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Short communication

Potential interaction between β-cyclodextrin and amylose–lipid complex in retrograded rice starch

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ABSTRACT

The aims of this study were to investigate the interaction between β-cyclodextrin (β-CD) and amylose–lipid complex in retrograded starch and to propose a model related to the interaction for exploring the retardation of β-CD on starch retrogradation. Results obtained from differential scanning calorimetry (DSC) and X-ray diffraction (XRD) showed that β-CD competed with amylose to disrupt the formation of amylose–lipid complex and that a potential amylose–β-CD–lipid inclusion complex was formed in the retrograded starch. The formation of the complex obviously caused the association of starch chains due to the short and fat aggregates observed using atomic force microscopy (AFM). These findings indicated that the formed amylose–β-CD–lipid complex was responsible for the retardation of starch retrogradation.

1. Introduction

Amylose–lipid complex has been well documented in many researches (Nebesny, Kwaśniewska-Karolak, & Rosicka-Kaczmarek, 2005; Tufvesson, Wahlgren, & Eliasson, 2003). The formation of this complex is upon both biosynthesis of native starch and heating of starch slurry at gelatinization temperature and above. In the complex, the carbon chain end of the lipids is located into the helix of amylose molecules and this combination mode eventually leads to the inclusion complex formation (Keetels, Van Vliet, Jurgens, & Walstra, 1996; Nebesny et al., 2005; Tufvesson et al., 2003).

β-Cyclodextrin (β-CD) is a cyclic oligosaccharide comprised of seven glucose units arranged in a donut-shaped ring (Lindner & Saenger, 1982). Its hydrophobic core can combine with a variety of organic and inorganic molecules and its hydrophilic wall can interact with the compounds which contain polar groups to form non-inclusion complexes (Lindner & Saenger, 1982; Loftsson & Duchêne, 2007). These special properties of β-CD make it widely used in food, cosmetic and pharmaceutical industries (Del Valle, 2004). In food industry, for example, β-CD has recently been used to reduce undesired taste, extend the shelf life of food products (Szente & Szejtli, 2004) and improve the gelatinization properties of rice starch (Kim & Hill, 1984; Gunaratne & Corke, 2007). β-CD also retards the short-term and the long-term retrogradation of rice starch (Tian et al., 2009a, 2009b). Even the disruption of amylose–lipid complex by β-CD has been explored in a simulated amylose/lipids gel (Gunaratne & Corke, 2007). However, in a retrograded starch, there are no systematic reports about the disruption and the effect of this disruption on the retrogradation of starch.

This work presented here had two aims: first, to further investigate the interaction between β-CD and amylose–lipid complex in a retrograded starch; second, to propose a model corresponding to the interaction for investigating the retardation of β-CD on starch retrogradation.

2. Experimental

2.1. Materials

Rice starch was extracted and purified from fresh grain (Shandong Mei-Jing Rice Inc., China) using the procedures described by Sodhi and Singh (2003). It contained 0.3% proteins, 1.2% free lipids and 23.8% amylose content. β-CD was purchased from Seebio Biochemical, Inc. (Shanghai, China). All other chemicals and solvents were of analytical grade unless otherwise noted.

2.2. Preparation of retrograded starch/β-CD samples

Three gram of rice starch was added to β-CD solutions, which were prepared by dissolving 30 and 90 mg of β-CD in distilled water (6 mL). The resultant slurries were heated and gelatinized

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at 85 °C for 30 min to melt the native crystallite corresponding to amylopectin but not to dissociate the amylose–lipid complex involved in starch. Each of these gelatinized gels with 40% of solid content was cooled and stored at 4 °C for 2 h in a sealed container to perform a retrogradation process. The obtained retrograded samples were dried at 35 °C in a vacuum oven, milled to powder and passed through a 100-mesh sieve. Rice starch without β-CD was subjected to the same treatment to prepare retrograded starch as a reference.

2.3. Differential scanning calorimetry (DSC)

Thermal analysis was performed using a Pris 1 DSC (Pekin-Elmer Inc., USA) under ultrahigh-purity nitrogen atmosphere. Three milligram of the each prepared sample and 6 μL of distilled water were sealed into aluminum pans and equilibrated at 25 °C for 30 min. These sealed samples were scanned from 30 to 110 °C at a constant rate of 8 °C/min to collect the enthalpy change in phase transitions.

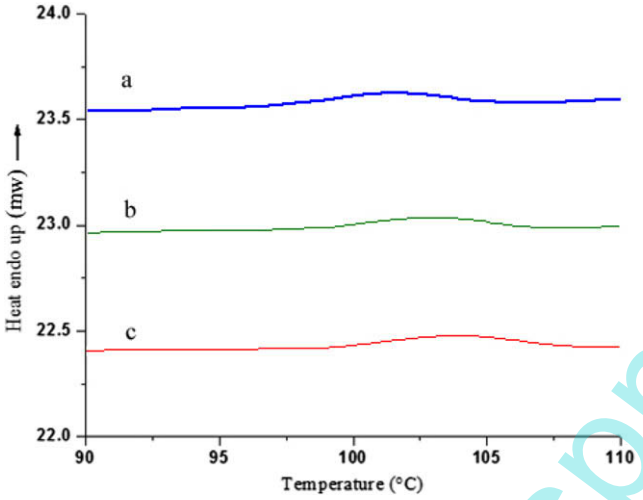

Fig. 1. DSC curves of the prepared samples: (a) retrograded starch, (b) retrograded starch with 1% β-CD, (c) retrograded starch with 3% β-CD.

2.4. X-ray diffraction (XRD)

One gram of each prepared sample was equilibrated for 2 h at 75% of relative humidity in a sealed vessel before the XRD test. The diffractograms of these samples were scanned from 5° to 35° at a scanning rate of 6°/min using a Bruker D8-Advance XRD instrument (Bruker AXS Inc., Germany) under the conditions of 40 kV and 30 mA. Relative crystallinity (RC) and the X-ray pattern of the samples were calculated and analyzed by a Jade 5.0 software (Materials Data Inc., California).

2.5. Atomic force microscopy (AFM)

Each of the prepared samples was diluted to the final concentration of 0.002% (w/w) using warm distilled water (35 °C). The resultant solution (3 μL) was directly deposited onto the mica and allowed to evaporate under ambient conditions (25 °C and 75% of relative humidity) for drying prior to observation. The measurement was performed in tapping mode at room temperature using a CSPM4000 SPM (Being Nano-Instruments Ltd., China). Image data including shape and size of the deposited macromolecules were analyzed by the Imager 4.50 software of the microscope.

3. Results and discussion

3.1. Thermal properties analysis

For the retrograded rice starch, single endothermic peak (around 102 °C) derived from the dissociation of amylose–lipid complex was observed (Fig. 1a). This result was consistent with the study described by Richardson, Kidman, Langton, and Hermansson (2004). One percent of β-CD also caused one peak occurrence but obviously decreased the enthalpy change (ΔH) of this peak from 2.7 to 2.1 J/g (Fig. 1b). This decrease indicated that the amylose–lipid complex was partly disrupted by β-CD.

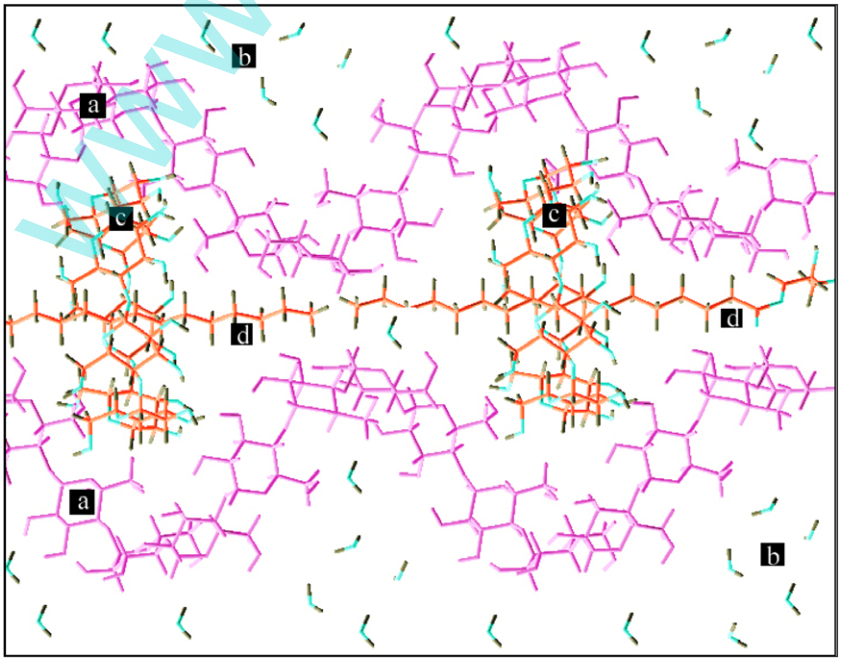

Fig. 2. One of the possible models proposed for amylose–β-CD–lipid complex. (a) Amylose helixes, (b) water molecules, (c) β-CD molecules, (d) monoglyceride molecules.

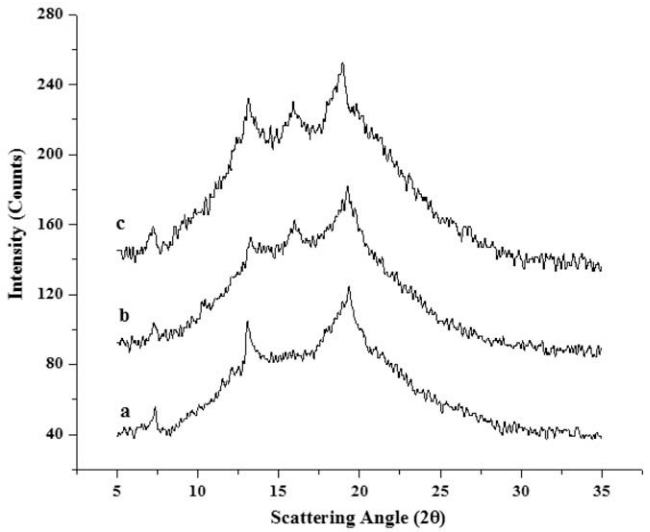

Fig. 3. Effect of β-CD on XRD pattern of the prepared samples: (a) retrograded starch, (b) retrograded starch with 1% β-CD, (c) retrograded starch with 3% β-CD.

The disruption was interpreted by the fact that β-CD might compete with amylose to form β-CD–lipid inclusion complex in a simulated amylose–lipids system (Gunaratne & Corke, 2007). 3% of β-CD, however, increased the melting temperatures including the onset temperature (T_o), peak temperature (T_p) and conclusion temperature (T_c) of the detected peak. Furthermore, it increased the ΔH from 2.7 to 2.9 J/g (Fig. 1c). These results revealed that β-CD drove a new inclusion complex formation. This potential complex was probably resulted from amylose–β-CD–lipid complex since β-CD interacted not only with lipids but also with amylose to form amylose–β-CD complex in a pure amylose/β-CD system (Gunaratne & Corke, 2007; Tian et al., 2009a). One of the possible models for the amylose–β-CD–lipid complex was further proposed in Fig. 2.

3.2. X-ray diffraction (XRD) pattern analysis

Retrograded starch presented peaks at 7.3°, 13.0° and 19.8° (Fig. 3a). It indicated that a structure characterized by V-type crystallite was detected (Zobel, 1988). This crystallite pattern was related to the formation of amylose–lipid complex according to previous study reported by Hibi, Kitamura, and Kuge (1990). One percent of β-CD weakened peaks at 7.3° and 13.0°, and decreased the relative crystallinity (RC) from 16.5% to 14.3% (Fig. 3b). This decrease further confirmed that β-CD disrupted the formation of amylose–lipid complex contained in the retrograded starch. Nevertheless, 3% of β-CD increased the RC from 16.5% to 17.2% and drove a new peak development at 16.2° (Fig. 3c). These findings indicated that another crystallite, amylose–β-CD–lipid complex, was indeed formed in the retrograded starch when β-CD was added.

3.3. Atomic force microscopy (AFM) images analysis

The macromolecules of the retrograded starch appeared as fairly branched aggregates with typical height of 3–8 nm and length of 200–400 nm (Fig. 4a). The aggregates, however, became short and fat with typical coil conformation in the presence of β-CD (Fig. 4b). This coil conformation probably caused by the po-

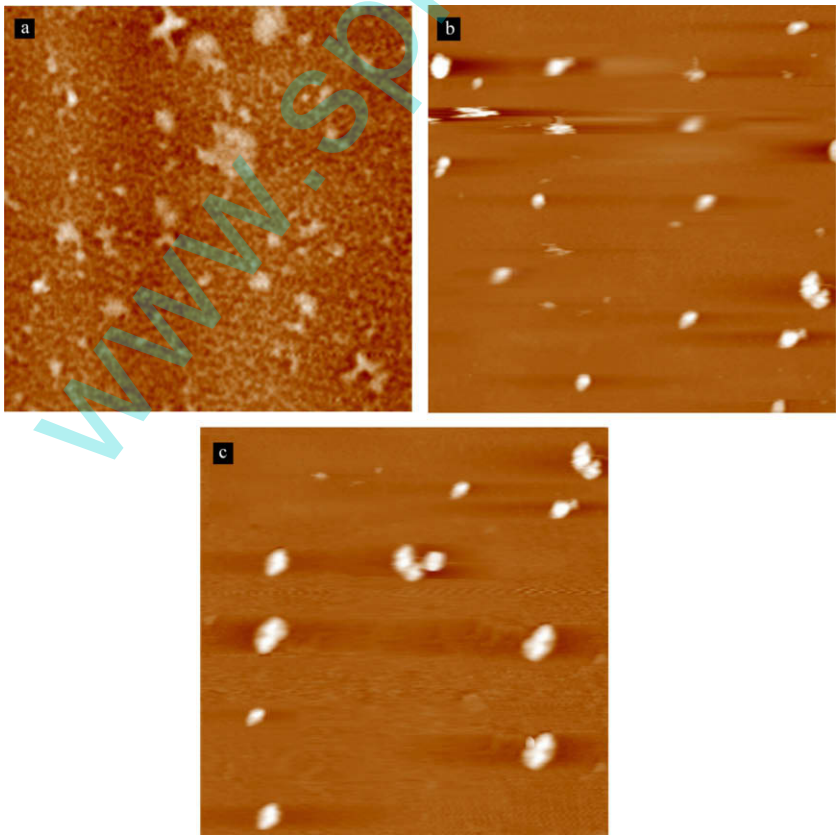

Fig. 4. AFM images (5 μm × 5 μm) of (a) retrograded starch, (b) retrograded starch with 1% β-CD, (c) retrograded starch with 3% β-CD. The scale of black-to-white color is 0–10 nm.

tential amylose–β-CD–lipid complex was found more significant when the addition volume of β-CD increased to 3% (Fig. 4c). It indicated that the potential complex caused the formation of the disordered starch molecules. Further, Gunning et al. (2003) reported that short and fat molecules were difficult to crystallize in a starch gel. It thus suggested that the amylose–β-CD–lipid complex retarded a transition of starch molecules from a disordered conformation to an ordered one. In other words, the complex found in the retrograded gel was responsible for the retardation of β-CD on starch retrogradation.

4. Conclusions

This study made clear that the interaction between β-CD and amylose–lipid complex occurred in the retrograded starch. This interaction was twofold: first, β-CD disrupted the formation of amylose–lipid complex and competed with amylose to form β-CD–lipid inclusion complex; second, β-CD directly interacted with amylose to form amylose–β-CD complex. This work also demonstrated that a potential amylose–β-CD–lipid complex was formed and the new complex caused the starch molecules conformation disordered. These findings suggest that the retardation of β-CD on starch retrogradation is attributed to the formation of the potential amylose–β-CD–lipid inclusion complex.

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