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Physical stabilities of taro starch nanoparticles stabilized Pickering emulsions and the potential application of encapsulated tea polyphenols

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ABSTRACT

In this research, Pickering emulsion stabilized by taro starch nanoparticles was successfully prepared, and the potential application of encapsulating tea polyphenols was investigated. The nanoparticle size (about 460 nm) and contact angle (81.5°) of taro starch indicate that it is suitable for adsorbing on the oil-water interface and forming a dense interfacial layer. Emulsion stability at different particle concentrations, oil-water ratios, and sodium chloride concentrations has been systematically studied. By considering the particle size, zeta potential, and stability index of Pickering emulsion, it is considered that the emulsion has the best stability when the particle concentration is 7% and the oil fraction is 0.5. Low concentration of salt ions (0.04 mM NaCl) will cause a slight flocculation to improve the stability, but adding high concentration of salt will make emulsion break. In addition, we found that this Pickering emulsion could encapsulate the tea polyphenols greatly with a retention rate of up to 67%. The findings may have great significance for the design and fabrication of native starch particle stabilized emulsion.

1. Introduction

Solid particles of nanoscale and microscale dimensions as novel natural macromolecules, replaced emulsifier to fabricate Pickering emulsion. Different from the traditional emulsion, Pickering emulsion stabilized solely by colloidal particles. In 1903, Walter Ramsden first recognized this effect [1], and in 1907, Pickering first published observations of this phenomenon [2]. Suitable size and contact angle of particles are two key factors of stabilizing the Pickering emulsion. The suitable contact angle makes it possible for the particles to adsorb on the oil-water interface. Particles that are too hydrophilic or hydrophobic can cause excessive wetting in a phase, which does not conducive to the formation of a uniform and stable emulsion. The proper particle size can make the emulsion system have a great desorption energy. According to the energy for detachment (ΔE) [3], it has been confirmed that solid particles of nanoscale and microscale dimensions stabilized Pickering emulsion can be stable for months. Compared with conventional emulsions stabilized with surfactants, Pickering emulsions show great stability against creaming and coalescence due to its unique stability mechanism [4]. For emulsions with densely packed particle surfaces, adjacent particle layers enter physical contact due to an irreversible absorption process, but remain separated on the oil-water interface [5].

Many fundamental studies have used macromolecular as particle-stabilizer. Protein is kind of biomacromolecules in the food. Marie Chevallier et al. provided a possible solution to the heat stability of whey protein emulsions by using whey proteins previously aggregated [6]. Jie Xiao et al. fabricated kafirin into spherical nanoparticles and studied tunable interface structure [7]. Insoluble polysaccharide is also a natural macromolecule suitable for stabilizing the Pickering emulsion. Negar Kasiri and Milad Fathi extracted pistachio cellulose with acid hydrolysis and use it to fabricate stable emulsion against heating and stresses. It provided a novel practical application of agro-waste source [8]. Li et al. studied the stability and mechanism of O/W Pickering emulsions stabilized by regenerated cellulose [9]. Due to the aggregation and formation of the three-dimensional structure of the cellulose particles, the oil-water interfacial film is enhanced. Starch is one of the most commonly used macromolecular carbohydrates in the food industry and human diet. Many experiments have shown that polysaccharides have the effect of improving human health [10, 11]. Hisfazilah Saari et al. used waxy maize small particles modified with octenyl succinic anhydride to produce the Pickering emulsion [12]. Small emulsion droplet increased stability against creaming. Ali Marefati et al. constructed Pickering emulsion stabilized with quinoa starch and encapsulated curcumin to explore the effectiveness for delivering bioactive substances [13].

The good biocompatibility of starch makes it widely applied. In the food field, starch-rich food materials are commonly used in baking, candy, condiments, dairy products and other fields [14]. Starch is a

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promising biomaterial who has a wide range of sources, low cost, and a wide range of applications. There are many studies have reported physical or chemical modification starch stabilized Pickering emulsions. OSA modification is a recognizable chemical method to increase the hydrophobicity of starch particles [15, 16]. Moreover, milling is a familiar physical method to decrease the size of starch particles [17, 18]. Characteristic of native taro starch show that it is suitable for preparing Pickering emulsion. Taro starch is the most abundant ingredient in dry-base of taro. The *Colocasia esculenta* (L.) Schott, also known as taro, is a perennial monocotyledonous herbaceous wet plant of the genus Colanasia Schott of the family Araceae. It is widely distributed in the tropical and subtropical regions of Asia and Oceania. It is one of the world's largest food crops and economic crops that integrates edible, medicinal and ornamental values. Starch is easily prepared into colloidal particles as it can be partially wetting by the aqueous and oil phases without being completely dissolved in each phase. The native taro starch has a relatively small particle size range after milling, which provides a possibility for densely adsorption at the oil-water interface. Taro is a unique agricultural product in Zhejiang Province of China with high yields but a single application. Most taro are limited to cooking. We chose taro starch as the research object, which can easily obtain a large amount of raw materials and at the same time develop the application value of taro.

After exploring the physical stability of taro starch particles-stabilized Pickering emulsion, we predicted the possibility of embedding functional factors. Nanotechnology provides a new way for the delivery of nutrients in foods [19]. Pickering emulsion is one of the important methods. Tea polyphenols have great physiological activities, but oral catechins have very low bioavailability [20]. The sensitivity of catechins to the digestive environment, low intestinal transport efficiency, and rapid metabolism and clearance of catechins in the body is some reason that caused this phenomenon. The catechins are not stable in the digestive environment and can be degraded or form polymers of varying degrees. In terms of the bioavailability of phenolic compounds, monomers have a higher absorption rate than polymers. The formation of polymers during the digestion process limits the physiology of catechins. If the proper food matrix is selected, the effect of the small intestine environment on catechins can be reduced, thereby improving their in vivo digestive recovery and absorption in the small intestine. In starch-based food systems, the addition of tea polyphenols can also delay starch digestion and slow glucose absorption by inhibiting the activity of digestive enzymes. Therefore, if the tea polyphenols and starches are used together, the post-prandial blood glucose response may be delayed. Therefore, we chose tea polyphenols to encapsulate Pickering emulsion.

In this article, taro starch is extracted by sodium hydroxide soaking method. We investigate the particle size, morphology, and wettability of taro starch to determine if it is suitable for stabilize emulsion. Pickering emulsion with water-MCT and taro starch fabricated by high-speed shear homogenization. Optical microscopy, particle size analysis, ζ-potential and the stability index were used to characterize the emulsions. We systematically studied the effects of particle concentration, oil-water ratio, and sodium chloride concentration on the stability of the emulsion. A detailed explanation is provided for the mechanism of starch stabilization for Pickering emulsion. In addition, we tried to encapsulate functional factors in Pickering Emulsion to predict its potential for controlled release delivery.

2. Material and methods

2.1. Materials

Taro roots are purchased from Lianhua Supermarket (Hangzhou, China). According to the manufacturer, the producing area of taro is in Fenghua district, part of Ningbo City, Zhejiang Province. Medium chain triglyceride (MCT) was obtained from KLK Oleo, Ltd. (Malaysia), which contains 58 wt% C8 fatty acid and 42 wt% C10 fatty acid, and has a relative density of 0.95 g/ml. Tea polyphenols, Na_2SO_3, ascorbic acid and NaOH were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium chloride was purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). All other chemicals were of analytical grade. Deionized water is used for preparing all solutions. All experiments were performed at a constant temperature of 25 °C.

2.2. Extraction of taro starch

Taro blocks were peeled and cut into $3cm^3$ blocks. The taro blocks were soaked in 0.01% sodium hydroxide solution for 4 h, 0.02% sodium sulfite and 0.01% ascorbic acid was added in advance. The mixture was ground for 3 min using a plant tissue breaker (JYL-Y20, Joyoung Co., Ltd.) and then break it for 5 min using a colloid mill (Hundom technology Corp., China). The mixture was left standing at 20 °C for 6 h. The liquid mixture was passed through an 80-mesh sieve and the filtered liquid to stand for 4 h. The filtered liquid was passed through a 260-mesh sieve for further screening taro starch. The filtered liquid was centrifuge by centrifuged separator (L535R, Cence Corp., Changsha, China) at 10000 rpm 15 min. The supernatant was discarded and the precipitate was washed twice with deionized water. The precipitate was dried at 45 °C for 24 h in drying oven (GZX-9146 MBE, Boxun medical biological instrument corp., Shanghai, China). Extracted taro starch was broke up by a grinder (Xuzhong Machinery Equipment Co., Ltd. Hangzhou, China).

2.3. Characterization of taro particles

Starch particle size distribution measured by dynamic light scattering particle size analyzer (Brookhaven instrument Corp., New York, NY). 1 g starch was dispersed in 100 ml deionized water. Measurements were made at a fixed scattering angle of 90°at 25.0 ± 1.0 °C. The morphology of starch particles was investigated by scanning electron (SEM). Spray a little amount of starch on the plate, the system was covered by gold before measurement. A scanning electron microscope (SU810, Hitachi, Ltd., Japan) was used at a high voltage (3.0 kV) with working distance of 9 mm to capture the morphology of native starch granules. To verify the wettability of taro starch particles between water and MCT, the water-in-air contact angle of starch film was measured by an OCA50AF optical contact angle measuring device (Data Physics Instrument. Germany). Taro starch is laminated into a circular flake by tableting press at 10 metric tons. Then the starch flakes stick to a glass slides. Slide placed on the instrument's measurement platform. Water dripping by the electric injection system, and capture the contact angle image by CDD camera timely. Repeat measurements ten times on average.

2.4. Preparation of emulsions

Pickering emulsions (total volume 10 ml) with different starch concentration (3%, 5%, 7%, 9%), were prepared by mixing taro starch particle suspensions with various oil fractions ø (0.3, 0.4, 0.5, 0.6) in a glass vial. Sodium chloride with different concentration (0, 0.02, 0.04, 0.06 mM) was added in a continuous phase and then prepared emulsion. Then Mixtures homogenized by using a high-speed homogenizer (IKA-ULTRATURRAX T10 basic, IKA, Inc., Germany) with an 8 mm dispersion probe at 12,000 rpm for 2 min.

2.5. Emulsion particle size distribution

The droplet size distribution was measured by dynamic light scattering particle size analyzer (Brookhaven instrument Corp., New York, NY). Measurements were made at a fixed backscattering angle at 25.0 ± 1.0 °C. Duration set was 2 min, and equilibration time was 1 min. The Refractive index of water was 1.530, MCT was 1.452, and

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