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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.