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Inclusion complexes of tapioca starch with flavour compounds

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Abstract

Tapioca starch inclusion complexes with primary and secondary alcohols having various chain lengths as well as ketone compounds were studied by DSC. The formation of complexes was confirmed by X-ray diffraction. The thermal properties of tapioca–alcohol complexes from DSC showed that melting temperature increased linearly with chain length of alcohol from 1-heptanol to 1-decanol and also the alcohol complexes had higher melting temperatures than the ketone complexes. Enthalpy values of the complexes showed that alcohols had higher complexing ability than ketones and that the complexing ability increase with increase chain length, with the short chain alcohol (1-hexanol) having the lowest complexing ability. Type I (amorphous) and type II (crystalline) complexes were found in samples depending on the flavour and formation condition. The results from X-ray crystallography showed the typical V-amylose pattern for all flavour complexes, although this was less well-defined for the ketones.

Keywords: Tapioca starch; Inclusion complex; V-amylose; Aliphatic alcohol; Ketone

1. Introduction

Starch contains two main types of polysaccharides, namely amylose and amylopectin. Amylose is a linear polymer consisting of (1→4)-α-D-glucose units with a very small extent of α-(1→6) linked branches while amylopectin possess much more of α-(1→6) branch points (Hoover, 2001). Amylose is able to form inclusion complexes with various types of ligands where the hydrophobic parts of the ligands are entrapped in the hydrophobic helical cavity of amylose. This type of complex, resulting in the so called V-type X-ray pattern, normally has six glucose residues per turn to form left-handed single helix and have been found with iodine and linear ligands such as monoglycerides, fatty acids and alcohols (Helbert & Chanzy, 1994; Kuge & Takeo, 1968; Le Bail, Rondeau, & Buleon, 2005; Zobel, French, & Hinkle, 1967). Different V-pattern structures for the complexes depending on the type of ligands have been suggested. For example, sixfold single helices but with space between helices larger than that of normal V-pattern or in some cases seven glucose unit per turn has been reported with *n*-butanol, isopropanol, thymol, linalool and menthone (Nuessli, Putaux, Bail, & Buleon, 2003; Rondeau-Mouro, Le Bail, & Buleon, 2004; Rutschmann & Solms, 1990; Yamashita & Hirai, 1966). Moreover, eight glucose units per turn were found for bulky molecules such as α-napthol (Le Bail et al., 2005). The amylose complexes exist in two polymorphic forms, type I and II, characterised by the temperature of their dissociation in differential scanning calorimetry (DSC) (Biliaderis, 1992; Biliaderis & Galloway, 1989; Eliasson, 1994). Type I polymorphic form melts at a temperature about 10–30° below those of type II, depending on the types of ligands and the experimental conditions (Eliasson, 1994; Kowblansky, 1985; Whittam et al., 1989). As type II has a crystalline structure while type I is amorphous state, type II is also detected in X-ray crystallography, showing the typical V-pattern as stated before (Biliaderis & Seneviratne, 1990; Tufvesson & Eliasson, 2000).

Inclusion complexes with active ligands particularly flavour compounds with amylose are an emerging technique

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for nanoencapsulation because the single helix structure of amylose is comparatively the same structure of cyclodextrins and a common property of many flavour compounds is a hydrophobic character (Conde-Petit, Escher, & Nuessli, 2006; Zeller, Saleeb, & Ludescher, 1999). In the literature, it is suggested that starch-flavour complexes will provide protection during processing and storage because the complexes melt at high temperature (Heinemann, Conde-Petit, Nuessli, & Escher, 2001; Le Bail et al., 2005; Nuessli, Sigg, Conde-Petit, & Escher, 1997). Moreover, the release of the complexes can be manipulated by various factors such as temperature, water activity and enzyme action (Wulft, Avgenaki, & Guzmann, 2005).

Besides pure amylose, potato starch was used in most of studies on inclusion complex with ligands. The main reason for this is that because potato starch contains little or no internal lipid which interferes with the formation of the complex. Studies using tapioca starch which like potato starch contains a low amount of internal lipid (<0.1%) (Moorthy, 2002) are limited.

The aim of this study was therefore to investigate whether tapioca starch has the ability to form complexes with flavour compounds. The flavour molecules, aliphatic alcohols containing between 6 and 10 carbons, were chosen to study the effect of chain length on complex formation with amylose. Furthermore, the effect of different functional groups has been compared as well. Differential scanning calorimetry (DSC) was used to detect the formation of complexes and wide angle X-ray diffraction was used to determine the structure of the complexes.

2. Materials and methods

2.1. Materials

Native tapioca starch was from Avebe Group (Veendam, Netherlands). Moisture content determined by vacuum drying at 60 °C was 12.00%. The amylose content was determined to be 20.26%. Pure potato amylose was from MP Biomedical, Inc. (Ohio, USA).

L-α-Lysophosphatidylcholin (LPC, 99% pure) from egg yolk was from Sigma. All other reagents were of analytical grade.

All of the flavour compounds including 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 2-nonanol, 3-nonanol, 5-nonanol, 1-decanol, 2-octanone and 2,6-dimethylcyclohexanone (DMCH) were obtained from Sigma–Aldrich Company (Schnelldorf, Germany). The purity of the compounds was more than 98%. Their physicochemical properties and odour descriptor are presented in Table 1.

2.2. Preparation of tapioca-flavour complexes

Complex of tapioca starch and each flavour compound was prepared in pressure cell reactor. Each flavour compound was mixed with tapioca starch and water in a 0.1:1:3 weight ratio in the reactor vessel. The mixture was heated from 20 to 120 °C at 2 °C/min, and then cooled immediately from 120 to 20 °C at 1 °C/min. The complexes were then frozen with liquid nitrogen and subsequently freeze-dried.

2.3. Wide angle X-ray diffraction

The freeze-dried samples were equilibrated over saturated NaCl solution (75% RH) in a closed box at 4 °C for at least 48 h before analysis. The samples were transferred to a round sample holder. The measurements were carried out by a Bruker AXS D5005 wide angle X-ray diffractometer (AXS GmbH, Karlsruhe, Germany) using CuKα radiation (1.54 Å) with 30 mA and 40 kV. The relative intensity was recorded in a scattering angle range (2θ) of 4–30° with an angular interval of 0.05° and sample exposure time of 12 s. Relative crystallinity was calculated as the ratio of the area of the crystalline to the total region of the X-ray diffractograms.

2.4. Differential scanning calorimetry measurements

DSC thermograms were recorded using the Perkin-Elmer DSC-7 instrument. The freeze-dried samples approximately 10–20 mg were accurately weighed into stainless

Table 1
Physicochemical properties and odour descriptors of flavour compounds

	Chemical formula	Mw (g mol^{-1})	Bp (°C)	Water solubility at 25 °C (mg/L)	Odour descriptor
1-Hexanol[a]	$C_6H_{14}O$	102.18	156–158	7135.9	Fruity odour
1-Heptanol[a]	$C_7H_{16}O$	116.20	175	2356.7	Fragrant, woody, green, fatty
1-Octanol[a]	$C_8H_{18}O$	130.23	195	767.0	Fatty, citrus, rose, sweet
1-Nonanol[a]	$C_9H_{20}O$	144.26	212–214	246.7	Oily, floral, petal
1-Decanol[a]	$C_{10}H_{22}O$	158.29	233	78.61	Sweet. orange
2-Nonanol[b]	$C_9H_{20}O$	144.26	198.5	413.4	Fatty, green, melon, orange
3-Nonanol[b]	$C_9H_{20}O$	144.26	194.7	413.45	Herbaceous, spicy, earthy, sweet
5-Nonanol[b]	$C_9H_{20}O$	144.26	195	413.4	—
2-Octanone[c]	$C_8H_{16}O$	128.21	173	1219.5	Apple, floral, green, herbaceous
2,6-DMCH[c]	$C_8H_{16}O$	126.20	174–176	5186.3	—

[a] Primary alcohol.
[b] Secondary alcohol.
[c] Ketone.

steel pans and distilled water was added to give a weight ratio of 3:1. Pans were allowed to equilibrate overnight prior to analysis. The system was calibrated with indium and cyclohexane standards. An empty stainless steel pan was used as a reference. DSC scans were performed from 1 to 140 °C at heating rate of 10 °C/min. The samples were cooled at 10 °C/min and reheated under the same conditions. The Pyris software was used to calculate onset temperature (T_o), peak temperature (T_p) and end temperature (T_e). The enthalpies were calculated as J/g amylose.

DSC determination of amylose content was done according to the procedure described by Mestres, Matencio, Pons, Yajid, and Fliedel (1996). Pure amylose (about 5 mg) and tapioca starch (about 8 mg) were weighed accurately into a stainless steel pan. Then, 40 µl LPC solution (2% w/v in water) was added directly in the pan before hermetic sealing. The reference sample was a pan with 40 µl water. The samples were heated from 35 to 160 °C (heating rate 15 °C/min), cooled to 45 °C (cooling rate 10 °C/min) and reheated to 160 °C at the same heating rate. Energy data were collected during cooling, and the enthalpy of complex formation was determined. Amylose content was deduced from the ratio of the sample enthalpy to that of pure amylose.

2.5. Measurement of complexing index

The complexing index (CI) was used to determine the degree of starch-flavour complex formation. Measurement of the index is based on the method of Gilbert and Spragg (1964). Iodine solution was prepared by dissolving a mixture of 0.1 g of potassium iodide and 0.02 g I_2 in 50 ml distilled water. Starch-flavour complexes (0.1 g) were added to 25 ml distilled water. A control only containing tapioca starch processed in the pressure cell was used. The sample suspension was mixed with a vortex mixer for 2 min and centrifuged at 3500 rpm for 15 min. The supernatant (2.5 ml) was mixed with 200 µl of iodine solution and 300 µl of distilled water. Then, the absorbance was measured at 600 nm. CI was deduced from the absorbance ratio of the flavour-complexes to that of the control.

3. Results and discussion

3.1. DSC investigation of tapioca starch-flavour complexes

In the present experiment, the complexing abilities of tapioca starch with flavour complexes were determined by DSC. The transition temperatures and enthalpies of the complexes are summarised in Table 2. Typical DSC thermograms for complex melting and formation are shown in Figs. 1 and 2, respectively.

Amylose-flavour complexes can be formed by gelatinizing starch in the presence of flavour molecules such as alcohols and ketones as DSC thermograms show peaks corresponding to endothermic (Fig. 1) and exothermic (Fig. 2) processes in the sample during the temperature scans. The results indicated the formation of the complexes is thermoreversible, as also found for amylose–lipid complexes (Biliaderis, Page, Slade, & Sirett, 1985). The endothermic event from the first heating scan was used to indicate the complexes that have been formed during sample preparation while the endotherm from the rescan was used to indicate the reorganization of complexes. Moreover, the exothermic event from the cooling scan was used to investigate complex reformation (Le Bail et al., 2005).

Based on the studies of amylose–lipid complexes (Biliaderis & Seneviratne, 1990; Eliasson, 1994; Karkalas, Ma, Morrison, & Pethrick, 1995) two types of the complex can be formed. Type I complex is the amorphous form that melts at the lower temperature in the DSC whereas type II complex is more crystalline and melts at the higher temperature. For primary alcohols, during the first scan only endothermic processes at high temperature were detected and this may be assumed to be the melting of type II amylose–alcohol complex. Transition peak temperatures of the complexes were in the range of 101–115 °C (Table 2). During cooling the complexes were reformed at lower temperature than the first heating scan. The rescan of complexes showed two endothermic transitions, which might be due to the melting of complex type I and II. The melting temperatures of type II complexes were about 28 °C higher than those for type I. A difference of 25 and 23 °C was observed for the complex of corn and pea amylose, respectively with alcohol (C4–C14), (Kowblansky, 1985; Whittam et al., 1989). The variation among these experiments could be explained by the dissimilar conditions to prepare the complex as well as the source of amylose. It was interesting to note that the formation temperatures of both complexes for all samples were lower than their corresponding melting temperature (Figs. 3 and 4).

A type I complex with an endothermic peak at lower temperature is observed during the rescan due to the rapid cooling of the complexes in the DSC after dissociation in the first heating (Whittam et al., 1989). The crystalline complex will need more time to reform the ordered structure while the low-temperature complex (amorphous state) requires less time.

The melting temperatures of the complexes vary with the alcohol chain length (Table 2 and Fig. 3) both during the first and the second scan. Data in Fig. 3 show that the melting temperatures of the first and rescan were virtually the same. With increasing chain length the melting temperature of both types I and II complexes increase. For type I complexes the temperature increased with chain length by about 2–3 °C per carbon atom from 1-heptanol to 1-decanol whereas the increase in type II was about 2 °C per carbon atom. It should be noted that the melting temperature of 1-hexanol is much lower than the other complexes and cannot follow in the same trend of the complexes containing between 7 and 10 carbons. Whittam et al. (1989) also reported that the melting temperature of both type of complexes increased with chain length from 1-butanol to 1-octanol. Moreover, Kowblansky (1985) found that the

increase in melting temperature with chain length was steep between 4 and 8 carbons and gradual from 8 to 14 carbon chain length of alcohol. In the case of different ligands such as fatty acid, it was found that the melting temperature of potato amylose complex increased with chain length of saturated fatty acid from C10 to C18, melting temperature for both type of complexes increased by a similar amount with chain length (3 and <2 °C, respectively for one carbon increase) (Tufvesson, Wahlgren, & Eliasson, 2003). It was interesting that the effect of chain length of linear alcohols and fatty acids were the same. This phenomenon could be explained as the acyl chain length included in the amylose helix for the alcohol and fatty acid are the same, when hydrocarbon chain increases, the van der Waals and hydrogen bonds interaction of the molecular complex increases, result in greater stability and thus a higher melting temperature (Karkalas et al., 1995).

The different functional groups and their position influenced what type of complexes could be formed. Ketone compounds (2-octanone and DMCH) showed two endotherm peaks on the first heating scan. The first peak appeared at temperatures lower than the second peak corresponding to complex type I and II transition, respectively (Table 2). During the rescan the same pattern of transition appeared again. For the same carbon chain length but different position of the functional group (1-nonanol, 2-nonanol, 3-nonanol and 5-nonanol), a single endotherm corresponding to transition of type II complex were detected at first heating scan and complex I was formed only during the rescan for 1- and 3-nonanol, whereas two endotherms corresponding to transition of complex I and II were found at both scans for 2-nonanol. In contrast, 5-nonanol complex showed only a single endotherm corresponding to transition of complex II for both the first heating and rescan. It should be noted that the stability of 2-octanone complexes was very low compare to the other complexes (Table 2 and Fig. 4). Both transition temperatures of complex type I and II were about 60 and 90 °C, respectively.

The melting temperatures of the secondary alcohols (nonanol isomers) were in the range of 104–114 °C for type II complexes (Table 2). When the hydroxyl group is located far from the first carbon atom, the melting temperatures decreased except for 5-nonanol. Complex of 5-nonanol had more stability than 2 or 3-nonanol but still less than 1-nonanol. This could indicate that the position of the hydroxyl

Table 2
Transition temperatures and the corresponding enthalpies of different tapioca starch-flavour complexes determined by DSC

Sample	DSC-scan	T_p (I) (°C)	ΔH (I) (J/g)	T_p (II) (°C)	ΔH (II) (J/g)	$\sum\Delta H$ (J/g)
1-Hexanol	First scan			101.85 ± 1.02[a]	8.14 ± 2.50	8.14 ± 2.50
	Cooling	58.13 ± 1.41	15.92 ± 0.01			15.92 ± 0.01
	Rescan	75.17 ± 1.65	4.38 ± 0.30	103.92 ± 0.12	5.76 ± 0.34	10.15 ± 1.61
1-Heptanol	First scan			110.04 ± 0.83	17.26 ± 0.29	17.26 ± 0.29
	Cooling	62.78 ± 0.68	16.87 ± 2.18			16.87 ± 2.18
	Rescan	80.62 ± 0.30	7.06 ± 0.10	109.81 ± 0.04	13.00 ± 0.02	20.06 ± 0.85
1-Octanol	First scan			112.30 ± 0.71	23.21 ± 1.70	23.21 ± 1.70
	Cooling	65.99 ± 0.57	18.73 ± 0.02			18.73 ± 0.02
	Rescan	84.56 ± 0.39	9.00 ± 0.66	112.65 ± 0.03	13.95 ± 0.01	22.95 ± 1.30
1-Nonanol	First scan			114.36 ± 0.10	24.27 ± 3.75	24.27 ± 3.75
	Cooling	68.02 ± 0.31	18.75 ± 0.08			18.75 ± 0.08
	Rescan	86.64 ± 0.55	9.87 ± 0.08	114.98 ± 0.28	12.83 ± 0.32	22.70 ± 0.39
1-Decanol	First scan			115.59 ± 0.71	19.15 ± 1.37	19.15 ± 1.37
	Cooling	68.43 ± 0.19	18.96 ± 0.01			18.96 ± 0.01
	Rescan	88.81 ± 0.08	16.12 ± 0.18	116.01 ± 0.06	3.97 ± 1.14	20.09 ± 0.09
2-Nonanol	First scan	72.97 ± 0.01	4.37 ± 0.50	105.79 ± 0.37	13.66 ± 0.46	18.03 ± 2.37
	Cooling	56.98 ± 0.26	14.11 ± 1.48			14.11 ± 1.48
	Rescan	73.90 ± 0.12	7.38 ± 0.03	102.53 ± 0.96	16.13 ± 0.23	23.51 ± 0.03
3-Nonanol	First scan			104.67 ± 0.54	21.42 ± 0.35	21.42 ± 0.35
	Cooling	57.05 ± 0.21	16.73 ± 0.24			16.73 ± 0.24
	Rescan	75.70 ± 0.01	2.49 ± 0.02	103.62 ± 0.12	18.56 ± 0.12	21.05 ± 0.24
5-Nonanol	First scan			112.17 ± 0.82	22.73 ± 3.48	22.73 ± 3.48
	Cooling	60.44 ± 0.69	24.99 ± 0.95			24.99 ± 0.95
	Rescan			109.41 ± 0.70	23.52 ± 0.84	23.52 ± 0.84
2-Octanone	First scan	59.17 ± 0.47	7.54 ± 0.12	89.84 ± 0.23	0.66 ± 0.07	8.20 ± 0.21
	Cooling	36.26 ± 0.00	10.42 ± 0.14			10.42 ± 0.14
	Rescan	58.45 ± 0.35	2.85 ± 0.06	89.62 ± 0.35	2.19 ± 0.30	5.04 ± 0.62
2,6-DMCH	First scan	85.50 ± 0.24	4.27 ± 0.22	101.59 ± 0.12	3.24 ± 0.18	7.51 ± 0.09
	Cooling	37.47 ± 0.71	9.39 ± 0.14			9.39 ± 0.14
	Rescan	84.78 ± 0.35	3.81 ± 0.26	101.29 ± 0.12	2.97 ± 0.08	6.77 ± 0.42

[a] Mean and standard deviations of three replications.

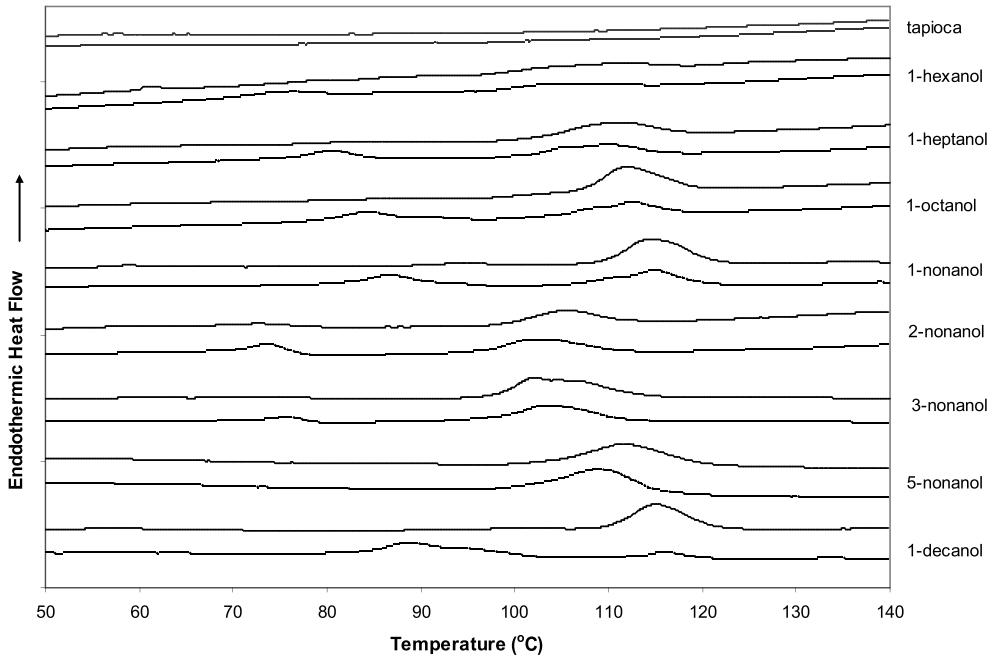

Fig. 1. DSC thermogram of heading scan (upper line is 1st run and lower line is 2nd run) for tapioca-flavour complexes.

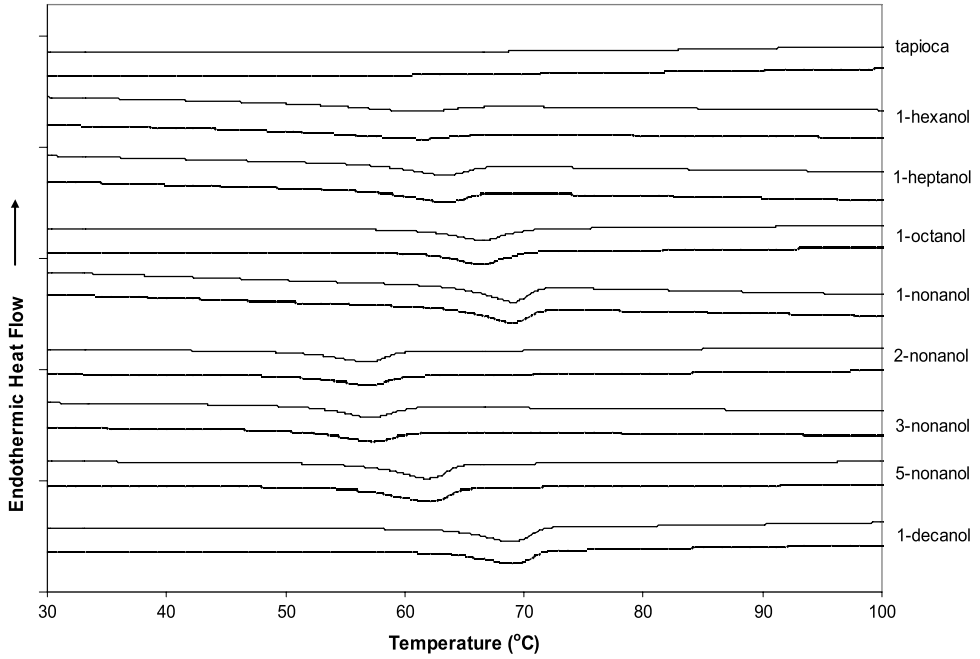

Fig. 2. DSC thermogram of cooling scan (upper line is 1st run and lower line is 2nd run) for tapioca starch-flavour complexes.

group had an effect on the formation and stability of the amylose complex.

The transition enthalpy of the complexes varied with the types of flavours. For complex type I, it was observed that enthalpy values increased with chain length from 1-hexanol to 1-decanol (Fig. 5). For complex type II, enthalpy increase from the complex of 1-hexanol to 1-heptanol, and then the values were comparable among 1-heptanol and 1-nonanol. The transition enthalpy of 1-decanol was the lowest. Complex form II were obtained more than complex I for 1-hexanol to 1-nonanol, whereas the result was opposite for 1-decanol. Under the conditions where a mixture of both form of complexes occurred (during rescan), the total enthalpy of the two complexes was close to the transition enthalpy of the complexes when only one form was present (first scan) as shown in the inserted graph in Fig. 5.

The transition enthalpy varied for the different functional group of compounds. The amount of complex type I

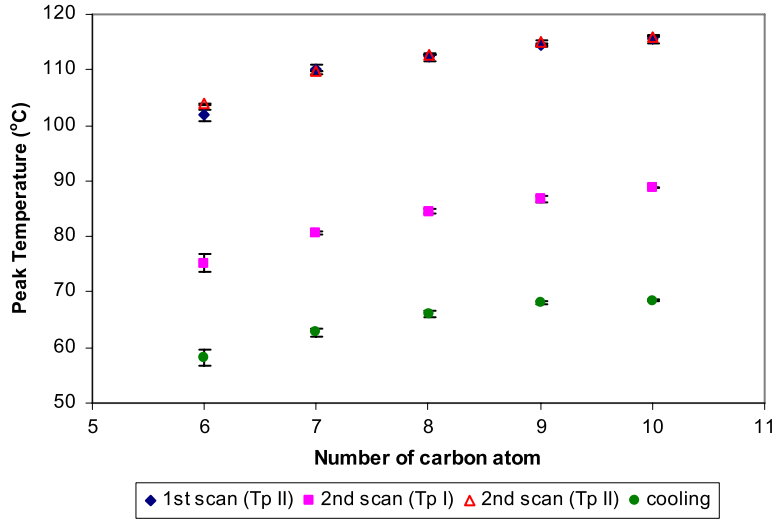

Fig. 3. The effect of chain length on transition peak temperature of tapioca–alcohol complexes.

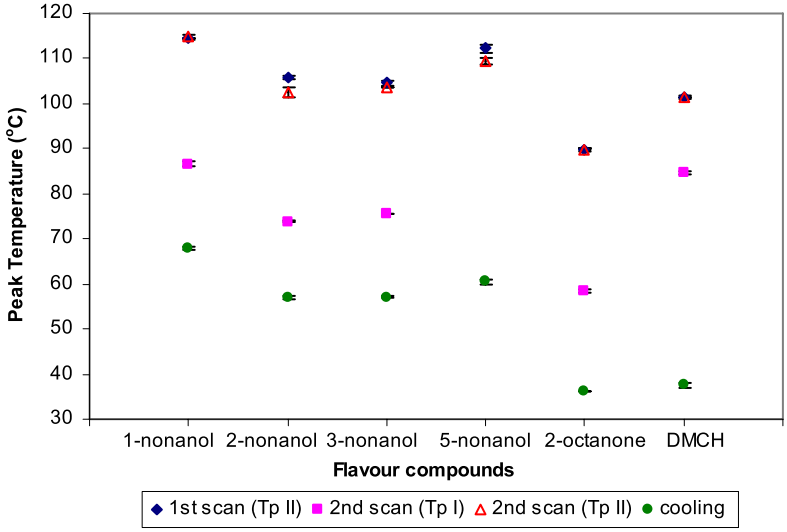

Fig. 4. The effect of functional group and their position on transition peak temperature of complexes.

and II were lowest for ketone compounds (2-octanone and DMCH) (Fig. 6). Among the alcohol group, 5-nonanol yielded the highest transition enthalpy corresponding to complex type II.

For most of the complexes the enthalpy of dissociation for type II complexes was higher than that for type I complexs (Figs. 5 and 6). This is because in the crystalline state (type II) there are more intermolecular interactions which are the hydrogen bonding between adjacent helices. To melt the crystal more energy is needed to overcome these interactions.

The transition enthalpy can be used to indicate the amount of complex formed. The enthalpy of the first scan in Table 2 presented that amount of complex obtained from the original preparation. It was found that most of the nonanol and 1-octanol complexes yielded a highest value of enthalpy (>20 J/g amylose) followed by 1-decanol, 2-nonanol and 1-heptanol (17–19 J/g amylose) and 1-hexanol, 2-octanone and 2,6-DMCH had the lowest amount of complexes (7–8 J/g amylose). Thus it can be assumed that the length of 1-hexanol and the ketone functional group was not suitable for formation of complexes with amylose. However, it is of concern that values of enthalpy may be not precise because some samples may contain a proportion of free amylose and their enthalpies will be artificially low or in some case the polymorphs were in an intermediate polymorphic state (Karkalas et al., 1995). Thus, the iodine binding method was used to determine the quantity of complexes as well. The percent complexing index of the samples was presented in Table 3. 1-Hexanol showed the lowest complexing ability, followed by increase with the increasing chain length of alcohol. Although, 5-nonanol and 2-nonanol showed the highest complexing ability there was no difference compared with 1-decanol. Comparing to alcohol and ketone compounds, it was found that both 2-octanone and 2,6-DMCH yielded the lower complexing ability than all the alcohol complexes. These results are in agreement with the enthalpy values discussed above.

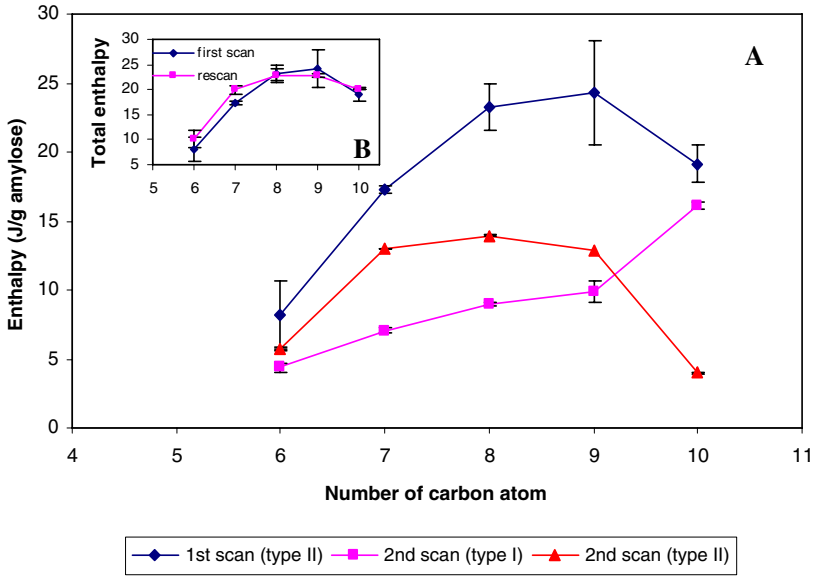

Fig. 5. The effect of chain length on transition enthalpy of tapioca–alcohol complexes (A); total enthalpy of tapioca starch with alcohols of different chain length (B).

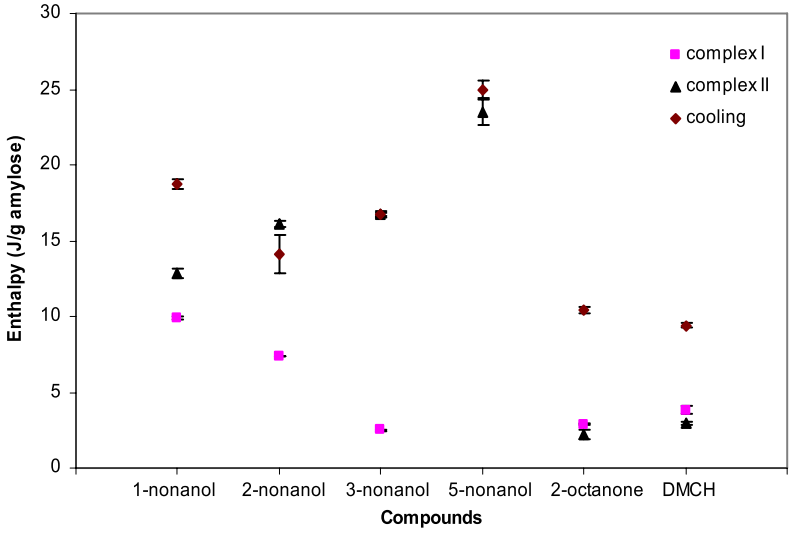

Fig. 6. The effect of functional group and their position on enthalpy of complexes.

Table 3
Percent crystallinity and complexing index of tapioca starch-flavour complexes

Sample	% Crystallinity	Complexing index (CI)
1-Hexanol	4.57 ± 0.03[a]	40.31 ± 0.18
1-Heptanol	6.29 ± 0.02	78.92 ± 1.26
1-Octanol	7.45 ± 0.43	87.76 ± 0.10
1-Nonanol	7.85 ± 0.04	91.20 ± 0.42
1-Decanol	5.30 ± 0.85	89.98 ± 0.82
2-Nonanol	6.07 ± 1.51	80.34 ± 0.26
3-Nonanol	7.55 ± 0.07	82.33 ± 0.82
5-Nonanol	6.97 ± 1.36	91.48 ± 0.45
2-Octanone	0.17 ± 0.01	23.56 ± 1.19
2,6-DMCH	2.34 ± 0.06	34.23 ± 0.08

[a] Mean and standard deviations of three replications.

The degree of crystallinity determined from WAXD was used to indicate the formation of the type II complex. The crystallinity of starch–alcohol complexes were higher than that of starch–ketone complexes, 2-octanone showed the lowest crystallinity. Among the alcohol complexes, the crystallinity increased with increasing chain length from 6 to 9 carbon atoms and 1-decanole showed the lowest crystallinity.

The relationships between crystallinity or complexing index and enthalpy values were demonstrated in Fig. 7. The enthalpy values of the complexes (data from the first scan) showed a positive correlation with the degree of crystallinity and the complexing index.

3.2. Crystalline structure of tapioca-flavour complexes

The crystalline structure of tapioca-flavour complexes was characterized by X-ray diffraction. Freeze-dried tapioca starch dispersion without addition of flavour compounds served as reference. The diffraction diagrams of the

reference and of the starch-flavour complexes are presented in Figs. 8 and 9. The percent crystallinity of complexes is presented in Table 3.

The X-ray diffraction pattern of freeze-dried tapioca starch dispersion without addition of flavour compounds can be described as an amorphous halo (Fig. 8). This indicated that no retrogradation of starch occurred during sample preparation. The X-ray diffraction patterns in the presence of aliphatic alcohols showed reflections at 7.6°, 13.1° and 20.1°. This scattering angles corresponding to those described for the V_h amylose, which is obtained with linear alcohols (Brisson, Chanzy, & Winter, 1991; Buleon, Delage, Brisson, & Chanzy, 1990; Whittam et al., 1989). Therefore, it can be assumed that the linear alcohol from 6 to 10 carbon atoms were included in the sixfold left-handed helix of amylose. Although the result from Jouquand, Ducruet, and Le Bail (2006) showed that 1-hexanol can form complexes with potato amylose and corn starch, a different V-amylose pattern was obtained. The complexes displayed V_{6II} type which was comparable to those obtained for butanol–amylose complex, suggested that hexanol molecules could also be entrapped between helices.

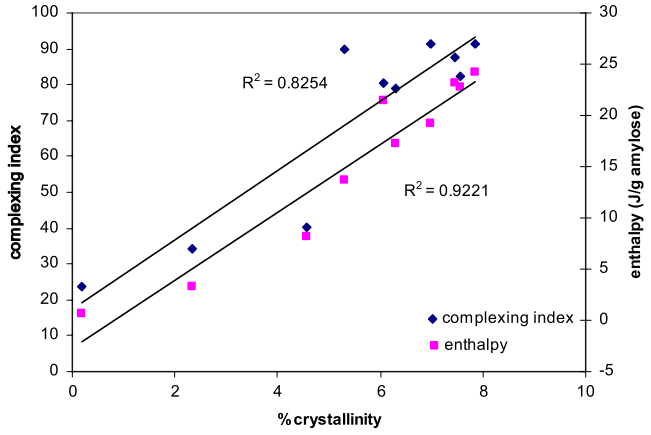

Fig. 7. Relation between relative complexing index of starch-flavour complex versus the enthalpy value as well as the relative crystalling obtained from WAXD.

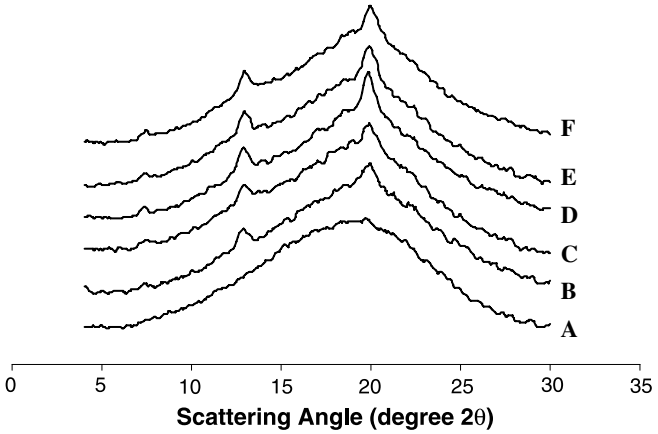

Fig. 8. X-ray diffractometer scans of complexes: (A) tapioca starch; (B) 1-hexanol; (C) 1-heptanol; (D) 1-octanol; (E) 1-nonanol; (F) 1-decanol.

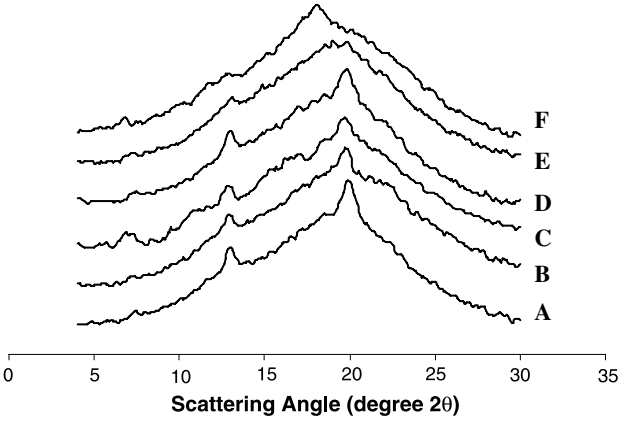

Fig. 9. X-ray diffractometer scans of complexes: (A) 1-nonanol; (B) 2-nonanol; (C); 3-nonanol; (D) 5-nonanol; (E) 2-octanone; (F) DMCH.

Although the functional group influenced the diffraction pattern of complexes the position of functional group did not. As we can see from Fig. 9, 2-nonanol, 3-nonanol and 5-nonanol showed the reflections at $2\theta = 7.6°$, 13.0° and 20.1° which was the same as 1-nonanol and it also correspond to V_h amylose pattern. In contrast, tapioca starch with addition of ketone compounds namely 2-octanone showed a small reflection at $2\theta = 7.6°$, 13.0° and broad reflections around 20.0° while DMCH showed the reflections at $2\theta = 7.0°$, 12.9° and 18.2°. These X-ray patterns suggest that 2-octanone compounds had less ability to induce amylose to form typical V_h complex which compose of six glucose units per turn. Although Jouquand et al. (2006) suggested that ketone (2-hexanone) was able to prevent the formation of complexes with potato amylose and corn starch the result obtained from this experiment showed that ketone compounds can form complexes with tapioca starch as we can seen from the transition behavior from DSC and also the their structure pattern from X-ray diffraction. This may due to the different of starch and conditions for preparing the complexes. The X-ray pattern of DMCH might suggested a complex that contains seven glucose residues per turn of helix because their reflection were similar to the results of Shogren, Fanta, and Felker (2006), Yamashita and Hirai (1966) who reported that three rather broad peaks at $2\theta = 7.0°$, 11.9° and 18.1° were consistent with a complex in which the unit cell contained V_7 helical chains.

3.3. Comparisons of tapioca starch inclusion complexes with other starch system

It is of interest to compare the properties of tapioca starch inclusion complexes with those of other starches. This current work revealed:

(a) The presence of two types of complex with different melting points, the higher melting points (100–115 °C) which corresponds to the crystalline complex and the lower melting points (74–88 °C) which corresponds to amorphous complex.

(b) An increase in stability with the chain length of alcohol.
(c) The transition enthalpy of complexes varies among different flavour compounds. Ketone compounds had a lower enthalpy than the alcohol compounds.
(d) The crystalline pattern of complexes could be composed of six or seven glucose units per turn depend on the size of flavour compounds. With linear molecules, they showed the V_h amylose pattern with sixfold single helix of glucose per turn while the cyclic molecule such as 2,6-DMCH showed the crystalline pattern that contain seven glucose units per turn.

Previous studies on other starches such as corn, pea and potato starch have shown some of those features. For example, Kowblansky (1985) reported that amylose from corn starch can form two different complexes with 1-decanol, the complex with a melting temperature of 82 and 106 °C, respectively. Besides 1-decanol, other linear aliphatic alcohols as well as carboxylic acid exhibited the same behaviour. Also Whittam et al. (1989) found that complexes of amylose from pea starch with linear alcohols having chain lengths varying from 4 to 8 carbon atoms yielded either crystalline or amorphous forms depending on preparation conditions. Additionally, the complex stability of corn and pea starch increased with the chain length of compounds. Regarding potato starch, Jouquand et al. (2006) reported that two forms of complexes were found at the melting temperature of 93 and 123 °C with potato starch–hexanol complex.

The enthalpy of complex dissociation did not vary significantly with alcohol chain length in the case of pea starch. For amorphous complexes, the enthalpy has a value of 0.90 ± 0.07 J/g starch regardless of alcohol chain length, whilst for crystalline complexes the enthalpy was 1.58 ± 0.05 J/g starch (Whittam et al., 1989). These values are lower than those for the tapioca starch complexes in this work which are in the range of 1.60 ± 0.88–2.74 ± 1.29 J/g starch, respectively for amorphous and crystalline complexes. These values for our work were obtained from the mean rescan enthalpies of alcohol complexes shown in Table 2 assuming an amylose content of 20.26% for the tapioca starch used. The difference from pea starch could be partly because of different starch amylose contents and difference ways in which the complexes have been prepared. However, there are similarities between the two pieces of work in that the enthalpy of the crystalline complexes are higher than the amorphous complexes formed from linear alcohols of chain length from 6 to 8 carbon atoms.

The X-ray diffraction pattern of flavours with other starches showed various patterns depending on type of flavour molecules. The complexes of pea amylose, potato starch and corn starch with linear alcohols (1-butanol, 1-hexanol, 1-octanol and 1-decanol), and linear aldehydes (*t*-2-hexenal and decanal), gave the diffraction patterns which indicate a helix having six D-glucose units per turn. Furthermore, complexes of potato with cyclic compounds as well as nonlinear molecules (1-menthol, 1-menthone, β-pinene, carvone, fenchone, geraniol, campher and thymol) presumably indicate a helix with seven D-glucose units per turn (Nuessli et al., 1997; Osman-Ismail & Solms, 1972; Whittam et al., 1989).

As can be seen from the results of this work and previous work, it can be concluded overall that the ability of tapioca starch to form complexes with certain compounds is broadly similar to the other starches however; the thermostability and crystallinity of the complexes show some differences between starches. Since amylose is the common element it is assumed that the properties of flavour compounds as well as method used to prepare the complexes are responsible for these differences.

4. Conclusion

Tapioca starch is able to form inclusion complexes with flavour compounds, in particular with aliphatic alcohols. Physicochemical properties of guest molecules such the nature and position of the functional group and the length of the linear chain influenced the extent of starch complexation, as well as the thermal behaviour and the structure of complexes. In the present investigation the combination of DSC and wide angle X-ray diffractometer was used to investigate the formation of complexes. However, certain aspects such as the effect of the molecular structure of ligand on complexing ability are still not clear. This work suggests it is possible to develop a new carrier, tapioca starch, for flavour encapsulation.

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