrast to amylose complexed with lipids. Large molecules of β-CD and HPβ-CD could

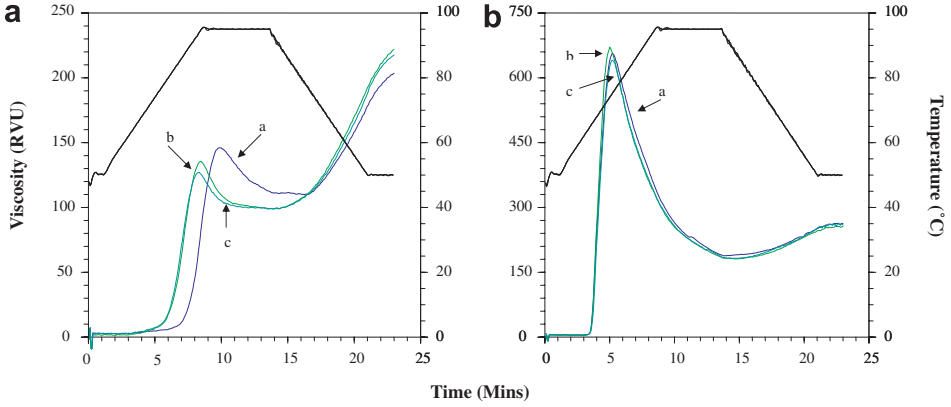

Fig. 5. Pasting curves of representative (a) cereal (wheat), (b) tuber, and root (potato) starches in the presence of β-CD and HPβ-CD. a, with water; b, with β-CD; c, with HPβ-CD.

Table 4
Development of peak viscosity of cereal, tuber and root starches with α-amylase (fungal and bacterial) and β-amylase

Starch	Starch (no enzyme)	α-Amylase (bacterial)	α-Amylase (fungal)	β-Amylase
Wheat	146 ± 0.8[b]	9 ± 0.8	32 ± 0.8	74 ± 0.7
+β-CD[a]	135 ± 0.7	9 ± 0.5	18 ± 0.6	70 ± 0.6
+HP-β-CD[a]	128 ± 0.7	9 ± 0.6	19 ± 0.4	66 ± 0.5
Maize	212 ± 0.7	8 ± 0.4	96 ± 0.3	178 ± 1.3
+β-CD	209 ± 0.8	8 ± 0.4	91 ± 0.7	191 ± 0.6
+HP-β-CD	205 ± 0.6	8 ± 0.9	92 ± 0.6	188 ± 0.8
Rice	110 ± 7	6 ± 0.3	12 ± 0.4	59 ± 0.9
+β-CD	108 ± 6	6 ± 0.3	9 ± 0.5	73 ± 0.6
+HP-β-CD	108 ± 9	6 ± 0.7	9 ± 0.4	65 ± 0.8
Potato	658 ± 0.9	7 ± 0.2	74 ± 0.6	326 ± 1.6
+β-CD	670 ± 1.2	5 ± 0.6	71 ± 0.5	366 ± 0.4
+HP-β-CD	640 ± 0.8	5 ± 0.8	78 ± 0.4	345 ± 1.1
Sweet potato	388 ± 0.6	48 ± 0.7	250 ± 1.2	346 ± 1.6
+β-CD	397 ± 0.9	40 ± 0.4	245 ± 0.8	360 ± 1.8
+HP-β-CD	398 ± 1.2	43 ± 0.6	238 ± 0.6	357 ± 0.9
Yam	52 ± 0.4	3 ± 0.4	12 ± 0.6	16 ± 0.4
+β-CD	55 ± 0.8	3 ± 0.7	10 ± 0.5	22 ± 0.3
+HP-β-CD	48 ± 0.9	3 ± 0.5	9 ± 0.4	18 ± 0.5

[a] 0.01 M.
[b] Values are mean of at least duplicate determination ± standard deviation.

interfere with the association of amylose chains, and their physical characteristics such as chain length may partly explain the decreased cold paste viscosity and setback in maize and rice starch. The cold paste viscosity and setback of potato starch were decreased in the presence of β-CD and HPβ-CD while yam and sweet potato starches showed slight increase or no change.

3.5. Enzymatic hydrolysis

Kim and Hill (1984a) reported that β-CD can inhibit α-amylase hydrolysis, finding a slight increase of peak viscosity of wheat starch containing α-amylase. However, using a Rapid Visco-Analyser Li et al. (2000) showed that β-CD did not inhibit α-amylase hydrolysis of wheat starch, but it did have an inhibitory effect on wheat flour.

In this study, we tested different types of α-amylase (fungal and bacteria), and β-amylase in the presence of β-CD and HPβ-CD. Peak viscosity of all starches was decreased by the amylases. Among these, bacterial α-amylase showed the highest hydrolysis of starch under the given conditions followed by fungal α-amylase and β-amylase (Table 4). Decrease of peak viscosity was additive in the presence of both β-CD and HPβ-CD for all starches with α-amylases. This indicates that neither β-CD nor HPβ-CD could inhibit the α-amylase hydrolysis. However, peak viscosity was increased in starches (except wheat starch) containing β-amylase in the presence of β-CD or HPβ-CD (Table 4). β-Amylase requires an end group to initiate the hydrolysis of α-(1 → 4) linkage. Therefore, β-amylase cannot hydrolyze either type of cyclodextrin compounds. Unhydrolyzed cyclodextrin molecules could hinder the reaction between starch and β-amylase probably by inhibiting the reaction site of β-amylase. This could be the reason why peak viscosity of starches containing β-amylase slightly increased in the presence of both β-CD and HPβ-CD. However, α-amylases that do not need end group to initiate the hydrolysis process can possibly hydrolysis the cyclodextrin molecules. The development of peak viscosities in starches containing amylase enzymes in the presence of β-CD and HPβ-CD was not consistent, thus it is difficult to show which one has generally more effect on enzyme hydrolysis (Table 4).

4. Conclusions

This study clearly demonstrated the disruption of amylose–lipid complex by both β-CD and HPβ-CD by complexing with starch lipids. The mode of action of β-CD and HPβ-CD in interacting with starch granules (disruption of amylose–lipid complex) appeared similar, however, higher magnitude of swelling factor, solubility, early swelling, decreased transition energy of both native and synthesized amylose–lipid complex, and complex forming ability with native starch lipids by HPβ-CD than that of β-CD may indicate HPβ-CD has greater interaction with starch granules in the disruption of amylose–lipid complex and formation of a new cyclodextrin–starch lipid inclusion.

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.

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