Journal of Food Engineering 142 (2014) 100–110

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Formulation engineering of water in cocoa – Butter emulsion

Antonio Sullo *, Marcela Arellano, Ian T. Norton

Centre for Formulation Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

ARTICLE INFO

Article history:
Received 18 March 2014
Received in revised form 27 May 2014
Accepted 30 May 2014
Available online 14 June 2014

Keywords:
Emulsion
Cocoa butter
Microstructure
Rheology
Texture
Particle size
DSC

ABSTRACT

This research studied the effect of κ-carrageenan concentration and emulsifier mixture of soybean lecithin (LEC) and/or polyglycerol polyricinoleate (PGPR) on the physical properties of water-in-cocoa butter emulsions. Emulsions were prepared using bench scale margarine line process, consisting of a scraped surface heat exchanger and a pin stirrer. Results show that droplet size increases as the concentration of κ-carrageenan and/or LEC increases. Emulsions crystallise mainly in form V (β_2), however when the concentration of κ-carrageenan increases to 1.5 wt% less stable polymorphic forms (II) were also observed. The rheological properties of the emulsions at 40 °C were mainly controlled by the concentration of LEC which causes droplets to flocculate and as consequence viscosity increases. Finally, behaviour under large deformation showed that the presence of water droplets weakens the emulsions structure, due to the reduction in the density of the cocoa butter matrix bearing the load.

1. Introduction

Conventional chocolate falls into the category of high energy density food products as it is mainly made of sugar and cocoa solids suspended in an oil continuous cocoa butter phase (30–40% in dark chocolate) (Beckett, 2000). This combined with the overall major drive in today's society for a healthier way of living are presenting the modern food manufacturer with one of its biggest challenges to date which is the development of low-calories chocolate without compromising the classic needs of texture and mouth feel. One way of achieving this is to replace some of the fat with water in the form of water-in-oil emulsions. Previous studies carried out by this group (di Bari et al., 2014; Norton and Fryer, 2012; Norton et al., 2009) have shown that stable water-in-cocoa butter emulsions containing up to 60% water, can be produced by using bench scale margarine processing line (consisting of a scraped surface heat exchanger and a pin stirrer). Indeed, this process makes it possible to temper water-in-cocoa butter (CB) emulsions, so as to ensure crystallisation of cocoa butter in the desirable polymorph form V (β_2) which confers to the chocolate the expected sensory attributes of glossy appearance, good snap and good in-mouth melting properties (Afoakwa et al., 2008; Beckett, 2000).

It is thought (Norton et al., 2009) that water-in-cocoa butter emulsions are Pickering emulsions, where the fat crystals produced during the crystallisation of cocoa butter under shear act as Pikering particles which absorb at the oil/water interface. Further stability is given by sintering of the fat crystals at the interface forming a rigid interfacial shell and preventing water droplets coalescence (Frasch-Melnik et al., 2010). During storage the fat crystals form a coherent network which immobilises the dispersed phase, conferring to the product the required long term stability. (Ghosh and Rousseau, 2011). Emulsifiers have been found to play a key role in the stabilisation of those emulsions as most fat crystals are not naturally surface active. Emulsifiers modify the surface of the fat crystals, increasing their polarity thereby improving their ability to absorb at the oil/water interface (Frasch-Melnik et al., 2010; Garti et al., 1998; Hodge and Rousseau, 2005). Johansson and Bergenståhl (1995) found that the addition of LEC increases the polarity of β-form tristearin crystals and improves the stability of water-in-oil emulsions. Garti et al. (1998) observed that the addition of 1% PGPR to water-in-oil emulsions enabled microcrystalline (α-form) fat crystals to adsorb to the water–oil interface and improved the emulsion stability. The stability of the emulsions improves with the addition of hydrocolloids as the increase in the viscosity of the dispersed aqueous phase limits coalescence of water droplets (Mounsey et al., 2008). Moreover, polysaccharides such as κ-carrageenan have been found to improve the sensory properties of low-fat spreads water-in-oil emulsions (Alexa et al., 2010).

This research is a continuation of a study dedicated to understand the effect of processing and formulation parameters on the microstructure and physical properties of water-in-cocoa butter (oil) emulsion as potential route for the production of low fat

* Corresponding author. Tel.: +44 079646999864.
E-mail address: sulloa@bham.ac.uk (A. Sullo).

http://dx.doi.org/10.1016/j.jfoodeng.2014.05.025
0260-8774/

Nomenclature

$d_{2.3}$	surface-weighted mean droplet diameter, μm
$d_{3.3}$	volume-weighted mean droplet diameter, μm
σ	standard deviation of the logarithm of the droplet diameter, μm
ε	true strain, –
σ_s	true stress, Pa
F	compression force, N
H_0	initial height of the cylindrical sample, m
ΔH	the height difference due to compression, m
d	diameter of the cylindrical sample, m
σ_w	stress to fracture of dispersed phase, Pa
σ_e	stress to fracture of water-in-cocoa butter emulsion, Pa
σ_{CB}	stress to fracture of pure cocoa butter, Pa
A	adhesion parameters, [0, 1]
ϕ_w	volume fraction of the dispersed phase, –
S	strength reduction parameter [0, 1]
η_r	relative viscosity, Pa s
η_d	dispersed phase viscosity, Pa s
ηc	continuous phase viscosity, Pa s
K	emulsion viscosity ratio, $\left[K=\frac{\eta_d}{\eta_c}\right]$
ϕ_{eff}	effective volume fraction of dispersed phase, –
ϕ_n	nominal volume fraction of dispersed phase, –
K_o	change in ϕ_{eff} due to the absorbed layer of surfactant, $\left[K_o=\frac{\phi_{eff}}{\phi_n}\right]$

chocolate. Central to this study were the following questions: How do polysaccharides and mixture of emulsifiers change the microstructure of emulsions? What are the consequences of such changes on the rheological and mechanical behaviour of the emulsion? Two possible models appear to emerge based on the rigidity and interfacial properties of the water droplets. It is considered that these findings would make it possible to progress in the design of a process for continuous manufacturing of a low-calorie chocolate, with similar sensorial properties to that manufactured by traditional methods.

2. Materials and methods

2.1. Materials

Cocoa butter (CB) and polyglycerol polyricinoleate (PGPR) were kindly provided by Cargill Incorporated, Belgium. Lecithin (L-α-Phosphatidylcholine from soybean) (LEC) and κ-carrageenan were both purchased from Sigma, UK. The water used in all experiments was passed through a double distillation unit (Aquatron A4000D). All materials were used with no further purification or modification of their properties.

2.2. Methods

2.2.1. Pre-emulsion preparation

The oil phase was prepared with the following procedure: CB was heated to ~60 °C using a hot plate stirrer (Stuart, UK) and held at this temperature for approximately two hours, to remove any crystal memory. The emulsifier was then added while keeping the solution agitated using a magnetic stirrer (Stuart, UK). Mixtures of PGPR and LEC were used as emulsifier (1 wt% overall) in varying ratios (1/0; 3/1; 1/1; 1/3; 0/1). The dispersed phase was an aqueous solution of κ-carrageenan at different concentrations, ranging from 0.5 to 2 wt%. This was prepared by dispersing κ-carrageenan powder in distilled water at 25 °C using a magnetic stirrer. The dispersion was then heated to 85 °C for 1 h with continued mixing by using a hot plate stirrer (Stuart, UK) until the κ-carrageenan was fully dissolved. Once the κ-carrageenan was fully dissolved the solution was cooled to 60 °C prior to addition to the oil phase. A pre-emulsion was obtained by mixing the required amount of water (10–60 wt%) into the oil phase using an overhead stirrer (RW20 digital, IKA-Werke GmbH & Co.) fitted with an anchor-shaped stirrer for roughly 5 min or until the mixture appeared homogeneous (visual inspection).

2.2.2. Emulsification process (the margarine line)

Water-in-cocoa butter emulsions were produced in a bench scale margarine line which is made of two jacketed units: a scraped surface heat exchanger (“A-unit”: volume of 40 mL) followed by a pin stirrer (“C-unit”: volume of 170 mL). A schematic of the process is reported in Fig. 1. The technical specifications of this equipment have been given elsewhere (Norton and Fryer, 2012; Norton et al., 2009). Briefly, the pre-emulsion is first pumped through the A-unit from a “feeding beaker”, at a constant flow rate of 30 mL/min, with a Masterflex Easy-Load II L/S pump (Cole-Parmer Instrument Company, UK) and a silicon flexible pipe (inner diameter of 3.2 mm; ESCO, SLC, UK). The temperature of the cooling jacket of the A-unit was held at 25 °C and the shaft speed was 1350 rpm. The emulsion then enters the C-unit where the jacket temperature was 35 °C and the pin stirrer speed was 700 rpm. The outlet temperature of the C-unit was roughly 33 °C. This combination of shear and temperature profile was carefully chosen to allow the tempering of the CB. After processing, the emulsions were stored at 20 °C.

2.2.3. Droplet size measurements

The droplet size was measured by using nuclear magnetic resonance (NMR, Minispec Bruker Optics, UK), with a water droplet size application specifically for water-in-oil emulsions. NMR has previously been used to assess water droplet size distributions in food emulsions (van Duynhoven et al., 2002). Samples were placed into 10 mm NMR tubes, using a metal plunger, and filled to a height of 10 mm. All NMR measurements were carried out the day following emulsion manufacture. Droplet size values are the mean of at least three replicates. The surface-weighted mean diameter of the droplets ($d_{3.2}$) was calculated by using the equation proposed by van Duynhoven et al. (2002):

$$d_{3.2} = d_{3.3}e^{-0.5\sigma^2} \quad (1)$$

where $d_{3.3}$ is the volume-weighted mean droplet diameter and σ is the standard deviation of the logarithm of the droplet diameter. Results were reported as the average and standard deviation of at least 3 replicates.

2.2.4. Thermal analysis

The thermal analysis of the CB emulsions was carried out using a differential scanning calorimeter (Perkin Elmer DSC 7, UK). About 10 mg of each sample were precisely weighed into aluminium pans of 40 μL, which were hermetically sealed. An empty aluminium pan was used as a reference. Scans were performed from 0 to 60 °C at a controlled constant rate of 10 °C/min. This method was used to determine crystal (polymorphic) forms, which were identified by