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Preparation and encapsulation properties of double Pickering emulsions stabilized by quinoa starch granules

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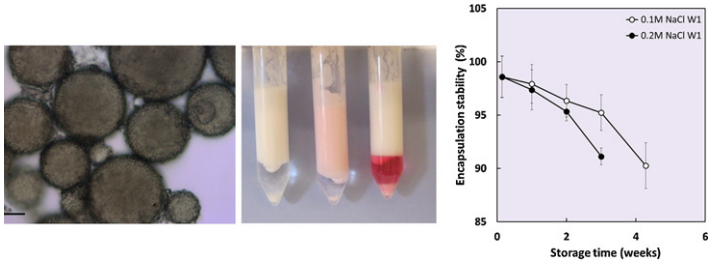
HIGHLIGHTS

- Quinoa starch granule stabilized W/O/W double Pickering emulsions were prepared.
- Encapsulation stability of a hydrophilic inner water phase as a function of time was determined.
- Initial encapsulation efficiency was over 98.5% immediately after emulsification.
- The encapsulation stability remained over 90% after 21 days.

GRAPHICAL ABSTRACT

Release of hydrophilic marker from Quinoa starch granule stabilized double emulsions.



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ABSTRACT

Double emulsions have potential applications in the food, cosmetic and pharmaceutical industries as vehicles for encapsulation and delivery of nutrients during food digestion or for drug release. The major drawback of this type of emulsions is that they are often difficult to stabilize. Particle stabilized emulsions, known as Pickering emulsions, show special features, such as being extremely stable with respect to coalescence. Starch granules have proved to be a suitable stabiliser for food grade Pickering emulsions. In this work, starch double $W_1/O/W_2$ Pickering emulsions were prepared and their encapsulation stability was studied as well as the impact of varying the lipophilic emulsifier (PGPR90) content and the salt concentration in the W_1 inner aqueous phase. Encapsulation properties were quantified by monitoring the release of a hydrophilic dye from the inner aqueous phase spectrophotometrically. Two double emulsion systems were studied, one with an inner aqueous phase with 0.1 M NaCl and the other with 0.2 M NaCl. The initial encapsulation efficiency was over 98.5% immediately after emulsification production. The encapsulation stability (ES) remained over 90% after 21 days for both systems studied, where 0.1 M NaCl W_1 emulsion had a ES of 95.2% and the 0.2 M NaCl W_1 emulsion had a ES of 91.1% respectively.

1. Introduction

The simplest multiple emulsions are called double emulsions and are ternary systems, having either a water-in-oil-in-water ($W_1/O/W_2$) or an oil-in-water-in-oil ($O_1/W/O_2$) structure, whereby the dispersed droplets contain smaller droplets of a different phase [1] essentially an emulsion in an emulsion. Multiple emulsions have been studied since their first description in 1924 by Seifriz [2]. The structural properties of this kind of multiple emulsions allow a controlled release of a component from the inner to the outer phase which leads to a number of potential applications in the fields of medicine, pharmacy, cosmetics and separation processes [1,3–10]. Double emulsions have also applications in the food industry [4,9,11–16].

Water-in-oil-in-water ($W_1/O/W_2$) type emulsions considered in this study have several food applications such as in the formulation of reduced fat-food products (by replacing some of the volume of

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the oil droplets with entrapped water drops) and as vehicles for encapsulation and delivery of hydrophilic nutrients [12]. For example to fortify foods with water soluble vitamins [17–19] or minerals [20], to entrap poorly tasting bio-actives in taste-masking applications, and to protect probiotics against the harsh effects of bile acids and gastric juices [21]. Through designing W/O/W structure taste perception can be controlled modifying the release of internal aqueous phase which interacts with oral surfaces [12]. Sensory tests have indicated that there is a significant taste difference between W/O/W emulsions in which there is a delayed release of flavour and O/W emulsions containing the same ingredients [8].

The main reasons why $W_1/O/W_2$ emulsions have not been yet widely used is that they are more complicated to produce because they have an additional internal surface (and the excess free energy associated with it) of the W_1/O emulsion which needs to be stabilized in addition to the surface of the secondary emulsion [1]. Furthermore homogenisation conditions must also be such that they can create the secondary emulsion but at the same time keep the primary W_1/O emulsion more or less intact. Progress in the development of stable double emulsions as food ingredients depends on replacing small-molecule emulsifiers and synthetic polymeric stabilizing agents by food-grade components . One way to produce emulsions with a high degree of stability is through the use of Pickering type emulsions. The use of particles to stabilize emulsions has received substantial and increasing research interest as of late due to their distinctive characteristics and promising technological applications in a range of fields including foods. The stabilization of emulsion droplets by particles is possible due to their partial dual wettability. This allows for the spontaneous accumulation of particles at the oil–water interface and stabilizing it against coalescence by volume exclusion and steric hindrances [22], i.e. the particles prevent oil–water interfaces of oil droplets from coming in to direct physical contact.

There are numerous varieties of particles reported in the literature for stabilizing Pickering type emulsions, and due to advances in nano technology and micro-manufacturing their availability and design ability will no-doubt increase in the future. Examples where food based/edible stabilizing particles have been studied have included: fat crystals, globular proteins and aggregated hydrocolloids [10], insoluble flavonoid particles [24], cellulose–ethyl cellulose complexes for stabilizing emulsions and foams [25], freeze fractured starch granules and protein mixtures [25,26], and chitin-nano crystals stabilized emulsions [27]. For comprehensive reviews on particle stabilized emulsions, applications and related theory please refer to [28], Aveyard et al. [22] Hunter et al. [29], and for food emulsion in particular see [23,30]. Recent work where Pickering type double emulsions have been studies include those using fat-crystals to stabilize the inner emulsion of a W/O/W emulsions [31] and combinations of fat-crystals and particles producing highly stable Pickering-in-Pickering double emulsions. This novel design enables food technologists to achieve a significant fat replacement in a way that is imperceptible to the consumer [32].

Starch is one of the most common food ingredients, and after hydrophobic modification intact starch granules has been shown to have novel and useful emulsifying properties [20,33–35]. In our previous studies starch granules isolated form quinoa were modified with octenyl succinic anhydride (OSA) and used to produce Pickering emulsions with excellent stability. Quinoa starch granules were chosen as Pickering agents because the granules are relatively small (0.5–3 μm in diameter) with a unimodal size distribution. Small size is of interest as it reduces the amount required (mg starch per ml oil) to stabilize a given emulsion droplet interface. The size of the emulsion drops produced were a function of the starch to oil ratio used, but were independent of the overall dispersed phase content over a range of 7–33% v/v oil [37]. Furthermore these emulsions have shown an outstanding degree of stability being un-changed after 2 years of storage under perikinetic conditions [35]. By taking advantage of starches' distinctive physical–chemical characteristics and careful application of heat we have been able to increase the cohesively of the partially gelatinized starch layer to increase resistance to lipolysis by up to 70% [37]. Although the drop size of starch granule stabilized emulsions was relatively large, their excellent stability and barrier properties can prove suitable for applications such as encapsulation of various ingredients in food and pharmaceutical products with the starch particles controlling the release properties. In order to achieve encapsulation of hydrophilic ingredients a double emulsion system may be a good choice of system. Thus, in this study, starch granule stabilized double Pickering emulsions were prepared and their encapsulation stability of a hydrophilic inner water phase as a function of time was determined.

2. Materials

Starch was isolated form quinoa (Biofood-Biolivs AB, Sweden) by a wet-milling process and OSA-modified with a degree of substitution of 1.8% using the method described in Rayner et al. [33] (processed by Lyckeby-Culinar AB, Sweden). The external water phase of the double emulsions (W_2) was a 5 mM phosphate buffer with 0.2 M NaCl. As internal water phase (W_1) two (0.1 M and 0.2 M NaCl) solutions were used. The oil phase was the medium-chain triglyceride oil Miglyol 812, density 945 kg/m^3 at 20 °C (Sasol GmbH, Germany) was prepared containing several concentrations (1–5% w/v) of polyglycerol polyricinoleate PGPR 90 (Grinsted Danisco AS, Denmark). Polyglycerol polyricinoleate (PGPR) is a powerful water-in-oil emulsifying agent commonly used with limited concentrations in food formulations [9]. The encapsulation efficiency was determined with carmine, an approved pigment food colouring agent (E120). It is stable to heat and light but sensitive to low and high pH. At neutral pH it has a bright red colour with a maximum UV light absorption at 520 nm [38]. Carmine was purchased as commercial water-soluble red dye solution from the local supermarket (Ekströms röd hushållsfärg, Procordia Foods AB, Sweden).

3. Methods

3.1. Preparation of primary (W1/O) water in oil emulsions

Water in oil emulsions (W_1/O), 20% W_1 and 80% oil-phase with a total volume of 7 mL were prepared. The W_1 disperse phase was deionized water containing carmine dye solution (4 μL dye/mL deionised water) with the corresponding amount of NaCl added to obtain either 0.1 M or 0.2 M. The continuous oil phase consisted of Miglyol 812 with varying concentrations 1–5% (w/v) of PGPR90 as lipophilic surfactant dissolved into it by stirring the oil phase in a covered container at 25–30 °C for 1 h at 240 rpm. The 5.6 mL of continuous and 1.4 mL of dispersed phase were emulsified in glass test tubes by high shear mixing in an Ystral X10 mixer (Ystral GmbH, Germany) with 6 mm dispersing tool at 24,000 rpm for 10 min.

3.2. Preparation of double $W_1/O/W_2$ emulsions

Double Pickering ($W_1/O/W_2$) emulsions consisting of total phase volumes: 8.25% v/v internal aqueous phase containing carmine dye (W_1), 33% v/v Miglyol 812 oil phase including 5% w/v PGPR (O), and 58.75% v/v outer aqueous phase (W_2). The total dispersed phase fraction was 41.25%. A sodium phosphate buffer was used in the outer aqueous phase as it has been shown to enable the separation of oil droplets by centrifugation and also promotes a more accurate measurement of some polymeric dyes, used as