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Short communication

Identification and releasing characteristics of high-amylose corn starch–cinnamaldehyde inclusion complex prepared using ultrasound treatment

Yaoqi Tian, Yanqiao Zhu, Mohanad Bashari, Xiuting Hu, Xueming Xu, Zhengyu Jin*

The State Key Laboratory of Food Science and Technology, School of Food Science and Technology, Jiangnan University, Wuxi 214122, China

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ABSTRACT

In this study, the high-amylose corn starch–cinnamaldehyde inclusion complex was prepared by an ultrasound treatment and its releasing characteristic was investigated. The results showed that the ultrasound treatment (35 °C, 10 min and 250 W) generated a higher encapsulation rate of 40.2% than the conventional treatment (encapsulation rate, 5.7%). Data obtained from Fourier-transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA) indicated that cinnamaldehyde was successfully encapsulated by high-amylose corn starch and the encapsulation significantly increased the dissociation temperature of cinnamaldehyde by around 70 °C. Compared to the physical mixture of high-amylose corn starch and cinnamaldehyde, the formed inclusion complex had good retention ability and reduced the releasing rate of cinnamaldehyde from 57.5% to 28.4% in the first week. These results suggest that cinnamaldehyde could be encapsulated by high-amylose corn starch with an ultrasound treatment for presenting the releasing behavior in food preservation.

1. Introduction

Cinnamaldehyde, a food antimicrobial agent, can effectively inhibit the growth of *Aspergillus flavus*, *Aspergillus niger* and *Penicillium citrinum* and it is available in foods for prolonging the shelf-life (Gutiérrez, Escudero, Batlle, & Nerin, 2009; Xing, Li, Xu, Yun, & Lu, 2010). Nevertheless, the direct use of cinnamaldehyde in foods has many disadvantages: the irritating smell of cinnamaldehyde affects the intrinsic flavor of foods and large quantities of active ingredients are also neutralized by free cinnamaldehyde in foods (Arfa, Preziosi-Belloy, Chalier, & Gontard, 2007; López, Sánchez, Batlle, & Nerín, 2007). Therefore, Cevallos, Buera, and Elizalde (2010) and Jiang, Li, and Jiang (2010) have prepared β-cyclodextrin–cinnamaldehyde inclusion complex for improving the stability of cinnamaldehyde, based on the displacement of water molecules in the cavity of β-CD by guest compounds. However, β-cyclodextrin transformed from starch by CGTase is relatively expensive.

Starch is a more resourceful and cheaper bioresource than β-cyclodextrin. In neutral aqueous solution, the single amylose helix was observed, when hydrophobic guests, such as pesticides, aliphatic alcohol and lactone, were present (Heinemann, Escher, & Conde-Petit, 2003; Lesmes, Barchechath, & Shimoni, 2008). The hydrophobic section of the guests was incorporated into the hydrophobic helix of amylose, thus resulting in the formation of the V-type amylose-guest inclusion complex (Zabar, Lesmes, Katz, Shimoni, & Bianco-Peled, 2009). It was also evident that the position of the guests located in the hydrophobic cavity of amylose helix was directly related to the molecule size of the guests (Tian et al., 2009, 2010).

Cinnamaldehyde is a hydrophobic compound with a benzene ring and an aldehyde group. It may cause starch molecules to form a V-type inclusion complex and its stability was increased by starch encapsulation (Itthisoponkul, Mitchell, Taylor, & Farhat, 2007). Nevertheless, native starch could not well encapsulate cinnamaldehyde due to the lack of enough surface activity in reaction system (Arfa et al., 2007). Mongenot, Charrier, and Chalier (2000) reported that the ultrasound treatment could generate starch suspension into a stable emulsion and significantly increase the encapsulation efficiency. The ultrasound treatment, therefore, was designed to encapsulate cinnamaldehyde by high-amylose corn starch in this study. The encapsulation product was identified and its releasing behavior was also estimated.

2. Experimental

2.1. Materials

Cinnamaldehyde was purchased from Sinopharm Chemical Reagent Inc. (Shanghai, China). High-amylose corn starch was gifted from Dingfeng Starch Inc. (Tianjin, China). Its amylose

* Corresponding author. Tel.: +86 510 85913299; fax: +86 510 85913299.
E-mail addresses: yqtian@jiangnan.edu.cn (Y. Tian), jinlab2008@yahoo.com (Z. Jin).

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content was determined by the spectrophotometric method described by Hoover and Ratnayake (2001). All other chemicals and reagents were of analytical grade unless otherwise stated.

2.2. Preparation of high-amylose corn starch–cinnamaldehyde inclusion complex

The high-amylose corn starch–cinnamaldehyde inclusion complex was prepared using the ultrasound method described by Zhu, Tian, Xu, Wang, and Jin (2012). In brief, 8 g of high-amylose corn starch was dissolved in 100 mL distilled water at 100 °C for 30 min with continuous stirring until it became a homogeneous paste. After the paste was cooled to 25 °C, 800 μL of cinnamaldehyde dissolved in anhydrous ethanol (8 mL) were added and mixed by successive stirring. The starch/cinnamaldehyde mixture (10:1, g/mL) was then treated at 35 °C for 10 min using a 250 W ultrasound generator (Zhisun Instrument Inc., Shanghai). The resultant sol was kept at 45 °C for 12 h to prepare the crude starch–cinnamaldehyde inclusion complex before it was dried at 45 °C for 5 h. The amount of surface cinnamaldehyde was removed by a washing procedure with 10 mL of anhydrous ether for at least three times. The remaining solids were dried at 40 °C in a vacuum oven and milled to pass through 100-mesh sieve to obtain the pure starch–cinnamaldehyde inclusion complex.

2.3. Determination of the included cinnamaldehyde

A simple procedure described by Li, Jin, and Wang (2007) was used to determine the included cinnamaldehyde. In brief, high-amylose corn starch–cinnamaldehyde inclusion complex was dispersed in anhydrous ethanol and incubated at 45 °C for 30 min. The absorbance at 286 nm of the ethanol was determined using a UV spectrophotometer (TU-1900, Persee General Instrument Inc., Beijing). The included cinnamaldehyde and the encapsulation rate (E_r) were obtained using following Eqs. (1) and (2):

$$A = 181.48C - 0.0244 \quad (R^2 = 0.9954) \tag{1}$$

$$E_r = \frac{M_i}{M_t} \times 100\% \tag{2}$$

where A is the absorbance of the ethanol solution, C is the concentration of cinnamaldehyde, expressed in μL/mL, M_i is the cinnamaldehyde content in the inclusion complex, and M_t is the total cinnamaldehyde content in reaction system.

2.4. Fourier-transform infrared (FT-IR) spectroscopy

FT-IR spectra of cinnamaldehyde, high-amylose corn starch, the high-amylose corn starch/cinnamaldehyde mixture, and the high-amylose corn starch–cinnamaldehyde inclusion complex were scanned using an infrared spectrophotometer (5DXC FTIR, Nicolet Co., USA). The analysis parameters were set as: wave number range, from 4000 to 400 cm^{-1}; resolution, 4 cm^{-1}; number of scans, 64; and scan speed, 0.63.

2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was conducted with a Mettler-Toledo TGA/SDTA851E under dynamic atmosphere of helium (99.99%) at 20 mL/min. Five milligrams of sample (each sample was equilibrated in a sealed vessel with saturated sodium chloride for one week before the test) were determined from 30 °C to 500 °C at a heating rate of 10 °C/min to evaluate the thermal stability.

Table 1
Apparent amylose content and encapsulation rate of high-amylose corn starch–cinnamaldehyde inclusion complex prepared using the ultrasound treatment.

Treatments	Apparent amylose content (%)	Encapsulation rate (E_r, %)
Control	42.6 ± 1.3a[a]	5.7 ± 0.3a
Ultrasound treatment	64.9 ± 0.8b	40.2 ± 0.5b

[a] Samples means with different lowercase letters in the same column are significantly different ($P < 0.05$).

2.6. Cinnamaldehyde releasing behaviors of the inclusion complex

Three grams of the pure starch–cinnamaldehyde inclusion complex were tiled into culture dishes. The culture dishes were put into a desiccator and stored at 25 °C and relative humidity of 75% for 0, 1, 2, 3, 4 and 5 weeks. Part of the stored sample (0.05 g) was taken out to determine the remaining cinnamaldehyde. The releasing rate (R_r) was estimated using the following formula (3):

$$R_r = \left(1 - \frac{M_s}{M_{ti}}\right) \times 100\% \tag{3}$$

where M_s is the remaining cinnamaldehyde dissolved in ethanol solvent and M_{ti} is the total included cinnamaldehyde in the starch–cinnamaldehyde inclusion complex.

2.7. Statistical analysis

The data were expressed as means of triplicate determinations. Statistical significance was assessed with one-way analysis of variance (ANOVA) using ORIGIN 7.5 (OriginLab Inc., USA) for windows program. A probability $P < 0.05$ was considered significant throughout the study.

3. Results and discussion

3.1. Preparation of starch–cinnamaldehyde inclusion complex

The results showed that the encapsulation rate of the high-amylose corn starch/cinnamaldehyde mixture was 5.7%, while the encapsulation rate reached 40.2% for the inclusion complex prepared by the ultrasound treatment at 35 °C for 10 min (Table 1). The ultrasound treatment also increased the apparent amylose content of high-amylose corn starch sample from 42.6% to 64.9%. This increase indicated that the ultrasound could partly break the glycosidic bond linked between glucose units. Corn starch with more amylose fraction was easily encapsulating cinnamaldehyde (Arfa et al., 2007). On the other hand, higher emulsifying property presented during the ultrasound treatment also benefited the encapsulation process (Zhu et al., 2012).

3.2. FT-IR spectra analysis

FT-IR spectra showed that the main adsorption peaks for pure cinnamaldehyde, $C_6H_5CH{=}CHCHO$, were 1620 cm^{-1} and 1675 cm^{-1} (Fig. 1). These were ascribed to the skeletal vibration of aromatic nucleus and carbonyl band stretch, respectively. With regard to the mixture of starch and cinnamaldehyde, the main absorption peaks of cinnamaldehyde around 1620 cm^{-1} and 1675 cm^{-1} were still observed, while the mixing increased the stretch vibration of the 1675 cm^{-1}. The increase might result from an overlap of carbonyl stretch vibration of high-amylose corn starch and cinnamaldehyde. However, the skeletal vibration of aromatic nucleus around 1620 cm^{-1} disappeared for the prepared starch–cinnamaldehyde inclusion complex. This indicated

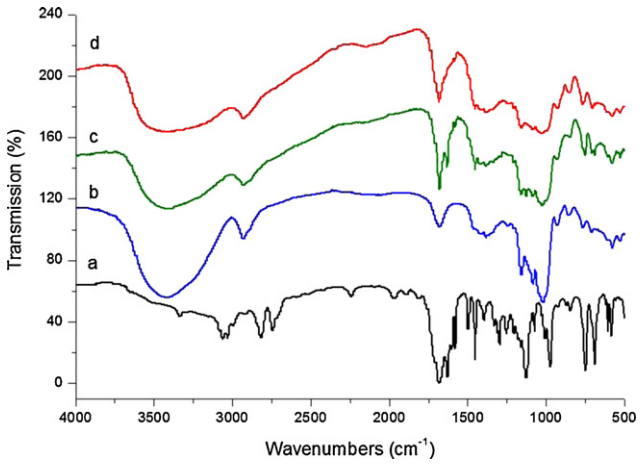

Fig. 1. The FT-IR spectra of (a) cinnamaldehyde, (b) high-amylose corn starch, (c) the mixture of high-amylose corn starch and cinnamaldehyde, and (d) the high-amylose corn starch–cinnamaldehyde inclusion complex.

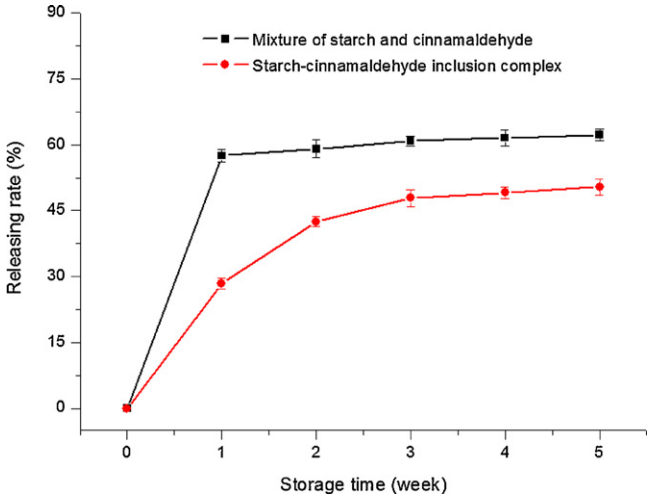

Fig. 3. Releasing characteristics of the included cinnamaldehyde in the high-amylose corn starch–cinnamaldehyde inclusion complex.

that the aromatic nucleus of cinnamaldehyde was incorporated into the helix of amylose. These findings suggested that the starch–cinnamaldehyde inclusion complex was successfully formed using the ultrasound method.

3.3. Thermogravimetric analysis (TGA)

The TGA data showed that the high-amylose corn starch showed a two-step thermogravimetric curve (Fig. 2). The first weight loss step at 120 °C was caused by the water evaporation and the second one around 280 °C was ascribed to the decomposition of starch. For the mixture of starch and cinnamaldehyde, the first mass loss around 125 °C was observed for the water evaporation and the volatilization of cinnamaldehyde and another mass loss step at 280 °C was similar to the curve of high-amylose corn starch. Nevertheless, the dissociation temperature of the starch–cinnamaldehyde inclusion complex was around 190 °C and the second mass loss around 300 °C was responsible for the decomposition of starch. This indicated that the thermal stability of cinnamaldehyde was increased by the encapsulation and also demonstrated the formation of starch–cinnamaldehyde inclusion compound.

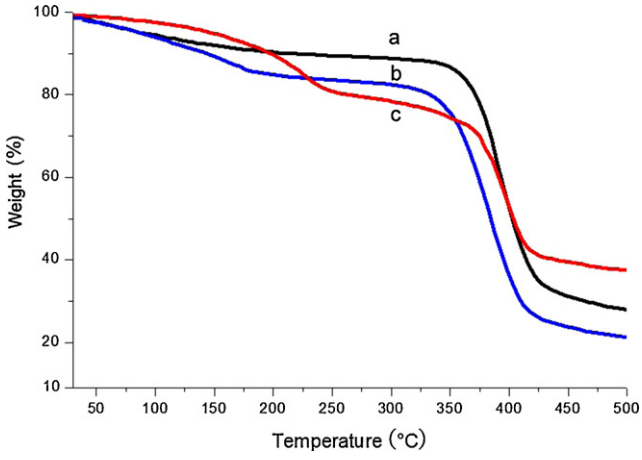

Fig. 2. Thermogravimetric curves of (a) high-amylose corn starch, (b) the mixture of high-amylose corn starch and cinnamaldehyde, and (c) the high-amylose corn starch–cinnamaldehyde inclusion complex.

3.4. Releasing behaviors of the starch–cinnamaldehyde inclusion complex

The results revealed that the releasing rate of the starch/cinnamaldehyde mixture rapidly increased from zero to 57.5%, while the releasing rate of the starch–cinnamaldehyde inclusion complex only increased from zero to 28.4% in the first week (Fig. 3). The lower releasing rate indicated that the prepared inclusion complex had good retention ability and effectively reduced the releasing rate of cinnamaldehyde. The releasing mechanism might be interpreted by the fact that the included cinnamaldehyde was replaced by water to release free cinnamaldehyde for an equilibrium state during storage (Eq. (4)).

$$\text{Starch–cinnamaldehyde inclusion complex} + \text{Water} \Leftrightarrow \text{Starch} + \text{Cinnamaldehyde} \quad (4)$$

4. Conclusions

The work demonstrated that cinnamaldehyde was successfully encapsulated by high-amylose corn starch to form starch–cinnamaldehyde inclusion complex. The encapsulation increased the stability of cinnamaldehyde and generated a good releasing behavior. The ultrasound treatment could reduce the molecular weight of high-amylose corn starch and increase the production yield of the inclusion complex. These suggest that high-amylose corn starch with an ultrasound treatment is one of most advantageous techniques for the encapsulation of cinnamaldehyde in food industry.

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