



# Dispersed droplets as tunable fillers in water-in-oil emulsions stabilized with fat crystals

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## ARTICLE INFO

**Keywords:**  
Emulsion  
Droplet size  
Fat crystal network  
Rheology  
Interfacial crystallization  
Fillers

## ABSTRACT

The role of water droplets as rheology modifiers in fat crystal-stabilized emulsions is not widely studied, but relevant to many fields and industries such as foods and cosmetics. The degree to which water droplets interact with the surrounding fat crystal network can impart a significant effect on rheology. The objective of this study was to investigate how the rheology of water-in-oil (W/O) emulsions stabilized by a surrounding fat crystal network is impacted by the ability of emulsifiers that promote interfacial fat crystallization and whether droplet size is a contributing factor. Three emulsifiers imparting different interfacial characteristics were chosen: glycerol monooleate (GMO) and glycerol monostearate (GMS) both promoted interfacial crystallization in the presence of hydrogenated soy oil (HSO) whereas polyglycerol polyricinoleate (PGPR) did not. Different homogenization methods were used to create emulsions with two distinct average droplet sizes with narrow size distributions for each emulsifier. Amplitude sweeps showed that GMS emulsions, independently of droplet size, displayed the highest elastic modulus ( $G'$ ) values followed by GMO, and then PGPR. Reinforcement ( $R = G'_{\text{emulsion}}/G'_{\text{HSO network}}$ ) values increased with each emulsifier over time, but its extent was dependent on emulsifier-mediated droplet-droplet interactions. In both GMO and GMS-stabilized emulsions, smaller droplets enhanced reinforcement whereas the opposite was observed in PGPR-stabilized emulsions. This study has shown that, through the use of different emulsifiers, the droplet interface should be considered a functional component that can be used to tailor the consistency of fat crystal-stabilized W/O emulsions.

## 1. Introduction

Fat crystal-stabilized emulsions are complex mixtures present in consumer products including spreads such as butter and margarine as well as cosmetic preparations as cold cream and lipstick. They comprise a dispersed aqueous phase sterically stabilized by a 3D matrix of crystallized triacylglycerols (TGs) (de Man and Beers, 1988; Hodge and Rousseau, 2005). Droplets in such emulsions can be stabilized by various means, namely small-molecule emulsifiers or solid species present at the droplet surface (Dickinson, 2013; Douaire et al., 2014; Duffus et al., 2016; Ghosh et al., 2011; Ghosh and Rousseau, 2011; Haj-shafiei et al., 2013; Pickering, 1907; Ramsden, 1903; Rayner et al., 2014). The latter is commonly known as Pickering stabilization. Importantly, emulsifiers can play a role in promoting solid particle adsorption to surfaces by modifying the wettability of the particle itself (Binks, 2002; Chevalier and Bolzinger, 2013) or mediating interfacial crystallization by providing a non-polar droplet surface amenable for fat crystallization (Frasch-Melnik et al., 2010; Ghosh and Rousseau, 2012). The latter possibly involves templating or small crystals adsorbing to the

surfactant monolayer and undergoing crystal growth, with both mechanisms providing the droplet with a mechanically rigid interface that is stable against coalescence (Douaire et al., 2014). In fat-continuous systems, monoacylglycerols (MAGs) are thought to facilitate interfacial crystal formation via heterogeneous nucleation at the droplet surface (Beri et al., 2013; Douaire et al., 2014; Frasc-Melnik et al., 2010; Ghosh and Rousseau, 2012; Krog and Larsson, 1992; Libster et al., 2009; Rafanan and Rousseau, 2017).

It is well-known that in the liquid state, incorporation of a dispersed phase within a continuous phase is likely to increase relative viscosity (Barnes, 1994). Furthermore, the extent to which dispersed droplets interact with the surrounding matrix can have a marked impact on rheology. When droplets reinforce material properties compared to an unfilled matrix, as denoted by an increase in elastic modulus ( $G'$ ) or viscosity, they are known as active fillers. Alternatively, if they weaken or cause no change, they are known as inactive fillers. Much of the work in this area has been carried out in oil-in-water (O/W) emulsion gels, where it has been found that filler activity depends on factors such as droplet surface characteristics, aggregation behaviour and average

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<https://doi.org/10.1016/j.jfoodeng.2018.09.001>

Received 18 February 2018; Received in revised form 31 August 2018; Accepted 2 September 2018

Available online 05 September 2018

0260-8774/ © 2018 Published by Elsevier Ltd.

**Abbreviations**

DSD	droplet size distribution
GMO	glycerol monooleate
GMS	glycerol monostearate
DSD	droplet size distribution
HSO	hydrogenated soy oil
MAG	monoacylglycerol

NMR	nuclear magnetic resonance
O/W	oil-in-water
PGPR	polyglycerol polyricinoleate
RCF	relative centrifugal force
SFC	solid fat content
TG	triacylglycerol
W/O	water-in-oil
XRD	X-ray diffraction

particle size and size distribution (Anton et al., 2001; Dickinson and Chen, 1999; Fröhlich et al., 2005; van Vliet, 1988). Filler “activity” is governed by different interparticle forces, depending on the nature of the continuous medium and the dispersed species. Attractive forces are mainly responsible for the increase in reinforcement seen with active fillers whereas repulsive forces are responsible for lack of change or weakening observed with inactive fillers. The forces governing viscosity and overall rigidity in colloidal dispersions also dictate the rheological behaviour of composite mixtures, namely Brownian motion, hydrodynamic forces and colloidal forces, which work in concert to give composites their material properties, depending on the shear stress (or rate) applied. Properties such as emulsion viscosity and elasticity can be further modified by altering the type, concentration and physical state of emulsifiers present at the oil-water interface.

Though less studied, similar findings have been found with water-in-oil (W/O) emulsions, where promotion of interactions between aqueous droplets and surrounding fat crystals can enhance emulsion elasticity whereas minimized droplet-fat crystal interactions yield little effect on rheology (Rafanan and Rousseau, 2017). For example, in microcrystalline wax systems, particle-stabilized droplets were shown to exhibit higher  $G'$  values over non-Pickering droplets (Le Révérend et al., 2011). In crude oil, asphaltene-resin colloids adsorbed at the interface have been shown to alter emulsion stability and flowability (Kumar et al., 2001).

Solid particles dispersed within a fat matrix, also considered a composite material, have been investigated as texture modifiers in food products, a prime example being chocolate where sugar, cocoa mass and potentially milk powder are dispersed in a continuous cocoa butter phase. Studies delving into particle size effects on molten chocolate flow properties have shown that a higher degree of particle interactions results in an increase in viscosity, but that increasing particle size counters this effect (Luckham and Ukeje, 1999). Specifically, the particle size distribution of solids dispersed in cocoa butter may enhance shear-thinning effect, depending on the particle size, the size distribution width, and fat content (Afoakwa et al., 2008; Do et al., 2007). Such studies demonstrate that control of particle-particle interactions in fat-continuous matrices may place a significant role in altering the rheology of the resulting composite.

Although fat crystal-stabilized emulsions are conceptually similar to composite materials containing solid particles, dispersed droplets are rarely thought of in the same light. The objective of the present study was to demonstrate how the presence of a dispersed aqueous phase significantly influences the viscoelastic properties of W/O emulsions, with a focus on the role of droplet size and distribution and extent of interactions with neighbouring droplets and fat crystals. Three emulsifiers yielding different interfacial characteristics were employed: glycerol monooleate (GMO) and glycerol monostearate (GMS) both promoted interfacial fat crystallization whereas polyglycerol polyricinoleate (PGPR) showed little influence. Emulsifiers were chosen not only for their ability to emulsify, but their ability to create a functional interface with attractive/repulsive qualities that are optimized with respect to droplet size distribution. Such an approach offers the opportunity to systematically enhance certain textural properties with minimal changes to ingredients, for a wide range of applications including low-fat spreads, cookie fillings, coatings and ganaches.

**Table 1**

Emulsion and blank compositions (wt.%) used in the present study. The aqueous phase consisted of 0.02 mM Rhodamine B as dye and 5 mM NaCl to prevent double emulsification.

	Water (wt. %)	HSO (wt. %)	Emulsifier (wt.%)	Canola oil (wt. %)
GMO	20.0	14.4	1.6	64.0
GMS	20.0	14.4	3.2	62.4
PGPR	20.0	14.4	0.4	65.2
GMO blank	0.0	14.4	1.6	84.0
GMS blank	0.0	14.4	3.2	82.4
PGPR blank	0.0	14.4	0.4	85.2

**2. Materials and methods****2.1. Materials**

All fat crystal-stabilized emulsions consisted of a 20 wt% aqueous phase dispersed in an 80 wt% oil phase made up of 14.4 wt% high-melting fat, 0.4–3.2 wt% emulsifier and 62.4–65.2 wt% canola oil (Table 1), with these compositions selected based on extensive preliminary experiments. All emulsions were made using one of three emulsifiers selected for this study: glycerol monooleate (GMO, Mono-muls90-O18, BASF Canada, Mississauga, ON, Canada, HLB ~ 3.4), glycerol monostearate (GMS, Alphadim SBK, Corbion, Mississauga, ON, Canada, HLB ~ 3.8), or polyglycerol polyricinoleate (PGPR, Nealanders, Mississauga, ON, Canada HLB ~ 3). Canola oil was purchased from a local supermarket (acid value < 0.2%) and used without further purification whereas hydrogenated soy oil (HSO) was used as the high-melting fat (acid value < 0.02%, bulk m.p. 72 °C of  $\beta$  polymorph) and consisted primarily of tristearin (Bunge, Bradley, IL, USA).

**2.2. Emulsion preparation**

The aqueous phase consisted of 0.05 M NaCl and 0.15 mM Rhodamine. NaCl was added to prevent the formation of double emulsions during high pressure valve homogenization (Pradhan and Rousseau, 2012). Rhodamine allowed for better discernment of oil phase separation (oiling-off) vs water separation as liquid phase pooling would be colourless in the case of oil migration and pink for aqueous separation. Given the viscosity of the emulsions after cooling and over time, separation may be seen in pockets throughout the storage vial, not necessarily localized at the bottom or top as is seen with less viscous liquid emulsions. The addition of NaCl and Rhodamine had no impact on emulsification droplet size, stability or interfacial characteristics based on preliminary tests. The experimental timeframe was 4 weeks, which consisted of weekly testing.

Note that each emulsifier required different concentrations to produce kinetically stable emulsions with significantly different number-weighted droplet size ( $d_{50}$ ) values and narrow droplet size distributions (DSDs). Emulsions with either the smaller or larger  $d_{50}$  values are hereafter referred to as ‘small DSD’ and ‘large DSD’.

**2.2.1. Monoacylglycerol-stabilized emulsions**

Two MAGs with different melting points were used: GMO (bulk

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