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# Investigation into the potential ability of Pickering emulsions (food-grade particles) to enhance the oxidative stability of oil-in-water emulsions

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ABSTRACT

In this study the potential ability of food-grade particles (at the droplet interface) to enhance the oxidative stability was investigated. Sunflower oil-in-water emulsions (20%), stabilised solely by food-grade particles (Microcrystalline cellulose (MCC) and modified starch (MS)), were produced under different processing conditions and their physicochemical properties were studied over time. Data on droplet size, surface charge, creaming index and oxidative stability were obtained. Increasing the food-grade particle concentration from 0.1% to 2.5% was found to decrease droplet size, enhance the physical stability of emulsions and reduce the lipid oxidation rate due to the formation of a thicker interfacial layer around the oil droplets. It was further shown that, MCC particles were able to reduce the lipid oxidation rate more effectively than MS particles. This was attributed to their ability to scavenge free radicals, through their negative charge, and form thicker interfacial layers around oil droplets due to the particles size differences. The present study demonstrates that the manipulation of emulsions' interfacial microstructure, based on the formation of a thick interface around the oil droplets by food-grade particles (Pickering emulsions), is an effective approach to slow down lipid oxidation.



## 1. Introduction

The susceptibility of lipids to oxidation is a major concern for food manufactures as lipid oxidation has negative effects on food qualities such as, taste, appearance, texture and shelf-life, and also leads to the formation of off-flavours (rancidity) and toxic compounds. In oil-in-water emulsions, lipid droplets are dispersed in an aqueous phase and stabilised by emulsifiers or surfactants [1,2]. There are various factors that can influence the rate of lipid oxidation in emulsion-based foods, including the molecular structure of lipids, temperature, the structure of the interfacial layer and the presence of antioxidants and pro-oxidants (transition metals) in the system [3–5]. One of the major mechanisms that causes lipid oxidation in emulsions is the interaction between lipid hydroperoxides located at the droplet surface and transition metals (sited in the aqueous phase), which accelerates the breakdown of lipid hydroperoxide into free highly reactive radicals, such as alkoxyl and peroxyl radicals [2,6]. One potential approach to enhance the lipid oxidation stability is to inhibit iron's ability to interact with hydroperoxide. The effective factors that can influence iron's ability are the physical location of pro-oxidants in the continuous phase (to prevent pro-oxidant to come into close contact with the droplet's surface), and the droplet interfacial characteristics (charge, thickness, etc.) [7].

So far, a great deal of research has been carried out on the ability of natural or synthetic antioxidants to inhibit the rate of lipid oxidation in emulsions, by chelating iron in the continuous phase or by scavenging free radicals [2,8–10]. Elias et al. reported that the lipid oxidation in menhaden oil-in-water emulsions stabilised with Brij 35 significantly decreased when 250 or 750 μg of β-Lg (β-lactoglobulin) was added into the continuous phase, mainly due to the ability of β-Lg to scavenge free radicals through their amino acid residues and chelate pro-oxidants in the continuous phase [11]. Another effective approach to alter the physical location of pro-oxidant in the system is the use surfactants that can form micelles in the continuous phase. It has been demonstrated that the lipid oxidation rate of corn oil-in-water emulsions was reduced as the concentration of Brij increased from 0.5% to 2%. This was ascribed to the fact that Brij micelles were able to decrease the iron–hydroperoxide interaction by separating pro-oxidants (in the continuous phase) from hydroperoxides (sited at the droplet interface) [4].

A number of studies suggest that the rate of lipid oxidation in emulsions can be also controlled by the charge of the droplets' interface. Proteins are able to reduce lipid oxidation, when either present at the droplet interface, or in the continuous phase [12,13]. Kellerby et al. showed that the rate of lipid oxidation in hexadecane-in-water emulsions stabilised with β-Lg was slower at pH values below the pI of the protein. This is because at pH < pI β-Lg is positively charged.

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Hence, positively charged droplets electrostatically repel iron and decrease the lipid oxidation rate [14]. Moreover, Mancuso et al. observed that the lipid oxidation rate of salmon oil-in-water emulsions was the highest for negatively charged droplets (stabilised with sodium dodecyl sulphate (SDS)), intermediate for uncharged droplets (stabilised with Tween 20), and the lowest for positively charged droplets (stabilised with dodecyl trimethyl ammonium bromide (DTAB)). These results indicate that negatively charged droplet interfaces were electrostatically attracted to positively charged pro-oxidant (iron), hence, pro-oxidants were in closer proximately to hydroperoxides and oxidation was promoted [15].

In addition to molecular surfactants and proteins, solid particles have also been shown to improve the lipid oxidation stability of emulsions due to their ability to form thick interfacial layers. In a previous study, by Kargar et al., it was shown that silica particles (at pH 2), when used to stabilised the emulsion interface, are able to increase the lipid oxidation stability due to partitioning irons from hydroperoxide [16]. The concept that solid particles can absorb at the oil–water interface and stabilise emulsions was first reported by Pickering over a century ago [17]. A wide range of solid particles have been used as emulsifiers for Pickering emulsion, including silica, clay, latex, etc. [18–20]. Recently, such emulsions have been receiving increasing level of attention, due to a variety of reasons such as, their remarkable stability against coalescence, their high stability against changes to processing conditions (pH, salt concentration, temperature, etc.) and also because they are present in a wide range of industrial applications (food, pharmaceutical and cosmetics) [18–20]. Many researchers have reported that the effectiveness of particles in stabilising emulsions depends on various parameters, such as the particle wettability [21], particle concentration [22], shape and size [23,24].

Despite the huge potential of these systems, applications in food industry are still limited by the absence of suitable food-grade Pickering particles. For this reason, we have used Microcrystalline cellulose (MCC) and modified starch (MS) as emulsifiers to form food-grade Pickering emulsions. MCC is prepared from cellulose powder, which is subjected to acid hydrolysis. Therefore, the chemical structure of MCC is the same as cellulose; however MCC has a shorter chain length due to hydrolysis [25]. Modified starch, classified as a smart food, is a starch that has been altered to perform additional functions. There are several methods available to modified starch. In this study, the waxy maize starch has been modified with alkenyl succinic anhydrides in order to increase its hydrophobic nature. As such, this modified starch (octenyl succinate anhydrides) possesses certain surface active properties which allow its usage as an emulsifier/stabiliser for oil-in-water emulsions [26].

The objective of this research was to increase the stability of oil-in-water emulsions against coalescence and lipid oxidation, in the presence of food-grade particles. Oil-in-water emulsions were stabilised by either MCC or MS at different processing conditions. The lipid oxidation rates in these systems were monitored for 1 week, using spectrophotometric methods to quantify the primary and secondary oxidation products.

## 2. Experimental

### 2.1. Materials

Distilled water and commercially available sunflower oil were used as the water and oil phases for all the prepared oil-in-water emulsions. MCC and MS were used as the Pickering particle species in this study and were provided by Sigma Aldrich (UK) and National Starch Food Innovation (UK), respectively. Ferrous sulphate, barium chloride, hydrochloric acid, cumene hydroperoxide, para anisidine and ammonium thiocyanate were all used as reagents for measuring lipid oxidation rates and were all purchased from Fisher Scientific (UK). Isooctane, isopropanol, butanol, and methanol were all used as solvents during the measurements of the rate of lipid oxidation and were all provided by Fisher Scientific (UK). All materials were used with no further purification or modification of their properties.

### 2.2. Methods

#### 2.2.1. Preparation and characterisation of aqueous food-grade particles dispersion

MCC and MS particles were added in distilled water and the resulting aqueous solutions were mixed for 40 min at 45–50 °C. The pH of all aqueous solutions was varied from pH 2 to 8 using 0.1 M HCl or NaOH. The particles dispersions were characterised at room temperature using a Delsa™ Nano C (Beckman Coulter). This instrument provides data on both the size of the particles and also their charge in their aqueous solutions at different pH conditions. The average particle sizes of MCC and MS after dispersion in aqueous solution were 415 nm ± 1.5 and 120 nm ± 3.2 respectively[2].

#### 2.2.2. Preparation and characterisation Pickering emulsions

MCC and MS particles were used at concentrations from 0.1% to 2% (wt/wt)[3] to stabilise 20% oil-in-water emulsions. Initially, particles dispersions were prepared and their pH was adjusted, as described above. Then the oil phase was added to the aqueous dispersion and the mixture was emulsified at ~10,000 rpm for 7 min using a Silverson L4RT with a fine emulsion screen of 19 mm diameter. Droplet size distributions ($D_{3,2}$ and $D_{4,3}$) were measured (in triplicates) immediately after emulsification and also after 21 and 40 days, using a Mastersizer 2000 (Malvern Instruments, UK) an integrated light scattering device. The creaming stability of the prepared emulsions was studied according to the Keowmaneechai and McClements method [27]. The samples were poured in glass test tubes (2.8 cm diameter 7.5 cm high) and were sealed to prevent evaporation. Samples were monitored for 3 days. The emulsions separate into a top "cream layer" and a bottom "serum layer" (Hs). The creaming index (CI) was calculated as:

$$\mathrm{CI}(\%) = (\mathrm{Hs}/\mathrm{He}) \quad (1)$$

where Hs is the serum layer high and He is the total emulsion height. The emulsions' microstructure was visualised using a Cryo-SEM (Philips XL-30 FEG ESEM) device. Samples were shock-frozen in liquid nitrogen, and dusted with gold particles prior to analysis in the SEM.

#### 2.2.3. Measurements of lipid oxidation

Immediately after formation, emulsions (10 mL) were placed in a sealed screw cap glass tubes and kept in an oven for 7 days at 40 °C to accelerate oxidation rate. The primary lipid oxidation product was measured by the peroxide value method (PV) according to Shantha and Decker's method [28]. In addition, the secondary products were measured using the anisidine value (ρ-AV) technique described in the American Oil Chemical Society (AOCS) CD 18–90 (1998) [29]. The experiments for measuring both primary and secondary lipid oxidation products followed the procedure described by Kargar et al. [16].

[2] The both particles are expected to be present in the solution as aggregate but the term particles is used in this study.

[3] Particle concentrations in this study were all calculated as weight of substance over total solution.