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Preparation and characterization of starch nanoparticles through ultrasonic-assisted oxidation methods

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ABSTRACT

In this work, starch nanoparticles (SNPs) were prepared from waxy corn starch (WCS) through ultrasonic-assisted oxidation. Three SNPs samples were produced by one time oxidation followed by ultrasonic treatment (O1U1-SNPs), twice oxidation and twice ultrasonic treatment (O2U2-SNPs) and TEMPO-mediated oxidation with ultrasonic treatment (TEMPO-SNPs), respectively. Differential scanning calorimetry (DSC), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy were used to characterize the thermal properties, morphology, and structure of the ensuing nanoparticles. The results revealed that the size of the O1U1-SNPs, O2U2-SNPs, and TEMPO-SNPs particles reached 30–50 nm, 20–50 nm and 20–60 nm, respectively. Compared to WCS, the crystallinity of the O1U1-SNPs, O2U2-SNPs and TEMPO-SNPs samples decreased from 36.32% to 11.35%, 1.64% and 1.72%, respectively. The O1U1-SNPs, O2U2-SNPs and TEMPO-SNPs exhibited smaller or no endotherms. The SNPs had higher carboxyl and carbonyl content.

1. Introduction

Starch is a primary source of stored energy, and reserves carbohydrates synthesized in many parts of plants. Starch is the second most abundant biomass material on Earth, next to the organic compound cellulose (Eliasson, 2004). The starch molecule is composed of an amorphous region (amylose) and a crystalline region (amylopectin). The shortcomings of native starch, such as poor tolerance to a broad range of processing conditions and poor functional properties, can be overcome through physical, chemical or enzyme modification, and this property has made starch a useful polymer. A common chemical modification of starch is oxidation. Oxidized starch is commonly produced by reacting starch with a specified amount of oxidizing agent under controlled temperature and pH (Wurzburg, 1986). Several oxidizing agents have been applied to starch oxidation, including sodium hypochlorite (NaOCl), bromine, periodate and the 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated system.

Ultrasonic technology has been widely applied in chemical processes. Application of ultrasonic irradiation in food processing has been increasing over the past few years because it shortens the processing times required and lowers energy consumption, creating an effective process (Jambrak, Lelas, Mason, Krešić, & Badanjak, 2009; Mason, Paniwnyk, & Lorimer, 1996). Ultrasonic treatment is a physical method for modifying starch (Azhar & Hamdy, 1979; Chung, Moon, Kim, & Chun, 2002; Iida, Tuziuti, Yasui, Towata, & Kozuka, 2008; Zuo, Knoerzer, Mawson, Kentish, & Ashokkumar, 2009). Ultrasonication generates ultrasonic cavitation in the solution and causes micro-bubbles. When micro-bubbles collapse, high energy is released and converted to high pressure and high temperature. The process causes degradation of polymers and/or catalytic acceleration of reactions (Kawasaki, Takeda, & Arakawa, 2007).

In recent years, nanoparticles originated from biopolymers have received considerable attention as novel and biofunctional materials in diverse industries. For example, in drug delivery systems, polysaccharide nanoparticles may exhibit prominent sustained release profiles, with assured safety (Lin, Huang, Chang, Feng, & Yu, 2011). Furthermore, increasing interest in nanoparticles of natural origin and their unique properties has led to intensive research in nano-sized particles from natural polysaccharide polymers such as starch (LeCorre, Bras, & Dufresne, 2010). Starch nanoparticles (SNPs) can be readily obtained with mechanical treatment such as ultrasonication (Bel Haaj, Magnin, Pétrier, & Boufi, 2013; Chong, Uthormporn, Karim, & Cheng, 2013), extrusion (Giezen, Jongboom, Gotlieb, & Boersma, 2000), high-pressure homogenization (Liu, Wu, Chen, & Chang, 2009), enzymatic treatment (Kim, Park, and Lim, 2008) and acid hydrolysis (Kim, Lee, Kim, Lim, & Lim, 2012; Putaux, Molina-Boisseau, Momaur, & Dufresne, 2003, Angellier, Choisnard,

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Molina-Boisseau, Ozil, & Dufresne, 2004). A combined process of acid hydrolysis for a short period (2 days at 40 °C) followed by facile ultrasonication (60% amplitude, 3 min) has been reported for nanocrystal formation (Kim, Han, Kweon, Park, & Lim, 2013; Kim, Han, Park, Kim, & Lim, 2013).

In this paper, the combined process of oxidation for a short period and ultrasonication produced SNPs. During ultrasonic-assisted oxidation waxy corn starch, carbonyl and carboxyl groups which produced by oxidation could be introduced to the surface of SNPs. The surface charges of SNPs caused by carbonyl and carboxyl groups generated electrostatic repulsive energy. The repulsive forces were strong enough to repulse SNPs away from each other and produced stable suspensions. Therefore, this influence might decide the dispersity and stability of SNPs suspension. To the best of our knowledge, no study has been reported on the different ultrasonic-assisted oxidation methods for preparing SNPs. This approach is easy and efficient.

2. Materials and methods

2.1. Materials

Waxy corn starch (WCS, 11.6% moisture) was obtained from Zhucheng Xingmao Corn Development Co., Ltd. (Shangdong, China). Sodium hypochlorite (Sinopharm Chemical Regent Co. Ltd., China) containing 10 g active chlorine/100 g was used in this experiment. All other chemicals used were of analytical grade.

2.2. Preparation of O1U1-SNPs and O2U2-SNPs

The oxidized starch was prepared by following Wang and Wang's (2003) method with some modifications. The WCS slurry (35 g/100 g solids) was prepared with distilled water and maintained at 35 °C in a heating mantle. The pH was adjusted to 9.5 with 2 M NaOH. Sodium hypochlorite (1 g/100 g active chlorine concentration) was slowly added into the starch slurry over 30 min while the pH was maintained at 9.5 with 1 M H_2SO_4. After NaOCl was added, the pH of the slurry was maintained at 9.5 with 1 M NaOH for an additional 6 h. The slurry was then adjusted to pH 7.0 with 1 M H_2SO_4, filtered by suction with a Buchner filter funnel (Whatman filter #4), washed with a two-fold volume of distilled water and dried in a convection oven at 40 °C for 48 h.

The oxidized starch slurry was prepared by dispersing 10 g of oxidized starch in 100 ml of distilled water in a glass beaker, immersed in a water bath at a constant temperature of 5 °C. Sonication was carried out in an ultrasonic bath (KQ-500TDE, Kunshan, China) with power ultrasound of 500 W with 100% amplitude at a frequency of 40 kHz. Sonication was continued for 180 min under continuous stirring to prevent the oxidized starch granules from settling to the bottom. The mixture was separated by centrifugation at 3000 rpm for 10 min, the precipitate was used for the second oxidation and the supernatant was centrifuged at 10,000 rpm for 10 min. Then the precipitate was freeze-dried to obtain O1U1-SNPs (the yield was about 40%). The precipitate of centrifugation at 3000 rpm was treated according to this method for oxidation followed by ultrasonication for the second time. The precipitate was then freeze-dried to obtain O2U2-SNPs (the yield was about 70%).

2.3. TEMPO oxidation with ultrasonic treatment

TEMPO oxidation with ultrasonic treatment was prepared by following Qian et al.'s (2010) method with some modifications. A slurry of 10% WCS (100 g) was put in a beaker and held at 5 °C. The TEMPO (0.048 g, 0.01 mol per anhydroglucose unit of starch) and sodium bromide (0.635 g, 0.2 mol per anhydroglucose unit of starch) were dissolved in 100 ml distilled water. After TEMPO was completely dissolved, the solution was added to the starch solution at 5 °C. The pH of the solution was adjusted to 9.5 with 0.5 M NaOH. Then, 20 g of sodium hypochlorite solution was slowly added to the starch solution, and the pH was maintained at 9.5 by continuous addition of 0.5 M NaOH. The beaker was then dipped into the ultrasonic bath (KQ-500TDE, Kunshan, China) with power ultrasound of 500 W with 100% amplitude at a frequency of 40 kHz. Sonication was continued for 180 min under continuous stirring at 5 °C. The mixture was separated by centrifugation at 3000 rpm for 10 min, and the supernatant was centrifuged at 10,000 rpm for 10 min. The precipitate was washed with water and centrifuged three times. Then the precipitate was freeze-dried to obtain TEMPO-SNPs (the yield was about 50%).

2.4. Determination of carbonyl content

The carbonyl content was determined according to the titrimetric method as described by Smith (1967). A starch sample (2 g) was added to 100 ml of distilled water in a 500 ml flask. The suspension was gelatinized in a boiling water bath for 20 min, cooled to 40 °C and adjusted to a pH value of 3.2 with 0.1 M HCl. A hydroxylamine reagent (15 ml) was then added to the mixture. The flask was stoppered and placed in a 40 °C water bath for 4 h with slow stirring. The excess hydroxylamine was determined by rapidly titrating the reaction mixture to a pH value of 3.2 with standardized 0.1 M HCl. A blank determination with only the hydroxylamine reagent was performed in the same manner. The hydroxylamine reagent was prepared by first dissolving 25 g of hydroxylamine hydrochloride in 100 ml of 0.5 M NaOH, before the final volume was adjusted to 500 ml with distilled water. The carbonyl content was expressed as the quantity of carbonyl groups per 100 glucose units (CO/100 GU), as calculated with Eq. (1):

$$\frac{\mathrm{CO}}{100\,\mathrm{GU}} = (Vb - Vs) \times M \times 0.028 \times \frac{100}{W} \quad (1)$$

where Vb is the volume of HCl used for the blank (ml), Vs is the volume of HCl required for the sample (ml), M is the molarity of HCl and W is the sample weight (db).

2.5. Carboxyl content

The carboxyl content of the oxidized starch was determined according to Chattopadhyay, Singhal, and Kulkarni's (1997) procedure with some modifications. Approximately 2 g of a starch sample was mixed with 25 ml 0.1 M HCl, and the slurry was stirred occasionally for 30 min with a magnetic stirrer. The slurry was then vacuum-filtered through a 150 ml medium porosity fritted glass funnel and washed with 400 ml distilled water. The starch cake was then carefully transferred into a 500 ml beaker, and the volume was adjusted to 300 ml with distilled water. The starch slurry was heated in a boiling water bath with continuous stirring for 15 min to ensure complete gelatinization. The hot starch dispersion was then adjusted to 450 ml with distilled water and titrated to a pH value of 8.3 with standardized 0.01 M NaOH. A blank test was performed with unmodified starch. The carboxyl content was expressed as the quantity of carboxyl groups per 100 glucose units (COOH/100 GU), as calculated with Eq. (2):

$$\frac{\mathrm{COOH}}{100\,\mathrm{GU}} = (Vs - Vb) \times M \times 0.045 \times \frac{100}{W} \quad (2)$$

where Vs is the volume of NaOH required for the sample (ml), Vb is the volume of NaOH used to test the blank (ml), M is the molarity of NaOH and W is the sample weight (db).