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Particle-stabilizers modified from *indica* rice starches differing in amylose content

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ABSTRACT

Octenyl succinic anhydride (OSA) starches were prepared from four cultivars of native *indica* rice starches with amylose contents of 1.90%, 18.01%, 25.40% and 26.98% (w/w). The emulsion stability and microstructure of the oil-in-water Pickering emulsions (soybean oil/water, 1/2, v/v) stabilized by OSA starch particles were investigated. Results indicated that the average droplet sizes of the emulsions were in the range of 10–70 μm, depending on starch cultivars. During 100 days of storage, the emulsions made from OSA starches (degree of substitution: 0.0287–0.0294) were stable. Optical microscopy showed that starch particles were accumulated at the oil–water interface in the form of a densely packed layer, which prevented the flocculation and coalescence of oil droplets by a steric mechanism. Moreover, the emulsification of particle-stabilizers was positively correlated with degree of substitution ($P < 0.01$) but had no obvious correlation with amylose content and pasting properties.

1. Introduction

Pickering emulsion is an emulsion that is stabilized by solid particles, which are adsorbed onto the interface between the oil and water phases. This type of emulsion was named after Pickering's publication over a century ago (Pickering, 1907), although the effect was first recognised by Ramsden (1903). The solid particles were called particle-stabilizers, which have been used widely in cosmetics, personal products, and some foods (Lee, Chan, & Mohraz, 2012). Compared with the traditional stabilizers, particle stabilizers have the advantages of strong interfacial stability, non-toxicity, eco-friendliness and low cost (Yu, Lin, & Li, 2013).

The common particle-stabilizers used for Pickering emulsions are silica, wax, chitin, clay particles, and boehmite alumina, etc. (Binks & Rocher, 2009; Chen et al., 2011; Gao et al., 2009; Tzoumaki, Moschakis, Kiosseoglou, & Biliaderis, 2011). Although there have been many studies conducted on particle-stabilizers, fairly few are directly related to food (Dickinson, 2012). In food products, natural and processed lipids are frequently used in the form of emulsions. Some examples of food Pickering emulsions are homogenised and reconstituted milks (stabilized by casein micelles), margarines and fat spreads (stabilized by triglyceride crystals) (Hunter, Pugh, Franks, & Jameson, 2008). However, apart from high fat spreads, the majority of food emulsions are in the oil-in-water form (O/W). Some potentially food-compatible particle-stabilizers that have been used in O/W Pickering emulsions include cellulose (Wege, Kim, Paunov, Zhong, & Velev, 2008), chitin (Tzoumaki et al., 2011), flavonoids (Luo et al., 2012), and fat crystals (Rousseau, 2013). Recent research has shown that the hydrophobic modified starch with small granule size and regular shape could be used as particles to stabilize oil-in-water emulsions (Marku, Wahlgren, Rayner, Sjöö, & Timgren, 2012; Tan et al., 2012; Timgrena, Rayner, Sjööa, & Dejmek, 2011; Yusoff & Murray, 2011). Moreover, Kargar, Fayazmanesh, Alavi, Spyropoulos, and Norton (2012) reported that microcrystalline cellulose and modified starch could be used as particle stabilizers in oil-in-water emulsions to reduce the oxidation rate of sunflower oil.

Starch is an accepted food ingredient and pharmaceutical excipient. The starch granule is abundant, inexpensive, and can be obtained from natural sources. However, the native starch granule is not naturally hydrophobic, and thereby generally not suitable to be adsorbed into the oil–water interface. Starch granules can be hydrophobically modified to stabilize O/W emulsions if they

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Abbreviations: AC, amylose content; BDV, breakdown viscosity; CPV, cool paste viscosity; DS, degree of substitution; D_{50}, median particle diameter; D_{av}, average particle size; D_{90}, 90% v/v particles are less than this size; D_{starch}, the particle size of starch granule; ES, emulsion stability; HPV, hot paste viscosity; OSA, octenyl succinic anhydride; PKV, peak viscosity; PT, peak temperature; RVA, rapid visco analyzer.

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remain intact and are predominantly wetted by the aqueous phase. Our previous study indicated that the rice starch had no change on the crystalline pattern and granule structure but slightly rough surfaces after octenyl succinic anhydride (OSA) modification in the aqueous slurry systems (He, Song, Ruan, & Chen, 2006; Song, He, Ruan, & Chen, 2006). Rice is one of the primary dietary sources of carbohydrates worldwide. Rice starch consists of tiny granules (⩽5 μm) with a narrow size distribution. Rice starch is white in colour and has a neutral odour, making it an ideal material for preparing particle stabilizers. However, no works have been reported on the preparation and properties of particle-stabilizers from rice starch.

In this study, the hydrophobic starch particles were created from *indica* rice starches with different amylose contents (AC) by OSA modification in aqueous slurry systems. *Indica* rice is largely planted in southern China (Sun, Wang, Liu, & Zhao, 2013), but its inferior eating and cooking qualities lead it to a lower price (He, Song, Ruan, & Chen, 2006). So *indica* rice could be a cheap alternative starch source for use in food products on the commercial scale. The physical properties (pasting properties and particle size) of the starch particles and emulsifying properties (emulsion stability and microstructure) of the soybean oil-in-water emulsions stabilized by hydrophobic rice starch particles were investigated using a rapid visco analyzer (RVA), a laser particle size analyzer and an optical microscope. This investigation is very important for the development of new starch-based particle stabilizers in the food and related industries.

2. Materials and methods

2.1. Materials

The *indica* rice used in this study were Te-nuo 2072 (TN), Te-you 2035 (TY), II-you 838 (IIY) and Gang-you 188 (GY), which were kindly provided by Xinyang Institute of Agricultural Sciences (Henan Province, China). OSA was purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). All other reagents were of analytical grade. Edible soybean oil was purchased from Yihai Kerry Investment Co., Ltd. (Shanghai, China).

2.2. Starch separation

Rice starch was separated by the traditional alkali method (Dias, Zavareze, Spier, Castro, & Gutkoski, 2010; He, Song, Ruan, & Chen, 2006). Moisture content of samples was determined by air–oven methods. The amylose content of rice flour was determined according to the iodine-binding method (Morrison & Laignelet, 1983).

2.3. OSA starch particle preparation

30 g of rice starch was mixed with 70 mL distilled water. Different amounts of OSA, from 3.0% to 7.0% (in proportion to starch, w/w), were slowly added over 2 h. The starch slurry was adjusted to pH 8.5 during the reaction using NaOH solution. The esterification lasted for 5 h at 35 °C. The pH of the slurry was finally adjusted to 6.5 using HCl solution. The slurry was washed with distilled water followed by alcohol/water (70:100, v/v), respectively. The deposition was dried at 45 °C for 24 h, and then passed through a 120-mesh sieve (125 μm opening).

2.4. Degree of substitution measurement

A titration method was used to calculate the degree of substitution (DS) of OSA modified starch (Song et al., 2006; Sweedmana, Tizzotti, Schäferb, & Gilbert, 2013). OSA starch (5 g, dry weight) was dispersed in 25 mL of 2.5 mol/L HCl-isopropyl alcohol solutions and then stirred for 30 min. A total of 100 mL 90% isopropyl alcohol solution (in proportion to water, v/v) was added to the suspension, followed by stirring for an additional 10 min. The suspension was filtered through a glass-filter and the residue was washed with 90% isopropyl alcohol solution until no Cl^- was detected (using 0.1 mol/L $AgNO_3$ solution). The residue was re-dispersed in 300 mL distilled water, and then the dispersion was cooked in a boiling water-bath for 20 min. The starch solution was titrated with 0.1 mol/L standard NaOH solution, using phenolphthalein as an indicator. A blank titration of the native starch was simultaneously performed as a control. DS was calculated by the following equation:

$$DS = \frac{0.162 \times (A \times M)/W}{1 - [0.210 \times (A \times M)/W]} \tag{1}$$

where A is the titration volume of standard NaOH solution, mL; M is the molarity of standard NaOH solution, mol/L, and W is the dry weight of OSA modified starch, g.

2.5. Pasting properties

The pasting properties of native starch and OSA starch were determined using a super 4D RVA (Newport Scientific Instruments, Warriewood, Australia). Starch (3.0 g) was suspended in 25 mL distilled water. The analysis was based on the American Association of Cereal Chemists (AACC) approved method 61-02.01 (1999). Each sample was held at 50 °C for 1 min, heated to 95 °C in 3.75 min, held at 95 °C for 2.5 min, cooled to 50 °C in 3.85 min and then held at 50 °C for 1.4 min. The rapid visco analyzer (RVA) parameters of peak viscosity (PKV), hot paste viscosity (HPV), cool paste viscosity (CPV), breakdown viscosity (BDV), and peak temperature (PT) were determined.

2.6. Emulsion preparation

Starch (3.0 g, dry weight) was suspended in 100 mL distilled water in a 250 mL glass beaker. After that, the starch suspension was mixed with 50 mL soybean oil using a high speed homogenizer (IKA T18, IKA-Werke GmbH & Co., KG, Germany) at 11,000 r/min for 2 min with 20 s intervals. A 25 mL emulsion was placed in a sealed glass test tube. Storage stability was determined as the volume of cream stored for 1 h, 6 h, 1, 2, 5, 35 and 100 d at room temperature (25 °C). At the same time, another 25 mL of the emulsion was placed in a colorimetric tube, and then a photograph was taken after storage at room temperature for 100 days using a digital camera (Digital Ixus 115 HS, Canon, Japan).

2.7. Microstructure of the emulsions

The emulsions were left for two days at room temperature. Iodine solution (0.2 g iodine and 2.0 g potassium iodide were dissolved in 100 mL distilled water) was used to stain the starch granules. A small drop of emulsion was place in a microscope slide with cavity. After being stained, the droplet images of the O/W emulsions stabilized by starch particles were captured by optical microscopy (Eclipse 80i, Nikon Instruments Inc., Japan) fitted with a digital sight (DS-Fi1, Nikon Instruments Inc., Japan). Micrographs of each sample were taken at 10× and 100× magnifications, respectively.