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Effect of processing on the microstructural properties of water-in-cocoa butter emulsions

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ABSTRACT

A bench scale margarine line (a scraped surface heating exchanger followed by a pin stirrer) was used to produce stable tempered water-in-cocoa butter emulsions. A wide set of processing parameters was explored and correlated to the microstructural properties ($d_{3,2}$ and main crystal polymorphic form) of emulsions containing 10% or 20% (w/w) aqueous phase. The droplets size ($d_{3,2}$) was evaluated using pulsed field gradient NMR measurements and related to the applied shear profile. In particular, the effect of each mixer on the final $d_{3,2}$ values was examined. Results obtained from DSC analysis of fast cooled emulsions were used to understand the effect of continuous shear on the main polymorphic form of cocoa butter. The behaviour of this fat in an emulsified system is still mostly unknown. The results allow us to better understand the mechanism of the emulsifying process occurring in the margarine line, and show a clear dependence of the crystallising behaviour on the applied mechanical shear. Finally, droplets size data was fitted with a power law model used in literature for high shear mixers.

1. Introduction

An emulsion consists of two immiscible liquids (usually oil and water), with one of the liquids dispersed as small spherical droplets within the other (McClements, 2005). In emulsified systems which contain an oil phase that exhibits crystalline behaviour (during and/or post-emulsification), the change in its physical state can affect the stability according to the type of emulsion and processing conditions. In case of oil-in-water (o/w) emulsions under Couette flow, it has been shown that fat crystals protruding through the droplets interface reduce stability, by inducing coalescence (van Boekel and Walstra, 1981). For water-in-oil (w/o) emulsions several authors have shown that emulsion stability could be improved by controlling the crystallisation of the external phase (Hodge and Rousseau, 2005; Rousseau, 2000). In particular, two mechanisms seem to play a major role on stabilisation: (1) the development of a fat crystal network which immobilises the water droplets, reducing the effect of back reactions (mainly coalescence) and (2) the development of fat crystal nuclei that act as Pickering particles sitting at the w/o interface. These nuclei will then grow, sintering together to form a fat-crystal shell (Frasch-Melnik et al., 2010; Garti et al., 1998; Ghosh and Rousseau, 2011). In fact, using scanning electron microscopy, the presence of a crystalline fat shell making up the interface for these systems has been observed (Norton et al., 2009, Frasch-Melnik et al., 2010). The sintering at the interface is thought to be critical for the overall stability of the emulsion.

Although stable water-in-oil emulsions may have a wide range of applications in the food, cosmetic or pharmaceutical industry, there is a lack of literature concerning their systematic production, both at lab-scale and larger scale. In this article, we describe the use of a bench scale margarine line to produce stable water-in-cocoa butter emulsions. The use of this device as a continuous emulsifying apparatus to produce stable emulsions has already been described (Norton et al., 2009; Norton and Fryer, 2012; Frasch-Melnik et al., 2010).

Cocoa butter (CB) is widely used in the food industry. For example, in chocolate it is the main fat component (Afoakwa et al., 2009; Do et al., 2007), determining many of the mouth-feel related properties. Although CB polymorphic behaviour has been debated for a long time, generally six polymorphic crystal forms are thought to exist (Wille and Lutton, 1966). The tempering process, commonly carried out in chocolate manufacture, aims to ensure that the fat crystallise in the V (β_2) polymorphic form, which is desired for its sensorial related properties (melting in the mouth, glossiness, snap) (Afoakwa et al., 2008, 2009; Stapley et al., 1999). In the last century, several works have extensively studied cocoa butter microstructure and the effect of processing conditions on its crystallising behaviour (Sonwai and Mackley, 2006; Mazzanti et al., 2003) and other physical properties (Brunello et al., 2003). However, the behaviour of this fat within an emulsified system is mostly unknown. Works by Norton et al. (2009, 2012) are the only two attempts in literature referring to the production and

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characterisation of water-in-cocoa butter emulsions. In the present work, some parameters and their combinations studied by Norton and Fryer (2012) were explored in more detail to better understand the role that the process plays on determining some of the microstructural properties of this type of emulsion. The margarine line (see Section 2.2.1.) was chosen as emulsifying device as it offers several advantages, including the possibility to mimic the emulsifying process occurring on larger scale, the high internal sheared area and versatility in terms of range of processing conditions available (i.e., shearing profiles, residence time, temperature conditions, etc.). The experimental parameters studied in this paper were the combination of different shear profiles, jacketing temperatures, and residence time.

2. Materials and methods

2.1. Materials

2.1.1. Ingredients

Cocoa butter and PGPR (sugin 476 M, Cargill, Spain) were used without any further purification. The aqueous phase was prepared by dissolving analytical grade sodium chloride (Fisher Scientific, UK) in double distilled water to a final concentration of 0.02 M. After the addition, the aqueous phase conductivity was approximately 1.0 mS/cm, i.e., a thousand times higher than the distilled water to perform conductivity tests on liquid emulsions (see Section 2.2.6.).

2.2. Methods

2.2.1. Experimental section

All the dispersions were produced according to two formulations, differing in the aqueous phase volume fraction (10% wt and 20% wt) and containing the same amount of PGPR (1% wt overall). PGPR is a powerful emulsifier; it is known to sterically stabilise the interface through the water binding capacity of its chain (Márquez et al., 2010; Garti et al., 1998). Particular attention was given to understanding the relationship between the applied shear and the obtainable average droplets size of the dispersed phase and polymorphic behaviour of the continuous phase. The effect of some key processing parameters on mean droplets diameter and melting profile was also investigated. All the dispersions were also studied for storage stability, i.e., any change in droplets size over the time.

2.2.2. Pre-mix preparation

For each sample, 400 g of pre-mix were prepared. Using a hotplate stirrer (Stuart, UK), cocoa butter was firstly heated for two hours at about 65 °C (±5.0 °C), i.e., well above its final melting point, in order to delete any crystal memory. The protocols referred in the literature to erase liquid crystalline memory in cocoa butter vary considerably from author to author. Using a DSC method, it was established that a holding step at 65 °C for 15 min is sufficient to melt all homogeneous nuclei of cocoa butter (Foubert et al., 2003). In this work, due to the larger amounts used compared to a DSC sample, the holding step was extended to two hours. Weighed amounts of molten cocoa butter were added to PGPR in an 800 mL beaker. To ensure homogeneous distribution of the emulsifier in the whole volume, the mixture was stirred using a magnetic stirrer on a hotplate (Stuart, UK), while the temperature was slowly decreased up to approximately 50 °C (±1.0 °C). Then, the aqueous phase, heated approximately the same temperature as the lipid phase, was added. The blending was carried out for about ten minutes using an overhead "lab egg" stirrer (IKA® RW 11, Sigma–Aldrich, UK) and a magnetic stir bar until the coarse emulsion appeared to be creamy and homogeneous (judged by eye). During the premixing stage and emulsification, the evaporation of water from the feeding vessel was avoided by covering it with aluminium foil.

2.2.3. The margarine line

Water-in-cocoa butter emulsions were produced using a bench scale margarine line (technical specifications can be found in Norton et al. (2009, 2012)). This device is a continuous emulsification apparatus consisting of two stainless steel mixers in series: a scraped surface heat exchanger (SSHE, but commonly called an "A unit") followed by a pin stirrer (PS, also known as a "C unit"). A SSHE allows the processing of high-viscous fluids, generally in combination with improved heat transfer compared to other stirred vessels (Dumont et al., 2000; Trommelen and Beek, 1971). A PS is also a mixing vessel able to provide shear, which has been used for different purposes: on its own for the production of fluid gels (Gabriele et al., 2010; Garrec and Norton, 2012), or after a SSHE to achieve the desired textural properties in margarines and other low fat spreads (Norton et al., 2006). Being jacketed units, the temperature can be controlled during emulsification.

2.2.4. Overall set up for emulsions production

The pre-emulsion was pumped through the margarine line using a peristaltic pump (Masterflex L/S Digital Pump System with Easy-Load II Pump Head, Cole-Parmer, UK) through one meter long silicon pipeline (inner diameter of 3.2 mm; SLS, UK). The same pipes were used to connect each unit to a water bath (Julabo, UK) providing a constant countercurrent jacket flow. The jacketing temperature was set at 25 °C and 35 °C, for the SSHE and the PS, respectively. T-junctions, attached at the inlet and outlet of both the units, were used to monitor the temperature, using a Data Logger Thermometer (omega, UK) fitted with K-type thermocouple (±0.2% accuracy). The SSHE inlet temperature was kept at 40 °C (±0.5 °C), i.e., very close to the starting crystallising point of cocoa butter. The SSHE and PS outlet temperatures were 26.0 °C (±0.5 °C) and 33.5 °C (±0.5 °C), respectively, while the temperature at the SSHE outlet and PS inlet was the same.

For both units, four levels of rotor speed were chosen. In Table 1 the rotor speed and the corresponding tip speed provided by each mixer is referred. Twelve shearing combinations were investigated in details.

By controlling the shear-temperature profile within the margarine line, tempering was mimicked. The average processing profile saw a cooling step under continuous shearing to start crystallisation in the SSHE, followed by a re-warming and mixing step in the PS, thus controlling crystallisation by melting out the unstable forms and distributing more homogeneously the higher melting point crystals. The flow rate was set at 30 mL/s (although the effect of a 60 mL/s flow rate was also studied, see Section 3.4.), having an average residence time of 56 s and 320 s for the SSHE and PS, respectively. The final emulsions were collected in 40 mL sample pots and cooled using a rate of 0.6 °C/min before being analysed. Samples for thermal analysis were collected (see Section 2.2.8.)

2.2.5. Conductivity measurements

Conductivity measurements were performed on freshly prepared emulsions (still in a liquid-like state) using a bench top conductivity meter (Mettler Toledo, UK), in order to characterise the dispersed system; the detection of conductivity would indicate the presence of water not in the form of droplets.

2.2.6. Droplet size measurements

For all of samples, droplet size analysis was performed with a pulsed field gradient (PFG) NMR (Minispec, Bruker Optics, UK), operating at 0.47 T (20 MHz for ^{1}H) with a water droplets size application. This method of measuring droplet size has been