ULTRA-STABLE SELF-FOAMING OILS

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ABSTRACT

1   This paper is concerned with the foaming of a range of fats in the absence of added foaming 2agent/emulsifier. By controlling the temperature on warming from the solid or cooling from the melt, 3crystals of high melting triglycerides form in a continuous phase of low melting triglycerides. Such 4crystal dispersions in oil can be aerated to produce whipped oils of high foamability and extremely 5high stability. The foams do not exhibit drainage and bubbles neither coarsen nor coalesce as they 6become coated with solid crystals. The majority of the findings relate to coconut oil but the same 7phenomenon occurs in shea butter, cocoa butter and palm kernel stearin. For each fat, there exists an 8optimum temperature for foaming at which the solid fat content reaches up to around 30%. We 9demonstrate that the oil foams are temperature-responsive and foam collapse can be controllably 10triggered by warming the foam to around the melting point of the crystals. Our hypothesis is given 11credence in the case of the pure system of tristearin crystals in liquid tricaprylin.

Highlights

- Stable air-in-oil foams without added foaming agent
- Crystals of high melting solid fat coat air bubbles in liquid oil of low melting fat
- Temperature-responsive oil foams

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1. INTRODUCTION

Literature on the preparation and properties of oil foams (or gas-in-oil) is very scant compared with that on aqueous foams despite their importance in a number of industries. Due partly to the lower surface tension of most oils compared with water, common surfactants are not surface-active at the oil-air surface and hence do not stabilise oil foams. In a series of papers, Shrestha and co-workers however succeeded in stabilising foams of a range of oils using mono- and diglyceride fatty acid esters (Shrestha, Aramaki, Kato, Takase & Kunieda, 2006; Kunieda, Shrestha, Acharya, Kato, Takase & Gutierrez, 2007; Shrestha, Shrestha, Sharma & Aramaki, 2008; Shrestha, Shrestha, Solans, Gonzalez & Aramaki, 2010). These surfactants formed either lamellar liquid crystals or surfactant particles in oil which were effective at preventing air bubbles from coalescence for a limited time. For a lubricating oil of poly(dec-1-ene), we showed likewise that various surfactants and polymers enabled foam stabilisation at conditions close to phase separation of the additive in oil (Binks, Davies, Fletcher & Sharp, 2010). By contrast, different kinds of solid particle have recently been shown to be excellent foaming agents of many oils, provided the oil surface tension is not too low and that particles have the appropriate wettability (Murakami & Bismarck, 2010; Binks & Rocher, 2010; Binks, Rocher & Kirkland, 2011; Binks & Tyowua, 2013; Binks, Sekine & Tyowua, 2014; Binks, Johnston, Sekine & Tyowua, 2015). These foams can be ultra-stable due to the irreversible adsorption of colloidal particles to the liquid surface (Binks & Horozov, 2006). For hydrocarbon-containing oils, particles of low surface energy are required and these have included oligo- or polytetrafluoroethylene (Murakami & Bismarck, 2010; Binks & Rocher, 2010; Binks, Rocher & Kirkland, 2011), fluorosilica (Binks & Tyowua, 2013) or fluoroclay (Binks, Sekine & Tyowua, 2014; Binks, Johnston, Sekine & Tyowua, 2015) particles of a variety of shapes and sizes.

A strategy used recently to prepare stable oil foams has been to allow crystals of the additive to form within the oil phase on cooling which, after aeration, adsorb to air bubble surfaces endowing the foam with high stability to drainage, coalescence and disproportionation. These mixtures can be thought of as a high melting point additive (forms crystals) within a low melting point oil (continuous phase). In the four examples studied so far, the latter has been a vegetable oil with applications to aerated foods, but this is not a requirement (Garvey, 2014). The systems have been a commercial mono/diglyceride surfactant in rapeseed oil (Brun, Delample, Harte, Lecomte & Leal-Calderon, 2015), long chain alcohols in sunflower oil (Fameau, Lam, Arnould, Gaillard, Velev & Saint-Jalmes, 2015), a long chain carboxylic acid in high oleic sunflower oil and other vegetable oils (Binks, Garvey & Vieira, 2016) and a saturated triglyceride in a soybean-rapeseed oil mixture (Mishima, Suzuki, Sato & Ueno, 2016). The oils above are examples of triacylglycerides (TAGs) in which a high proportion of the long

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fatty acid (FA) chains are unsaturated such that the melting point of the oil is low (< 0 °C) and hence the oils are liquid at room temperature.

Edible compositions in which fat is the continuous phase like butter, margarine and liquid oils are well known. They are commonly used as the fat ingredient in baking, as a frying medium or even consumed directly like the topping on pancakes or bread. The fat phase of the above is typically a mixture of liquid oil (fat that is liquid at room temperature) and fat (which is solid at room temperature). The solid fat (sometimes called the hardstock fat) structures the fat phase and, if water is present as droplets, aids in stabilising the emulsion by forming a fat crystal network in thecontinuous phase. It is ideal if the solid fat melts or dissolves around the temperature within the mouth otherwise there may be a waxy mouth feel. In addition to the ongoing need of manufacturers to reduce costs, health conscious consumers desire reduced fat-containing compositions these days. One way to achieve this is to replace part of the fat with an edible gas. Such aerated food compositions are known, *e.g.* ice cream, whipped cream and mousses, but these are complex colloidal formulations containing many other ingredients (Campbell & Mougeot, 1999). Normally, the gas is present as dispersed bubbles but, in the case of aerated fats/oils, their stability is frequently low. Thus, during storage, coarsening and coalescence of the bubbles can occur as well as drainage of liquid oil which reduces the aesthetic quality of the product. There is thus a need to develop aerated fat-continuous products exhibiting high stability. At the same time, some consumers deem it unhealthy to consume a product which contains synthetic ingredients like fatty acids, E-number emulsifiers and sugar. Unlike the studies referred to above, we put forward here a novel idea for stabilising aerated oils which does not require any additive. Our main objectives are: (a) to manipulate the temperature of a fat/oil such that oil foams stabilised by fat crystals can be be formed in the absence of any additive and (b) to determine if these crystal-stabilised foams are sensitive to temperature approaching the melting point of the crystals. We select triglyceride oils/fats of medium chain length (mainly C_8-C_{12}) which contain predominantly saturated FA chains such that their melting points are around or above room temperature. Since such oils are composed of a mixture of TAGs of different chain length/composition, we make use of the selective crystallisation of those TAGs of higher melting point within liquid oil of those TAGs of lower melting point, *i.e.* an oil dispersion of crystals forms from one and the same oil. We acknowledge that TAGs can also exist in several polymorphic forms exhibiting different melting temperatures. The question is whether crystals of particular TAGs adsorb around air bubbles dispersed in liquid oil composed of other TAGs. The studies focus on the case of coconut oil, whose use is currently experiencing a renaissance (Cassiday, 2016), but we give examples for other oils containing saturated TAGs. We also demonstrate the thermo-responsive nature of these oil foams by destabilising them around the melting point of the crystals. In order to verify our hypothesis that crystals of certain TAGs enable foaming of liquid oil of the remaining TAGs, we show

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that stable foams in a pure short chain liquid TAG (tricaprylin, C_8) can be prepared which contain adsorbed crystals of a pure long chain solid TAG (tristearin, C_{18}).

2. MATERIALS AND METHODS

2.1 Materials

Refined, bleached and deodorized (RBD) coconut oil (*Cocos nucifera*) was a gift from AAK, Sweden (batch B0364E) with the free FA content being < 0.02%. Coconut oil is an edible oil extracted from the kernel of mature coconuts harvested from the coconut palm. RBD oil is made from dried coconut kernel, which is placed in a hydraulic press with added heat, from which the oil is extracted. Because of its high saturated fat content, it is slow to oxidise (Moigradean, Poiana & Gogoasa, 2012) and is thus resistant to rancidification. Coconut oil contains mainly saturated TAGs (> 90%) and is an excellent source of medium chain fatty acids that can be easily burnt for energy. Typically, coconut oil contains around nine FAs of different melting point being caproic (Co, C6:0) 0.7%, caprylic (Cy, C8:0) 8.1%, capric (Ca, C10:0) 6.3%, lauric (La, C12:0) 48.3%, myristic (M, C14:0) 18.1%, palmitic (C16:0) 8.4%, stearic (C18:0) 2.4%, oleic (C18:1) 5.9% and linoleic (C18:2) 1.8%. Using HPLC-MS, the most abundant TAGs greater than 5% were LaLaM, LaLaLa, LaLaCy, CyLaM and CaLaM accounting for over 43% of the TAGs detected (Neff, Byrdwell & List, 2001). Palm kernel oil (*Elaeis guineensis*) Encore 100 was a gift from Cargill Food Ingredients, USA and is in fact palm kernel stearin (Personal communication, 2016). It also contains over 90% saturated TAGs (mainly C12:0 and C14:0). Refined cocoa butter (*Butyrum theobroma cacao*) and refined shea butter (*Butyrospermum parkii*) were purchased from Naissance, UK and contained no added fragrances or colours. Cocoa butter contains around 60% saturated TAGs (mainly C16:0 and C18:0, Firestone, 2013) whereas shea butter contains only around 45% saturated TAGs (mainly C16:0 and C18:0, Firestone, 2013). Tricaprylin, a low melting triglyceride (99%, melting point 9.5 °C) and tristearin, a high melting triglyceride (80%, highest melting point 73 °C) were purchased from Sigma-Aldrich.

2.2 Melting and cooling of coconut oil

The solid fat content (SFC) of coconut oil was determined using a Bruker NMR minispec mq$_{one}$ SFC analyzer (AOCS Official Method, 2009). In these measurements, the oil was placed in an NMR tube and heated to 60 °C for 10 min. It was then cooled to 0 °C for 1 hr before being placed in a water bath at either 10, 20 or 30 °C for 30 min. before measurement of the SFC. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC-7 instrument using nitrogen as the

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purge gas (see *e.g*. Chiavaro, 2015). Calibration was done using a sample of indium. Coconut oil (2.20 mg) was placed into a 20 µL aluminium pan which was sealed using a crimper. It was heated from -25 °C to 60 °C at 10 °C/min followed by cooling from 60 °C to -25 °C at 10 °C/min.

2.3 Aeration of oils

Apart from coconut oil, the other food oils were stored in the dark at 18 °C for various lengths of time before being warmed at a rate of approximately 0.1 °C/min. Coconut oil was stored in the fridge at 6 °C for up to 12 h and subsequently warmed at the same rate. A 250 mL polypropylene bowl containing 70 g of a solid vegetable oil (coconut oil, shea butter, cocoa butter or palm kernel stearin) was placed in a thermostated water bath. A Brannan England thermostat probe was also used to measure the temperature of the sample inside the bowl. For the majority of experiments, the initial temperature of the water bath was set at 18 °C and it was increased gradually at an approximate rate of 0.1 °C/min. This process continued until the desirable temperature was achieved between 19 and 42 °C depending on the type of vegetable oil. For coconut oil, experiments were also conducted in which a clear solution at 30 °C was cooled gradually to a set temperature before whipping. At the temperature of interest, the aeration of the sample was made with the use of a hand held double beater electric whisk (Argos value range, blade size 6 cm) on speed setting 1 (reaching 1,100 rpm). The whipping technique included 5 min whipping following by a 5 min resting interval. The procedure was repeated for a total period of 45 min, *i.e*. actual whipping time of 25 min. At the resting intervals, digital photographs were taken to monitor the foamability of the samples. At the end of whipping, a homogeneous sample of the whipped oil was transferred into volumetric cylinders or glass beakers to monitor its foam stability under the same temperature conditions. The samples were photographed at fixed times to record the foam volume for at least one month.

2.4 Tristearin in tricaprylin dispersion and aeration

2.12 g of tristearin was added to 10 mL of tricaprylin and heated to 75 °C to ensure that the tristearin was fully dissolved. The transparent oil dispersion prepared at 75 °C was gradually left to cool to 15 °C at an approximate rate of 2 °C/min. At 15 °C, a semi-solid white opaque oil dispersion was formed. At this temperature, the aeration of the sample was achieved with the use of an IKA Ultra–Turrax T25 homogeniser equipped with a metal head of diameter of 18 mm (due to the low volume of this dispersion). This included 5 min at 13,000 rpm followed by a 5 min resting interval. As in the case of the vegetable oils, the total procedure was repeated for a total of 45 min.

2.5 Microscopy of whipped oils

The average bubble diameter was measured by optical microscopy with the use of an Olympus BX51 microscope equipped with an Olympus DP70 camera. A small sample of the non-aqueous foam was placed within a dimple cell microscope slide with a coverslip on top. 8-bit grey scale images of 1360 x 1024 pixel resolution were taken and analysed with ImageJ software. The average bubble size distribution was determined from the measurement of 150 individual bubbles (three images of 50 bubbles each). The optical microscopy images were captured at fixed intervals immediately after preparation and throughout the investigation of foam evolution. A reflected light analyser (U-AN, Olympus) and a U-POT polariser were used to cross-polarise the light. Images were captured of the same sample at the same temperature for both non-polarised and polarised miscroscopy. For cryo-scanning electron microscopy (SEM), a sample of foam was deposited on a 12 mm aluminium SEM stub and submerged into liquid nitrogen slush. The mounted frozen sample was transferred to the cryo system (Quorum Technologies PP3010T) held at -140 $^{\circ}$C and 10^{-6} mbar in a nitrogen gas atmosphere. Once coated with platinum, the sample was inserted into the chamber of a Zeiss EVO 60 SEM at – 140 °C using a beam voltage of 10 kV for examination.

3. RESULTS AND DISCUSSION

We first describe what happens to coconut oil upon heating or cooling including values of the SFC at various temperatures and the morphology of the crystals. This is followed by the findings on the aeration of coconut oil as a function of temperature in which the foamability and foam stability are quantified. For an otherwise stable oil foam, we then show its thermo-responsive nature by progressively destabilising it upon warming. The self-foaming of a range of other vegetable oils, which vary both in the extent of saturation and most abundant chain lengths, is then demonstrated. Finally, evidence is given for the foaming of a pure short chain triglyceride stabilised by crystals of a pure long chain triglyceride.

3.1 Effect of temperature on coconut oil

The melting point of coconut oil is quoted as around 25 °C but, because it contains numerous different TAGs, it melts over a range of temperatures and ≈ 25 °C is in fact the temperature when all the sample is deemed liquid. The melting and crystallisation curves obtained by DSC are given in Figure S1 which are in close agreement with those published by Maruyama *et al*. (Maruyama, de Martini Soares, D'Agostinho, Goncalves, Gioielle & da Silva, 2014) Coconut oil exhibits an onset

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melting temperature of 14.0 °C with a peak melting temperature of 21.8 °C and an enthalpy change ΔH of 63.7 J/g. It displays two distinct but overlapping exothermic peaks on cooling, one at 5 °C (crystallisation of saturated TAGs, ΔH = -19 J/g) and the other at – 9.8 °C (crystallisation of unsaturated TAGs, ΔH = -8 J/g). Using solid-state NMR, the SFC can be determined at different temperatures. This is shown in Figure 1 which contains data from our own sample and a different sample reported in the literature (Clarke, 2012). The agreement between the two is excellent. Relevant to the foaming discussed later, the solid content of the oil increases from 0% to around 30% between 27 °C and 21 °C.

A sample of coconut oil was taken from the fridge at 6 °C and warmed progressively without shaking at a rate of ≈ 0.1 °C/min using a water bath. Representative photographs of the vessel are shown in Figure 2(a) at specific temperatures (the complete set is shown in Figure S2). Between 6 °C and 24 °C, the sample is solid of white/yellowish colour. The first sign of the liquid state appears at 25 °C (outer surface of sample) and an opaque liquid which interestingly foams naturally on release of trapped air bubbles occurs between 27 °C and 29 °C. From 30 °C upwards, a transparent yellow liquid is formed which no longer foams. At fixed temperature of 29 °C, the natural foam collapses progressively until none remains after 6 hr. The appearance of the vessel on cooling the oil from 35 °C is shown in Figure 2(b), with the complete set being shown in Figure S3. Between 35 °C and 25 °C, the oil is liquid and yellow in colour. The first sign of solidification appears at 24 °C (cloudy) and this increases progressively down to at least 20 °C. The slight hysteresis in behaviour between warming the solid and cooling the liquid is common in mixtures and results from the kinetics of either crystal dissolution or crystal formation being slow relative to the rate of temperature change used. Crystal dissolution is expected to involve little or no energy barrier and is likely to be fast, whereas crystal formation occurs by nucleation and growth which normally requires an energy barrier to be overcome and hence can be slow. The crystals which form at 27 °C (35 °C → 20 °C → 27 °C) are present as spherulites of around 100 μm in diameter, whose edges showed small needles (Maruyama, de Martini Soares, D'Agostinho, Goncalves, Gioielle & da Silva, 2014) of length around 50 μm as seen in Figure 2(c). Using polarised light microscopy, the isotropic liquid oil appears black and the anisotropic solid crystals appear blue.

3.2 Aeration of coconut oil at different temperatures

In the light of the above, we chose to aerate coconut oil at a variety of fixed temperatures achieved by either warming a sample from the fridge (solid) or cooling a sample from 30 °C (liquid). A known mass of solid coconut oil was whipped at constant temperature using a double beater for a total time of 45 min, involving 5 min of whipping and 5 min resting alternately. Whipping was conducted on

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separate samples at ten temperatures between 19 °C and 30 °C. As representative examples, we show in Figure 3 the appearance of the sample during whipping for a low, medium and high temperature. At 19 °C (a), the solid oil flakes can be aerated slightly turning into a creamy white paste; the incorporation of air remains constant however beyond the first 5 min of whipping. At 28 °C (c), the initial cloudy liquid oil clarified during whipping but no air could be incorporated. By contrast, at 23 °C (b), the initial semi-solid oil can be aerated to a high degree with the extent of air incorporation increasing with whipping time. Observations during whipping at some other temperatures are given in Figure S4.

As a measure of foamability, we define the over-run as (vol. after aeration – vol. before aeration)/(vol. before aeration); thus a doubling in volume due to aeration has an over-run of 100% corresponding to an air volume fraction of 0.5. The influence of whipping time on the over-run for samples whipped at different temperatures is shown in Figure 4(a). Apart from 23 °C for which the over-run increases progressively with time, the results for most of the other temperatures show an increase in over-run initially followed by a slight decrease to a constant value with whipping time. Both trends are reminiscent of the results by Mishima *et al*. (Mishima, Suzuki, Sato & Ueno, 2016) for added fat in a liquid oil system, although their variable was the type of tempering applied to the mixture prior to aeration. The effect of the whipping temperature on the over-run at the end of whipping is given in Figure 4(b) where a marked maximum is seen around 23 °C. At temperatures where coconut oil is too solid-like little foaming occurs, whereas at temperatures where it is completely liquid no foaming is possible. The result at 28 °C and higher is significant and implies that molecules of any of the TAGs (or low levels of mono- or diglycerides if present) do not adsorb at the air-oil surface. This is in agreement with the lack of foaming observed in molecular mono-/diglycerides in hydrocarbons (Shrestha, Aramaki, Kato, Takase, & Kunieda, 2006) or rapeseed oil (Brun, Delample, Harte, Lecomte & Leal-Calderon, 2015). At intermediate temperatures however, where a mixture of crystals and liquid oil coexist, appreciable foaming becomes possible which is very temperature dependent. It occurs for SFC values up to 20% (Figure 1). The implication is that TAG crystals which form act as the foaming agent and are thus surface-active.

The appearance of the foams with time stored at the temperature of preparation can be seen in Figure 5 for selected temperatures. Those at all other temperatures are given in Figure S5. At 19 °C (a), the whipped oil was so viscous that it could only be transferred to a wide glass beaker for monitoring. Its volume remains constant for over 2 weeks and no drainage of oil occurs. Similar excellent foam stability is witnessed at 23 °C (b) although it is less viscous and can be transferred to a graduated cylinder. By contrast, at 27 °C (c), the less viscous foam is stable for at least 2 h but reduces in volume within 24 h mainly by the drainage of clear liquid oil containing no crystals. This continues up to around 120 h after which no more oil is released. It is noteworthy that the remaining foam (of higher air

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volume fraction than initially) is subsequently stable. All the crystals in the system are associated with the foam layer as judged by the clear oil layer below. As a measure of foam stability, we calculate the ratio F being the foam volume after 1 month to that initially. F is equal to 1.00 ± 0.05 for all temperatures between 19 °C and 25 °C, decreasing to 0.5 ± 0.05 at 27 °C and finally to 0 at 28 °C and higher.

Optical micrographs of the foams at different storage times are given in Figure 6 for the three temperatures shown in Figure 5. At all temperatures, bubble surfaces are rough and textured (due to adsorbed TAG crystals) and some bubbles are non-spherical in shape which is characteristic of particle-coated interfaces. This is due to jamming of adsorbed particles which prevents relaxation of the interface to a spherical geometry (Subramaniam, Abkarian, Mahadevan & Stone, 2005). Importantly, there is no noticeable change in the average bubble size with time either demonstrating the superior stability to both coalescence of bubbles and disproportionation of gas between bubbles. The average bubble diameter is relatively small compared with surfactant-stabilised aqueous foams, being around 22 μm at 19 °C, 27 μm at 23 °C and 15 μm at 27 °C. Using crossed polarisers, anisotropic TAG crystals are clearly evidenced mainly at the air-oil interfaces of bubbles but also within the continuous oil phase, the latter enabling gelation and thus reducing the tendency for oil drainage. This is in agreement with the findings in Mishima *et al*. (Mishima, Suzuki, Sato & Ueno, 2016) using polarised light microscopy and microprobe infra-red spectroscopy showing that, during whipping, the relative concentration of fat crystals in oil decreased as they adsorbed and stabilised newly created air bubbles. Microscope images of the foams prepared and stored at all other temperatures are shown in Figure S6 and display the same behaviour. Cryo-SEM images in Figure S6(d) of the foam made at 23 °C confirm the bubble sizes and reveal the location of TAG crystals at their surfaces.

We decided to investigate how these mixtures whipped after being cooled from 30 °C (as opposed to warming) to set lower temperatures being 19, 21, 23, 25 and 27 °C. Photos of the vessels during whipping are given in Figure S7 and microscopy of the whipped oils after whipping is seen in Figure S8 at these temperatures. These mixtures can be aerated to similar over-run values at the corresponding temperature as samples which were warmed, apart from at 23 °C where the over-run is significantly less (see Figure 4(b)). A possible explanation for this is that the SFC-temperature curve can display hysteresis between heating and cooling cycles where the SFC on heating is higher than that of cooling at the same temperature. This is all linked to the kinetics of melting or crystallisation relative to the rate of temperature change. Given the relatively fast cooling rate employed here, we suspect that the concentration of crystals formed at 23 °C on cooling is less than that on heating leading to a lower over-run. Despite this, the oil foams prepared at temperatures between 19 °C and 25 °C were stable to drainage and coalescence for over 1 month (F = 1.0) with no change in the average bubble diameter. By

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27 °C however (as opposed to 28 °C earlier), no foam could be prepared.

3.3 Influence of storage temperature on coconut oil aerated at 23 °C

Given the fact that in a stable coconut oil foam the air bubbles are coated with TAG crystals in addition to crystals present in the continuous oil phase, such foams should be temperature-responsive on warming as the crystals begin to melt (Fameau, Lam, Arnould, Gaillard, Velev & Saint-Jalmes, 2015; Binks, Garvey & Vieira, 2016). We chose to investigate this possibility with the whipped oil prepared at 23 °C (upon warming) which is otherwise completely stable at rest at this temperature. After a period of one week at 23 °C, the foam was warmed in a water bath by 1 °C every 12 h until the final temperature of 30 °C was reached. The appearance of the foam at different temperatures after heating is shown in Figure 7. Between 23 °C and 27 °C, the foam appearance and stability remains unchanged at least for 12 h. At 28 °C, visible oil drainage occurs below theremaining foam and larger bubbles are visible within the foam. The extent of oil drainage increases at 29 °C and the foam shows extensive signs of collapse with very large bubbles forming as well as huge air voids developing between the foam and the vessel walls. Virtually no foam remains at 30 °C and the system reverts to a clear, yellow liquid oil. The influence of storage temperature on both the volume of foam and the volume of drained oil is shown in Figure 8. A progressive destabilisation of the foam begins just above 27 °C and ends at 30 °C. The melting of crystals within the foam occurs at similar temperatures to the melting observed in samples of neat coconut oil (Figure 2(a)). As adsorbed crystals around air bubbles melt, they no longer prevent coalescence between bubbles and foam collapse ensues. Microscopy images of the foam at different temperatures upon warming are given in Figure S9. The average bubble diameter remains constant at 25 ± 2 μm up to 27 °C after which it increases markedly due to coalescence. We also confirmed that a stable oil foam could be prepared again after cooling the solution formed at 30 °C to either 25 °C or 23 °C demonstrating the reversible nature of the melting and crystallisation of the crystals and their ability to stabilise foams.

3.4 Aeration of other medium chain length vegetable oils

In order to verify if fractional crystallisation of an oil enables its subsequent aeration, we investigated three other vegetable oils of relatively high saturated fatty acid content of medium chain length. These were palm kernel stearin, cocoa butter and shea butter which possess different melting temperature ranges. The results refer to the case where the oils were warmed from room temperature (all solid) to the respective temperature. After whipping, the variation of the over-run with whipping

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temperature is given in Figure 9 where the data for coconut oil is included for comparison (Figure S10 displays how the over-run varies with whipping time at different temperatures for these oils). In all cases, the over-run exhibits a maximum value at a particular temperature which varies from 23 °C to 34 °C depending on the oil. The maximum over-run for cocoa butter and shea butter is similar and slightly lower than that of coconut oil, whereas that for palm kernel stearin is markedly lower. At the optimum temperatures, the SFC is between ≈ 15% and ≈ 30% for these oils (Personal communication, 2016; Torbica, Jovanovic & Pajin, 2006; Salas, Martinez, Bootello, Venegas & Garces, 2011), *i.e.* best aeration occurs when they are quite soft solids. No foaming is possible at temperatures where the oils are completely liquid. It is worth noticing that the curve for cocoa butter is very sharp between 34 °C and 35 °C, consistent with its widespread use in chocolate which melts within the mouth around this temperature. Photos of the whipped vegetable oils and microscope images of bubbles within them are given in Figure 10. In all cases, non-spherical bubbles exist and anisotropic crystals are predominantly arranged at bubble surfaces giving them a textured appearance. Foams prepared at the optimum temperature were stable for at least 2 months when stored at this temperature; they could however be controllably destabilised upon warming as with coconut oil above.

It is likely that the lamellar planes (or faces) of the TAG crystals are aligned parallel to the air-oil surface of bubbles but are randomly arranged within the continuous oil phase. This has recently been shown unequivocally using micro-X-ray diffraction experiments on foams stabilised by crystals of a commercial saturated TAG in salad oil (Mishima, Suzuki, Sato & Ueno, 2016). The driving force for the adsorption of the TAG crystals from the oil phase to the air-oil surface is to reduce the relatively high surface energy of the latter, *e.g.* the surface tension of the liquid triglyceride triolein is around 31.6 mN/m compared with that of the hydrocarbon decane which is 23.8 mN/m at 20 °C (Jasper, 1972). Since the surface energies of TAG crystals are not available, we take the case of the *β*-crystals of stearic acid (C_{18}) as an example. Calculations reveal that the surface energy of the faces (001 plane) was 43.5 mN/m whereas that of the edges (100 plane) is much higher at 86.5 mN/m (Beckmann & Boistelle, 1984). A plausible arrangement of the TAG crystals here is such that their faces composed of low energy methyl ($-CH_3$) groups are in contact with the air phase on one side and the oil phase on the other, whilst their edges composed mainly of methylene ($-CH_2$) groups and glycerol units interact with each other laterally through neighbouring crystals adsorbed at the air-oil surface.

3.5 Tristearin in tricaprylin system

In order to support our hypothesis that crystals of a particular TAG (or TAGs) stabilise air bubbles in liquid oil comprising other TAGs, we briefly investigated the pure system of tristearin (high

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melting) in tricaprylin (low melting). For 20 wt.% tristearin in tricaprylin, Figure 11 shows that it is a clear solution at 75 °C (a) but then becomes a crystal dispersion on cooling to 15 °C (b). The optical microscope image of this dispersion reveals a high concentration of aggregated tristearin crystals (c). Several isolated crystals can be discerned however (right hand side of image) and these are plate-like of side length around 10 μm (see also Figure S11(a)). It was shown recently that the crystals were exclusively those of the β polymorph (Fletcher, Roberts & Urquhart, 2016). Since we were limited to low volumes (due to the expensive tristearin), we aerated the dispersion using a rotor-stator homogeniser. Figure 12 (and Figure S11(b)) reveals that air can be incorporated as bubbles, some of which are non-spherical, with anisotropic crystals bring present both at bubble surfaces and in the continuous tricaprylin phase. The foam was stable for at least 2 weeks at 15 °C. The over-run is much higher however in oil foams in which commercial fat crystals of fully hydrogenated rapeseed oil rich in behenic acid are added to liquid salad oil (Mishima, Suzuki, Sato & Ueno, 2016).

4. CONCLUSIONS

For fats containing a substantial proportion of saturated fatty acids in their triglyceride chains, we show that whipped oils can be produced in the absence of any other additive simply by controlling the temperature. Upon warming from the solid or cooling from the melt, crystals of high melting TAGs form in liquid oil of low melting TAGs. These dispersions can be aerated and the foams so produced are extremely stable containing bubbles coated with crystals. The over-run exhibits a maximum with respect to temperature and optimum foaming occurs when the solid fat content is around 20-30%. The foams are temperature-responsive and can be progressively collapsed upon increasing their temperature to around the melting point of the crystals. The work opens up the possibility of preparing aerated food compositions containing no additive, a challenge currently being addressed by several companies.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/...

Declaration of interest

The authors confirm that there is no conflict of interest with regards to the work contained herein.

Author contribution

BPB had the original idea, designed the experiments, analysed the data and wrote the paper. IM carried out the experiments, analysed the data and proof-read the paper.

REFERENCES

Official Methods and Recommended Practices of the AOCS. (2009). 6th ed. 2011-2012 Methods and Additions and Revisions. AOCS Official Method Cd 16b-93. Solid fat content (SFC) by low-resolution nuclear magnetic resonance-the direct method.

Beckmann, W., & Boistelle, R. (1984). Calculations of the intermolecular potential and surface energies of stearic acid, *Journal of Crystal Growth*, *67*, 271-277

Binks, B.P., & Horozov, T.S. (eds.) (2006). *Colloidal Particles at Liquid Interfaces*. Cambridge: Cambridge University Press.

Binks, B.P., Davies, C.A., Fletcher, P.D.I., & Sharp, E.L. (2010). Non-aqueous foams in lubricating oil systems, *Colloids and Surfaces A*, *360*, 198-204.

Binks, B.P., & Rocher, A. (2010). Stabilisation of liquid-air surfaces by particles of low surface energy, *Physical Chemistry Chemical Physics*, *12*, 9169-9171.

Binks, B.P., Rocher, A., & Kirkland, M. (2011). Oil foams stabilized solely by particles, *Soft Matter*, *7*, 1800-1808.

Binks, B.P., & Tyowua, A.T. (2013). Influence of the degree of fluorination on the behaviour of silica particles at air-oil surfaces, *Soft Matter*, *9*, 834-845.

Binks, B.P., Sekine, T., & Tyowua, A.T. (2014). Dry oil powders and oil foams stabilised by fluorinated clay platelet particles, *Soft Matter*, *10*, 578-589.

Binks, B.P., Johnston, S.K., Sekine, T., & Tyowua, A.T. (2015). Particles at oil-air surfaces: Powdered oil, liquid oil marbles, and oil foam, *American Chemical Society Applied Materials and Interfaces*, *7*, 14328-14337.

Binks, B.P., Garvey, E.J., & Vieira, J. (2016). Whipped oil stabilised by surfactant crystals, *Chemical Science*, *7*, 2621-2632.

Brun, M., Delample, M., Harte, E., Lecomte, E., & Leal-Calderon, F. (2015). Stabilization of air bubbles in oil by surfactant crystals: a route to produce air-in-oil foams and air-in-oil-in-water emulsions, *Food Research International*, *67*, 366-375.

Campbell, G.M., & Mougeot, E. (1999). Creation and characterisation of aerated food products, *Trends in Food Science & Technology*, *10*, 283-296.

Cassiday, L. (2016). Coconut oil boom, *Inform*, *27*, 5-13.

Chiavaro, E. (2015) ed. *Differential Scanning Calorimetry-Applications in Fat and Oil Technology*. Boca Raton: CRC Press.

Clarke, C. (2012). *The Science of Ice Cream*. Cambridge: The Royal Society of Chemistry (p.52).

Fameau, A-L., Lam, S., Arnould, A., Gaillard, C., Velev, O.D., & Saint-Jalmes, A. (2015). Smart nonaqueous foams from lipid-based oleogel, *Langmuir*, *31*, 13501-13510.

Firestone, D. (2013). *Physical and chemical characteristics of oils, fats, and waxes.* , (3rd ed.) Urbana: American Oil Chemists Society Press..

Fletcher, P.D.I., Roberts, N.A., & Urquhart, C. (2016). Solubility behaviour, crystallisation kinetics and pour point: A comparison of linear alkane and triacyl glyceride solute/solvent mixtures, *Journal of Industrial and Engineering Chemistry*, *34*, 382-389.

Garvey, E.J. (2014). Ph.D. thesis, University of Hull (UK).

Jasper, J. (1972). The Surface Tension of Pure Liquid Compounds, *Journal of Physical Chemistry Reference Data*, *1*, 841-948.

Kunieda, H., Shrestha, L.K., Acharya, D.P., Kato, H., Takase Y., & Gutierrez, J.M. (2007). Super-stable nonaquous foams in diglycerol fatty acid esters-non polar oil systems, *Journal of Dispersion Science and Technology*, *28*, 133-142.

Maruyama, J.M., de Martini Soares F.A.S., D'Agostinho, N.R., Gonçalves, M.I.A., Gioielli, L.A., & da Silva, R.C. (2014). Effects of emulsifier addition on the crystallization and melting behavior of palm olein and coconut oil, *Journal of Agricultural Food Chemistry*, *62*, 2253-2263.

Mishima, S., Suzuki, A., Sato, K., & S. Ueno. (2016). Formation and microstructures of whipped oils composed of vegetable oils and high-melting fat crystals, *Journal of American Oil Chemists Society*, *93*, 1453-1466.

Moigradean, D., Poiana, M-A., & Gogoasa, I. (2012). Quality characteristics and oxidative stability of coconut oil during storage, *Journal of Agroalimentary Processes and Technologies*, *18*, 272-276.

Murakami, R., & Bismarck, A. (2010). Particle-stabilized materials: Dry oils and (polymerized) non-aqueous foams, *Advanced Functional Materials*, *20*, 732-737.

Neff, W.E., Byrdwell, W.C., & List, G.R. (2001). Triacylglycerol structures of food fats high in saturated acids by HPLC and mass spectrometry, *Journal of Liquid Chromatography & Related Technology*, *24*, 837-854.

Personal communication with Cargill (Minneapolis, USA) in Dec. 2016.

Salas, L.J.J., Martinez, F.E., Bootello, G.M.A., Venegas, C.M., & Garces, R. (2011). High melting point sunflower fat for confectionary, *WO 2011048169 A1* assigned to Consejo Superior De Investigaciones Cientificas.

Shrestha, L.K., Aramaki, K., Kato, H., Takase, Y., & Kunieda, H. (2006). Foaming properties of monoglycerol fatty acid esters in nonpolar oil systems, *Langmuir*, *22*, 8337-8345.

Shrestha, L.K., Shrestha, R.G., Sharma, S.C., & Aramaki, K. (2008). Stabilization of nonaqueous foam with lamellar liquid crystal particles in diglycerol monolaurate/olive oil system, *Journal of Colloid and Interface Science*, *328*, 172-179.

Shrestha, R.G., Shrestha, L.K., Solans, C., Gonzalez, G., & Aramaki, K. (2010). Nonaqueous foam with outstanding stability in diglycerol monomyristate/olive oil system, *Colloids and Surfaces A*, *353*, 157-165.

Subramaniam, A.B., Abkarian, M., Mahadevan, L., & Stone, H.A. (2005). Non-spherical bubbles, *Nature*, *438*, 930.

Torbica, A.M., Jovanovic, O., & Pajin, B. (2006). The advantages of solid fat content determination in cocoa butter and cocoa butter equivalents by the Karlshamns method, *European Food Research & Technology*, *222*, 385-391.

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Figure 1. Variation of the solid fat content of coconut oil with temperature for our sample (open points) and the sample used in Clarke (2012) (filled points).
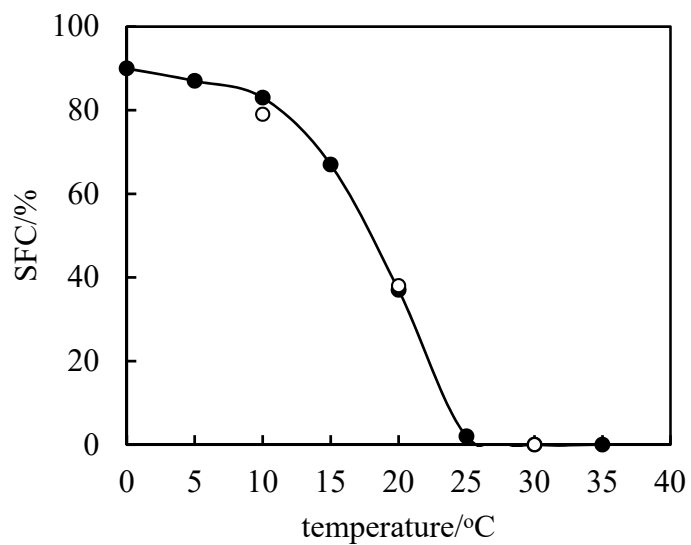
Figure 2.   (a) Close up photos of the vessel containing 5 g of coconut oil as it is warmed at 0.1 °C/min from 6 °C. Inset is a photo' of the entire vessel.

(b) As in (a) but in which the liquid oil at 35 °C is cooled at 0.1 °C/min.

(c) Polarised optical micrograph of coconut oil at 27 °C (after heating from 6 °C to 35 °C and then cooling to 20 °C) showing spherulites of needle-like crystals dispersed in liquid oil.

(a)

(b)

(c)

20
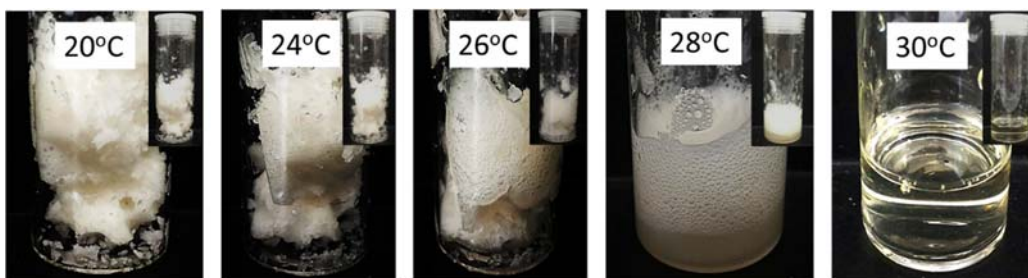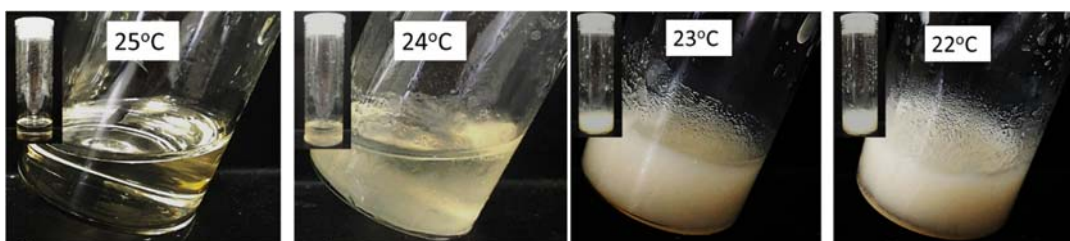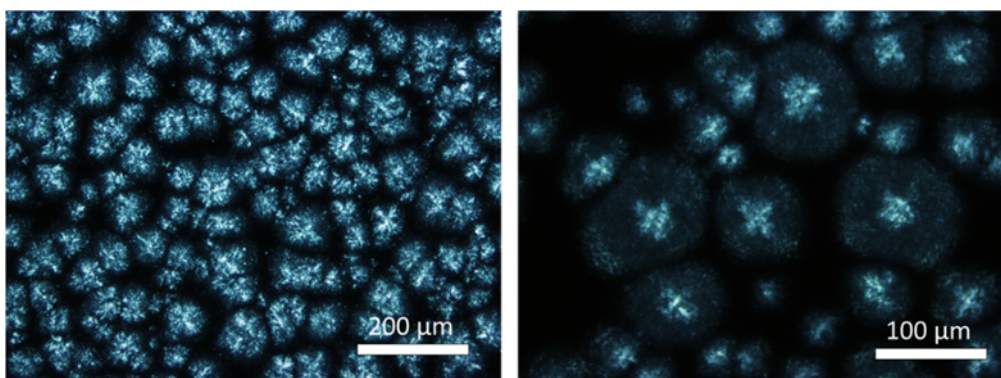
Figure 3. Photographs from above during whipping of coconut oil after warming from 6 °C to either (a) 19 °C, (b) 23 °C or (c) 28 °C. Inset is photo' from vessel side.

21
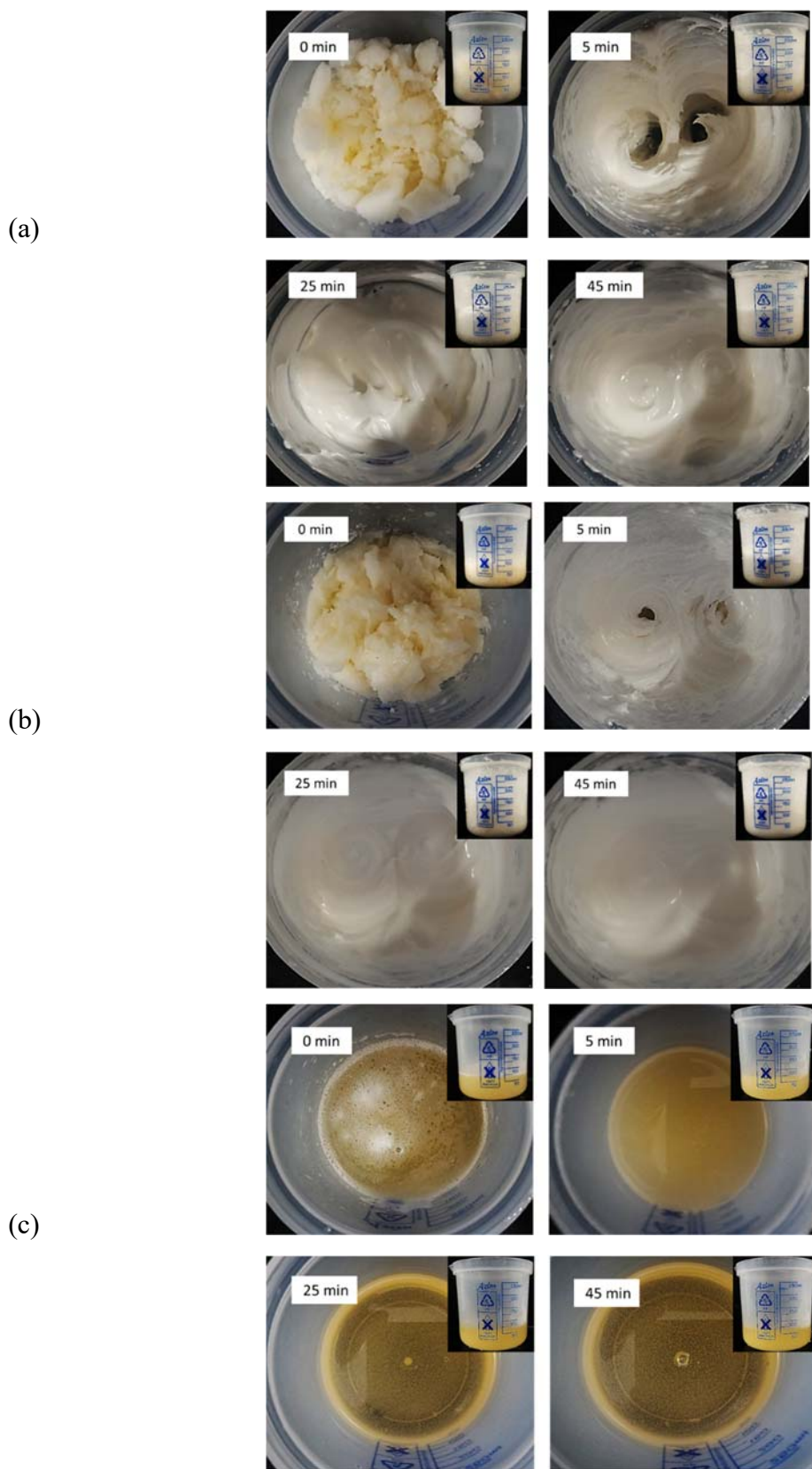
Figure 4. (a) Over-run of coconut oil at different times during whipping for different whipping temperatures (given). Samples were warmed from 6 °C.

(b) Over-run of coconut oil after whipping *versus* whipping temperature. Samples are either after warming from 6 °C (filled points) or after cooling from 30 °C (open points).

(a)

(b)

22
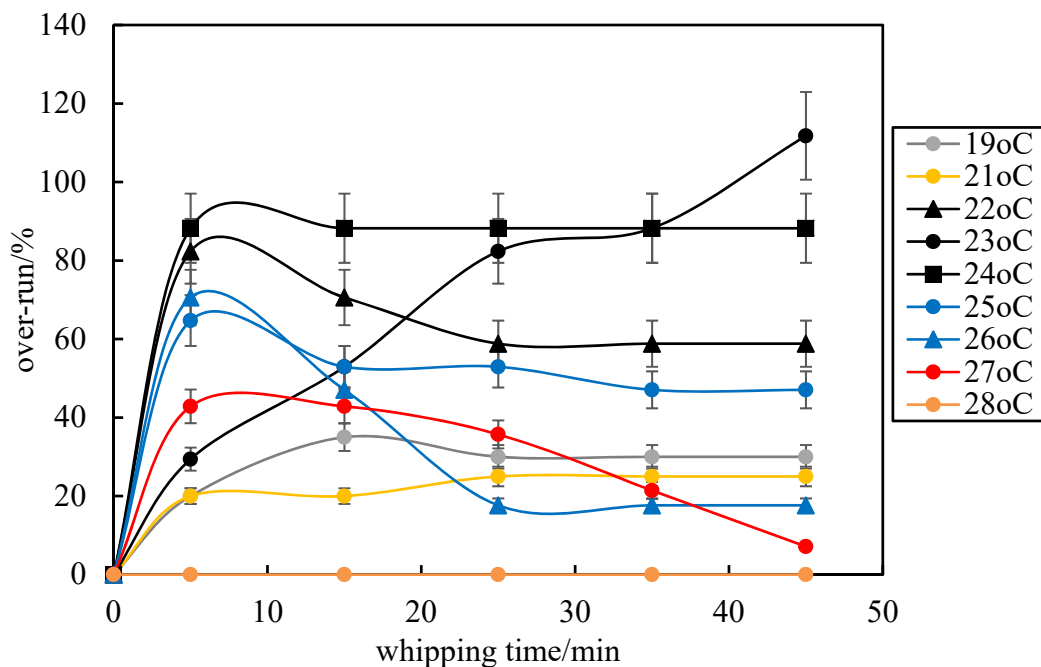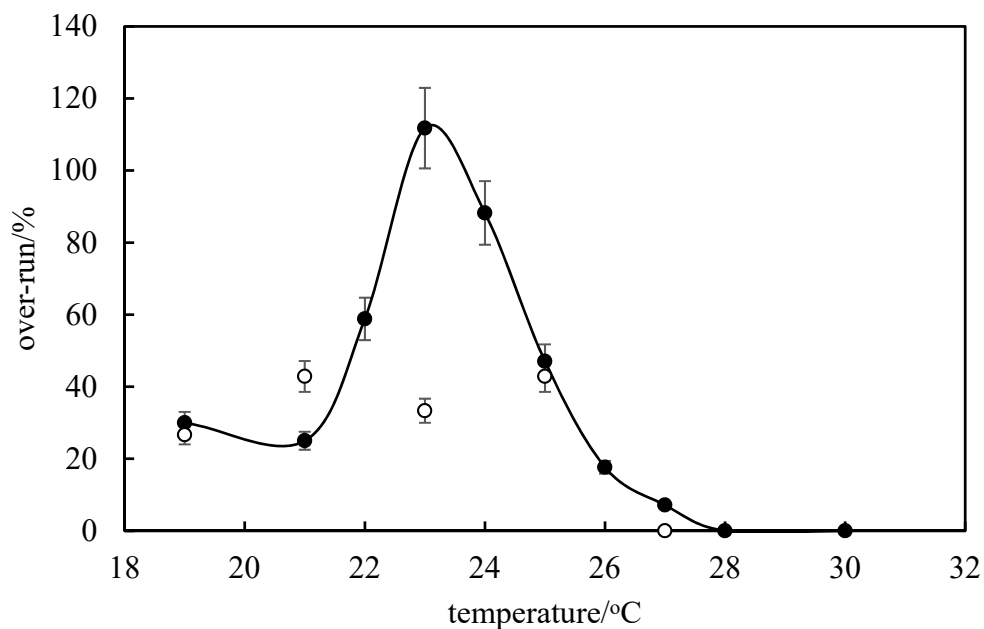
Figure 5. Appearance of whipped coconut oil as a function of storage time (at the temperature of whipping) for samples whipped at (a) 19 °C, (b) 23 °C and (c) 27 °C after warming from 6 °C.

(a)
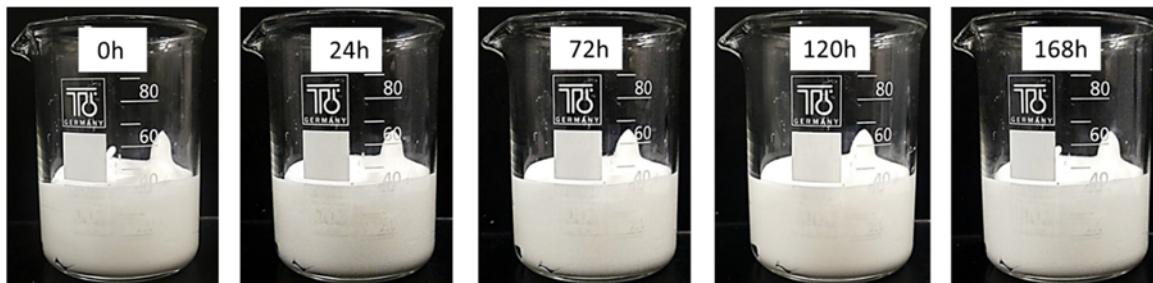
(b)
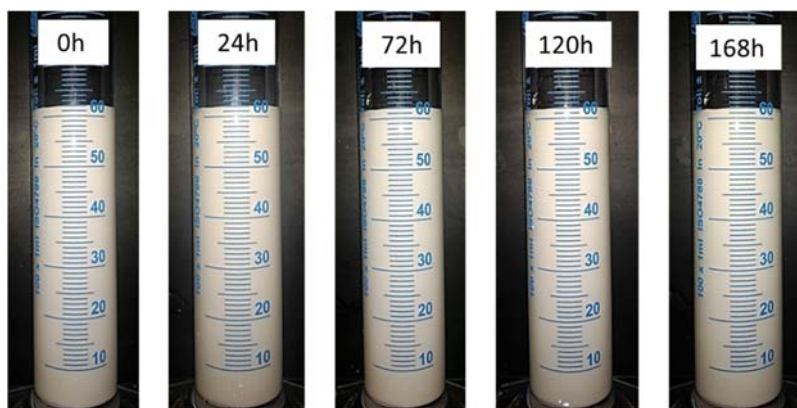
(c)
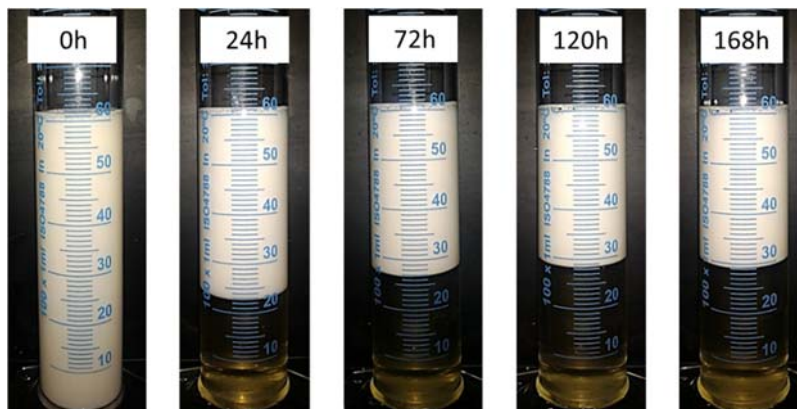
Figure 6. Optical microscopy of coconut oil whipped and stored at different temperatures for different times after preparation (warmed from 6 °C); (a) 19 °C, (b) 23 °C and (c) 27 °C. The first two images for 23 °C refer to 24 h and include a polarising microscopy image whilst the third refers to 168 h.

(a)

(b)

(c)

24
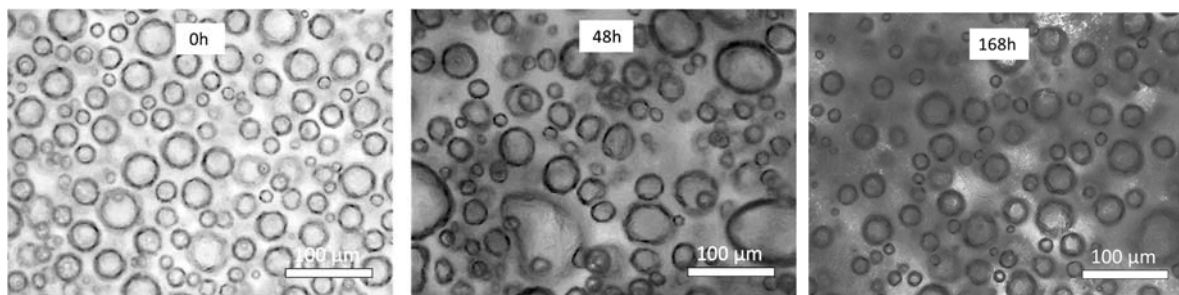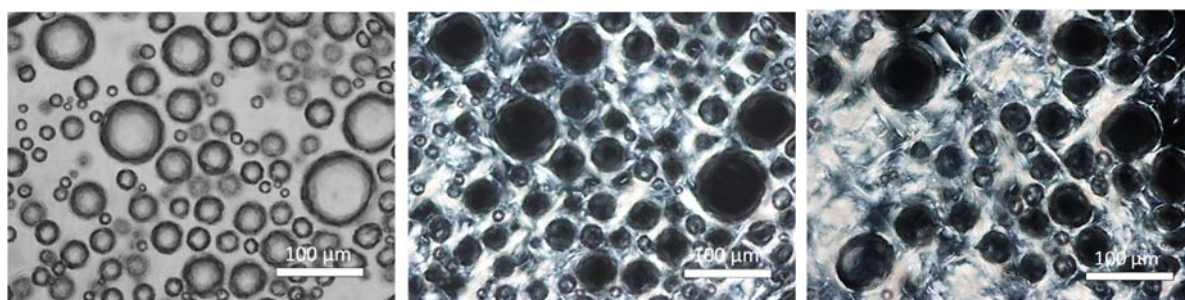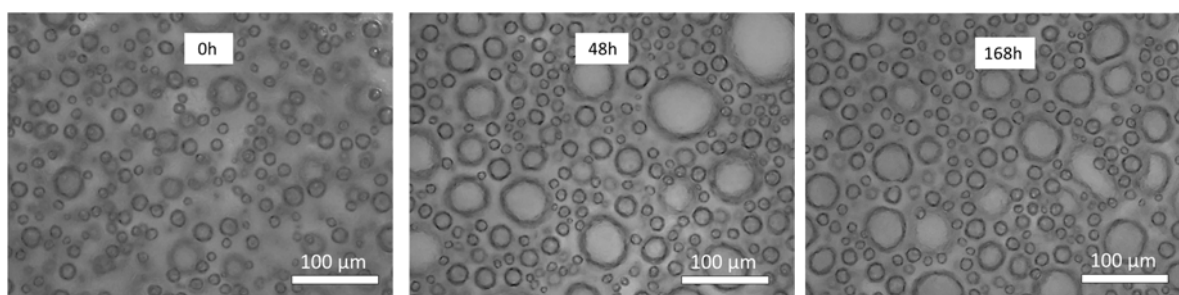
Figure 7. Photos of vessel containing coconut oil whipped at 23 °C as it is warmed to different temperatures given.
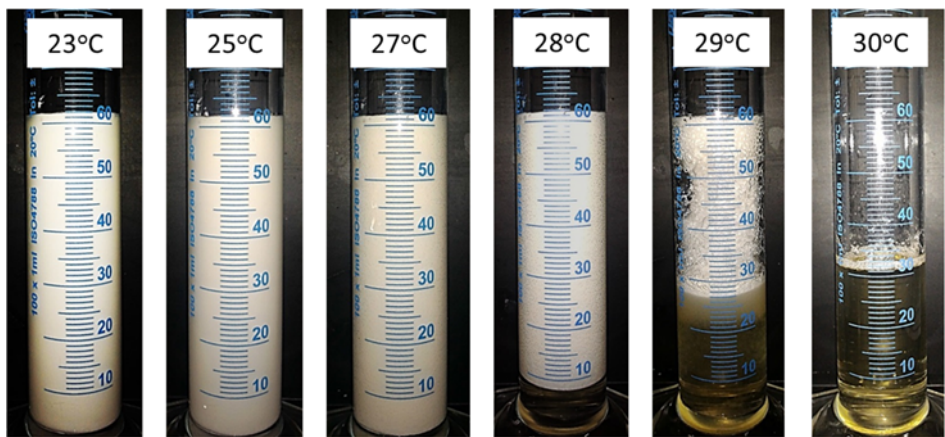
Figure 8. Variation of foam volume (filled points) and released oil volume (open points) after 12 h with storage temperature for coconut oil whipped at 23 °C.
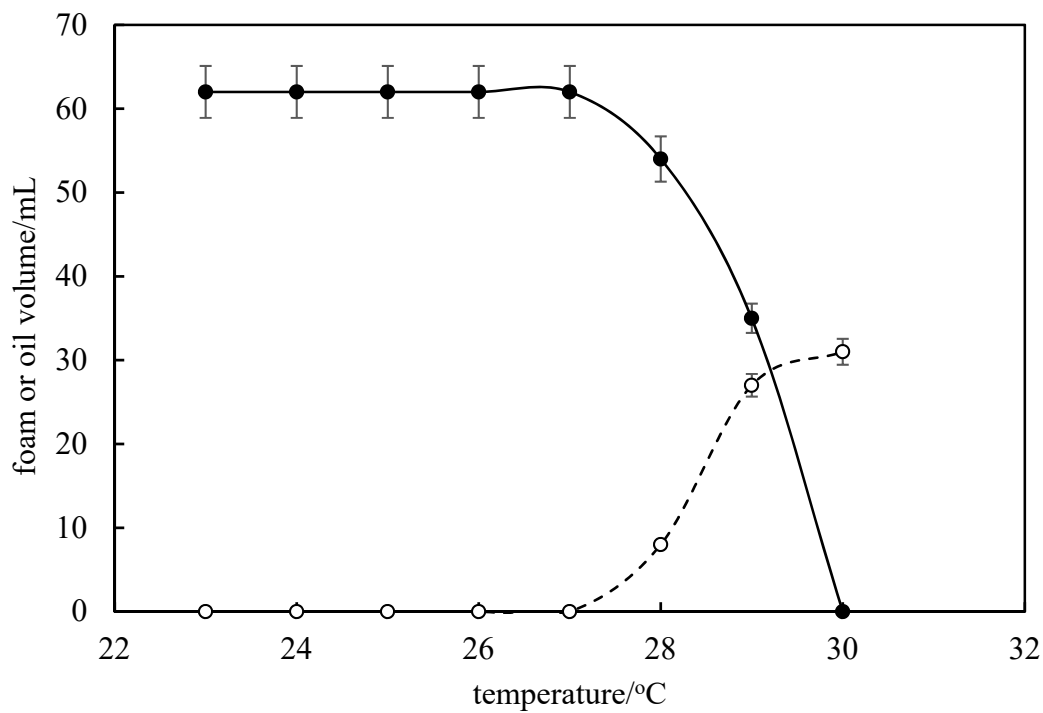
Figure 9. Over-run of coconut oil (filled circles), palm kernel stearin (open circles), shea butter (filled diamonds) and cocoa butter (open triangles) after whipping *versus* whipping temperature. Samples were warmed from room temperature.
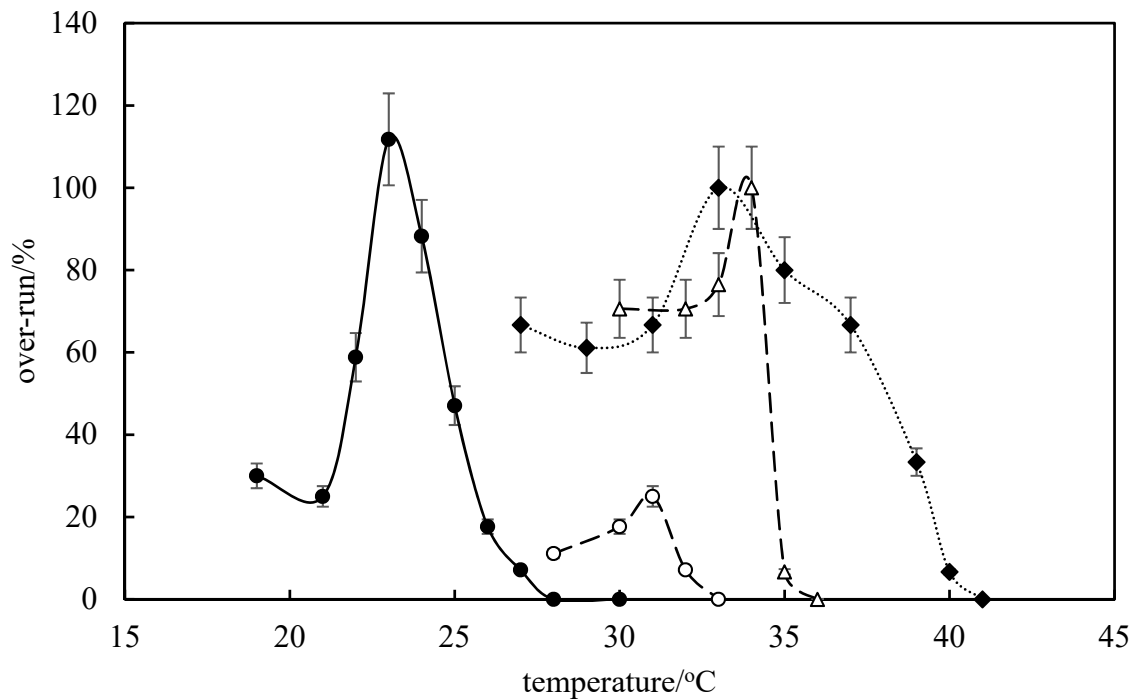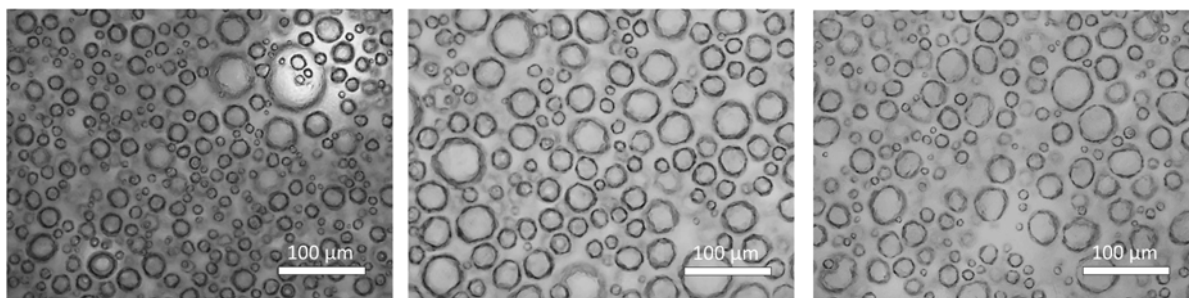
Figure 10. (a) Photos from above of whipped shea butter at 33 °C (left), whipped cocoa butter at 34 °C (middle) and whipped palm kernel stearin at 31 °C (right) immediately after whipping. Inset is photo' from vessel side.

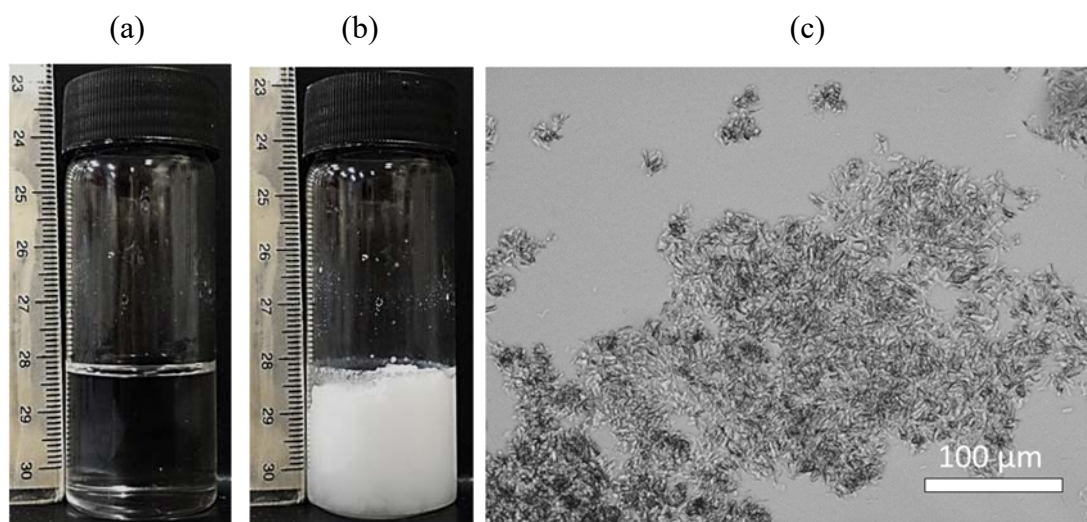(b) Optical microscope images for systems in (a) respectively.
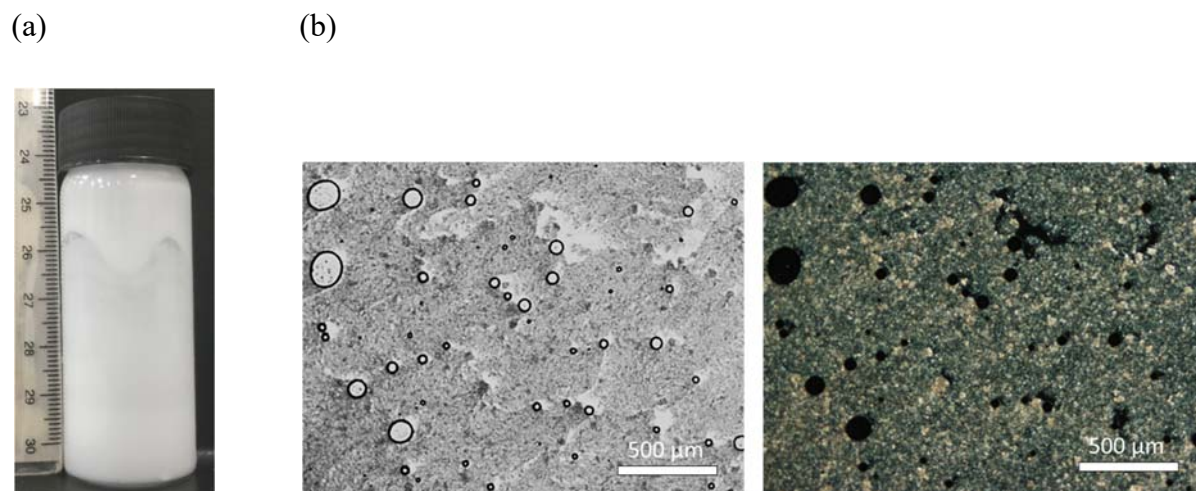
(a)
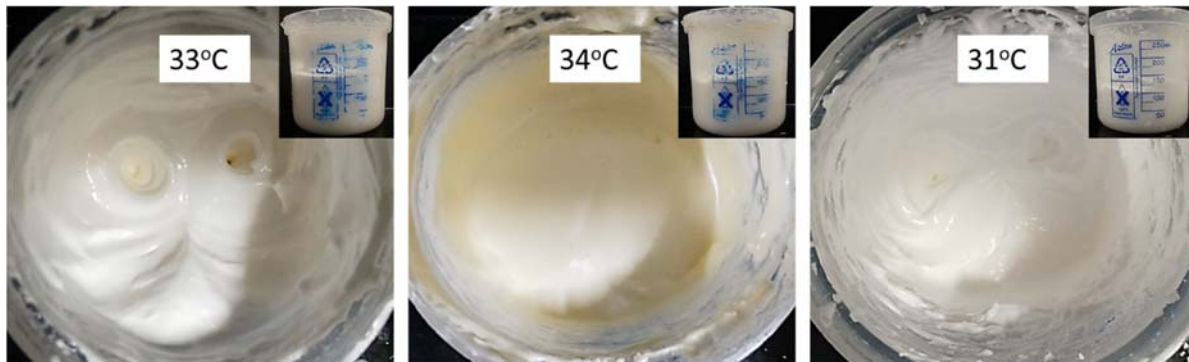
(b)

Figure 11. Photo' of vessel containing 20 wt.% tristearin in tricaprylin (a) after warming to 75 °C and (b) after cooling to 15 °C. (c) Optical microscopy of oil dispersion at 15 °C.

(a) (b) (c)

29

Figure 12. (a) Appearance of 20 wt.% tristearin in tricaprylin after whipping at 15 °C and (b) optical and polarised microscopy of system in (a).

(a)   (b)

TOC

Ultra-stable self-foaming oils

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