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Freezing and freeze-drying of Pickering emulsions stabilized by starch granules

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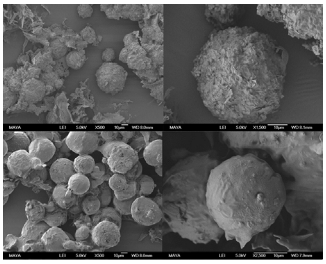
HIGHLIGHTS

- Oil powders with 80% oil were produced from starch granule stabilized emulsions by freeze-drying.
- The oil powders could be reconstituted to stable emulsions.
- Partial gelatinization of starch increased freeze-drying stability of emulsions.
- Dispersed phase melting point affected freeze-drying stability of the emulsions.
- Different freezing methods imposed different changes on stability of the droplets.

GRAPHICAL ABSTRACT

Oil containing powders can be produced with relatively high oil content (80%) from starch granule stabilized Pickering emulsions where adsorption and partial gelatinization of starch granules at the oil–water interface protects the integrity of droplets during freezing and freeze-drying.



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ABSTRACT

The aim of this study was to investigate the possibility to produce novel powder materials based on chemically modified starch granule stabilized Pickering oil-in-water (O/W) emulsions. This study also investigated the effect of partial starch gelatinization *in situ*, dispersed phase type (two oil types with different melting points), freezing method and thawing, and freeze-drying and rehydrating on the overall properties of the emulsions. The emulsions showed high freeze–thaw stability. The results of this study demonstrated the feasibility of the production of oil containing hydrocolloid-based powders, through combination of heat treated or even non-heat treated starch Pickering emulsions and freeze-drying. The final powders comprised high weight percentage of oil (over 80%, w/w). Upon rehydration of powders, the starch stabilized oil drops were found to be only moderately affected by the process with some aggregation observed.

1. Introduction

Emulsions are mixtures of two immiscible liquid phases where one is dispersed in the other as spherical droplets. These systems are not thermodynamically stable, thus stabilizers are required to prolong their stability [1]. Surfactants, proteins and hydrocolloids are the main types of stabilizers in food emulsion systems [2] and function by enhancing droplet stability by lowering the interfacial tension, increasing steric hindrance, and/or electrostatic repulsion between droplets [3]. In Pickering emulsions, solid particles stabilize emulsions by being essentially irreversibly adsorbed at the oil–water interface, creating a thick physical/mechanical barrier [4]. Pickering emulsions demonstrate long-term stability [5–7]. Starch granules have been shown suitable for Pickering type stabilization after chemical modification with octenyl succinic anhydride (OSA) to adjust their wetting behaviour [8]. Previously, emulsions stabilized by quinoa starch granules were found to remain stable over a two-year storage period with no phase separation or change in droplet size [9]. Depending on the botanical

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source, starch granules vary in size, shape and composition. For Pickering emulsions, small and uni-modal granules such as quinoa starch were found preferable [9,10]. The physicochemical properties of starch enable the adjustment of the Pickering emulsion droplet barrier by careful application of heat treatment causing partial *in situ* gelatinization of the starch granules adsorbed at the oil–water interface [11].

Dehydration of emulsion systems could be used to increase shelf life, improve their use, and facilitate transportation [12–14]. However, dehydration may alter the interfacial properties and lead to disruption [15–17]. There are several approaches to maintain the stability of emulsions during drying and subsequent storage. A common way is to add a solid hydrophilic carrier to the aqueous phase in amounts ranging between 30% and 80% of the total weight of the final powder [18,19]. Examples of such carrier compounds include lactose, glucose, maltodextrin, and cellulose [13,20]. As an alternative and to avoid carrier compounds, multiple or layer by layer (LBL) deposition of polyelectrolytes that crosslink on the droplet surface, crosslinking of protein-stabilized interfaces, and protein–polysaccharide conjugates have also been applied [21–23].

Freeze-drying is a process where the solvent (usually water) is crystallized at low temperature and then sublimated directly from the frozen state into vapor by decreasing the pressure around the product. Compared to other drying methods, freeze-drying causes less damage to sensitive structures and thus useful for preservation of heat sensitive food materials as well as of other biological products [24].

Upon freezing of emulsions, the water and oil phases start to crystallize which introduces a number of destabilization mechanisms [25,26]. Ice formation in the continuous phase increases droplet-droplet interaction and less water is available to hydrate the emulsifier on the droplet surface. The formation of ice crystals also results in an increased concentration of solutes in the unfrozen aqueous phase, causing a change in ionic strength and pH. This can lead to disruption of electrostatic repulsion between the droplets [14,27]. Notably, Pickering emulsions stabilized by quinoa starch granules were previously shown to be highly stable towards changes in ionic strength (in the range 0.2–2 M NaCl) of the continuous phase [8]. When an oil-in-water emulsion is cooled to temperatures where the oil phase starts to crystallize, partial coalescence may occur since lipid crystals of one droplet can penetrate into the liquid region of another droplet upon collision. Complete or partial crystallization of oil in droplets during the production or storage of emulsions may have a large negative impact on the emulsion stability [14,28]. Additionally, due to the volumetric expansion of water upon freezing, ice crystals may penetrate oil droplets and possibly rupture the interfacial layer, which enables oil-to-oil contact [16,31]. Droplets covered by a thick film have been found better protected against crystal penetration and partial coalescence [29,30]. The rate of coalescence during freezing has been correlated to the size of the stabilizing agent [31,32]. The large particles used in starch Pickering emulsions form a dense layer around droplets and therefore provide higher resistance against crystal penetration. The reasons are mainly the large size relative to the ice crystals and the high energy required to remove a micron sized particle from the oil–water interface [4].

The objective of this work was to produce oil-filled powders by freeze-drying without the need of additional carrier compounds. Pickering emulsions stabilized by OSA modified quinoa starch were used as initial emulsions; with the aims to further study the effect of *in situ* heat treatment to induce a partial gelatinization of the starch granules adsorbed at the oil–water interface prior drying, and to evaluate the influence of the dispersed phase oils with different melting temperatures. Furthermore, the freezing step, as a prerequisite of freeze-drying, was studied. Overall properties of initial emulsions, frozen and thawed emulsions, and dried and rehydrated powders were analyzed.

2. Materials and methods

2.1. Materials

The materials used were hydrophobically modified quinoa starch granules with 1.8% OSA isolated and modified as described previously [8], phosphate buffer (5 mM, pH 7, 0.2 M NaCl), and two different dispersed phases: Miglyol 812 (density 945 kg m^{-3}, melting point −12.5 °C, Sasol GmbH, Germany) or shea nut oil (density 910 kg m^{-3}, melting point 32–34 °C, a kind gift from AAK, Karlshamn, Sweden), respectively.

2.2. Methods

2.2.1. Emulsion preparation

Oil (7%, v/v), buffer (93%, v/v) and starch (214 mg/mL oil) in a total volume of 7 mL were weighed into a glass test tube and emulsified first using a vortex mixer (10 s) and then homogenized using a high-shear homogenizer Ystral (D-79 282; Ystral GmbH Ballrechten-Dottingen, Germany) at 22 000 rpm for 30 s. Since the melting point of shea nut oil is above room temperature (∼20 °C) it was kept in a water bath at 40 °C before emulsification. After emulsification, partial *in situ* gelatinization was induced in half of the samples by heating the emulsions in a water bath (*i.e.* maintaining the emulsions at 70 °C for 1 min, with a total heat treatment time of approximately 3 min including warm up time monitored using a type K, 0.1 mm thermocouple). All samples were produced in duplicate.

2.2.2. Freeze–thaw cycling

The freeze–thaw cycling experiment was performed on non-heat treated samples to see the effect of the freezing step. A total volume of 10 mL of each emulsion type was transferred to stainless steel trays, covered by aluminium foil, and thereafter frozen overnight using a freezer room (−18 °C). Thereafter, the emulsions (previously frozen in -18 °C) thawed during 4 h in room temperature. For comparison, and in order to see the effect of the rate of freezing on overall properties of emulsions, an additional set of emulsions were produced and flash frozen by dipping the trays into liquid nitrogen (−196 °C) and kept in the freezer overnight before thawing. Miglyol emulsions were flash frozen from its liquid state at room temperature. Shea nut oil emulsions were flash frozen either directly from the liquid state at 40 °C or after the dispersed phase was solidified at room temperature for 3 h.

2.2.3. Freeze-drying

Samples were frozen in freezer room as described in Section 2.2.2. All samples were then kept in the freezer before being transferred to the freeze dryer. The emulsions were freeze-dried during 5 days using a laboratory freeze dryer (CD 12, Hetosicc, Denmark) with 20 °C in the drying chamber, −50 °C in the cooling unit, and a vacuum of 10^{-2} mbar. The aluminium foil covering the containers of frozen emulsion was punctured before freeze-drying.

2.2.4. Characterization of emulsions and powders

The microstructure of the initial emulsions, freeze–thawed emulsions, and re-hydrated powders (restored to the original emulsion concentration using MilliQ water) were characterized by light microscopy (Olympus BX50, Japan) with 100–500 times magnification and using a digital camera (DFK 41AF02, Imaging source, Germany) together with the software ImageJ (NIH, Version 1.42 m). Each emulsion drop was diluted with 5 drops MilliQ water. Dried