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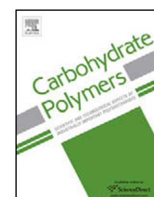

Synthesis and characterization of amylose–zinc inclusion complexes

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ABSTRACT

Amylose–zinc inclusion complexes were synthesized using zinc chloride and amylose, which is obtained by completely debranching potato starch using pullulanase. Based on the zinc content (W–Zn) and zinc conversion (C–Zn), the reaction parameters, such as reaction time, reaction temperature, pH value and amount of zinc chloride added, were evaluated. The W–Zn and C–Zn of the zinc-loaded amylose, which was prepared under optimal conditions, were 128 mg/g and 82.05%, respectively. The Raman spectra showed that amylose formed a special single helix structure after complexing with zinc. X-Ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC) results showed that starch and zinc could formate the inclusion complexes. Moreover, the formation of amylose–zinc inclusion complexes was confirmed by the results of X-ray photoelectron spectroscopy (XPS) and ^{13}C CP/MAS NMR, which suggests that zinc was mainly coordinated to the oxygen atoms of the glucose unit, 6-CH_2OH. Thermal properties of the complexes were influenced by the zincatation process. This approach not only enlarged the number of fields for amylose use but also exhibited the extensive potential applications for zinc nutrition fortifier research. The study suggested that potato amylose might be a good carrier of zinc for nutritional supplementation purposes.

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1. Introduction

Major concerns exist related to the mineral nutritional status of human populations all over the world (Drews, Kies, & Fox, 1979). Elemental zinc is an essential nutrient required by people and animals for promoting growth and development, maintaining a normal sense of taste, smell and vision, building proteins, triggering enzymes, creating DNA and maintaining a healthy immune system (Wintergerst, Maggini, & Horning, 2006; Luo et al., 2013). If the body is deficient in elemental zinc, some symptoms may emerge, such as stunted growth, tardive wound healing, dermatitis, low sexual function, impaired appetite, taste abnormalities and depressed immunity (Staroszczyk & Janas, 2010). Zinc deficiencies have been defined in human populations in many countries (Drews et al., 1979).

Dietary fiber, especially anionic hydrocolloids, has been reported as having a strong adsorption ability to metal cations (Debon & Tester, 2001). However, the non-digestible properties of dietary fiber have been shown to impair the absorption of minerals and trace elements in the small intestine because of their binding and/or sequestering effects (Bosscher, Van Caillie-Bertrand, Van Cauwenbergh, & Deelstra, 2003). Moreover, many zinc compounds still exhibit problems, such as stimulating the stomach and a low absorption rate (Woo, Bassi, Maningat, Ganjyal, & Zhao, 2014).

Amylose and amylopectin are the two major polysaccharide components of reserve starch in plants, both of which are widely used in food and bio industries (Ghiasi, Varriano, & Hoseney, 1982; Nakamura, Yamamori, Hirano, Hidaka, & Nagamine, 1995; Schirmer, Höchstötter, Jekle, Arendt, & Becker, 2013). Amylose, a type of linear polysaccharide composed of D-glucose mainly linked by α-1,4-linkages, can form crystalline complexes with a variety of small ligands (Brisson, Chanzy, & Winter, 1991). Furthermore, amylose can hold ions within its spiral cavity because of its unique single helical structure (Eliasson, 1985; Heinemann, Conde-Petit, & Nuessli, 2001). In addition, the cavity has a hydrophobic

Abbreviations: W–Zn, zinc content; C–Zn, zinc conversion; URPA, uncomplexed retrograded potato amylose; ^{13}C CP/MAS NMR^{13}, C cross-polarization/magic angle spinning nuclear magnetic resonance; XPS, X-ray photoelectron spectroscopy; FWHM, full width at half maximum.

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interior and hydrophilic exterior; hence, amylose can encapsulate hydrophobic guest molecules by weak intermolecular hydrophobic interaction, forming inclusion complexes (Putseys, Lamberts, & Delcour, 2010). As a helical polysaccharide, amylose has been widely used for biomedical applications, including pro-drug preparation, encapsulation of bovine hemoglobin and oral drug delivery (Cai, Yang, Zhang, & Qing, 2010). Metal ions can also be coordinated to the hydroxyl oxygen atoms of amylose, which leads to the formation of inclusion complexes (Senti & Witnauer, 1948; Sarko & Biloski, 1980). However, knowledge of the formation of amylose–zinc inclusion complexes is limited.

In our previous study, starch–zinc complexes were synthesized by the reaction of zinc acetate with cassava starch, which was enzymatically modified by combining α-amylase and glucoamylase (Luo et al., 2013). However, the content of zinc ions loaded in starches still needs improvement. The objective of the present study was to investigate the complexation ability of amylose with zinc ions. Based on the digestion of pullulanase, amylose was obtained from native potato starch, which has a stronger complexation capacity compared to that of native starch from other resources according to numerous pre-tests (data not show). The optimization of the experimental conditions, including reaction time, reaction temperature, pH value and the initial amount of zinc chloride, was investigated. Furthermore, the prepared amylose–zinc inclusion complexes were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), ^{13}C cross-polarization/magic angle spinning nuclear magnetic resonance (^{13}C CP/MAS NMR) and scanning electron microscopy (SEM). The present study may provide a potential new pathway for the preparation of zinc nutrition fortifier by the complexation reaction of amylose and zinc ions.

2. Materials and methods

2.1. Materials

Commercial food-grade potato starch was purchased from Wisconsin biological engineering Co., Ltd. (Qinghai, China). Pullulanase (OPTIMAX L300, activity 1000 ASPU/mL) was supplied by DuPont Genencor® Science. One unit of pullulanase activity corresponds to the amount of enzyme that liberates 1 g of glucose from pullulan per hour at pH 4.5 at 60 °C. Analytical grade zinc chloride was purchased from Shanghai Qiangshun Chemical Reagent Co., Ltd (Shanghai, China). All other chemicals and reagents used were of analytical grade.

2.2. Preparation of amylose (debranched starch)

Native potato starch (50 g, dry basis) was dispersed in water (450 g) in a three-necked flask. The slurry was adjusted to pH 4.5 with stirring by using 0.5 mol/L HCl and then gelatinized in a boiling water bath for 1 h. After gelatinization, the mixture was cooled to 60 °C and the debranched reaction was initiated by adding pullulanase (10 ASPU/g starch). To completely debranch the starch, the solution was incubated at 60 °C at pH 4.5 for 4 h. The sample was slowly cooled to ambient temperature and then stored at 4 °C for 18 h. After centrifuging, washing, drying and crushing with 100 mesh sieve, the retrogradaed potato amylose (URPA) powder was prepared. The completeness of the debranching reaction was confirmed by ^{1}H NMR, which can distinguish the α-1,6- from α-1,4-linkages of the starch (Gidley, 1985).

2.3. Preparation of amylose–zinc inclusion complex

Zinc chloride solutions (2 mol/L) of different volumes (20, 30, 40, 50 and 60 mL) were added into the prepared amylose solutions dropwise (pH 7.0) with continuous stirring. The pH of the mixture was adjusted to a certain value (5, 6, 7, 8 or 9) by adding 0.5 mol/L NaOH or 0.5 mol/L HCl solution. After reacting at a temperature of 40, 50, 60, 70 or 80 °C for 1, 2, 3 or 4 h, respectively, the mixture was slowly cooled to ambient temperature and then stored at 4 °C for 18 h. The samples were neutralized to pH 4.5 with 0.5 mol/L HCl, filtered, and washed with deionized water to remove all residual free zinc ions. Finally, the prepared samples were dried in an oven at 40 °C for 24 h. As a control, a potato amylose solution without zinc, called uncomplexed retrograded potato amylose (URPA), was prepared according to the foregoing procedures. The products prepared under the optimal conditions were used for further analysis.

2.4. Determination of the zinc content and zinc conversion rate

The zinc content in the samples, after their wet mineralization with HNO_3 and $HClO_4$, was determined by a Z-5000 flame atomic absorption spectrophotometer (AAS) (Hitachi co. Ltd, Tokyo, Japan) according to a standard procedure of AAS (Varma, 1984). The zinc conversion rate (Y) was calculated by the following equation:

$$Y = \frac{(m_1 - m_0)}{m} \times 100\% \quad (1)$$

where m_0 (g) is the zinc content of the enzyme-modified starch, m_1 (g) is the zinc content of the starch–zinc complexes, and m (g) is the zinc content of the added zinc chloride.

2.5. Characterization of amylose–zinc inclusion complexes

2.5.1. Raman spectroscopic analysis

The Raman spectra of the samples were obtained using a laser confocal Raman microscopy system (LabRAM Aramis, France). The spectrometer was equipped with a quartz beam splitter and a liquid-nitrogen-cooled germanium detector with excitation at 632.81 nm obtained using a Nd:YAG laser. The laser power was set to 100 mW and 256 scans per sample were accumulated with a spectral resolution of 1.0 cm^{-1}.

2.5.2. XRD determination

X-ray diffraction was conducted with a RU200R X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu $K\alpha$ radiation at 40 kV and 40 mA, incident wavelength at 0.1524 nm, a theta-compensating slit, and a diffracted beam monochromator. The XRD spectra of URPA and amylose–zinc inclusion complex were recorded between 5° and 60° (2θ), the scanning length at 0.02°, scanning speed at 0.1 s/step.

2.5.3. DSC measurement

Gelatinization temperatures were determined and recorded on a Perkin-Elmer DSC-8000 (PerkinElmer Co., Waltham, USA) differential scanning calorimeter, equipped with a thermal analysis data station. sample (5 mg, dry basis) in the DSC pans, which were then sealed. The scanning temperature range and the heating rate were 30–400 °C and 10 °C/min, respectively. The thermograms were recorded with an empty pan as a reference.

2.5.4. ^{13}C CP/MAS NMR determination

^{13}C CP/MAS NMR experiments were conducted using a Bruker AVANCE 400 MHz spectrometer (Bruker Corporation, Fallanden, Switzerland) operated at 6000 r/min by using a standard broadband MAS probe. The spectra were harvested at 25 °C with a pulse sequence of CP TOSS and a spectral width of 295.8 ppm, contact ion time of 17 ms and a relaxation delay time of 2 s. All chemical shifts were reported in parts per million (ppm).

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