



# Crystallisation in water-in-cocoa butter emulsions: Role of the dispersed phase on fat crystallisation and polymorphic transition



Vincenzo Di Bari<sup>a,b,c,\*</sup>, William Macnaughtan<sup>a</sup>, Jennifer Norton<sup>c</sup>, Antonio Sullo<sup>c</sup>, Ian Norton<sup>b,c</sup>

<sup>a</sup> University of Nottingham, Food Sciences, Sutton Bonington Campus, Loughborough, LE12 5RD, United Kingdom

<sup>b</sup> Centre for Innovative Manufacturing in Foods (CIM), United Kingdom

<sup>c</sup> The University of Birmingham, School of Chemical Engineering, Edgbaston, Birmingham, B15 2TT, United Kingdom

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## ABSTRACT

The present work is one of the first to focus on the role of emulsified water droplets on the crystallisation behaviour of water-in-cocoa butter emulsions under quiescent conditions (i.e. absence of any externally applied force). Cocoa butter (CB) systems were designed to progressively increase the number of heterogeneous nuclei within the CB matrix, and the crystallisation behaviour was studied at four temperatures (5 °C, 10 °C, 15 °C and 20 °C). Information on the crystallisation kinetics and polymorphism was obtained by pulsed nuclear magnetic resonance and differential scanning calorimetry, respectively. This work provides evidence that dispersed water droplets have two key effects on the phase transition of the continuous fat phase: (1) increase the crystallisation rate and (2) enhance the polymorphic evolution. Emulsions crystallised faster (larger Avrami kinetic constant) than the bulk phase at intermediate-low levels of supercooling, although the mechanisms of nucleation did not change across systems. Moreover, at all temperatures, emulsified CB evolved faster towards more stable polymorphs. In these systems, a mechanism of ‘interfacial heterogeneous templating’ seems unlikely considering that the emulsifier (polyglycerol polyricinoleate) does not crystallise. This result was attributed to the presence of an emulsifier liquid-like layer surrounding the water droplets where the polymorphic evolution could be locally enhanced by the structural re-arrangement of CB triglycerides.

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## 1. Introduction

Water-in-cocoa butter (CB) emulsions represent a novel ingredient developed to reduce the fat content in chocolate (Norton, Fryer, Parkinson, & Cox, 2009). The effect of process and formulation on the microstructure of these emulsions has been described in the literature (Di Bari, Norton, & Norton, 2014; Norton & Fryer, 2012; Sullo, Arellano, & Norton, 2014). Water-in-CB emulsion kinetic stability is provided by both PGPR molecules and fat crystallisation. CB solidification contributes to droplet stability by both network formation and Pickering stabilisation.

*Abbreviations:* TAGs, triacylglycerols; CB, cocoa butter;  $T_c$ , crystallisation temperature; DSC, differential scanning calorimetry; NMR, nuclear magnetic resonance; O/W, oil-in-water; W/O, water-in-oil; PGPR, polyglycerol polyricinoleate.

\* Corresponding author at: University of Nottingham, Food Sciences, Sutton Bonington Campus, Loughborough, LE12 5RD, United Kingdom.

E-mail address: [vincenzo.dibari@nottingham.ac.uk](mailto:vincenzo.dibari@nottingham.ac.uk) (V. Di Bari).

Norton and Fryer (2012) were the first to suggest that CB fat crystals contribute to emulsion stability through Pickering stabilisation. The role of CB crystals on emulsion stability was later confirmed by the evidence that stable emulsions could be produced without the addition of PGPR (Di Bari, 2015). In addition, in these systems, the development of a fat crystalline shell surrounding the water droplets was observed, suggesting a mechanism of Pickering stabilisation: the interfacially adsorbed crystals eventually sinter together to form a solid shell. This latter phenomenon implies a process of interfacial crystallisation at the water droplet interface. Although the process of interfacial crystallisation in oil-in-water (O/W) emulsions has been studied in detail, the role of the dispersed phase in fat continuous systems has gained attention only in recent years and remains mostly unknown (Bayés-García et al., 2015). For O/W emulsions, triacylglycerol (TAG) crystallisation behaviour is affected by interfacial layer composition. When high-melting point emulsifiers are at the interface, ‘interfacial heterogeneous nucleation’ occurs if there are structural similarities between the emulsifiers

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and oil TAGs. The presence of a layer of crystalline molecules induces the ordering of the TAGs located near the droplet interface, which results in the formation of different polymorphs compared to bulk fat crystallisation (Douaire et al., 2014). Using a model emulsion system, Ueno et al. (2003) reported the formation of a pseudo-hexagonal crystal form resulting from the interaction between *n*-alkane and additive molecules solidified at the interface. This polymorphic form was not observed in bulk phase with and without the high melting point additives and in O/W emulsions without the same additives. The authors concluded that the solid ‘template film’ formed by the additive molecules drives the nucleation into the new arrangement by a mechanism of ‘interfacial heterogeneous nucleation’. This process may also induce an increase in the nucleation rate (Arima, Ueno, Ogawa, & Sato, 2009; Ueno, Hamada, & Sato, 2003). Less evidence of interfacial local ordering and its effect on fat phase polymorphism is available for W/O emulsions. Saturated monoglycerides have been shown to solidify directly at the interface, which in turn might induce continuous fat phase TAG nucleation by ‘interfacial heterogeneous templating’ (Ghosh & Rousseau, 2011). The same phenomenon may occur in monomeric liquid surfactant-stabilised droplets in the presence of crystallising bulk TAGs (Rousseau, 2013). Rousseau (2013) has hypothesised that interfacial crystallisation cannot occur for polyglycerol polyricinoleate (PGPR), which was attributed to its liquid physical state and complex interfacial arrangement (not fully elucidated). This arrangement would not allow the necessary TAG–emulsifier interaction and local ordering for interfacial crystallisation to occur. The present study aimed to investigate the crystallisation and polymorphic behaviour of water-in-CB emulsions produced using PGPR as an emulsifier. To the best of our knowledge, this is the first study on the kinetics of crystallisation of water-in-oil (W/O) emulsions. This is because emulsions quickly destabilise when fat is melted (Rousseau, Ghosh, & Park, 2009). In the present study, we showed that water droplets stabilised by PGPR remain stable under quiescent condition even when CB is molten, which offers the opportunity to study the crystallisation behaviour of emulsions. In another recent study, it was shown that freshly produced water-in-CB emulsions stabilised by PGPR remain stable at 50 °C but can destabilise when cooled to freezing temperatures (up to –80 °C) (Rivas, Zelga, Schneider, & Rohm, 2016). The authors also showed that the use of a 50% sucrose solution as dispersed phase resulted in a significant increase in the freeze-thaw stability of emulsions; this result was attributed to higher viscosity and osmotic effects. This study focuses on the polymorphic and crystallisation behaviour of water-in-CB emulsions. It was hypothesised that water droplets would act as seeds promoting CB crystallisation compared to bulk CB. The effect of the interface on the polymorphism of water-in-CB emulsions is more difficult to predict. This is because of the lack of studies investigating the role played by oil-soluble surfactants on the polymorphism of crystallising TAGs in W/O emulsions. To test the hypothesis, the crystallisation behaviour of bulk CB was compared with that of CB enriched with PGPR and of two emulsions containing 19% and 38% (vol%,  $\Phi$ ) aqueous phase. To evaluate the effect of CB system microstructures, samples were melted to erase the crystal memory and crystallised at four temperatures. This allowed the investigation of the combined effect of microstructure and degree of supercooling on CB crystallisation.

The findings of this work are relevant from a fundamental science perspective and for food applications. From an application point of view, the use of water-in-CB emulsions in chocolate manufacture would provide two key advantages: reduced calorie density of the product and evolution towards the desired polymorphic form.

## 2. Materials and methods

### 2.1. Materials

The emulsion lipid phase was prepared by blending the appropriate mass of molten CB with PGPR as the emulsifier. The mixing was performed at 60 °C for 15 min. Both ingredients were of standard food grade (Cargill, Vilvoorde, Belgium) and were used without any further purification prior to use. Double distilled water (Aquatron, A4000D, Bibby Scientific Limited, UK) was used as dispersed phase for emulsions.

### 2.2. Methods

#### 2.2.1. Emulsification

Two emulsion formulations containing 19% and 38% (vol%) dispersed phase were investigated. Emulsions were produced by adding the water to a lipid phase containing 5% PGPR (expressed as weight percentage of the dispersed phase) and using a bench-scale scraped surface heat exchanger (SSHE). The optimised process developed by Di Bari et al. (2014) was used with the following settings: 25 °C for the temperature of the water circulating in the SSHE jacket, 30 mL/min as flow rate for the emulsion circulation through the SSHE and maximum SSHE rotor speed (1315 rpm). As reference materials, bulk CB and CB containing 1% PGPR were crystallised using the same process used for emulsification. After production, all samples were stored in 30-mL sealed plastic pots at 4 °C until analysis. All samples were produced in triplicates.

#### 2.2.2. Droplet size determination

Emulsion droplet size was determined using a benchtop pulsed nuclear magnetic resonance (pNMR) spectrometer (Minispec, Bruker Optics, UK) equipped with a droplet size application. The measurement settings used were selected as reported by Di Bari et al. (2014). The average droplet size expressed as ‘Sauter mean diameter’ ( $d_{32}$ ) and free water (i.e. percentage of the dispersed droplets having a diameter of >50  $\mu\text{m}$ ) were reported. Measurements were performed in triplicate.

#### 2.2.3. Solid fat content

Isothermal crystallisation of CB systems was investigated using pNMR. Solid fat content (SFC) evolution of the systems was determined with the spectrometer described in Section 2.2.2 using the ‘indirect method’. This method relies only on the determination of the point at 70  $\mu\text{s}$  of the free induction decay curve, where the signal decay of the liquid component can be considered negligible and the signal of the solid is less than 0.1% of the original value (Van Putte & Van Den Enden, 1974). A measurement is then performed at a temperature at which all fat is completely melted, and the SFC can be calculated using Eq. (1):

$$\text{SFC}(\%) = \frac{c \times S_m - S_L}{c \times S_m} \times 100\% \quad (1)$$

where  $S_m$  is the signal produced by the molten fat,  $S_L$  is the signal produced by the liquid fraction at the measuring temperature;  $c$  is a correction factor that considers the signal loss due to temperature increase on melting. The factor  $c$  is calculated from the ratio of the signal intensity of a reference oil (sunflower oil in this study) at working ( $c_t$ ) and melting temperature ( $c_m$ ) ( $c = c_t/c_m$ ).

Approximately 0.3 g per sample were weighted into glass tubes (1 mm internal diameter) and heated to 50 °C for 20 min using a dry hot plate to erase crystal memory. The selected sample mass was below the maximum amount required to fill the NMR radio-frequency coil (approximately 1 cm) to prevent any signal loss following thermal expansion on heating. After melting, the samples were transferred into the NMR probe-head (set at the

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