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Characterisations of oil-in-water Pickering emulsion stabilized hydrophobic phytoglycogen nanoparticles

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ABSTRACT

The medium-chain triacylglycerol (MCT)-in-water (O/W) Pickering emulsions were prepared using octenyl succinate phytoglycogen nanoparticles as stabilizer. The rheological properties and microstructure of emulsions with O/W ratio of 1 and 0.1 were investigated. All emulsions exhibited the typical pseudoplastic fluid characteristics at shear rates of 1–100 1/s. The modified phytoglycogen nanoparticles stabilized emulsions satisfied the Herschel-Bulkley rheological model. The increase of viscosity was pronounced at 5% of modified phytoglycogen nanoparticles and 50% of MCT fraction for emulsion preparation. The emulsion with high oil phase displayed G′ was higher than G″, and both G′ and G″ were independent of frequency, whereas G′ and G″ of low oil concentration emulsion showed ascending tendency with increasing frequency. Microstructure of emulsions revealed that the larger droplet size of O/W emulsion containing high oil phase with gel-like appearance was obtained, indicating that nanoparticles accumulated at the oil-water interface in the form of a barrier layer and a three-dimensional network had been formed. It was concluded that it is possible to employ modified phytoglycogen nanoparticles and high MCT content to produce food-grade Pickering emulsion with good long term stability.

1. Introduction

Phytoglycogen is a starch-related α-D-glucan in the endosperms of sugary-1 (su-1) mutants of maize, rice, sorghum or barley (Ball & Morell, 2003; Miao, Li, Jiang, Cui, Lu & Zhang, 2014; Powell et al., 2014). Different from starch, phytoglycogen is a water-dispersible amylopectin analogue with a more highly branched structure and does not show the semi-crystalline structure. For the starch biosynthesis pathway, the reactions for producing starch granules are co-ordinately catalysed by starch synthase, starch branching enzyme, and starch debranching enzyme (Fujita et al., 2012). The su-1 mutant endosperm cell is deficient in debranching enzyme, which is to trim abnormal branches that inhibit the formation of physically organized starch structure and solid particle, and the more highly branched phytoglycogen then accumulates to replace starch granules (Ball & Morell, 2003). It has been reported that the particle size of phytoglycogen is in the range of 30–100 nm (Putaux, Buléon, Borsali, & Chanzy, 1999; Wong et al., 2003). Also, phytoglycogen is made up both α-1,4 and α-1,6 linked glucose units with an average branch chain length of DP 10–12, and its branch density and molecular density is approximately 7–10% and 1000–2000 g/mol·nm^3, respectively (Huang & Yao, 2011; Inouchi, Glover, & Fuwa, 1987; Miao, Li, Jiang, Cui, Zhang & Jin, 2014; Yun & Matheson, 1993). Currently, phytoglycogen as a novel nanomaterial has received great interests for its biodegradability and functionality. Although several studies on the structure and properties of phytoglycogen have been conducted (Huang & Yao, 2011; Lu et al., 2016; Miao, Li, Huang, Ye, Jiang & Zhang, 2015; Miao et al., 2014; Powell et al., 2014; Ye, Miao, Lu, Jiang, & Cui, 2017; Yun & Matheson, 1993), little work has been reported for the modified phytoglycogen stabilized food-grade Pickering emulsion.

Emulsion is a mixture of two normally immiscible phases (oil and water) and plays a very important role in the formulation of food, cosmetics or pharmaceutical products. Emulsion is thermodynamically unstable and its preparation and stabilization is usually achieved by addition of small molecular surfactants, surface

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active biopolymers, including protein, polysaccharides and fat (Dickinson, 2012; McClements, 2005). Recently, Pickering emulsions stabilized by solid particles are of great practical interest because of their strong interfacial stability, eco-friendly and nontoxic (Chevalier & Bolzinger, 2013; Rayner, Timgren, Sjöö, & Dejmek, 2012; Timgren, Rayner, Sjöö, & Dejmek, 2011; Xiao, Li, & Huang, 2016). There have been considerable researches conducted on the solid particle-stabilizers, such as silica, wax, bentonite particle, chitin, cellulose nanocrystals (Binks & Rocher, 2009; Binks, Clint, & Whitby, 2005; Hu, Ballinger, Pelton, & Cranston, 2015; Midmore, 1999; Tzoumaki, Moschakis, Kiosseoglou, & Biliaderis, 2011), however, fairly few works were related with hydrophobic phytoglycogen nanoparticles. In this study, the hydrophobic nanoparticles were produced from su-1 maize phytoglycogen by octenyl succinic anhydride (OSA) modification and used as a nanoparticle stabilizer for Pickering emulsion. The rheological properties and microstructure of O/W emulsions using high and low oil phase content were also investigated by a combination of chemical and instrumental analysis, which would lead to helpful in development of novel nanoparticle stabilizer in the food and related industries for high quality emulsions.

2. Materials and methods

2.1. Materials

Su-1 maize kernels were purchased from the Chinese Academy of Agricultural Sciences (Beijing, China). Waxy maize starch was donated by Changchun Dacheng Industrial Group Co., Ltd. (Jilin, China). 2-Octen-1-ylsuccinic anhydride (OSA, 97%) was from Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). All other reagent-grade chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Preparation of phytoglycogen nanoparticles

The phytoglycogen nanoparticles were isolated from sugary-1 maize as described in a previous study (Miao et al., 2014). The sugary-1 maize endosperms were mixed with five times their weight of deionised water for overnight and then ground using a high-speed blender (SB102, Hangzhou Joyoung Co. Ltd., Zhejiang, China). The slurry was filtered through 100-mesh sieves and then centrifuged at 10,000 g for 10 min. Three volumes of ethanol were added to precipitate the soluble starch particle. After centrifugation and decanting for three cycles, the precipitate was collected and placed in a fume hood to remove the residual ethanol. The obtained material was soluble phytoglycogen nanoparticles. OSA was diluted in iso-propanol to a ratio of 1:5 (w/w) and added to an aqueous suspension of starch (30%, w/w) with agitation in 2 h at a level of 10% while the pH was maintained at 8.5 using 3% NaOH solution (Ye et al., 2014). After the reaction at 35 °C for 8 h, pH value was adjusted to 6.5 using 2.5 M HCl. The starch suspension was centrifuged at 3000 g and washed 3 times with distilled water and 3 times with ethanol. The collected material was hydrophobic phytoglycogen nanoparticles for further analysis.

2.3. Degree of substitution, particle size analysis and molecular weight of hydrophobic phytoglycogen nanoparticles

The degree of substitution (DS) was measured using the titration method as described in a previous study (Miao Li, Jiang, Cui & Zhang et al., 2014). DS was calculated using the following formula: $DS = \frac{0.162\times(A\times M)/W}{1-[0.210\times(A\times M)/W]}$, where A was the titration volume of NaOH solution, M was the molarity of NaOH solution, W was the dry weight of starch sample, 162 and 210 were the molecule weight of glucose unit and OS group, respectively. The zeta-potential and particle size distribution were obtained using a Zetasizer Nano ZS (Malvern Instruments Ltd., Malvern, UK). The starch sample (0.1%, w/v) was suspended in the distilled water before measurement. The weight-average molecular weight (Mw) was determined using the SEC-MALLS-RI methods of Miao et al. (2014) with a slight modification.

2.4. Solution observation

The starch sample was dissolved in distilled water with a concentration of 3% or 5% (w/v) at room temperature. The solution was stirred for 30 min and then was transferred to a glass tube. The appearance of solution was recorded using a digital camera (Canon, Shanghai, China).

2.5. Interfacial tension and contact angle measurements

The interfacial tension of oil-in-water (O/W) or air-in-water (A/W) system was done using a DCAT 21 automatic tensionmeter (DataPhysics Instruments GmbH, Germany). The measurement was carried out at 25 °C using the Wilhelmy plate method as reported by Ye et al. (2017). The contact angle analysis was conducted using an OCA15EC contact angle meter (DataPhysics Instruments GmbH, Germany) equipped with a video camera using sessile drop method.

2.6. Preparation of O/W pickering emulsion

The hydrophobic phytoglycogen nanoparticles were dispersed in deionised water in a concentration of 3% or 5% (w/w). Then the solution was mixed with different amounts of MCT under a given pH (7.0) using a high speed homogenizer (IKA T18 digital ULTRA-TURRAX®, IKA GmbH, Germany) at 18,000 rpm for 4 min.

2.7. Rheological measurement of emulsion

Rheological properties of emulsion stored for 1 d after preparation were determined using an AR-G2 rheometer (TA Instruments, New Castle, DE, USA) with a plate clamp (40 mm diameter, gap height 1 mm). The measurement temperature was kept at 25 °C using a circulating bath and a controlled Peltier system. The sample was continuously sheared from 0.1 to 10 1/s for the flow sweep testing. In order to determine the viscoelastic region, oscillation strain sweep experiment was measured in the oscillation strain ranging from 0.01 to 100% and the frequency was 1 Hz. The conditions of oscillation amplitude test were as follows: frequency 0.1–10 Hz and strain 0.2%. The storage modulus (G′) and loss modulus (G″) were calculated from the strain response.

2.8. Droplet size distribution of Pickering emulsion

The droplet size distribution of O/W emulsion was determined using a Microtrac S3500 particle size analyzer (Microtrac Inc., PA, USA). The instrument is composed of a tri-laser system of 658 nm wavelength for measuring the emulsion size distribution based on modified Mie theory. The refractive index of water and dispersed particles were 1.333 and 1.466, respectively. Droplet size measurement was reported as the volume-average droplet size (d_{43}).

2.9. Microscopy analysis of emulsion

The O/W emulsion stabilized using hydrophobic phytoglycogen nanoparticles was transferred to a glass tube and the appearance of emulsion was recorded using a digital camera (Canon, Shanghai,

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