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Starch particles for food based Pickering emulsions

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Abstract

Intact starch granules are a new source of particles for stabilizing emulsions, so called Pickering emulsions. Small (1-2 μm) and uni-modal starch granules at various concentrations have been used in this study to investigate the stability of the emulsions, the drop size dependence of the starch concentration and the barrier properties of the stabilizing starch layer upon heating. The granules were modified with octenyl succinic anhydride (OSA) to increase the hydrophobicity. The drops in the emulsions prepared in this study were in the 10-100 μm range depending on the starch concentration, and the drop size decreased with an increased amount of added starch granules. During the 8 week storage, the emulsion drops were stable to coalescence and the volume occluded by the emulsion phase was unaffected or even increased. In order to increase the barrier properties at the oil-water interface the emulsions were gently heated, which induced a partial gelatinization of the starch granules. The efficiency of the barrier was characterized by a lipolysis experiment where the activity of lipase was measured. The activity of lipase was decreased with nearly 70% compared to an unheated starch stabilized emulsion, which will be useful in applications where a controlled release of specific substances in the gastro intestinal tract is desirable.

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Keywords: Pickering emulsion; Starch granules; Storage stability; Barrier properties

1. Introduction

Food emulsions are generally stabilized by surfactants, proteins and hydrocolloids. However, the use of particles to stabilize emulsions has attracted substantial research interest due to their distinctive characteristics and promising technological applications [1]. Particle stabilized emulsions, so called Pickering emulsions [2], are known to display long-term stability even without the addition of surfactant. Through the choice of the size of the stabilizing particles, the surface layer thickness can be easily

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manipulated, and the effective density of the emulsion droplets tailored to achieve positive, negative or close to neutral buoyancy.

The stability of particle stabilized emulsions is ascribed to the fact that if the particles have favorable wetting conditions for the dispersed phase and are above a certain size (approximately 10 nm) they are effectively irreversible adsorbed at the oil-water interface and the desorption energy per particle is several thousand kT (where k is the Boltzmann constant and T is the absolute temperature) [3]. Practically this is an insurmountable energy barrier to droplet shrinkage beyond a tightly packed monolayer of particles. The strong adsorption of particles at the interface can thus explain their stability against coalescence and in some cases Oswald ripening.

In contrast to particles commonly used for Pickering emulsions such as latex, silica, and clay particles, starch (including hydrophobically modified starch) is an accepted food ingredient and pharmaceutical excipient. Starch granules are abundant, inexpensive, and obtained from natural sources. There is a large natural variation regarding size, shape, and composition of starch granules among its numerous botanical sources. Native starch is not naturally hydrophobic, and thereby generally not suitable to adsorb to the oil-water interface. However, the hydrophobicity can be increased for example by chemical modification using octenyl succinic anhydride (OSA). OSA modified starch with a degree of modification < 3%, E1450, is a well established food ingredient with no specific limitations on its use.

The properties of emulsions stabilized by starch granules can be further modified by heating in situ. When heated in aqueous media starch gelatinizes. The gelatinization process includes swelling of starch granules, amylose leakage from granules, loss of molecular and crystalline order, and at high temperatures, long times or high shear stresses finally leads to granule disintegration [4]. We surmised that with a judicious choice of heating conditions, the surface covering starch granules can be partially gelatinized and still remain bound to the surface and create an enhanced barrier to transport across the interface.

The objective of this investigation was to study the storage stability of starch granule stabilized oil-in-water emulsions and to draw on starches' physical-chemical characteristics to create barrier properties at the oil-water interface.

2. Materials and Methods

2.1. Starch granules

A source of starch with a small and uni-modal granule size distribution, quinoa (see Figure 1a), was selected. Starch was isolated from quinoa (Biofood, Sweden) by a wet-milling process and repeatedly washed using water, 3% NaOH, and citric acid (pH 4.5), respectively. The starch was treated with OSA to 1.8% by Lyckeby-Culinar AB, Sweden. The continuous phase of the emulsions was a 5mM phosphate buffer with pH 7 and 0.2M NaCl (density 1009.6 kg/m³ at 20°C), the dispersed phase was the medium-chain triglyceride oil, Miglyol 812 (density 945 kg/m³ at 20°C, Sasol GmbH, Germany).

2.2. Emulsification

The continuous and dispersed phases and starch were emulsified in glass test tubes by high shear mixing in an Ystral X10 mixer with a 6 mm dispersing tool (Ystral GmbH, Germany) at 22000 rpm for 30 s. To determine the effect of the amount of added starch on emulsion drop size, emulsions were prepared by combining 6.65 ml of continuous phase, 0.35 ml of dispersed phase and starch at varying amounts (12.5 mg - 400 mg). The samples were stored at 20°C for 1 day before drop size measurements. To determine the stability of the emulsions, buoyancy neutral emulsions, i.e. the starch covered oil drops had approximately the same density as the continuous phase, were prepared. The volume fractions of oil were 12.5, 16.6, 25.0 and 33.3%, the starch to oil ratio was constant at 214 mg starch/ml oil and the total