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Material properties of cocoa butter emulsions: effect of dispersed phase droplet size and compression speed on mechanical response

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Graphical abstract

Abstract

Water-in-cocoa butter (CB) emulsions material properties were investigated using uniaxial compression test. Emulsions containing 20% (wt%) water and with a range of droplet size were manufactured to assess the role of defect size on emulsions mechanical properties. Although differences were not significant within the tested droplet size range, results showed a decreasing trend in the values of mechanical parameters at fracture with increasing structural defect size. The mechanical response of bulk CB and emulsions was also investigated at different compressive rates. Materials visco-elastic behaviour was confirmed by their strain-hardening behaviour at increasing test speed with bulk CB always displaying the highest mechanical strength. In the light of these results and microscopy evidences, it was hypothesised that droplets are only partially bonded to the CB network therefore playing a stress-concentration role by promoting fracture initiation. The addition of water droplets also resulted in a reduction of the overall network internal degree of connectivity: when large deformations are applied, droplet-matrix de-bonding occurs at the particle-fat network interface promoting fracture propagation and thus explaining the weakening structural effect of droplets.

Keywords: cocoa butter, emulsions, fracture propagation, fracture initiation, particle gels

1. Introduction

Water-in-cocoa butter (CB) emulsions are a new food ingredient developed to reduce fat content in chocolate (di Bari et al., 2014, Norton et al., 2009, Rivas et al., 2016). With respect to their colloidal properties, similarly to margarine (van Vliet and Walstra, 1995), water-in-cocoa butter emulsions can be classified as particle gels formed by the aggregation of CB fat

crystals and crystal aggregates to produce a continuous three dimensional solid network, which traps the liquid oil and water, this latter phase dispersed in the form of droplets. Microstructure visualisation of water-in-cocoa butter emulsions using *cryo*-Scanning Electron Microscopy (Norton et al., 2009, Norton and Fryer, 2012) revealed the existence of a crystalline ‘shell’ around water droplets and a continuous bulk network both resulting from CB crystallisation. Therefore according to the classification reported in literature (Rousseau, 2013), these systems can be ascribed to the group of fat-crystals stabilised emulsions where both Pickering and network stabilisation occur. From a material science point of view, water-in-cocoa butter emulsions are complex composite materials where the filler phase (i.e. water droplets) is dispersed within a continuous polycrystalline semi-solid fat matrix (i.e. CB) (di Bari *et al.*, 2018a, submitted). The material properties of these emulsions will therefore depend upon the properties of both the continuous and dispersed phase and on the droplet-matrix interaction. Whilst the material behaviour of hydrocolloids based composite gels and their sensory perception has been investigated in literature (SALA et al., 2007, Sala et al., 2008), there is still a limited number of studies dedicated at understanding the mechanical behaviour of crystallising fats containing emulsified water droplets (Chronakis and Kasapis, 1995, Heertje, 1993, Sullo et al., 2014). To our knowledge, the material properties of these systems and the role played by the dispersed phase have been characterised mainly using small oscillatory rheology (Haj-shafiei et al., 2013, Rafanan and Rousseau, 2017). Although this approach yields important information on fundamental material properties, the deformations applied are smaller than those encountered in food applications, which limits the possibility to predict material behaviour in every-day scenarios where large deformations are met. In order to apply water-in-cocoa butter emulsions for fat reduction, it is necessary to understand their material properties at large deformations. This approach imposes deformations above the linear viscoelastic region, i.e. approximately 0.001 strain (Kloek et al., 2005a, Kloek et al., 2005b),

and allows to gain information on samples microstructure and functional properties (van Vliet, 1996). The aim of this study was to further elucidate the role of dispersed droplets and droplet-matrix interaction on CB emulsions material properties at large deformations. Material properties were characterised using uniaxial compression test until specimens fracture. In the light of findings reported in literature (di Bari *et al.*, 2018a, submitted; Sullo *et al.*, 2014), water droplets are known to act as ‘structural defects’ causing a reduction in the mechanical strength of emulsified CB compared to bulk CB. However, there is no information available on the effect of water droplet size and filler-continuous phase interaction on emulsions fracture behaviour. Since water droplet crystalline interface and the bulk network both results from CB crystallisation, it is reasonable to hypothesise the existence of droplets-matrix interactions. As clearly shown in model systems (Rafanan and Rousseau, 2017), these interactions are expected to influence the overall mechanical behaviour of emulsified systems, nevertheless very little is still known on the forces and mechanisms governing the interactions. In his review, Heertje (1993) reported that fracture occurred mostly around and through water droplets when saturated and unsaturated monoglycerides, respectively, were used to stabilise water droplets in margarine. This result was attributed to differences in the structure of the crystalline interfacial shell formed: a multi-layered and particulate interface for saturated and unsaturated monoglycerides, respectively. However, the type of bonds connecting the interfacial shell and the bulk network were not discussed in detail. In order to further advance the current understanding on the role of dispersed droplets and droplet-matrix interaction on emulsions material properties, two variables were investigated in this study: (1) role of structural defects size and (2) compression test speed on the large deformation behaviour of CB emulsions. The processing conditions applied to manufacture samples were tailored in order to minimise differences in the properties of CB phase (primarily polymorphism) and maintain focus on the role of the filler phase. The combination of mechanical analysis and microstructure

visualisation carried out in this study allowed to gain a deeper understanding of the role of water droplets and of the droplets-CB matrix interaction on material properties of emulsions.

2. Materials and Methods

2.1. Materials

Cocoa butter (CB) and the emulsifier polyglycerol polyricinoleate (PGPR) were of food grade, provided by Cargill (Vilvoorde, Belgium) and used without any purification. To normalise for any emulsifier effect, PGPR was always added to a final value of 5% of aqueous phase mass. Double distilled water (Aquatron, A4000D, Bibby Scientific Limited, UK) was used as aqueous phase of emulsions. Emulsions lipid phase was prepared by blending the PGPR with molten CB (60°C) stirring with a magnetic stirrer at 300 rpm for 15 minutes.

2.2. Methods

2.2.1. Cocoa butter emulsions manufacture

Emulsions were produced according to di Bari *et al.* (2014) using a laboratory scale scraped surface heat exchanger (SSHE) with its jacket temperature set to 25°C and a flow rate of 30 mL min⁻¹. In order to produce a 20% water emulsion with decreasing droplet size, four SSHE shaft rotational speeds (N_{SSHE}) were used: 170, 500, 930, 1315 rpm. Bulk CB (i.e. reference material) and the 40% (wt%) emulsion were produced using a shaft speed and 1315 rpm and keeping all the other processing parameters the same as above. Samples for droplet size and solid fat content determination (Section 2.2.4.) were collected and stored at 4°C until analysis.

2.2.2. Uniaxial compression test of CB systems

Samples preparation for parallel plates uniaxial compression test was carried out as described in di Bari *et al.* (2018a, submitted). The diameter of the compressive upper plate was over a factor of two larger than the specimen diameter, therefore it can be considered a compression test between two parallel infinite plates. The test was performed using a TA.XT.plus texture

analyser (Stable Micro-system Ltd., Surrey, UK) universal testing machine controlled by a desktop computer. A 30 kg loading cell fitted with a 40 mm diameter cylindrical aluminium probe was used with the trigger force set to 0.05 N. Both cylindrical probe (i.e. upper plate) and the static plate were covered with parafilm to reduce frictional effects at the plates - specimens' interfaces. At least ten specimens (height (H) /diameter (d) = 1.56) for each sample type were analysed at 25°C at 48h after production and applying an engineering strain of 10% to ensure complete specimen failure. The compression speed will be specified case-by-case. A sampling rate of 500 data point/s was used for data collection and the force-deformation curves were converted into engineering stress (σ_E)-strain (ϵ_E) curves according to di Bari *et al.* (2018a, submitted). From each stress-strain curve five mechanical characterizing parameters were extracted: (1) Apparent Young's modulus (E_{app}); (2) bulk modulus (BM), (3) stress (σ_{Fr}), (4) strain (ϵ_{Fr}) and (5) work to fracture (here synonymously called also 'work to failure'). Details on the calculation of these parameters and on their physical meaning have been reported elsewhere (di Bari *et al.*, 2018a, submitted).

2.2.3. Differential Scanning Calorimetry (DSC)

DSC of CB systems was used to gain an insight on their polymorphic. Analysis were carried out using a DSC 8000 (PerkinElmer, UK) equipped with an intracooler 2 and controlled by 'PyrisTM' software. Approximately 4 mg (± 1 mg) of material obtained after material testing was weighed for each sample directly into a 40 mL aluminium pan and hermetically sealed with an aluminium lid. An empty pan was used as reference using dry nitrogen (20 mL min^{-1}) to purge the system. On analysis samples were hold at 0°C for 5 minutes and then heated up to 50°C at 5°C min^{-1} . Tests were carried out at least in duplicate and heat flow data were normalised per gram of CB.

2.2.4. Droplets size and solid fat content determination

Sauter mean diameter ($d_{3,2}$) and free water (diameter above 50 μm) of the emulsions were calculated using a pulsed nuclear magnetic resonance spectrometer (Minispec, Bruker Optics, UK) equipped with a droplet size application. Measurements were performed according to Di Bari *et al.*, (2014). Solid fat content (SFC) determination in CB systems was performed using the 'indirect method' following the protocol described in literature (Di Bari *et al.*, 2017). All reported values are the average of three replicates.

2.2.5. Cryogenic electron scanning electron microscopy

Cryogenic electron scanning electron microscopy (*Cryo*-SEM) was used to gain an insight of emulsion structure. Images acquisition was done using a Phillips XL30 microscope equipped with a Gatan low temperature stage using the procedure detailed by Norton *et al.* (2009).

3. Theory

According to theories on fracture mechanics, defects (small cracks) or in-homogeneities occur in all materials and determine structural strength reduction: under deformation, stress-strain concentration occurs in the vicinity of structural defects, which can yield earlier material failure (Luyten and Van Vliet, 1995). Material fracture results from two processes: (i) initiation; (ii) propagation. Fracture initiation corresponds to the initial growth of a crack, which occurs only if the stress at the tip of the crack is higher than adhesion or cohesion stresses between building elements of the material. Fracture propagation represents the growth of a crack, which occurs only if the energy required for the growth is lower than the strain energy released (van Vliet and Walstra, 1995). Material failure occurs only if defects can grow enough to determine overall material breakdown. When deforming a system (for example in compression), only part of the mechanical energy supplied is used for fracture. The total supplied energy (W_{Tot}) is given by Equation 1 (Van Vliet, 1996):

$$W_{\text{Tot}} = W_e + W_{d,v} + W_{d,c} + W_{\text{Fr}} \quad (\text{Eq. 1}),$$

where, W_e is the elastically stored energy, $W_{d,v}$ is the energy dissipated due to the viscoelasticity of the system, $W_{d,c}$ is the energy dissipated due to frictions processes at large deformation, and W_{Fr} is the total work to fracture.

While the W_e can be estimated ($W_e = \frac{1}{2} E \varepsilon^2$) from the Young's modulus (E) and the strain (ε) and the W_{Fr} can be calculated from stress-strain curve until the fracture point, it is usually difficult to quantify the values of $W_{d,v}$ and $W_{d,c}$. This problem is usually overcome performing test at different compressive rates (Van Vliet, 1996). This aspect is investigated in detail in Section 4.2.

4. Results and Discussion

4.1. Effect of dispersed phase droplet size on the material properties of water-in-cocoa butter emulsions

The aim of the work presented in this section was to understand the effect of droplet size on the large deformation behaviour of 20% (wt%) water-in-cocoa butter emulsions. This was achieved by manipulating the processing conditions: emulsions were prepared using the SSHE at four rotational rates (N_{SSHE}) to obtain different average $d_{3,2}$ and free water content. In agreement with di Bari *et al.* (2014) the average $d_{3,2}$ and free water content value decrease at increasing N_{SSHE} , whereas the SFC content remained constant across systems (Table 1). To better understand the approach used, it should be recalled that the $d_{3,2}$ is the average droplet diameter, while free water represents the fraction of droplets with a $d_{3,2}$ above 50 μm . Considering the emulsions produced with a N_{SSHE} of 170 and 1315 rpm the difference in the engineered defect size can be easily appreciated: the values of $d_{3,2}$ and free water for a N_{SSHE} of 170 rpm are four and three times, respectively, larger than those values obtained with a N_{SSHE} of 1315 rpm. This consideration will be re-called later in this section to explain results. Finally, it should be pointed out that with the adopted experimental set-up it was not possible to produce emulsions having larger/smaller droplets than those reported here.

Table 1: Scraped surface heat exchanger (SSHE) rotor rate (N_{SSHE}) and microstructural parameters of emulsions produced at different N_{SSHE} .

SSHE Rotational rate (N_{SSHE})	$d_{3,2}$ (μm)	Free water (%)	SFC (%) ¹
170 rpm	14.0	15.7	78.7 ± 1.7
500 rpm	8.1	7.6	79.7 ± 1.6
930 rpm	3.8	5.4	76.3 ± 2.0
1315 rpm	3.5	5.1	78.3 ± 0.8

In Figure 1 the values of Apparent Young's modulus (E_{app}) and bulk modulus (BM) measured for the four emulsion systems are shown. No difference in the value of E_{app} was observed as a result of decreasing $d_{3,2}$. This result suggests that by increasing droplet size, the development of structural rigid junctions responsible for the elastic behaviour is not affected.

Also values of BM (Fig. 1) are the same among systems indicating that the overall matrix deformability is not affected by the size of in-homogeneities.

DSC analysis of samples revealed that they were all characterised by a melting peak between 32-33°C, suggesting CB was in Form V for all of tested samples irrespectively of the adopted SSHE crystallisation conditions (Fig. 2). This result confirms that the processing conditions allowed to control the polymorphic form so to maintain the focus on the effect of droplet size.

A better understanding of the emulsion structure and of the droplets-CB matrix interaction was gained *via cryo*-SEM visualisation of emulsions. In Figure 3 the structure of a 20% aqueous phase emulsion (produced at a SSHE of 1315 rpm) is shown (with the CB matrix

and water droplets indicated). Water droplets appear surrounded by a crystalline interfacial layer and embedded in the CB matrix. Furthermore, water droplets appear to be only partially sintered to the fat matrix in agreement with other findings (di Bari *et al.*, in preparation). Although some of the droplets-CB matrix solid bonds may have been broken on sample preparation, a limited number of droplets-matrix bonds appears to be a common pattern. This evidence may suggest that on crystallisation only a small number of solid bonds could be formed between the droplets interface and the continuous fat matrix. Therefore, it appears reasonable to hypothesise that in emulsions weak van der Waals forces may play a major role in determining interactions between fat crystals of the solid droplet interface and the bulk network. Finally, the majority of droplets appears to be intact. A similar result was referred by Heertje (1993) who proposed that this behaviour accounts for ‘surface fracture’: the fracture pattern suggests cracks propagating around the droplets rather than through the droplets.

Figure 4a shows the fracture stress (σ_{Fr}) and strain (ϵ_{Fr}) as a function of the average $d_{3,2}$. The σ_{Fr} remains constant with increasing droplet size (and free water content, data not shown), thus suggesting that within the investigated range material hardness is not affected by the size of in-homogeneities but it may rather depend on the total amount of disperse phase. The ϵ_{Fr} (Fig. 4a) decreases at increasing $d_{3,2}$ values of droplets. This result indicates that the material deformability at fracture is affected by the defect size: the presence of larger defects leads to an earlier failure.

Figure 4b shows the data of work to failure expressed as function of average $d_{3,2}$ (bottom x axis) and free water content (upper x axis) of emulsions. It can be seen that the profile of the data is the same: at increasing defect size, the mechanical energy needed for fracturing the material decreases. Despite this decreasing trend, the differences in work to fracture among emulsified systems within the tested droplet size were not significant and all emulsions were

characterised by brittle fracture. This evidence suggests that the overall fracturing behaviour is not changing as a result of water addition and is still dominated by CB. To understand the effect of droplet size on emulsions work to fracture two aspects must be considered: (1) by increasing the value of N_{SSHE} the obtained $d_{3,2}$ and free water values decrease and therefore the size of introduced structural defects decreases; (2) when larger in-homogeneities are dispersed within the fat matrix, the total number of defects decreases. As shown in Table 1, the defect size in emulsions produced with a N_{SSHE} at 170 rpm is approximately three times larger than the one obtained for N_{SSHE} at 1315 rpm. However, the values of work to fracture do not differ by a factor of three between the two systems. This result suggests that although larger defect lead to an earlier breakdown (ϵ_{Fr}), the work to fracture does not decrease linearly with the average size of in-homogeneities. By using compression and wire cutting experiments Kloeck *et al.* (2005a) calculated that the critical average defect length responsible for stress concentration in a fat crystal network is approximately $20\ \mu\text{m}$ (size range $8 - 130\ \mu\text{m}$). This value corresponds to a fat crystal aggregate at the gel point (the point at which the network is formed). Such a value is close to the defect size for the weakest system in this study (i.e. produced with a N_{SSHE} of 170 rpm). This evidence support the hypothesis that larger in-homogeneities may be responsible for a more pronounced stress concentration effect resulting in less tough structures. It can be speculated that an average water droplet size larger than $20\ \mu\text{m}$ would result in a significant lower work to fracture.

4.2. CB systems material properties as function of compressive rate

CB systems can be considered visco-elastic materials, which means that their behaviour incorporates aspects of liquid (viscous) and solid (elastic) components. Therefore, their mechanical response is expected to be test speed dependent. The study of the uniaxial load response over a wide range of test speeds would provide an understanding of how network relaxation and fracture propagation influence the failure behaviour of those materials (Zhang et al., 2005). Network stress relaxation is associated with energy dissipating mechanisms occurring on deformation, i.e. viscous flow and friction between structural elements, terms $W_{d,v}$ and $W_{d,c}$ in Eq. 1, respectively (Section 3).

The aim of work presented in this section was to characterise the dependence of the large deformation behaviour of CB systems on uniaxial compressive rate. To gain a deep understanding, a wide range of test speeds were evaluated: from 0.01 to 10 mm s⁻¹. Test specimens of bulk CB and of emulsions containing 20% and 40% (wt%) of dispersed phase were produced. The average $d_{3,2}$ (μm), free water (%), and SFC (%) for these systems have been compiled in Table 2. The two emulsions were characterised by the same droplet size and the SFC was the same for the three systems. For each compression rate and formulation, at least ten specimens were analysed and the average and standard error of the mean reported.

Table 2: Average droplet size $d_{3,2}$ (μm), free water (%), and SFC (%) for bulk cocoa butter (CB) and emulsions containing 20% and 40% (wt%) aqueous phase (plus/minus one standard error of the mean of triplicates).

Aqueous phase (%)	$d_{3,2}$ (μm)	Free water (%)	SFC (%)¹
0²	-	-	79.0 ± 0.8
20	3.1 ± 0.1	4.4 ± 0.2	78.3 ± 0.8
40	3.2 ± 0.1	5.6 ± 0.1	78.0 ± 2.0

¹ Percentage expressed as gram of solid fat per gram of total lipid.

² Reference material (i.e. bulk CB)

On compression, independently from the compressive speed, samples always fractured after a small deformation (below 10% of deformation). The most commonly observed failure pattern was characterised by a fracture along the central longitudinal axis with the formation of two cones in correspondence to the flat ends and several lateral pieces (as shown in di Bari *et al.*, 2018a, submitted). So for these systems, brittle fracture was also thought to occur.

The measured E_{app} values (Fig. 5) are independent of the compressive rate and formulation. This behaviour can be explained recalling that the behaviour of an ideal (Hookean) solid material is not deformation rate dependent: when a purely elastic element experiences a load (higher than its stiffness), it deforms instantaneously. Since the E_{app} of the CB systems is independent from the formulation within the investigated deformation time scale, it can be concluded that this mechanical property is strictly controlled by the deformability of solid bonds formed within the matrix (before introducing any permanent mechanical damage).

Values of BM (Fig. 6) increase at increasing compressive rate, suggesting materials display higher resistance to deformation at increasing compressive rate. This result can be explained considering that energy dissipation processes have a more pronounced effect at increasing test

speed which determines an increase in the overall mechanical resistance as measured by the BM (see also Fig. 7 and text).

Figure 7a, b, and c show results of fracture stress (σ_F) and strain (ϵ_F), and work to fracture, respectively. For all samples, the measured values of mechanical parameters at failure increased with increasing compressive rate. This result suggests that the fracture behaviour of CB systems is rate dependent, which is expected for visco-elastic materials. Bulk CB had a higher value for all of the fracture parameters at any compressive rate. Independently from the compression speed, the work to fracture of emulsions is lower than that reported for CB. This is in agreement with results in literature where a water-in-cocoa butter emulsion with a gelled internal aqueous phase was also shown to be characterised by a lower strength than bulk CB (Sullo *et al.*, 2014). In line with the initial hypothesis, this result suggests that addition of water droplets weakens CB structure. Furthermore, although for a cross-head speed up to 0.1 mm s^{-1} no significant difference was observed between 20% and 40% emulsified systems, at increasing test speed a larger amount of dispersed phase results in a significant reduction in material strength.

Fracture stress represents the hardness of materials and values measured for CB systems are shown in Figure 7a. Two regions can be observed: for all CB systems at a low cross head speed ($\leq 0.1 \text{ mm s}^{-1}$), the rate does not have a significant effect on the stress to fracture (σ_{Fr}), whereas at higher test speed, the σ_{Fr} for all materials increases with increasing compressive rate. This result may have important implications from a product design perspective: considering that the perceived hardness on biting is affected by both material properties and bite rate (usually above 10 mm s^{-1}), it is reasonable to think that the development of a product having a lower fat content may be achieved by tuning the material properties to deliver the expected mechanical behaviour in the mouth.

Data referring to fracture strain (ϵ_{Fr}) are shown in Figure 7b. Bulk CB displayed always a higher deformability at fracture than emulsions. Within the range of used compressive rates, results suggest that ϵ_{Fr} is less influenced than σ_{Fr} by the test speed: with increasing test rate up to 1 mm s⁻¹ there is no difference among ϵ_{Fr} values for each of the three CB systems. For all sample types an increase of ϵ_{Fr} occurs at 10 mm s⁻¹.

Work-to-fracture data are shown in Figure 7c. Results suggest a strain rate hardening behaviour for all of the CB systems: the mechanical energy required to fracture a material increases with increasing test speed. The small error bars suggest that test reproducibility was high overall. However, the error increases at higher compressive rates. A similar trend both in terms of strain hardening behaviour and increasing error with test rate was described on compressive analysis of butter (Rohm, 1993). To explain the observed strain hardening behaviour, it should be recalled that water-in-cocoa butter emulsions are viscoelastic (food) materials, where some of the mechanical energy supplied on deformation is stored in the elastic elements (solid bonds) and some is dissipated *via* viscous flow and friction between structural elements. While the mechanical behaviour of the elastic components does not depend on deformation rate, energy dissipating mechanisms are deformation rate dependent (Calzada and Peleg, 1978). As mentioned above (Section 3), the two main energy dissipating mechanisms occurring in the systems studied here are viscous flow and frictional effects between structural elements. However, it is very difficult (if at all possible) to determine the effect of each of these mechanisms on mechanical properties. The difficulty arises from the fact that each dissipating mechanism correlates differently with the strain rate, leading to results difficult to interpret (van Vliet and Walstra, 1995, van Vliet, 2002). At low compression rates, network stress-relaxation occurs over a broader time-scale, but the time available for fracture propagation is also longer. In this study the observed lower values of the failure parameters at low test speed suggest that fracture propagation occurs faster than network relaxation. However, at higher

uniaxial load rates, the deformation rate is faster than fracture propagation and stress relaxation mechanisms dominate. This behaviour results in a higher deformation at fracture (ϵ_{Fr}). Furthermore, it is likely that if a given deformation is applied faster, the sliding of structural elements against each other and viscous effects of the liquid oil trapped within the fat crystalline matrix are more pronounced. Therefore, more energy is dissipated and, as a result, the material appears to be harder and requires more energy to fracture, thus explaining the higher work to fracture measured for the tested materials.

To understand the fracture behaviour at the microstructural level, since the E_{app} (Fig. 5) is comparable among systems, it can be hypothesised that the same elastic energy ($\sim \frac{1}{2} E_{app} \cdot \epsilon^2$) is stored in all the systems and can be used for fracture propagation. The differences in the failure should therefore arise from differences in the number of microstructural defects (fracture initiation) and energy dissipation mechanisms (fracture propagation) occurring among CB systems. Droplets are likely to represent defects weakening the structure as suggested by the fact that less mechanical energy had to be supplied to emulsions to achieve final failure compared to bulk CB. The weakening structural role played by the droplets may be explained by considering two co-occurring factors: (1) water droplets are not (or only partially) connected to the network formed by CB thus representing inactive fillers (Fig. 3). This hypothesised structural scenario is in agreement with results from Rafanan and Rousseau (2017); (2) the presence of droplets hinders crystal-crystal aggregation processes, which results in the development of less solid bonds within the network. This second mechanism is in good agreement with literature (Le Révérend et al., 2011, Sullo et al., 2014). The reduction in the number in solid junctions within the CB matrix and their replacement by an inactive filler phase, only in part bound to the continuous phase, overall results in decreased material strength.

5. Conclusions

Water-in-cocoa butter emulsions can be considered composite materials, where water droplets are structural defects dispersed within the CB matrix. The material properties of these particle gels depend on the structure developed by selecting processing and formulation conditions and on the test speed. The presence of water droplets provides structural zones where stress concentration occurs. Therefore, by increasing the amount of water (hence the number of structural in-homogeneities) or the size of the defects, the system becomes more prone to collapse under large deformation and less mechanical energy has to be supplied to obtain local and overall material failure. Experimental evidences support the hypothesis that on compression the crack may initiate in the vicinity of the droplets (i.e. fracture initiation) and propagate around them (i.e. fracture propagation) by overcoming the adhesion stresses between fat crystals forming the bulk network and the droplets interface (Fig. 8). This evidence may support the hypothesis that fracture occurs according to a preferred growth pattern in emulsions determined by droplet size and number.

The visco-elastic nature of CB systems was confirmed by their strain hardening behaviour. Bulk CB showed higher hardness than emulsions at any compressive rate. However, the elastic properties of the systems were not influenced by either compression rate or formulation, suggesting that the fat crystal network dominates the behaviour at small deformation. Although a more quantitative understanding of the role of water droplets on the mechanical properties of emulsions has been developed here, further studies to characterise the interaction forces between the interfacial water crystalline layer and network are needed.

Finally, with respect to the performance of these novel food materials on consumption, the lower mechanical strength observed for emulsions compared to the bulk fat phase suggests that these systems will be perceived as different, mainly on first bite. A potential route to increase their mechanical strength may be the use of an emulsifier to increase the interfacial

crystallisation and the development of more solid bonds between interfacial and network crystals.

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Figure 1: Apparent Young's modulus (E_{app} , $\blacktriangle$) and bulk modulus (BM, Δ) expressed as function of the average dispersed phase droplet size ($d_{3,2}$, μm). Error bars represent one standard error of the mean. Solid lines serve only to guide reader's eye.

Figure 2: Melting behaviour of water-in-cocoa butter emulsions produced at four scraped surface heat exchanger (SSHE) rotational speeds. Endotherms correspond to samples produced with a SSHE rotor rate of (from top to bottom) 170, 500, 930, and 1315 rpm, respectively. Endotherms normalised per gram of cocoa butter (CB).

Figure 3: Cryo-SEM image of a 20% (wt%) water-in-cocoa butter emulsion (scale bar = 20 μm). Water droplets (covered by a continuous crystalline shell) and the cocoa butter (CB) matrix are indicated in the image.

Figure 4: (a) True stress ($\blacklozenge$) and strain ($\diamond$) to failure expressed as function of the average dispersed phase droplet size ($d_{3,2}$, μm); (b) specific work to failure as function of $d_{3,2}$ (μm) ($\blacksquare$) and free water ($\square$). Error bars represent plus/minus one standard error of the mean.

Figure 5: Apparent Young's modulus (E_{app}) as function of compressive rate. Systems tested were bulk cocoa butter (CB, $\diamond$), 20% (wt%) aqueous phase ($\square$) and 40% (wt%) aqueous phase ($\triangle$) emulsions. Error bars are plus/minus one standard error of the mean.

Figure 6: Bulk modulus (BM) as function of compressive rate. Systems tested: bulk cocoa butter (CB, $\diamond$), 20% (wt%) aqueous phase ($\square$) and 40% (wt%) aqueous phase (Δ) emulsions. Error bars are plus/minus one standard error of the mean.

Figure 7: (a) Fracture stress, (b) fracture strain, (c) work to fracture as function of compressive rate for bulk cocoa butter (CB, $\diamond$), 20% (wt%) aqueous phase ($\square$) and 40% (wt%) aqueous phase (Δ) emulsions. Error bars are plus/minus one standard error of the mean.

Figure 8: Schematic representation of the phenomena occurring on deformation of water-in-cocoa butter emulsions. When a compressive load is applied to a cylindrical specimen, the solid bond connecting the dispersed water droplets to the cocoa butter (CB) fat forming the crystal network are the first to break determining “fracture initiation”. Under the applied load the fracture may propagate mostly around the dispersed water droplets until complete material failure occurs.

ACCEPTED MANUSCRIPT