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Pickering emulsions stabilized by compound modified areca taro (*Colocasia esculenta* (L.) Schott) starch with ball-milling and OSA

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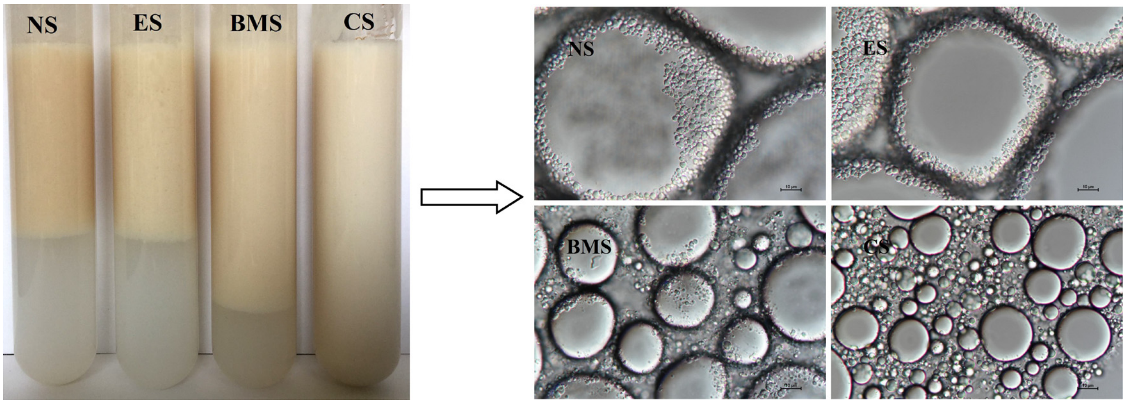
GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this study was to compare the emulsifying capacity and stability of soybean oil-in-water (O/W) Pickering emulsions stabilized by different areca taro starches (native starch, OSA esterified starch, ball-milled starch, and compound modified starch with ball-milling and OSA), and investigate the stability mechanism of Pickering emulsions. It was found that the compound modified starch showed strong surface activity and high emulsion viscosity, resulted in the best emulsifying capacity and stability. It could be clearly seen that the starch particles adsorbed at the oil-water interface of droplets to form physical barriers, and the upper and middle emulsion phases were uniform and stable after storage for 30 d. Thus, the ball-milling combined with OSA modification can be used as a viable and effective method to produce better starch-based particle emulsifiers.

1. Introduction

Conventional emulsions are usually stabilized by surfactants. Solid particle stabilized emulsions, called Pickering emulsions [1], have attracted extensive research interest due to their unique properties and potential technological applications [2]. Since the kinetic energy of collision between droplets is usually insufficient to desorb the particles once adsorbed at the oil-water interface, Pickering emulsions exhibit long-term stability against coalescence and Ostwald ripening compared to conventional emulsions [3,4].

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Although Pickering emulsions have been reported for over a century, systemic researches have mainly been in the last twenty years [5]. Inorganic solid particles are main materials to stabilize the emulsion, such as: silica [6], Laponite [7], montmorillonite [8], etc. In view of the safety of application in food industry, some natural food-grade particle stabilizers have been widely used in O/W Pickering emulsions, including starch [9], cellulose [10], protein [11], chitosan [12] and chitin [13]. Specifically, starch has been focused as a natural emulsifier in recent years due to the favorable characteristics of nontoxicity, biodegradability, biocompatibility and less environmental impact [14]. Representative starches are quinoa starch [9] and waxy maize starch [15]. Areca taro (*Colocasia esculenta* (L.) Schott), a root crop of the araceae family, is mainly planted in the tropical and subtropical regions [16]. Areca taro has a high starch content, accounting for about 85% of the total dry matter [17]. Areca taro starch particles are very small (1–5 μm in diameter), which is a good material for processing particle emulsifiers [17]. However, native starch particles generally cannot be used as Pickering stabilizers or at the best, stabilized emulsions with low efficiency, due to their strong hydrophilic properties [15].

The esterification with octenyl succinic anhydride (OSA) introduces hydrophilic carboxylic acid groups and hydrophobic long alkenyl chains, which endows starch with amphiphilicity, thereby increasing its surface activity [18]. OSA esterified starch has better emulsifying capacity and can increase emulsion viscosity and stability, so it is widely used in food, pharmaceutical and other fields [9,19,20]. Since native starch has a close crystalline structure, the esterification reaction occurs mainly on the surface of starch particles, making the degree of substitution lower [21]. Therefore, it is necessary to choose auxiliary means to change the crystalline structure or reduce the size of the crystalline region to increase the contact area of starch with OSA reagents. Ball-milling is a safe and economical physical method and is broadly applied in food production [22]. When the starch is modified by ball-milling, the starch particle and crystalline structure are severely damaged under the action of combined friction, collision and shear resulting from the grinding balls and the container wall [23]. The internal structure of the particles becomes loose and the molecular chains break, resulting in more exposure of hydroxyl groups to the reagent and an increase in solubility, which promotes the chemical activity and accelerates the reaction efficiency [24].

The ball-milling treatment can break the starch particles and reduce its size. OSA esterification modification can improve the amphiphilicity of starch. The objective of this work was to combine ball-milling with OSA esterification modification to improve emulsifying ability by possible synergistic effect. Refined soybean oil was used as the oil phase. Pickering emulsions were stabilized by native and three modified areca taro starch particles. The three modified starches were OSA esterified starch, ball-milled starch and compound modified starch with ball-milling and OSA, respectively. In order to evaluate the emulsifying capacity and stability, the appearance, emulsification index, droplet size and microstructure of emulsions were investigated. Furthermore, the stability mechanism of emulsion was explored. This study provides a new approach for processing particle emulsifier, which is beneficial to the development and application of food-grade Pickering emulsions.

2. Materials and methods

2.1. Materials

Native starch (NS) was isolated from areca taro (Fuding, China) by water extraction using the method described by Jiang et al. [25]. The esterified starch (ES) was prepared by mixing 35% (W/W) starch milk with 3% (based on the weight of starch, W/W) OSA at 35 °C, pH 8.0 and reacted for 4 h with constant stirring [26]. The ball-milled starch (BMS) was prepared by adding native starch to a mill pot at a ball ratio of 3:1, and then milled with a planetary ball mill (QM-3SP04, Nanjing University Instrument Plant, Nanjing, China) at 420 rpm for 5 h [23]. The ball-milled combined with OSA esterified starch, i.e., compound modified starch (CS), was prepared through the same method as ES except that 10% (W/W) BMS milk was used instead of 35% (W/W) native starch milk.

Table 1
DS of different modified starch samples.

Sample	*DS*
ES	0.01756 ± 0.00009b
CS	0.01994 ± 0.00015a

Data expressed as the mean ± SD (n = 3). Means in the same column with different letters are significantly different ($p < 0.05$).

Food-grade refined first-grade soybean oil was purchased from Darunfa Supermarket (Fuzhou, China). The 2-octen-1-ylsuccinic anhydride (OSA) was purchased from Sigma-Aldrich Chemical Co. (Saint Louis, MO, USA). The Nile Red (AR) was obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The Nile Blue (AR) was obtained from Alfa Aesar (Heysham, UK). Hydrochloric acid (AR), sodium hydroxide(AR), and sodium azide (NaN_3, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.2. Determination of degree of substitution (DS)

The DS of ES and CS were determined according to the procedure described by Królikowska et al. [27]. The DS was calculated using the following Eq. (1):

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

where A is the volume of NaOH solution consumed during titration (mL), M is the molarity of NaOH solution (mol/L), W is the dry weight of the starch sample (g), 0.210 is the millimolar weight of octenyl succinyl group (g/mmol), and 0.162 is the millimolar weight of per anhydroglucose unit (g/mmol).

2.3. Scanning electron microscopy (SEM)

The morphologies of starch samples were observed using a scanning electron microscopy (Phenom ProX, Phenom-World B.V., Eindhoven, Netherlands) with magnification of 20,000 ×. An accelerating voltage of 15 kV was used during imaging [28].

2.4. X-ray diffraction (XRD)

XRD patterns of the starches were measured using an X-ray diffractometer (Ultima IV, Rigaku Corporation, Tokyo, Japan) with Cu-Kα radiation at 40 kV and 40 mA [29]. The scanning range of diffraction angle (2θ) was from 5° to 35° with step intervals of 0.02° and a scanning rate of 6°/min. The relative crystallinity (%) was calculated using the MDI Jade 6.0 software (Materials Data Inc., Livermore, California, USA) according to the method of Nara et al [30].

2.5. Determination of surface tension

A series of different contents (0.1%, 0.5%, 1.0%, 2.0% and 3.0%, W/W) of NS, ES, BMS and CS dispersions were prepared using a high speed homogenizer (IKA T25 digital ULTRA-TURRAX®, IKA GmbH, Staufen, Germany) at 20,000 rpm for 1 min, and then cooled to 25 ± 0.1 °C. The surface tension of various starch dispersions was measured by the Wilhelmy plate method using an automatic surface/interfacial tensiometer (BZY-1, Shanghai Hengping Instrument and Meter Factory, Shanghai, China). The platinum plate was rinsed with distilled water, then burnt by a blue flame and left to cool before each measurement [20].