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Development and characterisation of tempered cocoa butter emulsions containing up to 60% water

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ABSTRACT

Cocoa butter water-in-oil emulsions, with up to 60% water, were created using both a high shear mixer and a bench scale margarine line. The high shear mixer gave a stable, fully emulsified emulsion with water content of up to 20%, and the polymorphic form required for good eating qualities was evident from differential scanning calorimetry measurements after the emulsions had been stored for 5 weeks or more at 5 °C. No further changes in polymorphic form occurred up to 24 weeks and no increase in droplet size or water loss was observed over this time. The bench scale margarine line allowed more control and greater flexibility in terms of the applied shear, the consistency of the applied flow fields and temperature profiles. Tempered emulsions could be produced by controlling the exit temperature from the pin stirrer (the final unit). Optical and electron microscopy showed droplets were between 1 and 10 μm in diameter, with a smooth shell of fat around the interface, which was hypothesised to impart emulsion stability. NMR measurements of droplet size were carried out for a range of emulsions produced with 20% water and up to 20% sucrose. These data confirm the droplets sizes obtained by microscopy, with all the results lying in the range of 1–5 μm. Electrical conductivity measurements on these emulsions showed that all the emulsions were fat continuous and contained no free water. Results suggest low-fat chocolate formulations using this route may be feasible.

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1. Introduction

1.1. The obesity problem

Obesity is increasing throughout the world. According to NHS reports, in the UK in 2005 23.1% of men and 24.8% of women were classified as obese, as compared with 13.2% and 16.4%, respectively, in 1993; here obesity was defined as a body mass index (BMI) of over 30. With obesity's known health risks, such as cardiovascular disease, diabetes, stroke, arthritis and some forms of cancer, the British Government is becoming increasingly concerned with the health and longevity of the nation (McPherson et al., 2007).

Dietary fat is very energy dense, but has a limited effect on suppressing appetite, compared to carbohydrate (Egger and Swinburn, 1997). This is related to "passive consumption" in which excess energy is ingested without a large quantity of food being consumed (Prentice and Jebb, 1995). Therefore, reducing dietary fat may reduce energy intake and help prevent obesity effectively. It is, therefore, desirable for the food industry to produce low-fat products. This seems to be especially true for foods which are not part of the staple diet, and provide only limited nutritional benefits, such as chocolate. Chocolate is a suspension of non-fat particles (sugar, cocoa solids and milk solids) in a continuous fat phase (cocoa butter). Conventional chocolate contains 30–40% fat, from both milk fat and cocoa butter (Beckett, 2000). In chocolate, the fat gives desirable physical characteristics, such as snap, gloss, creamy texture, rich taste and melt-in-the-mouth quality. As chocolate is notoriously high in calories (a gram of fat contains approximately nine calories), it may be detrimental to maintaining a healthy weight. There may thus be a gap in the market as low-fat chocolates with desirable taste and texture are currently not readily available. It is important to consider the polymorphic form of the cocoa butter emulsions. Cocoa butter has at least five crystal forms, each of which have different melting points (see Table 1). Although the thermodynamically stable form is form VI, consumers find V (β_2) the most attractive, as it melts between 32 and 34 °C (Beckett, 2000). This form is obtained by first tempering and then cooling at controlled rates. Stapley et al. (1999) have shown how the process of tempering is controlled by shear, whilst Tewkesbury et al. (2000) developed a model for the conventional cooling and phase change of chocolate. Le Révérend et al. (in press) built a model to

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Table 1
The cocoa butter polymorphs (Aronhime and Garti, 1988).

Polymorph	Melting point (°C)
I	17.3
II	23.3
III	25.5
IV	27.3
V	33.8
VI	36.3

describe rapid cooling rates that can predict the amount of tempered and untempered product.

1.2. Lower fat chocolate

Various methods of creating chocolate that is lower in calories have been proposed. Both Zumbe (1999) and Dubberke (1999) created reduced fat chocolates by manufacturing the chocolate as normal, then removing some of the fat. Dubberke (1999) processed a chocolate that contained less than 27% weight of fat, and claimed to have similar or better physical characteristics to standard chocolate. Whilst this approach sees a slight reduction in fat, it is inefficient as the fat is removed only after processing. Using lower calorie fat replacements may reduce the calorie content of chocolate. Cooper et al. (1990) patented a reduced calorie cocoa butter substitute that mimics melting properties of natural cocoa butter. However, cocoa butter substitutes are often incompatible with cocoa butter, so have to be used with cocoa powder, and are not fully digested.

An alternative microstructural approach is to add micron-size air cells to maintain the physical properties, but reduce the calories on a volume basis. Robert (2004) patented a method for making aerated chocolate, in which gas bubbles of approximately 25 μm in diameter were dispersed homogenously throughout the chocolate.

Chocolate contains a high percentage of sugar (typically 45%: Bouzas and Brown, 1995). Polyols and bulking agents have a greatly reduced calorie content compared with sucrose. Currently, although some brands offer diabetic chocolate in which maltitol replaces the majority of sugar, the calorie content is still high because fat content remains unchanged, or is even increased.

1.3. Water in chocolate

Although the methods mentioned above attempt to reduce the number of calories in chocolate, none seem to have been successful, without introducing additives that may be considered unnatural by the consumer. An alternative method might be to introduce water in the form of a water-in-oil cocoa butter emulsion: a cocoa butter continuous phase with an aqueous phase dispersed. By maintaining a continuous fat phase the product would continue to have attractive properties. Unfortunately, water within chocolate can affect quality, resulting in blooming and reduced snapability (Beckett, 2000). The addition of 3% or 4% of water (by weight) of water can result in a paste-like chocolate (Beckett, 2000). However, if water is introduced in the form of an emulsion (i.e. by making stable droplets and preventing water migration), calorie content could be greatly reduced. A number of patents describe processes or products which attempt to introduce water into chocolate. This may be to create a product suitable as a chocolate filling (Padley and Talbot, 1992). Baba et al. (1992) patented a method of creating water-containing chocolate by directly mixing a chocolate mix with an aqueous ingredient after rolling and conching, emulsifying with a nut paste to make a water-in-oil type emulsion. This water-containing chocolate is comparable with a ganache, a soft mixture made when adding cream to chocolate, which does not snap when broken (Beckett, 2000). Schlup and Lioutas (1995) patented a process for the production of a water-containing milk chocolate containing 1–16% water (by weight), in which the cocoa and aqueous ingredients were mixed independently and then blended to form a uniform mixture. The product made is a solid with desirable gloss, snap and hardness, and can be demoulded well. Tremblay and Mathur (1998) patented a method for manufacturing a reduced fat chocolate using defatted chocolate nib powder and lipid vesicles (containing a 40% lipid phase and a 60% aqueous phase). Processing involved mixing the lipid phase with the aqueous phase to form lipid vesicles (at 70–100 °C), and blending this with defatted chocolate.

Beckett et al. (2001) patented a process for manufacturing milk chocolate containing up to 30% water (by weight), which involved mixing a dark chocolate material with a water-in-oil emulsion and mixing to disperse the water (to below 10 μm) throughout, without creating a continuous phase. Hugelshofer (2000) investigated this method in depth. The water-in-oil emulsion was unstable in the presence of solid particles. However, Hugelshofer (2000) suggested that it is possible to produce a dark chocolate containing 10–15% water with sensorial properties similar to conventional chocolate. A similar method was patented by Traitler et al. (2000) who added a water-in-oil emulsion (with droplets of approximately 2 μm) to molten chocolate, with the intention of distributing the water in droplets throughout the chocolate mass, resulting in a chocolate with 1–40% water (by weight).

Here a number of cocoa butter emulsions were produced, using (i) a high shear mixer to create emulsions without considering the temper of the cocoa butter, or (ii) a bench scale margarine line (scraped surface heat exchanger followed by a pin mixer; supplied by Unilever). The margarine line is a continuous process, in which the temperature of the two jackets can be manipulated, so that tempering can occur during the emulsification stage through the control of shear and temperature. Both methods allow the production of emulsions with micron size droplets. The water-in-oil cocoa butter emulsions were produced with water contents from 10% to 60% by mass. Two different emulsifiers have been investigated (PGPR and soya bean lecithin). Both are used in commercial chocolate production (Schantz and Rohm, 2005). The aim of the work is to improve the understanding of water-in-oil cocoa butter emulsions, and to move towards a chocolate product containing water with the sensorial properties of conventional chocolate.

2. Materials and methods

2.1. Materials

The cocoa butter emulsions were made using commercially sourced pure cocoa butter, commercially sourced sugar (icing sugar and tricalcium phosphate (E341), Silver Spoon, UK), lecithin (L–phosphatidylcholine from soya bean, Type II-S, Sigma, UK) and polyglycerol polyricinoleate (PGPR, Kerry Bio-Science, UK). These were used in varying quantities.

2.2. Methods

2.2.1. High shear mixer

During this batch process, a Silverson L4RT (Silverson Machines Ltd, UK) high shear mixer was used to produce a range of cocoa butter emulsions. The cocoa butter and the emulsifier (either 2% soya bean lecithin or 1% PGPR) were melted using a water bath. The cocoa butter was heated to 45, 55 or 65 °C. A sugar solution (1% sugar) was then added. The whole mixture was emulsified for 3 min using the high shear mixer, fitted with a fine emulsifier screen. Following emulsification a sample of the emulsion was taken, which was sealed, and immediately refrigerated.

Table 2
Details of sample formulation and margarine line set up, along with exit temperature.

Sample	Sugar content (%)	Aqueous phase (%)	Fat content (%)	A unit shaft speed (rpm)	C unit shaft speed (rpm)	Through put (ml/min)	Exit temperature (°C)
1	1	21	78	1230	1320	50	29
2	1	21	78	1230	1320	30	35
3	1	21	78	1230	1320	70	35
4	1	21	78	800	1320	50	32
5	1	21	78	1350	800	50	37
6	10	30	69	1230	1320	50	–
7	20	40	59	1350	1320	50	–

2.2.2. A laboratory scale margarine line

Scrape surface heat exchanger (A unit) followed by pin stirrer (C unit): Supplied by Unilever (Sharnbrook, UK).

This provides a continuous process, where the cocoa butter and emulsifier (1% PGPR) were heated using the water bath to approximately 60 °C; this temperature was selected as it is above the final melting point of the cocoa butter crystals. The sugar solution (20% water) was also heated to 60 °C on a Stuart hotplate stirrer, and was stirred using a magnetic stirrer. The sugar solution was then added to the cocoa butter, and stirred using an overhead stirrer fitted with an anchor-shaped stirrer until the mixture looked homogeneous, which took approximately 3 min. This pre-emulsion was then pumped through the margarine line (Masterflex L/S Digital Economy Drive with a Masterflex Easy–Load II L/S pump, Cole–Parmer Instrument Company, UK), through silicon tubing (outer diameter 6.3 mm, inner diameter 3.2 mm; ESCO, SLC, UK). A unit: volume of 40 ml, 80 mm stirrer with two 10 mm blades; C unit: volume of 170 ml, 140 mm stirrer with sixteen 5 mm pins and sixteen 5 mm pins in the shaft. The A unit jacket temperature was held at 30 °C and the C unit at 40 °C for all the samples. These jacket temperatures were selected to start fat crystallisation in the A unit and control the polymorphic form of the cocoa butter in the C unit. The exit temperature was measured and was approximately 35 °C for all the samples. Settings were manipulated (see Table 2): shaft speeds (pin stirrer: 800, 1230 and 1350 rpm and scrape surface heat exchanger: 800 and 1320 rpm) and throughput (30, 50 and 70 ml/min). Following emulsification a sample of the emulsion was taken, which was sealed, and immediately refrigerated.

2.3. Determination of droplet size

The droplet size in the final emulsion and the percentage of emulsified water was measured by NMR analysis, using both a Maran 20 (MHz) NMR spectrometer (Resonance Instruments, UK) and a minispec NMR (Bruker, 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 (Callaghan, 1993; van den Enden et al., 1990; van Duynhoven et al., 2007). It is thought to be an accurate method of droplet size distribution, that is comparable to other methods, but has advantages, as it is non-perturbing, and is simple to use (van Duynhoven et al., 2002). The samples were put into 10 mm NMR tubes, using a metal plunger, and filled to a height of 10 mm. All NMR analysis was conducted in the week following emulsion manufacture.

2.4. Determination of melting properties

A differential scanning calorimeter (Perkin Elmer DSC Series 7, UK) equipped with thermal analysis software (Pyris) was firstly calibrated for temperature using indium and zinc, with an aluminum pan as a reference. Emulsion samples were loaded into 40 μL capacity aluminum pans, and sealed with aluminum covers. Pans were heated at a rate of 2 °C/min, from either 0 to 50 °C, or from 5 to 45 °C. This method was used to determine the dominant crystal (polymorphic) form, as shown by the temperature peak (°C) and the melting enthalpy (J g^{-1}) of the emulsions in comparison with pure cocoa butter. Melting properties were also compared with polymorphic information found in literature (Aronhime and Garti, 1988; see Table 1).

2.5. Microscopy

Cryo-SEM was performed, using a Philips XL-30 FEG ESEM (Quorum cryo system with a Polaron PolarPrep 2000 cryo preparation chamber), in which the sample was frozen to below −80 °C, coated with gold and scanned. Light microscopy was from a Polyvar II microscope (Reichert–Jung, Germany) in bright field mode.

3. Results and discussion

3.1. Emulsions made using the high shear mixer

3.1.1. Droplet size

Samples emulsified with soybean lecithin resulted in emulsions that appeared visually stable for 24 weeks i.e. showing no creaming on storage and no free water pooling on the surface of the sample. Measurements carried out by NMR (see Table 3a) indicated

Table 3a
Results of NMR analysis for cocoa butter emulsions produced using a high shear mixer. Emulsions were processed for 3 min on half power. Samples include 1% sugar and 2% soya bean lecithin. NMR measurements were taken in the first week after processing.

Percentage of water in sample	Percentage water in droplets >100 μm	Percentage water in droplets <100 μm
Soya bean lecithin		
10	3	97
20	9	91
30	21	79
40	23	77
50	34	66

Table 3b
Results of NMR analysis for cocoa butter emulsions produced using a high shear mixer. Emulsions were processed for 3 min on half power. Samples include 1% sugar and 1% PGPR. NMR measurements were taken in the first week after processing.

Percentage of water in sample	Percentage water in droplets >100 μm	Percentage water in droplets <100 μm	Droplet size measured by NMR (μm)	Distribution width
PGPR				
10	0	100	3.0	0.7
20	0	100	4.0	0.8
30	62	38	–	–
40	72	28	–	–
50	73	27	–	–
60	90	10	–	–

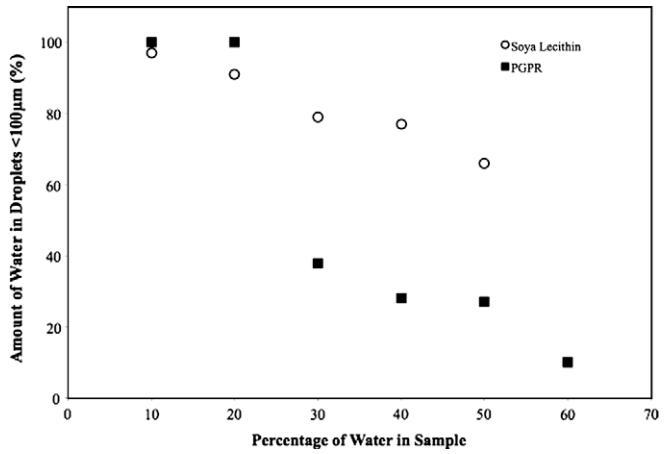

Fig. 1. Graph indicating the percentage of water in small droplets (<100 μm), taken from NMR analysis, for samples containing soya lecithin and PGPR. Samples contain 10%, 20%, 30%, 40%, 50%, and 60% water. All samples were emulsified using a high shear mixer and then refrigerated. NMR measurements were taken in the first week after processing.

that as the water content increased (i) the percentage of water in small droplets (<100 μm) decreased, and (ii) the percentage of water in droplets size greater than 100 μm increased. All the emulsions were found to be physically stable on storage for up to 24 weeks with no visible loss of water or fat continuity.

The samples emulsified with PGPR were again visually stable, over 24 weeks. NMR measurements (see Fig. 1 and Table 3b) indicated that all the water was contained in small droplets for the 10% and 20% water-containing emulsions. However, again as the water content was increased, there was an increasing amount of water contained in droplets greater than 100 μm.

As can be seen from Fig. 1, the use of soya bean lecithin gives emulsions with a narrow distribution in terms of percentage of water in small droplets (<100 μm), as compared to PGPR. Both emulsifiers have produced emulsions with small droplets (<100 μm) for 10% and 20% water. For emulsions with 10% or 20% water, PGPR appears to be favourable as 100% of the droplets were smaller than 100 μm.

3.1.2. Melting properties

DSC was used to analyse the melting profiles of the samples. The emulsion heated to 65 °C closely resembles pure cocoa butter, having a peak maximum at 32.4 °C (see Fig. 2). However, the results obtained for the emulsions processed at 45 and 55 °C have melting profiles that are very close to those reported for a whole range of chocolates (Afoakwa et al., 2008). The start, peak and end temperatures are given in Table 4. These results show that although a formal tempering process was not used, it appears that applying shear at temperatures between 45 and 65 °C, to cause nucleation of the fat, followed by cooling to 5 °C by placing the samples in the refrigerator is sufficient to 'temper' the fat.

Emulsions with different percentages of water (10%, 30% and 50%) emulsified with soya lecithin, were tested at varying time intervals after manufacture (see Figs. 3 and 4 and Table 5), to consider (i) whether the percentage of water affected melting proper-

Table 4
The melting properties of pure cocoa butter and three cocoa butter emulsions (in which the fat phase was heated to 45, 55 or 65 °C). Showing temperature start, peak and end, and melting enthalpy, as measured by DSC. Error bounds show 1 standard deviation.

Sample	T_{start} (°C)	T_{peak} (°C)	T_{end} (°C)	Melting enthalpy (J g^{-1})
Cocoa butter	30.2 (±1.3)	33.2 (±0.6)	34.9 (±1.9)	131 (±1.7)
45 °C	28 (±0.9)	31.4 (±0.02)	34.2 (±0.1)	145.3 (±3.2)
55 °C	27.7 (±1.5)	31.2 (±0.1)	33 (±1.1)	143.5 (±3.8)
65 °C	28.1 (±1)	32.4 (±0.3)	33.8 (±0.5)	129.5 (±2.8)

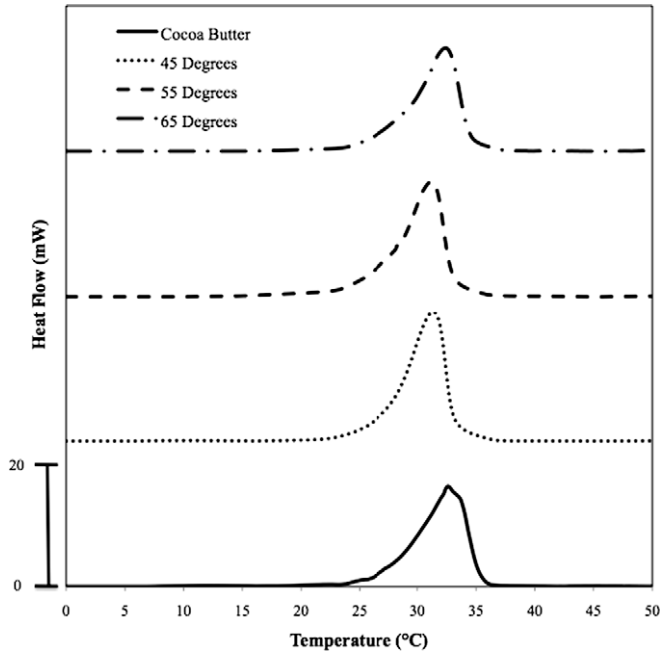

Fig. 2. DSC curves indicating melting temperatures of cocoa butter emulsions (all containing 30% water) emulsified using a high shear mixer. The fat phase of the emulsions was heated to different temperatures (40, 55 and 65 °C). Immediately after manufacture samples were refrigerated. Measurements taken 2 months after manufacture of emulsions. Pans were heated from 0 to 50 °C at a rate of 2 °C/min. Tempered cocoa butter is displayed as a comparison. These results have been normalised for both sample size and fat content. An empty pan was used as a reference.

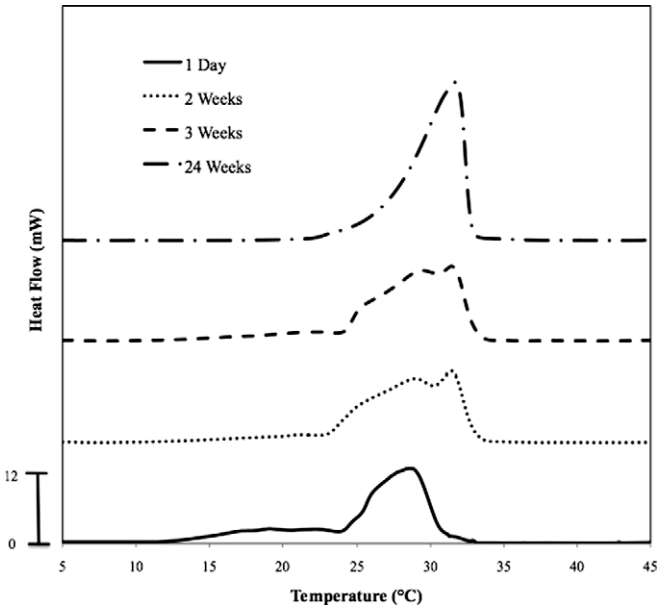

Fig. 3. DSC curves indicating the melting temperatures of the same emulsion (containing 30% water) after varying lengths of time. Pans were heated from 5 to 45 °C at a rate of 2 °C/min. These results have been normalised for both sample size and fat content. An empty pan was used as a reference.

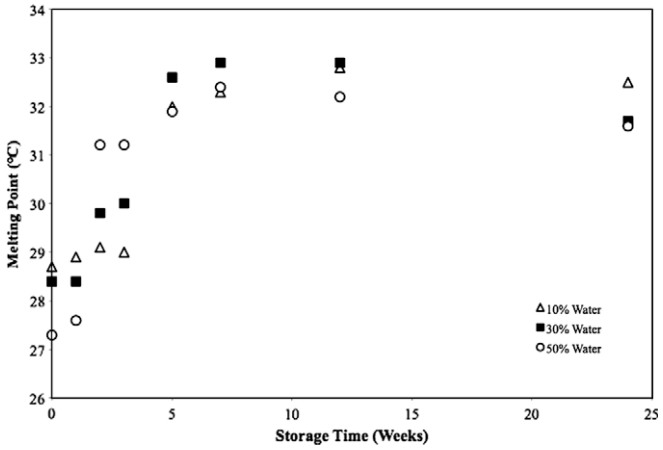

Fig. 4. Graph indicating average temperature peak of cocoa butter emulsions (containing 10%, 20% and 30% water) emulsified using a high shear mixer, at varying time intervals (from 1 day to 24 weeks).

ties, and (ii) whether the presence of water affected the behaviour of the emulsion over time. It can be seen that after one day and also after one week all the emulsions had a similar melting point (27–29 °C), which indicates that the cocoa butter is not in the desirable crystal form (see Table 1). After 2 or 3 weeks all three samples appeared to have a mixture of crystal forms, indicated by two different melting temperatures (see Table 5 and Fig. 3).

Although the samples initially appeared to change crystal form dramatically, indicated by a change in temperature peak and melting enthalpy, they remained stable from 5 weeks onwards at approximately 32.5 °C. After 12 weeks all three samples had a similar melting temperature (32.2–32.9 °C), indicating the presence of crystals in form V, although the melting energies varied considerably (see Table 5). After 24 weeks, a reduction in melting temperature is seen for all samples (melting between 31.6 and 31.7 °C), although this continues to suggest the presence of crystals in form V. These results suggest that storing the samples at 5 °C over 5 weeks and up to 24 weeks changes the melting temperature and enthalpy to that expected with a tempered cocoa butter in form V. Furthermore, it appears that this change is independent of the water content of the samples. The average temperature peaks followed the same pattern with time (see Fig. 4), suggesting that water content has little or no effect on the melting properties of the emulsions over time, although it does affect melting enthalpy.

3.2. Emulsions made on margarine line

A number of cocoa butter emulsions were prepared on a bench scale margarine line. These samples all had 20% water and 1% emulsifier (PGPR). The samples varied according to formulation (percentage of sugar and cocoa butter), and processing method (A and C shaft speeds and throughput; see Table 2). Each of the samples was tested for conductivity to determine whether the sample was an oil-in-water or water-in-oil emulsion. A conductivity of $0 \pm 0.1\ \mu S\ cm^{-2}$ for each sample suggested fully emulsified water-in-oil emulsion.

3.2.1. Droplet size

NMR analysis (see Table 6) indicated that all samples emulsified using the bench scale margarine line were fully emulsified, with no free water, and droplets of approximately 1 μm.

3.2.2. Melting properties

Calorimetry was carried out on the samples; the data in Table 7 are averages of triplicates. As can be seen, samples 1 and 4 gives the melting profile and the enthalpy of melting for polymorphic form 5 i.e. a temperature peak of between 31 and 32 °C and a melting enthalpy of approximately $127\ J\ g^{-1}$. These samples were produced when the exit temperatures from the process (from the pin stirrer) were 29 and 32 °C, respectively (see Table 2) i.e. below the melting temperature of the desired polymorphic form of the cocoa butter. All the other samples had exit temperatures at or above 35 °C, i.e.

Table 5
Results indicating the temperature onset, peak and end (all °C) and enthalpy ($J\ g^{-1}$) of the cocoa butter samples over time. Error bounds show 1 standard deviation.

Sample	T_{onset} (°C)	T_{peak} (°C)	T_{end} (°C)	Melting enthalpy ($J\ g^{-1}$)	Number of peaks
10% water					
1 day	24.6 (±0.6)	28.7 (±0.1)	30.9 (±0.2)	86.7 (±5.2)	1
1 week	23.4 (±0.1)	29.1 (±0.1)	30.9 (±0.1)	94.1 (±4.1)	2
2 weeks	23.0 (±0.2)	29.1 (±0.1)	31.5 (±0.5)	100.0 (±2.1)	2
3 weeks	24.4 (±0.2)	29.0 (±0.4)	32.2 (±1.3)	104.5 (±2.9)	1
5 weeks	26.3 (±3.4)	32.0 (±0.5)	33.5 (±0.4)	115.3 (±5.5)	1
7 weeks	26.2 (±2)	32.3 (±0.2)	33.7 (±0.2)	110.1 (±8.8)	1
12 weeks	27.6 (±2.7)	32.9 (±0.3)	34.1 (±0.1)	111.1 (±7.8)	1
24 weeks	28.3 (±0.2)	31.7 (±0.4)	33.7 (±1.5)	138.4 (±1.5)	1
30% water					
1 day	24.4 (±0.6)	28.8 (±0.5)	30.3 (±0.5)	106.2 (±7.2)	1
1 week	24.0 (±0.4)	28.4 (±0.3)	30.1 (±0.4)	102.1 (±1.4)	1
2 weeks	24.7 (±2.7)	29.8 (±1.5)	32.9 (±0.2)	111.9 (±2.2)	2
3 weeks	24.1 (±0.1)	30.0 (±1.2)	33.0 (±0.1)	115.8 (±0.8)	2
5 weeks	28.0 (±0.2)	32.6 (±0.1)	33.7 (±0.2)	136.1 (±0.3)	1
7 weeks	28.2 (±0.6)	32.9 (±0.7)	34.3 (±0.8)	141.7 (±2.2)	1
12 weeks	28.1 (±0.2)	32.9 (±0.1)	34.0 (±0.1)	136.9 (±2)	1
24 weeks	26.7 (±0.04)	31.7 (±0.05)	32.7 (±0.04)	141.0 (±2.8)	1
50% water					
1 day	24.0 (±0.7)	27.3 (±0.2)	29.3 (±0.1)	116.2 (±2.3)	1
1 week	23.4 (±0.3)	27.6 (±0.1)	29.5 (±0.2)	118.4 (±5.7)	1
2 weeks	26.4 (±3)	31.4 (±0.01)	32.6 (±0.3)	143.2 (±7.7)	2
3 weeks	24.5 (±0.7)	31.2 (±0.04)	32.7 (±0.1)	129.8 (±5)	2
5 weeks	28.1 (±0.6)	32.2 (±0.01)	33.4 (±0.1)	160.0 (±3.8)	1
7 weeks	28.2 (±0.6)	32.4 (±0.4)	34.2 (±0.8)	153.6 (±10.2)	1
12 weeks	27.7 (±0.02)	32.2 (±0.2)	33.5 (±0.1)	163.8 (±7.4)	1
24 weeks	26.8 (±0.1)	31.6 (±0.2)	32.7 (±0.04)	179.2 (±1.5)	1

Table 6
Results of NMR analysis for cocoa butter emulsions produced using the margarine line. Samples include 20% water and varying percentages of sugar.

Sample	Percentage water in droplets >100 μm	Percentage water in droplets <100 μm	Diameter of droplets (μm)
Margarine line samples			
1	0	100	1.6 ± 0.1
2	0	100	1.5 ± 0.1
3	0	100	1 ± 0.2
4	0	100	1.4 ± 0.1
5	0	100	0.6 ± 0.1
6	0	100	1.3 ± 0.3
7	0	100	4.9 ± 0.9

Table 7
Results of DSC analysis of cocoa butter emulsions made using the bench scale margarine line.

Sample	T_{start} (°C)	T_{peak} (°C)	T_{end} (°C)	Melting enthalpy (J g^{-1})	Conductivity (μS cm^{-2})
1	26.4 (±0.2)	31.8 (±0.1)	33.1 (±0.1)	127.0 (±0.4)	0
2	21.9 (±0.4)	29.2 (±0.4)	31.7 (±0.2)	86.9 (±0.9)	0
3	23.2 (±0.3)	29.9 (±0.4)	31.8 (±0.8)	81.9 (±7.7)	0
4	27.2 (±1.2)	31.2 (±0.2)	32.4 (±0.2)	127.1 (±2.1)	0
5	20.9 (±0.5)	28.6 (±0.7)	31.3 (±0.4)	90.1 (±1.6)	0
6	21.3 (±0.2)	28.9 (±0.1)	30.9 (±0.2)	96.0 (±1.2)	0
7	21.3 (±0.5)	28.6 (±0.4)	31.2 (±0.2)	82.0 (±0.8)	0

above the temperature for melting of form V. This suggests that all of the nuclei produced in the scraped surface heat exchanger have been re-melted in the pin stirrer, so that crystallisation then occurs into the lower melting polymorphic forms. A tempered emulsion is produced without a traditional tempering process, as demonstrated by the peak profile shown in Table 7.

3.2.3. Microscopy

Cryo-SEM images were taken of cocoa butter emulsions (cocoa butter, water, sugar and emulsifier) produced with the bench top margarine line (the A and C units). These results show that water within the fat phase is contained in droplets of relatively small size (5–15 μm; see Fig. 5). Although in the same order of magnitude, this is slightly larger than suggested by the NMR results. The image does reconfirm that the sample is fully emulsified, with evenly distributed, regular droplets. The image in Fig. 5 (left) shows the microstructure of the droplets contained in the emulsion, with a smooth crystalline shell of fat around the water droplets. Very similar microstructures to that displayed in Fig. 5 (left) have been observed in margarine (Norton et al., 2006) and ice cream (Goff et al., 1999).

In margarine it is this fat shell that imparts both the physical and microbiological stability to the emulsion. The water phase is contained in a solid structure on the application of mechanical forces (i.e. on spreading) and any microbial activity will be contained within a single droplet. It is therefore very likely that the same behaviour will be observed for our cocoa butter emulsions.

4. Conclusion

This investigation was intended to improve knowledge surrounding water-in-oil cocoa butter emulsions, to create water-in-oil cocoa butter emulsions with a high water content, which are stable, and do not cream on storage. Furthermore, the cocoa butter within the samples should be in polymorphic form V (β_2), which consumers find the most attractive, as it melts between 32 and 34 °C (Beckett, 2000). Two methods were employed: a high shear mixer and a bench scale margarine line (scrape surface heat exchanger and pin stirrer).

Using the high shear mixer resulted in a stable, fully emulsified emulsion with a water content of up to 20% water. The correct polymorphic form of the fat was evident when the cocoa butter was heated to 65 °C, and the emulsions processed at 45 and 55 °C had melting profiles that were very close to those reported for a whole range of chocolates (Afoakwa et al., 2008; see Table 4 and Fig. 2). The DSC results suggest that by storing the cocoa butter

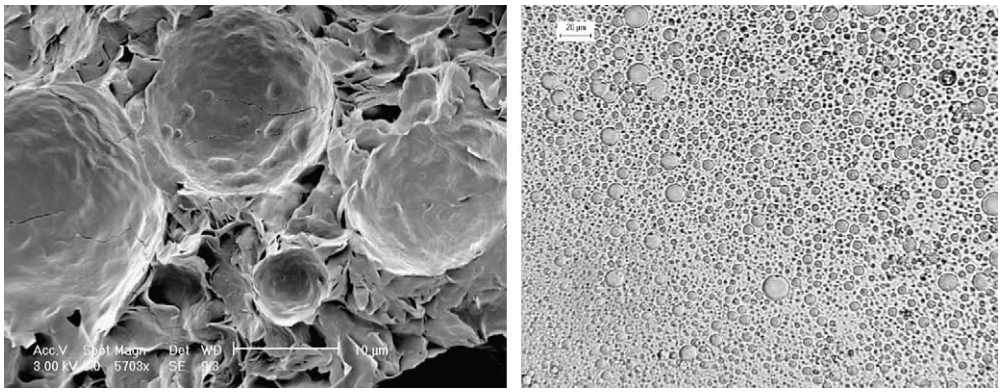

Fig. 5. Left: Cyro-SEM of a cocoa butter emulsion processed using A and C units indicating a continuous fat phase with water droplets dispersed (the water has been removed during the Cryo-SEM preparation process). This method of preparation appears to have resulted in a better defined emulsion structure. Right: Light microscope image of an emulsion made on the A and C units, showing the distribution of water droplets within the fat matrix.

emulsions at 5 °C over approximately a 5 weeks period, an emulsion with a melting point and melting enthalpy similar to tempered cocoa butter in form V was produced (see Table 5 and Fig. 3). Furthermore, this was independent of water content. Samples with 10%, 30% and 50% water all followed the same trend, changing from IV to V over a similar number of weeks.

It is thought that the bench scale margarine line is a better method of creating a cocoa butter emulsion. It is likely to be more successful for creating an emulsion of the correct polymorphic form as temperature and shear can be controlled with more precision. Controlling the temperature leads to seeding of the cocoa butter, resulting in a tempered emulsion in form V. It is also a better method for creating emulsions with a small droplet size. Furthermore, it is likely to be more appropriate for large-scale industrial production as it is a continuous process.

The methods of analysis (NMR, DSC, microscopy and conductivity readings) appear to be successful in gaining sufficient microstructural information about the cocoa butter emulsions.

Further work should aim to manipulate more variables, both in terms of formulation (for example, the percentage of emulsifier used), and processing. Future work should also consider the microbiological stability of cocoa butter emulsions.

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