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Effect of pH and ionic strength on the emulsifying properties of two Octenylsuccinate starches in comparison with gum Arabic

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ABSTRACT

Octenylsuccinate starches were obtained by combining esterification reaction and β-amylase hydrolysis treatment with (HOSE) and without (OSE) acid pretreatment. In the present study, the emulsions stabilized by gum Arabic (GA), OSE and HOSE starches were systematically compared in terms of molecular structure and emulsion properties. The molecular structure of three emulsifiers was analyzed using size exclusion chromatography, showing that the GA had a relative smaller molecular size distribution compared to OSE and HOSE starches. Emulsifying activity index (EAI), emulsifying stability index (ESI), droplet size ($d_{4,3}$) of emulsions at different emulsifier to oil ratios were determined to evaluate the emulsion properties of three emulsifiers under a wide range of pH and NaCl concentration. The GA stabilized emulsion showed the lowest droplet size at high emulsifier concentrations, but clear phase separation was observed after 7 days of storage at relatively low emulsifier concentrations (1:9 and 0.5:9.5). The emulsions stabilized by the HOSE starch showed excellent emulsion stability under a wide range of pH and NaCl concentration, and produced the small droplets with better storage stability, particularly at relatively low emulsifier concentrations (1:9 and 0.5:9.5).

1. Introduction

Emulsifier could stabilize an emulsion system with two immiscible liquids, normally containing both hydrophilic and hydrophobic groups, such as gum Arabic (GA) and hydrophobically modified starches. GA, one of the most widely used emulsifiers, could formulate cloud and flavor emulsions and prevent the oil droplets from aggregation, due to its high water solubility, low apparent viscosity and surface activity, as well as the ability to form a protective film around emulsion droplets (Sweedman, Hasjim, Tizzotti, Schäfer, & Gilbert, 2013; Given, 2009). However, high cost and limited sources of GA restrain the use in food and beverage industry, and it is required to find alternative emulsifiers such as chemically modified starches. Octenylsuccinic anhydride (OSA) modified starch has been identified as one of the most promising replacements for GA (Trubiano, 1995).

In the area of food and beverage applications, the emulsion stabilizer with low apparent viscosity is preferred, requiring less energy to flow during processing (Sweedman, Hasjim, Schäfer, & Gilbert, 2014). Acid or enzyme treatments with partial degradation on molecular size are the most commonly used methods to modify physicochemical properties of OS starches. Sweedman et al. (2014) modified OS starches by acid hydrolysis for stabilizing emulsion containing β-carotene. Our previous study has confirmed that the emulsions stability of OS starches can be enhanced by β-amylase hydrolysis (Xu, Huang, Fu, & Jane, 2015). The structural changes of OS starches hydrolyzed by β-amylase were also characterized, showing that β-amylase hydrolysis process could be stopped by either OS groups or α-1,6 glycosidic linkages, leading to an increase of both degree of substitution (DS) and degree of branching (DB) values (Bai, Kaufman, Wilson, & Shi, 2014; Sweedman et al., 2013; Xu et al., 2015).

In this work, we prepared OS starches with improved emulsion properties using combined acid and enzyme treatments, which have potential application in food and beverage industry. The aims

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of this study were to study effect of pH and NaCl concentration on the emulsifying properties of two OS starches in comparison with GA, and to find a novel emulsifier with a minimum concentration to stabilize emulsions.

2. Materials and methods

2.1. Materials

Waxy maize starch (moisture content, 14.6%) was provided by Cargill Co. (Minneapolis, MI, USA). GA was provided by Guangzhou Sunpart Food Co. (Guangzhou, China). 2-Octen-1-ylsuccinic anhydride was purchased from Vertellus Specialties Inc. (Nanjing, China). Food grade β-amylase was obtained from Novozymes Investment Co., Ltd (Wuxi, China), and its enzyme activity was 1230 U/g. One unit (U) is defined as the amount of enzyme that produces sufficient reducing sugars from a standard starch substrate to reduce 5 mL of Fehling's reagent. Brazil orange oil was purchased from Guangzhou Sunpart Food Science and Technology Development Co., Ltd (Guangzhou, China). Dimethyl sulfoxide (DMSO)-d_6 and trifluoroacetic acid (TFA)-d_1 were purchased from Sigma-Aldrich Pty. Ltd. (St Louis, MO, USA). Other chemical reagents were analytical grades.

2.2. OSA modified starch

Waxy maize starch (35%, w/v) was suspended in distilled water with agitation. A weighed quantity of OSA (3% of the dry starch basis, dsb) was added slowly within 1 h while maintaining the pH at 8.5. 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. The mixture was centrifuged and washed twice with distilled water and twice with ethanol. The OS starch was oven-dried at 40 °C for 24 h, and then passed through a 100-mesh nylon sieve (Wang et al., 2013).

2.3. OSA modified starch with acid hydrolysis pretreatment (HOS starch)

Waxy maize starch (35%, w/v) was suspended in deionized water with agitation. Various amounts of HCl solution (0.2 M) were added to the starch slurry in order to make different acidic conditions (i.e., pH 1.70, 1.35, 1.20 and 1.00, respectively). The slurry was heated in a 55 °C water bath for 1 h, and finally washed with distilled water for three times. The hydrolyzed starch samples were oven-dried at 45 °C overnight, then passed through a 100-mesh nylon sieve. The degree of hydrolysis was determined using the phenol-sulfuric acid method (Huang, Xie, Chen, Lu, & Tong, 2008). The hydrolyzed starch was modified with OSA (3% of the dry starch basis) as described above.

2.4. Apparent viscosity measurement

Acid hydrolyzed starch (20%, w/v) was suspended in deionized water, and then heated in a boiling water bath for 30 min with agitation. It was then cooled down to room temperature, and its apparent viscosity was analyzed at room temperature using a Brookfield viscometer (Massachusetts, USA) at a shear rate of 7.9 S^{-1}. The apparent viscosity of three emulsifiers (OSE and HOSE starches, GA, 12%, w/v) was analyzed at room temperature using Brookfield viscometer at a shear rate of 20.4 S^{-1}.

2.5. β-Amylase hydrolysis of starches

Enzyme treatment of OS and HOS starches were carried out following the method described by Xu et al. (2015). OS and HOS starch slurry (10% w/v) was adjusted to pH 5.5 with 0.1 M HCl solution, then heated in a 120 °C oil bath for 1 h. After cooling to 57 °C, various amounts of β-amylase were added (OS starch, 12.3 U/g, dsb; HOS starch, 6.2 U/g, dsb), and the mixture was incubated at 57 °C for 24 h followed by a heating step in a boiling water bath for 30 min to denature the enzyme. The resulting solution was frozen by liquid nitrogen immediately and freeze-dried. Thus the following emulsifiers were obtained: OSE starch, OS starch treated with β-amylase (12.3 U/g, dsb); HOSE starch, HOS starch treated with β-amylase (6.2 U/g, dsb).

2.6. Molecular size distribution

OS starches and GA (15 mg) were dissolved in DMSO (4 mL) by stirring at room temperature for 12 h, and then precipitated with ethanol followed by a centrifuged at 5000 *g* for 15 min. The precipitated starch was dissolved in 5 mL of hot water by heating in a boiling water bath for 30 min, and then filtered through a 1 μm filter (Millipore, Bedford, MA). The molecular size distribution of samples was determined using a size exclusion chromatography (SEC, Agilent Co., USA) equipped with a KS-803 column (8 mm × 300 mm, Shodex, Tokyo, Japan), an Agilent 1260 ISO pump (Agilent Co., USA) and an Agilent 1260 Refractive Index Detector (Agilent Co., USA). Samples were eluted through columns with distilled water at a flow rate of 1.0 mL/min. The columns were held at 70 °C, and the injection volume was 20 μL. The average molecular weight was calculated using a standard curve given in Fig. 2 (Xu et al., 2015).

2.7. Preparation and physicochemical properties of emulsions

2.7.1. Emulsions preparation

The emulsions were prepared with emulsifier and orange oil at various mass ratios (5:5, 3:7, 1.5:8.5, 1:9, and 0.5:9.5). The emulsifier was dispersed in deionized water and kept stirring for 2 h in a water bath at 70 °C, and then stored overnight to allow a complete hydration of molecules. The pH of the dispersions was adjusted to 6.0. Orange oil and sodium benzoate (0.15%, w/w) were added, and then the mixture was homogenized at 16,000 rpm for 3 min to obtain an initial emulsion. The mixed emulsion was then passing through a single-pass laboratory-scale jet homogenizer at 300 bar at room temperature to obtain a final emulsion. The final emulsion was sealed in a glass bottle, and stored at room temperature for 45 days for the stability measurement (Xu et al., 2015).

2.7.2. Emulsifying activity index (EAI) and emulsifying stability index (ESI)

The EAI and ESI values of emulsifiers were determined following a method described elsewhere (Pearce & Kinsella, 1978; Tan, Mailer, Blanchard, & Agboola, 2014). Emulsion (100 μL) was prepared using the method described in section 2.8.1 with the emulsifier to oil ratio at 2:1. The emulsion was diluted 500 times with sodium dodecyl sulfate solution (0.1%, w/w), and measured by a UV–Vis spectrophotometer at 500 nm. The EAI and ESI values were obtained using the following equations.

$$EAI = \frac{2 \times 2.303 \times A_0 \times DF}{\rho\varphi(1-\theta) \times 1000}$$

$$ESI = \frac{A_0}{A_0 - A_{10}}$$

where A_0 and A_{10} are observed absorbance of 0 min and 10 min; *DF*

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