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Octenylsuccinate starch spherulites as a stabilizer for Pickering emulsions

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ABSTRACT

This study investigated structure and morphology of starch spherulites prepared from debranched waxy maize and waxy potato starches. Debranched waxy potato starch favored the formation of B-type crystals with longer branch chains (average chain length, 26.14), whereas A-type polymorphic aggregates were generated from debranched waxy maize under same recrystallization condition. Spherulites had smaller particle size distribution (D[3,2], ~3.7 μm), higher dissociation temperature (80–120 °C) and crystallinity (80~90%), compared to native waxy starches. Intact spherulites could be used as an edible particle emulsifier after modifying by octenylsuccinic anhydride (OSA). The emulsion produced using 2 wt.% of octenylsuccinate (OS) starch spherulites as emulsifier was quite stable over 2 months, and its Pickering emulsions displayed protective effect on stability of oil droplets.

1. Introduction

Spherulites are semi-crystalline entities with some degree of radial symmetry displaying a 'Maltese cross' under polarized light. Starch spherulites can be formed by heating a starch suspension and then recrystallization through cooling without any disturbance (Singh, Lelane, Stewart, & Singh, 2010; Steeneken & Woortman, 2009; Ziegler, Nordmark, & Woodling, 2003). The morphology of spherulites is determined by multiple factors, such as molecular size and concentration of starch, heating temperature, cooling rate, and crystallization temperature (Cai & Shi, 2014). Ring, Miles, Morris, Turner, and Colonna (1987) prepared the B-type spherulites with a diameter of 10–15 μm through cooling an aqueous solution of amylodextrin (5–20%, w/w). In contrast, A-type spherulites with a diameter of ca. 10 μm can be produced by mixing ethanol with hot aqueous solutions of short chain amylose followed by slowly cooling to 4 °C for recrystallization (Helbert, Chanzy, Planchot, Buleon, & Colonna, 1993). Cai and Shi (2014) prepared A- and B-type spherulites (5–15 μm) with a yield of 70–90% by debranching waxy maize and waxy potato starch and then recrystallization in an aqueous environment.

In the current food, pharmaceutical and cosmetic industries, a large proportion of materials need to stabilize by emulsion (Xiao, Li, & Huang, 2015). Pickering emulsion is functioned by a solid particle stabilizer, which absorbs onto the interface between the oil and water phases. Compared with the traditional stabilizers, particle stabilizers have several advantages, such as strong interfacial stability, non-toxicity, environment-friendliness and low cost (Yu, Lin, & Li, 2013). Common Pickering emulsifiers used in industry are silica, fat crystals, proteins and hydrocolloids (Dickinson, 2010). The particle size of Pickering emulsions varies from nanometer to micrometer length scale. Starches (e.g., hydrophobically modified starches) are new sources for Pickering emulsion stabilizer (Rayner, Timgren, Sjöö, & Dejmek, 2012; Timgren, Rayner, Sjoo, & Dejmek, 2011). Yusoff and Murray (2011) first used octenylsuccinate (OS) starch which was degraded by freeze-milling as a particle stabilizer of Pickering emulsion. Timgren et al. (2011) used more intact granules in Pickering emulsion systems, and observed that such emulsions were related stable and exhibited excellent barrier properties. Song, Pei, Zhu, Fu, and Ren (2014) investigated four OS rice starch varieties with narrow size distribution (⩽5 μm) as Pickering emulsifier, and prepared the Pickering emulsion with droplet size of 10–70 μm and high stability.

Abbreviations: CL, chain length; CLSM, confocal laser scanning microscopy; D[3,2], volume-surface average diameter; DB, degree of branch; DS, degree of substitution; DP, degree of polymerization; DSC, differential scanning calorimetry; FACE, fluorophore-assisted capillary electrophoresis; NMR, Nuclear magnetic resonances spectroscopy; ΔH, enthalpy change; LSD, least significant difference; OSA, octenylsuccinic anhydride; SEM, scanning electron microscopy; T_c, conclusion temperature; T_o, onset temperature; T_p, peak temperature.

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Although several preparation methods and physicochemical properties of starch spherulites have been reported (Cai & Shi, 2014; Helbert et al., 1993; Ring et al., 1987), little information has been known as a particle stabilizer. In this study, we prepared starch spherulites by recrystallization of enzyme-debranched waxy maize and potato starches, and then modified by OSA. The structural and morphological properties of starch spherulites and their emulsions were investigated, which leads to new starch-based particle stabilizers in the food, pharmaceutical or cosmetic industries.

2. Materials and methods

2.1. Materials

Waxy maize starch was purchased from Dacheng Company (Changchun, China), and waxy potato starch was provided by Ingredion Inc. (Bridgewater, NJ, USA). OSA was obtained from Vertellus Specialties Inc. (Nanjing, China). Isoamylase was purchased from Megazyme International Ltd. (Co. Wicklow, Ireland) with activity of 1000 units/mL. Brazil orange oil was purchased from Guangzhou Sunpart Food Science and Technology Development Co., Ltd (Guangzhou, China). Other chemicals were reagent-grade.

2.2. Preparation of starch spherulites

Spherulites were synthesized according to the method reported with minor modification (Cai & Shi, 2014). Waxy starch (10 g, dry basis, db) was suspended in 30 mL of acetate buffer (0.01 M, pH 4.0). The slurry was heated in a boiling water bath with continuous stirring for 30 min, and then held in a 120 °C oil bath for another 30 min. After the mixture was cooled to 50 °C, isoamylase (30 units/g, dry starch basis, dsb) was added, and the mixture was stirred at 50 °C for 24 h, followed by heating in a boiling water bath for 30 min to denature the enzymes. The mixture was cooled to 50 °C, and held for 24 h to form starch spherulites. The precipitates were filtered, washed with water and ethanol, dried in a 40 °C oven overnight and gently ground.

2.3. Preparation of OS starch spherulites

Starch spherulites (5.0 g, db) were suspended in distilled water (35%, w/v) with agitation. OSA (3%, w/w, dsb) was added slowly within 1 h while maintaining the pH at 8.5 by NaOH (3%, w/w). The reaction was allowed to proceed for 2 h in total at 35 °C. After reaction, the reaction mixture was neutralized to pH 6.5 with diluted HCl solution (3%, w/w). The mixture was centrifuged and washed twice with distilled water and ethanol. OS starch spherulites were oven-dried at 40 °C for 24 h, and then passed through a 100 mesh nylon sieve (Wang, He, Fu, Luo, & Huang, 2015).

2.4. Amylopectin branch chain-length distribution

Branch chain length distribution of starch samples was measured by a fluorophore-assisted capillary electrophoresis (FACE, Beckman-Coulter, Brea, CA, SA) using the method reported elsewhere (Wu, Li, & Gilbert, 2014).

2.5. Particle size distribution

Particle size of starch spherulites and emulsions was measured by Mastersizer 2000 (Malvern Instruments Ltd., UK) following the method reported elsewhere (Wang, He, Huang, Fu, & Liu, 2013).

2.6. Microscopy

Light microscopy was performed on an Olympus BX-51 light microscope (Tokyo, Japan) under polarized light at 500× magnification. Images of starches were viewed with an EVO18 scanning electron microscope (SEM, Carl Zeiss, Germany).

2.7. X-ray diffraction

X-ray diffraction was conducted with a D/Max-200 X-ray diffractometer (Rigaku Denki Co. Ltd., Tokyo, Japan) (Wang et al., 2013).

2.8. Thermal properties

Differential scanning calorimetry (DSC) was analyzed with a differential scanning calorimeter (DSC 8000, Perkin-Elmer, Norwalk, CT, USA), following a published method (Zhang et al., 2014).

2.9. ^{1}H Nuclear magnetic resonance spectroscopy (NMR)

^{1}H NMR spectra were recorded on a Bruker 600 MHz (Bruker, Fallanden, Switzerland) at 30 °C with a pulse angle of 30°, a delay time of 10 s, and an acquisition time of 2 s. The degree of branching (DB) was calculated from the results of ^{1}H NMR using the integral measurements from the following peaks: α-1,6 linkages at approximately 4.75 ppm, α-1, 4 linkage was shown at 5.11 ppm (Bai & Shi, 2013; Tizzotti, Sweedman, Tang, Schaefer, & Gilbert, 2011).

$$DB = \frac{I_{\alpha-1,6}}{I_{\alpha-1,6} + I_{\alpha-1,4}} \times 100\%$$

Degree of substitution (DS) is the fraction of OS groups, identified using the proton signal of methyl protons in the OS group, approx. 0.85 ppm.

$$DS = \frac{I_{0.85}}{3(I_{\alpha-1,6+I_{\alpha-1,4}+I_{r-e}})}$$

where $I_{r\text{-}e}$ corresponds to the reducing chain ends. The DB values of native starch were around 3.0%, whereas the DB value of starch spherulites was about 0.02% (Table 1). It suggested that all of the α-1,6 branch linkages were completely hydrolyzed after debranching treatment.

2.10. Preparation and characterization of Pickering emulsions

2.10.1. Preparation of Pickering emulsions

OS starch spherulites were suspended in distilled water (2%, w/w), then orange oil (5%, w/w, based on the mass of OS-starch dispersion) and sodium benzoate (0.15%, w/w) were added, and homogenized at 150,000 rpm for 3 min using a high-speed homogenizer (FJ200-SH, Shanghai, China) to obtain an initial emulsion. To obtain the final emulsion, the initial emulsion was then passing through using a high pressure homogenizer (APV-1000, Denmark) at 300 bar, and sealed in a glass tube for the stability measurement at room temperature up to 60 days.

2.10.2. Confocal laser scanning microscopy (CLSM)

The Pickering emulsion (5 mL) was transferred into a centrifuge tube, and Nile red solution (0.01%, w/w, 15 μL) was added. The mixture was incubated in a shaker at room temperature for 3 h. A TCS SP5 CLSM equipped with an Argon ion laser (Leica, Wetzlar, Germany) was used for the detection of the fluorescence signal from the dye-stained starch granules. The Leica objective lens were 40×/1.25 oil, and excitation wavelength was set as 633 nm.