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Barrier properties of heat treated starch Pickering emulsions

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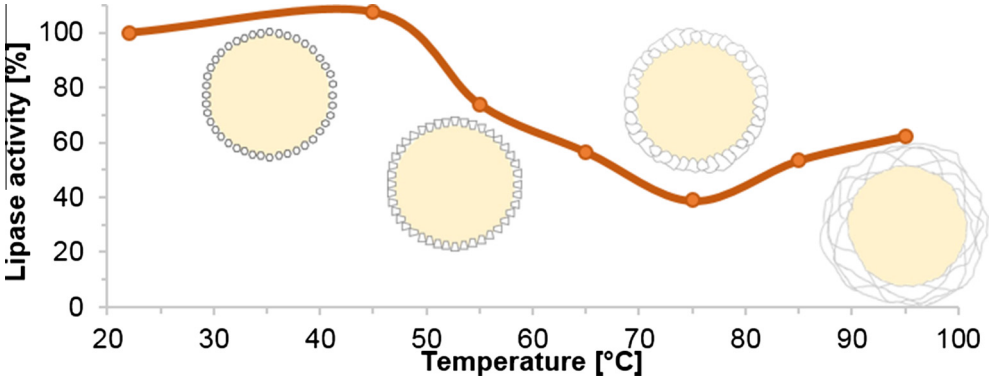
GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: There is a recognized technological need for delivery systems encapsulating lipophilic substances in food and pharmaceutical products. Pickering emulsions can provide well-defined and highly stable systems, but may not provide good enough barrier properties. Starch granules, recently being used for Pickering stabilization, have the advantage of the ability to swell during gelatinization. Hence, this property could be used to tune and control barrier properties.
Experiments: Oil-in-water Pickering emulsions stabilized by starch were subject to heat treatment at different conditions. The influence of temperature, time, and storage on emulsion drop characteristics was evaluated. In order to further evaluate the barrier properties, lipolysis using the pH-stat method was applied and the effect of starch concentration, treatment temperature, and preliminary oral conditions were also investigated.
Findings: A better encapsulating barrier was obtained by starch swelling at the oil drop interface. This was seen as reduced lipase activity. The internal oil drop size remained intact and the starch was kept at the interface during heat treatment. The extent of swelling could be controlled by the heating conditions and had impact on the ability to prevent lipase transport through the starch barrier layer. Addition of α-amylase simulating oral digestion only had minor impact on the barrier effect.

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1. Introduction

There is a recognized technological need for oral delivery systems that encapsulates, protects and gives controlled release of bioactive substances in food and pharmaceutical products [1]. Emulsions [1] or dried emulsions [2], either oil/water for lipophilic substances or double emulsions (w/o/w) for hydrophilic substances, can be interesting candidate formulations in this respect. However, such systems have a large surface area and will be susceptible to surface induced degradation, such as lipid digestion. However, by structuring the interface between oil and water one could achieve delayed lipid digestion and for example induce satiety [3,4], or targeted and controlled release of bioactive components within the gastro-intestinal tract [1,5]. Pickering emulsions have been seen to at least in some cases reduce lipid digestion in emulsions [6].

Emulsions made without the use of traditional emulsifiers has been of interest in application areas where the use of surfactant causes adverse effects such as air entrapment, foaming, irritancy, or biological interactions [7]. An elegant way to avoid surfactant use is to substitute emulsifiers by solid particles as drop stabilizing agents. Due to their distinctive characteristics and promising technological applications [8], the use of particles to stabilize emulsions has attracted substantial research interest. Particle stabilized emulsions, so called Pickering emulsions first observed over 100 years ago [9,10], are known to possess a high degree of stability even without the addition of surfactant [11,12]. A more detailed description of Pickering emulsions can be found in some recent reviews [13,14].

Lately starch granules have been studied for of use in Pickering emulsions [15–19]. Starch granules are biodegradable and well accepted for use in both food and pharmaceutical applications, even after hydrophobic modification with <3% octenyl succinic anhydride (OSA) [20]. Hydrophobic modification of starch is required in order to obtain affinity for the lipid phase. Starch naturally varies in size from 0.5 to almost 100 μm depending on the botanical source [21]. Previously, intact starch granules from quinoa (*Chenopodium quinoa* Willd.) was shown to efficiently stabilize oil-in-water emulsions [13,19]. This ability was attributed to the small granule size (0.5–2 μm), unimodal size distributions and distinctive morphology, i.e. rounded polyhedrons.

Due to the relatively large size of the stabilizing starch granules, at least in comparison to emulsifiers like surfactant molecules (0.4–1 nm), and globular proteins (1–5 nm) [8], there are relatively large spaces between them even if assuming a fully covered interface. Thus even though the starch granules are stabilizing the emulsion drop interface against coalescence, they are not likely providing equally good barrier properties. A huge advantage of using intact starch granules over other particles is therefore starch physicochemical properties in terms of gelatinization. This irreversible process, as defined by Atwell et al. [22] includes granular swelling, native crystalline melting, loss of birefringence, and solubilization, leading to collapse of molecular order. Depending on subsequent storage conditions, the gelatinized starch may then be further structured by recrystallization. Heat treatment causing starch gelatinization in Pickering emulsions has previously been shown to just slightly increase the emulsion drop size distribution although also introducing drop aggregation [2].

One method to quantify the relative impenetrability of an interfacial barrier for comparing differently treated emulsions is to measure the ability to decrease the rate of lipolysis [23]. The digestion of lipids is an interfacial process that involves the interaction of the lipase enzyme and its co-factors with the surface of the drops such that the enzyme can come into close contact with its substrate [1]. For this reason the interfacial area, i.e. the specific surface area of the emulsion is of importance and is given by:

$$S = \frac{6\varphi}{d_{32}}$$

where S is the surface area per unit volume of emulsion (m^2), φ is the oil volume fraction, and d_{32} is the Sauter mean diameter. The rate of digestion is often monitored using the pH-stat method [1,5,23]. This method partially mimic the physiological conditions in the small intestine although amylases known to break down starch are not generally included.

The aim of the present study was to modify the interfacial barrier properties of starch stabilized Pickering emulsion drops by partially or completely gelatinizing starch at the interface. The influence of starch surface packing, i.e. starch concentration, after heating to a specific temperature was evaluated. Furthermore, the influence of different degrees of gelatinization was studied as obtained by heating emulsions of a specific composition to different temperatures for selected periods of time. The focus was to evaluate the ability of the starch barrier to protect the lipid phase in general and not specifically to mimic gastrointestinal (GI) conditions. To quantify relative changes in initial rate of lipolysis as a measure of barrier properties the pH stat lipolysis method was used for analysis. This method was selected since the aim was not to quantify absolute bioavailability of the oil phase. However, to further mimic conditions at oral digestion, α-amylase was added in some experiments.

2. Experimental

2.1. Materials

The starch granules were isolated from quinoa grains (Biofood, Sweden) and chemically modified by OSA (2.9%) as described previously [24]. OSA donated by Lyckeby Culinar AB, Sweden was used for hydrophobic modification. Two different oils, paraffin (Merck Chemicals, Germany, 1.07174) and MCT-oil, Miglyol 812 (Sasol, Germany, 050 223), were used. All other chemicals was of PA quality and obtained from Sigma–Aldrich. The continuous phase of emulsions was a 5 mM phosphate buffer with pH 7 containing 0.2 M NaCl. A 1 mM Tris maleat buffer (pH 7.0) with 4 mM NaTDC, 1 mM $CaCl_2$ and 0.15 M NaCl was used as assay buffer for the lipolysis. Porcine pancreas lipase and co-lipase (L0382-100KU and C3028) were dissolved, 1 mg/ml, in assay buffer and aqueous solution, respectively. In some experiments α-amylase (A6814) was used at the concentration 100 U/ml.

2.2. Preparation of emulsions

Emulsions were prepared in glass test tubes by mixing with an Ystral (D-79282, Ballrechten-Dottingen, Germany) at 22000 rpm for 30 s. For studying the influence of starch concentration, emulsions with 2.7 ml of the continuous phase, 0.3 ml of the oil phase (10%) and 22.5–180 mg starch (75–600 mg starch per ml oil) were prepared. All other emulsions were prepared using 7% oil phase and 214 mg starch per ml oil.

After emulsification, emulsions were heat treated in a water bath at 45–100 °C. In order to compare different degrees of gelatinization the holding time at the desired temperatures was varied from 1 to 30 min. As comparison, starch was also heat treated in buffer and cooled to room temperature (22 °C) before emulsification. For lipolysis experiments the holding time was 1 min, and for experiments evaluating the influence of starch concentration, emulsions were heated to 70 °C.

In one storage experiment, heat treated emulsions with paraffin oil as dispersed phase were stored at 5 °C for 16 h and then kept at room temperature for 24 h, or as comparison kept only at room temperature for 48 h and 8 weeks, respectively. Emulsions used