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Formulation engineering of water in cocoa - butter emulsion

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Abstract

This research studied the effect of κ -carrageenan concentration and emulsifier mixture of soybean lecithin (LEC) and/or polyglycerol polyricinoleate (PGPR) on the physical properties of water-in-cocoa butter emulsions. Emulsions were prepared using bench scale margarine line process, consisting of a scraped surface heat exchanger and a pin stirrer. Results show that droplet size increases as the concentration of κ -carrageenan and/or LEC increases. Emulsions crystallise mainly in form $V(\beta_2)$, however when the concentration of κ -carrageenan increases to 1.5 wt% less stable polymorphic forms (II) were also observed. The rheological properties of the emulsions at 40°C were mainly controlled by the concentration of LEC which causes droplets to flocculate and as consequence viscosity increases. Finally, behaviour under large deformation showed that the presence of water droplets weakens the emulsions structure, due to the reduction in the density of the cocoa butter matrix bearing the load.

Key words: Emulsion; Cocoa butter; Microstructure; Rheology; Texture, Particle size, DSC.

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Introduction

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

It is thought (Norton et al., 2009) that water-in-cocoa butter emulsions are Pickering emulsions, where the fat crystals produced during the crystallisation of cocoa butter under shear act as Pickering particles which adsorb at the oil/water interface. Further stability is given by sintering of the fat crystals at the interface forming a rigid interfacial shell and preventing water droplets coalescence (Frasch-Melnik et al., 2010). During storage the fat crystals form a coherent network which immobilises the dispersed phase, conferring to the product the required long term stability. (Ghosh and Rousseau, 2011). Emulsifiers have been found to play a key role in the stabilisation of those emulsions as most fat crystals are not naturally surface active. Emulsifiers modify the surface of the fat crystals, increasing their

polarity thereby improving their ability to adsorb at the oil/water interface (Frasch-Melnik et al., 2010; Garti et al., 1998; Hodge and Rousseau, 2005). Johansson and Bergenstahl (1995) found that the addition of LEC increases the polarity of β -form tristearin crystals and improves the stability of water-in-oil emulsions. Garti et al. (1998) observed that the addition of 1% PGPR to water-in-oil emulsions enabled microcrystalline (α -form) fat crystals to adsorb to the water-oil interface and improved the emulsion stability. The stability of the emulsions improves with the addition of hydrocolloids as the increase in the viscosity of the dispersed aqueous phase limits coalescence of water droplets (Mounsey et al., 2008). Moreover, polysaccharides such as κ -carrageenan have been found to improve the sensory properties of low-fat spreads water-in-oil emulsions (Alexa et al., 2010).

This research is a continuation of a study dedicated to understand the effect of processing and formulation parameters on the microstructure and physical properties of water-in-cocoa butter (oil) emulsion as potential route for the production of low fat chocolate. Central to this study were the following questions: How do polysaccharides and mixture of emulsifiers change the microstructure of emulsions? What are the consequences of such changes on the rheological and mechanical behaviour of the emulsion? Two possible models appear to emerge based on the rigidity and interfacial properties of the water particles. It is considered that these findings would make it possible to progress in the design of a process for continuous manufacturing of a low-calorie chocolate, with similar sensorial properties to that manufactured by traditional methods.

2. Materials and methods

2.1. Materials

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

2.2. Methods

2.2.1. Pre-emulsion preparation

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

2.2.2. Emulsification process (the margarine line)

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

2.2.3. Droplet size measurements

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

replicates. The surface-weighted mean diameter of the droplets ($d_{3,2}$) was calculated by using the equation proposed by van Duynhoven et al. (2002):

Eq. (1)

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

2.2.4. Thermal analysis

The thermal analysis of the CB emulsions was carried out using a differential scanning calorimeter (Perkin Elmer DSC 7, UK). About 10 mg of each sample were precisely weighed into aluminium pans of 40 μ l, which were hermetically sealed. An empty aluminium pan was used as a reference. Scans were performed from 0 to 60 °C at a controlled constant rate of 10 °C/min. This method was used to determine crystal (polymorphic) forms, which were identified by the temperature peaks in the thermogram. The melting enthalpy was calculated from the area of the main endothermic peak (expressed in term of J g⁻¹ of CB) by using the equipment software (Pyris, Perkin Elmer DSC 7, UK). Results were reported as the average and standard deviation of at least 3 replicates.

2.2.5. Large deformation

Large deformation and failure behaviour of CB emulsions were assessed under compression using a TA-XT Plus texture analyser (Stable Micro Systems, Godalming, UK) fitted with a cylinder probe of 40 mm of diameter (P/40). Emulsion at the exit of the C-unit

(33°C) were poured into cylindrically shaped molds (internal diameter, $d = 22$ mm, height, $H_0 = 20$ mm) at the exit of the C-unit (at 33 °C), and stored for 24 h at 20 °C before measurement. All the measurements were made at a compression rate of 10 mm/s, the results were reported as the average and standard deviation of 8 replicates. Friction between the sample and the loading platens was negligible as shown by the absence of barrel shape of the loaded sample (Fig.2). The force/distance data, as obtained directly from the texture analyser, were converted into “true strain” (ε) and “true stress” (σ_s) according to equations 2 and 3, respectively (Tang et al., 1997):

Eq. (2)

Eq. (3)

where ε is the true strain, σ_s the true stress, F the compression force, the initial height of the cylindrical sample, the height difference due to compression, and d the diameter of the cylindrical sample.

2.2.6. Rheological measurements

Viscosity measurements were made using a control stress rheometer (Malvern Instruments Ltd., UK) with 4 blades vane geometry: (diameter of 25mm; length of 61mm and width of 1.5mm). Water-in-cocoa butter emulsions, after processing, were loaded onto the rheometer at 40 °C and equilibrated for 10 min. Steady shear viscosity was measured for a shear rate range from 0.01 to 800 s⁻¹.

3. Results and discussion

3.1. Effect of κ -Carrageenan, aqueous phase content and emulsifiers on droplet size

The quality of the water-in-cocoa butter emulsions, by means of droplet size is controlled by the interplay of water volume fraction, rigidity of the droplets and their interfacial properties. Fig. 3a and 3b show respectively, droplet size (surface-weighted mean diameter $d_{3,2}$), and percentage of free water (i.e. droplets with size greater than 100 μm) plotted as a function of κ -Carrageenan concentrations (0.5, 1, 1.5 and 2 wt %) for samples containing different water volume fractions (0.1, 0.4 and 0.6). Each emulsion contains only PGPR (1 wt %) as emulsifier. As can be seen from results in Fig. 3a, at low concentrations of κ -Carrageenan (0.5 and 1 wt %), emulsions with a small average droplet size were obtained ($\sim 4 \mu\text{m}$) which size remained constant for all the different water volume fractions used. At these concentrations of κ -Carrageenan the amount of free water was between 4 to 10%, this increased with increasing volume fraction of water in the emulsion (Fig. 3b). From Fig. 3a it can be seen that further addition of κ -Carrageenan up to 2wt% resulted in emulsions with large droplet sizes, ranging from 5 to 35 μm depending on the water volume fraction. Such dependence of droplet size on κ -Carrageenan concentration was particularly significant at low water fractions, and it became less apparent as the water volume fraction increases. This effect is explained by considering the effect of gelation of κ -Carrageenan on the viscosity of the dispersed phase. At high concentrations of κ -Carrageenan (2 wt %) gelation is fast enough to occur before the coarse enters into the A-unit, where the reduction in droplet size occurs. Gelation causes a significant increase in the aqueous phase viscosity, which prevents droplet break-up at a given velocity gradient (Walstra, 1993). As a consequence, emulsions with larger droplets are produced. However, this “viscosity ratio effect” (dispersed phase viscosity, /continuous phase viscosity,) is offset by the increase in the viscosity of the overall emulsion at high volume fractions of dispersed phase, which then results in an

increase of the stress exerted on each of the (gelled) water droplet at a given shear rate. This explains why at high volume fractions of dispersed phase, the water droplet size is less dependent on the concentration of κ -Carrageenan (Fig. 3a). Our results are in close agreement with the studies of Norton and Fryer (2012) for CB emulsion containing gelatine, as well as those of Alexa et al. (2010) for low-fat spreads containing κ -carrageenan. Alexa et al. (2010) reported that an increase in κ -carrageenan concentration in low fat-spreads leads to large water droplets, the effect of which was attributed to the increased viscosity of the aqueous phase and the induced gelation of the droplets during processing.

As anticipated earlier, the interfacial properties of the droplets also play a role in the final droplet size of the emulsion. This effect is shown in Fig. 4a and 4b, where the droplet size and percentage of free water are reported respectively, for emulsions containing mixed emulsifier, PGPR and LEC, in varying ratios with a total emulsifier content of 1 wt%. The dispersed phase of these emulsions contained a constant concentration of 1 wt % κ -Carrageenan, which was shown earlier to have a minimal effect on the droplet size. As can be seen from results in Fig. 4a, the smallest droplet size was obtained for emulsions containing exclusively PGPR as emulsifier; with a droplet size in the range between 3.8 to 5.6 μm . At this concentration of PGPR, the percentage of free water (Fig. 4b) ranged between 3 to 12%, which increased at high water volume fractions. In contrast, the emulsions containing only LEC produced the largest water droplets (Fig. 4a) and the highest percentages of free water (Fig. 4b), with droplet sizes that ranged from 4.5 to 19 μm , and free water from 16 to 48%. These results confirm that PGPR is more efficient as emulsifier than lecithin, enabling rapid droplet coverage and preventing the coalescence of the new droplets formed during processing. Interestingly, a certain amount of PGPR can be replaced by the co-surfactant LEC without significant changes in the droplet size of the emulsion. Indeed, Fig. 4a shows that a blend of PGPR/LEC in the ratio of 1/1 produces droplet sizes within the range 4.1 to

5.8 μm , which is very close, within the experimental error, to the value of droplet size obtained when solely PGPR is present. As the emulsifier ratio changes in favour of an increase in LEC, the droplet size increases dramatically. Once again, this effect becomes less apparent as the water volume fraction increases. This effect is thought to be due to the overall increase in the viscosity of the emulsion with increasing water volume fraction, which in turn prevents coalescence after processing as the activation energy for coalescence increases with the viscosity of the system (Kamogawa et al., 2003). Similarly, Ushikubo and Cunha (2014) found that water-in-oil emulsions with higher water content resulted in smaller droplets and increased emulsion stability, the effect of which was attributed to the increase in the apparent viscosity of the emulsions, thereby improving steric stabilisation.

3.2. Thermal Analysis

Melting behaviour of pure CB processed by using A+C unit is shown in Fig. 5a. The thermogram shows a single peak at 33 °C which corresponds to the crystal polymorph V (β_2). This form V(β_2) is one of the six crystalline arrangements or polymorphic forms exhibited by CB, which in order of increasing thermodynamic stabilities are: I (sub- α or γ), II (α), III (β_2), IV (β_1), V (β_2) and VI (β_1) (Willie, 1966). The importance of crystallising CB principally in Form V, through the tempering process, with regards to chocolate quality has been reviewed widely in the literature (Loisel et al., 1998; Loisel et al., 1997; Stapley et al., 1999). The polymorph form V imparts the desirable “in-mouth melting” behaviour (31-34 °C) of chocolate. Moreover, the less stable forms II and III, due to the monotropic nature of polymorphism of CB, will be transformed into more stable forms when given sufficient time (Ostwald’s rule of stages) (Nyvlt, 1995). This polymorphic transition is the cause of undesirable white spots appearing on the surface of chocolate during storage (Himawan et al.,

2006; Langevelde et al., 2001). In this research, temperature and shear profile in the two units (A and C) were carefully chosen to crystallise CB principally in form V.

Full details on the effect of process conditions on the crystallisation of CB have been recently published by Norton and Fryer (2012) and di Bari et al. (2014). Briefly, CB is first cooled to 25 °C in the A-unit where the distribution of the crystal polymorph (II, IV and V) in the system is dependent on the action of shear (di Bari et al., 2014). The shear in A-unit can accelerate the polymorphic transition towards the most stable form V, via induced orientation of the triacylglycerides chain, or transformation via partial melting of the crystals (MacMillan et al., 2002; Mazzanti et al., 2003). With the heating to 35 °C, in the C-unit, all the less stable forms are re-melted, leaving the only form V crystals which act as seed crystals. Fig. 5a shows the effect of κ -carrageenan concentration on the crystallisation of CB emulsions. For clarity, only samples at 0.6 water volume fraction are reported, as the water concentration had no effect on the shape of the thermogram (data not shown). As can be seen from results in Fig. 5a, emulsions containing 0.5 and 1 wt% of κ -carrageenan showed a melting profile close to that of pure CB with a single peak at ~32.8 °C, thus indicating that κ -carrageenan at concentrations < 1% has no influence on CB crystallisation. These results are in close agreement with the study reported by Norton et al. (2009) and Norton and Fryer (2012), where the increase in gelatine concentration had no significant effect on the melting profile and melting enthalpies of CB emulsions. It can also be seen from results in Fig. 5a, that emulsions prepared with κ -carrageenan at a concentration of 1.5 wt% showed three peaks which can be readily distinguished at temperatures of 15, 25 and 32 °C, which correspond to forms I, IV and V, respectively. It appears that form IV would be a heat-induced polymorphic transition from form II(α) to V(β 2) during the DSC run. This is indicated by the presence of an exotherm around 20 °C. The origin for the less stable form II is thought to be related to the effect that κ -carrageenan concentration has on the rate of gelation and consequently on the

rigidity of the water droplets. Indeed, the gelation of κ -carrageenan at a concentration of 1.5 wt% at a temperature of 25 °C is fast enough to occur in the A-unit, which means that crystallisation of CB occurs in the presence of rigid gel particles. The presence of rigid gel particles would be expected to decrease the local shear rates in the cocoa butter, for a given overall shear rate. This decrease in the shear rate would affect the shear induced orientation of the triacylglycerides and consequently, the polymorphic transition toward the more stable polymorph V. To this end, slower gelation rates as those obtained for emulsions containing 0.5 and 1wt% κ -carrageenan are not expected to significantly change the rigidity of the water phase, thus having a little impact on the CB crystallisation. Data reported by Norton and Fryer (2012) for emulsions containing gelatin are explained on the same basis, as gelatin is known for its slow gelation rate (Normand et al., 2000). It appears, therefore, that the polymorph distribution in the CB emulsions is controlled by the structuring of the water phase, through gelation κ -carrageenan, which occurs either at the beginning (in the A-unit) or at the end (in the C-unit) of the process.

Fig. 5b shows the effect of varying ratios of mixed emulsifiers (PGPR/LEC) on the crystallisation of water-in-cocoa butter emulsions. All the emulsions, independently of the emulsifier ratio, show one dominant peak at 29-30 °C, which is in the range of melting temperatures reported for form IV. Less evident is the appearance of a second peak around 17 °C for a PGPR/LEC ratio of 25-75. As it is further discussed in this section, LEC appears to retard the transition to the more stable form V, as compared to emulsions stabilised solely by PGPR.

Table 1 shows the peak temperature and enthalpy for the melting of pure CB and the different formulations of water-in-cocoa butter emulsions. Interestingly, the normalised endothermic total enthalpy for the emulsions containing 0.5 and 1% wt κ -carrageenan were comparable, within the experimental error, to pure CB. The total enthalpy is the amount of

heat required to melt a gram of crystalline matter, this means that the mass fraction of the crystalline solid in the emulsion relative to pure CB remained constant. As it will be further discussed in the next section, the total amount of crystalline material is an important physical parameter so as to understand and predict the large deformation properties of the material. The enthalpy of the CB emulsion decreased as the concentration of k-carrageenan increased to 1.5 wt%, due to the presence of a less stable crystal form. The presence of lecithin significantly decreased the enthalpy, thus there were fewer crystals present in these emulsions after 1 day, in comparison to pure CB. This effect, along with the lower peak temperature obtained (in comparison to pure CB), are suggested to indicate a retardation in the nucleation process of form V as mentioned earlier, which is in agreement with data in the literature. Dhonsi and Stapley (2006) observed an increase in the crystallisation induction times of CB and sugar mixtures with the increase in the concentration of LEC. This effect was attributed to the fact that lecithin is known to migrate to the sugar/fat interfaces, which would hinder the catalytic heterogeneous nucleation sites at the sugar surface, retarding thus crystallisation. Moreover, the retardation of the overall growth rate, represented by the reduction of enthalpy, might be attributed to the significant increase in viscosity in the sample containing LEC, the effect of which leads to a decrease in mass transport (Himawan et al., 2006).

3.3 Large deformation

The behaviour under large deformation yields important information on the structural and textural properties of CB emulsion. Fig. 6 shows typical stress-strain curves obtained for pure CB and water in CB emulsions at 0.2 and 0.6 water volume fractions. All the emulsions contain 1 wt% of k-carrageenan in the aqueous phase. In the case of pure CB, after a small elastic region, the stress grows exponentially until the strain to fracture is reached at 23kPa.

From this point the stress decreases suddenly under the action of the compression load. Fracture patterns characterised by low strain (less than 0.2 strains) and high stress, as for pure CB, are generally observed for brittle materials, where no plastic deformation slows down the propagation of the fracture (Aguilera, 1999). In pure CB, fracture occurs when the stress applied is sufficiently high to break interaction forces, Van der Waals or sintered crystal bonds between fat crystals, resulting in the breakdown of the material over a macroscopic length scale (Kloek et al., 2005).

According to the classic theory of fracture mechanics (Griffith, 1920), fracture is ultimately governed by the crack initiation at the level of the defects left in the network by the spatial arrangement of the crystals during the formation of the fat network. It is at level of those defects that the stress concentrates sufficiently to initiate and propagate cracking leading to the failure of the material; the larger the defect the greater the stress. As can be seen from results in Fig. 6, the water has a detrimental effect on the mechanical properties of CB, causing a significant shift of the stress-strain curve towards lower stress values with the increase in water volume fraction. Moreover, the CB emulsions exhibited significant strain-hardening behaviour (the rate of increase in stress is higher than that of strain), which becomes more apparent with high water fractions. Strain-hardening behaviour is the result of structure densification and compaction of crystals at the beginning of the breaking process, thus increasing the number of geometric restrictions on the deformation. As the water volume fraction increases, the material approaches what it appears to be a “transition” from brittle to plastic deformation. However, in contrast to the theoretical predictions (Aguilera, 1999), the ultimate strain to fracture does not increase significantly.

The stress and strain to fracture for CB emulsions at different water volume fractions are shown in Fig. 7a and 7b, respectively. Overall, the incorporation of water droplets resulted in a monotonic decrease of the stress to fracture at each concentration of κ -

carrageenan (Fig. 7a). The strain to fracture remains constant as the amount of water droplets in the sample increases. Our understanding of the large deformation of CB emulsions is based on the mechanistic model developed for particle filled composites, recently reviewed by Fu et al. (2008). In a similar fashion, the mechanical strength of CB emulsion is governed by adhesion between the CB matrix and the (κ -carrageenan) gel particles, the volume fraction of the gel particles and the strength of both the matrix and the particles. Adhesion through interfacial bonding accounts for the stress transferred from the CB matrix to the dispersed phase during compression, and it is thought to be mainly governed by the crystallisation at the CB/water interface (crystal shell). The mechanical behaviour of the CB matrix, instead, depends, among other factors, on the amount of crystals and their structure (size, shape and polymorphic form) as they ultimately influence the strength of interactions between crystals (Marangoni and McGauley, 2002; Narine and Marangoni, 1999). All these factors are taken into account into Eq. (4), originally proposed by Li et al. (2004):

Eq. (4)

where σ_c and σ_d are the stress to fracture of the emulsion, the stress to fracture of the dispersed phase (aqueous phase, i.e. κ -carrageenan gel particles) and the stress to fracture of the continuous phase (pure CB), respectively. α is the adhesion parameter [0,1] which accounts for the stress transfer between the two phases, ϕ is the volume fraction of the dispersed aqueous, and S a strength reduction parameter [0,1], which accounts for any changes in the CB network caused by the presence of the gel particles. Following this reasoning, the weakening of the structure with the increase in water content is explained mainly by the much lower rigidity of the water droplets compared to the CB crystal network. Since Eq. (4) reduce to Eq. (5).

Eq. (5)

Two important conclusions follow from Eq. 5. First, water droplets, disregarding the concentration of κ -carrageenan, can be considered as holes in the CB matrix which reduce the density of the CB matrix. Thus, the decrease in strength of the composite with the increase in the particles volume fraction (i.e. water droplets) is a reflection of the decreased cross-sectional area of the network bearing the load. Second, the origin of the apparent reduction in stress to failure with the increase in the concentration of κ -carrageenan (Fig. 7a) is explained by considering changes in the strength of the CB matrix. Such changes are described in Eq. 5, by the strength reduction parameter (S). This parameter is directly proportional to the amount of crystalline material in the CB phase, which can be approximated to the enthalpy ratio (enthalpy emulsion/enthalpy of pure CB) (cf. Table 1). To this end, it is worth mentioning that a linear relationship exists between amount of crystalline matter and the hardness of a crystalline fat network. This has been previously shown in literature for hydrogenated palm oil, soybean oil, and hydrogenated soybean oil, among others (Braipson-Danthine and Deroanne, 2004; Brunello et al., 2003).

Stress and strain to fracture for emulsion stabilised by PGPR/LEC at different ratios are shown in Fig. 8a and 8b, respectively. Eq. 5 predicts that samples containing exclusively LEC as surfactant will have the lowest stress to fracture amongst the emulsions tested, due to its lower enthalpy value compared to pure CB and consequently the lower strength of CB matrix (cf. Table 1). Surprisingly, differences in the stress to failure among these CB emulsions were not significant, which suggests that other factors such as droplet size distribution should be taken into account in order to explain the fracture behaviour of these CB emulsions (Fig. 8a). On the other hand a significant increase in strain to fracture was observed when LEC is present in the emulsions, which suggests an increase in plastic behaviour as the amount of solid crystal decreases in the system (Fig. 8b).

3.4 Rheology

In this section the rheology of the emulsions is discussed. Viscosity curves at 40 °C for emulsions containing 0.5 and 1.5 wt% κ -carrageenan in the aqueous phase are shown in Fig. 9a and 9b, respectively. Both emulsions are stabilised using PGPR at 1 wt % concentration, and they display very similar rheological behaviours. At a water volume fraction of 0.4 and below, the CB emulsions show Newtonian behaviour, that is, the viscosity remained constant and independent of shear stress. An increase in the water volume fraction resulted not only in an increased viscosity at low shear stresses (Newtonian plateau), but also in the appearance of a weak shear-thinning region (i.e. a shear stress dependence of the apparent viscosity). Such non-Newtonian effects have been reported for other emulsions in the upper boundary of the concentration domain (Pal and Rhodes, 1989). The origin of the shear thinning behaviour of CB emulsions stabilised with PGPR is suggested to be due to their non-flocculated nature. As the stress (shear rate) increases, the droplets change their distribution from isotropic to a more ordered one along the stream lines, thus reducing the disturbance of the continuous liquid flow (Barnes, 1994). A comparison between the two CB emulsions (i.e. Fig. 9a and 9b) indicates that the change in viscosity of the dispersed phase does not have a significant effect on the overall viscosity of the emulsion, which is mainly governed by the water droplet size and volume fraction.

Emulsions containing PGPR and LEC as surfactant in the ratio of 4/1 and 1/1 are shown in Fig. 8a and 8b, respectively. Emulsions stabilised only by LEC are not reported, as these samples were not stable at 40 °C and thus led to unreliable measurements. The emulsions show dramatically different rheological properties compared to those stabilised solely by PGPR (compare Fig. 10 to Fig. 9). Shear thinning behaviour was observed for each emulsifier ratio at water fractions which were well below the expected close packing concentration (0.65-0.8 for polydisperse emulsions) (Barnes, 1994). Moreover, emulsions

stabilised by mixed emulsifiers exhibit an apparent yield stress, that is, the point where the viscosity increases asymptotically as the applied shear stress is decreased. The yield stress becomes more evident with increasing water volume fraction and LEC concentration. The likely origin of the yield stress is ascribed to attractive forces between water droplets, which are dependent on the concentration and nature of the emulsifier (Pal, 1993, 1997). Interactions between droplets through depletion effect occur when surfactant molecules, or micelles, are excluded from the gap between two droplets approaching to each other, due to configurational entropy loss of the micelles (Barnes, 1994; Pal, 1993). The overall effect is that the two particles are pulled together (Barnes, 1994; Pal, 1993). This depletion flocculation of dispersed particles is also observed in suspensions containing non-adsorbing free polymer (Abdulmola et al., 1996; Pal, 1997). As result of depletion flocculation, the effective volume of the dispersed-phase (total available volume to the emulsifier) becomes higher than the nominal volume fraction (ϕ), leading to a viscosity increase. This phenomenon is shown in Fig. 11a, where data of relative viscosity as a function of water volume fraction for CB emulsions stabilised by solely PGPR or a mixture of PGPR/LEC (1:1 ratio) are compared. As can be seen from results in Fig. 11a, at equivalent water fractions, the presence of LEC resulted in a dramatic increase in the relative viscosity of the emulsion compared to emulsion stabilised solely by PGPR. Further insights in the effect of surfactant on the viscosity of the emulsion can be obtained from Eq. (6) (Pal, 2000):

$$\text{Eq. (6)}$$

where η_r is the relative viscosity, η_0 is the viscosity ratio and ϕ_{eff} the effective volume fraction of dispersed phase. The fitting parameter α accounts for the change in the effective volume due to the absorbed layer of surfactant, as described by Eq. (7):

$$\text{Eq. (7)}$$

where ϕ_n is the nominal volume fraction surfactant, obtained from the relative volumes (or weights) of the phases used in the preparation of the emulsions. K_o is constant for a given emulsion system, but it varies depending upon the nature and the concentration of the surfactant.

According to Eq. (6) the plots of $\ln(\phi_n)$ versus $\ln(\phi_n)$ are expected to be a straight line with an intercept of 1 and a slope of K_o (cf. Fig. 11b). A summary of K_o values together with the calculated surfacial layer thickness (Tadros, 1994) for all the emulsions is given in Table 2. A comparison was made between CB emulsions at a water volume fraction of 0.2 and with similar droplet size ($\sim 4\mu\text{m}$). Emulsions containing exclusively PGPR as surfactant are characterised by low values of K_o and a surfacial layer thickness of $0.07\mu\text{m}$, which is comparable with the thickness of the solvated surfactant at the surface of the drops. This confirms the minimal interaction between the water droplets surrounded by PGPR as it provides a good steric barrier by preventing droplets from flocculating in nonpolar media (Dedinaite and Campbell, 2000). The concentration of κ -carrageenan has no effect on the droplets effective volume, and thus it is solely determined by the nature and concentration of the surfactant. As can be seen from results in Table 2, K_o increases when LEC is present in the formulation. The surfacial layer thickness values obtained for CB emulsions stabilised by both, PGPR and LEC, in the ratio of 3/1 and 1/1 are 0.32 and $0.59\mu\text{m}$, respectively. This effect cannot be solely due to the degree of solvation of the surfactant layer, but instead suggests a high level of flocculation the water droplets with the addition of LEC (Knoth et al., 2005). This depletion flocculation has previously been reported to be dependent not only on the concentration of LEC, but also on the nature of the continuous phase, where long-chain lipids induce flocculation (Leal-Calderon et al., 1997).

4. Conclusion

In this study we reported the effect of κ -carrageenan and mixed emulsifiers on the structural and mechanical properties of the water in CB emulsion. The current observations are twofold. First, the quality of the emulsion, with regards to droplet size and polymorphic form obtained (due to tempering) are strongly determined by the rate of the gelation of the hydrocolloid within the aqueous phase, as well as the presence of different mixed emulsifier ratios. A fast gelation of hydrocolloid resulted in a significant increase in the aqueous phase viscosity, the effect of which reduced the droplet break-up for a given velocity gradients (Walstra, 1993). Consequently, CB emulsions with larger droplets were produced. It was suggested that the presence of rigid gel particles decreased the local shear stress in the cocoa butter phase for a given overall shear rate. This reduces shear orientation of triacylglycerides molecules and therefore affecting the crystallisation of CB in to form the polymorph V. The ratio of the two emulsifiers in the CB emulsion also plays a role in controlling droplet size, which value increases as the concentration of LEC increases. Results demonstrated that it was possible to replace 50 wt% of PGPR with LEC without affecting the droplet size. Second, the large deformation behaviour is controlled by the microstructural properties discussed above. To this end the weakening of the CB emulsions, as the water content increases, is explained mainly by the reduction of the density of the CB matrix, with less CB bearing the imposed load. In addition, the reduction in the amount of solid crystals and the changes to the polymorphic forms crystallised also had an impact to the strength of the CB emulsion. The nature of surfactant controls the rheological properties of the CB emulsions, where the presence of LEC favours the depletion flocculation of water droplets, and as a consequence the viscosity increases. We conclude that in order to produce a good quality tempered CB emulsion the rate of gelation should be low enough to occur after the processing, such that it does not interfere with the emulsification/crystallisation processes. Further research is currently ongoing to offset the reduction in strength upon the increase of water droplets,

which is an important factor in the manufacturing of low-calorie chocolate with desirable textural properties comparable to the full fat counterparts.

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Nomenclature

$d_{2,3}$	surface-weighted mean droplet diameter, μm
$d_{3,3}$	volume-weighted mean droplet diameter, μm
σ	standard deviation of the logarithm of the droplet diameter, μm
ε	true strain, -
σ_s	true stress, Pa
F	compression force, N
	initial height of the cylindrical sample, m
	the height difference due to compression, m
d	diameter of the cylindrical sample, m
	stress to fracture of dispersed phase, Pa
	stress to fracture of water-in-cocoa butter emulsion, Pa
	stress to fracture of pure cocoa butter, Pa
	adhesion parameters, [0,1]
	volume fraction of the dispersed phase, -

S strength reduction parameter [0,1]

relative viscosity, Pa.s

dispersed phase viscosity, Pa.s

continuous phase viscosity, Pa.s

emulsion viscosity ratio,

ϵ_{eff} effective volume fraction of dispersed phase, -

nominal volume fraction of dispersed phase, -

change in ϵ_{eff} due to the absorbed layer of surfactant,

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Fig. 1. Schematic representation of the emulsification process: the scraped surface heat exchanger (A unit) and the pin stirrer (C unit).

Fig. 2. Photographs of different stages during the uniaxial compression test of (a-d) pure cocoa butter or (d-g) water-in-cocoa butter emulsion at 0.2 water volume fractions. The sequence of photographs shows the absence of any barrel shape of the loaded samples.

Fig. 3. (a) Droplet size ($d_{3,2}$) and (b) percentage of free water of water-in-cocoa butter emulsions as a function of κ -Carrageenan concentration at different water volume fraction.

Fig. 4. (a) Droplet size ($d_{3,2}$) and (b) percentage of free water of water-in-cocoa butter emulsions as a function of PGPR/LEC ratio concentration at different water volume fractions.

Fig 5. Effect of κ -Carrageenan concentration (a) and emulsifier ratio (b) on DSC thermograms of water-in-cocoa butter emulsions at a water volume fraction of 0.6, 12 h after processing. Emulsions in Fig. 5a, are all stabilised using 1wt% PGPR, whilst emulsions in Fig. 5b contain 1wt% κ -carrageenan in the aqueous phase. All scans were carried out from 0 to 60 °C at a rate of 10 °C/min.

Fig. 6. Stress-strain curve for Pure CB and water-in-cocoa butter emulsions containing 1% κ -Carrageenan.

Fig. 7. Effect of κ -Carrageenan concentration on the (a) stress and (b) strain to fracture of water-in-cocoa butter emulsions.

Fig. 8. Effect of emulsifier ratio on the (a) stress and (b) strain to fracture of water-in-cocoa butter emulsion

Fig. 9. Viscosity flow curves at 40 °C for emulsions containing: (a) 0.5 wt. % and (b) 1.5 wt. % κ -carrageenan. Both emulsions were stabilised using 1 wt. % PGPR.

Fig. 10. Viscosity flow curves at 40 °C for emulsions containing 1% κ -carrageenan and stabilised by PGPR:LEC in the ratio of (a) 4:1 and (b) 1:1

Fig. 11. (a) Relative viscosity as a function of water volume fractions at 10 Pa for emulsions stabilised using either PGPR (square) or PGPR/LEC at ratio of 1:1 (circles). (b) Linearization of relative viscosity as a function of water volume fraction, based on Eq. 2

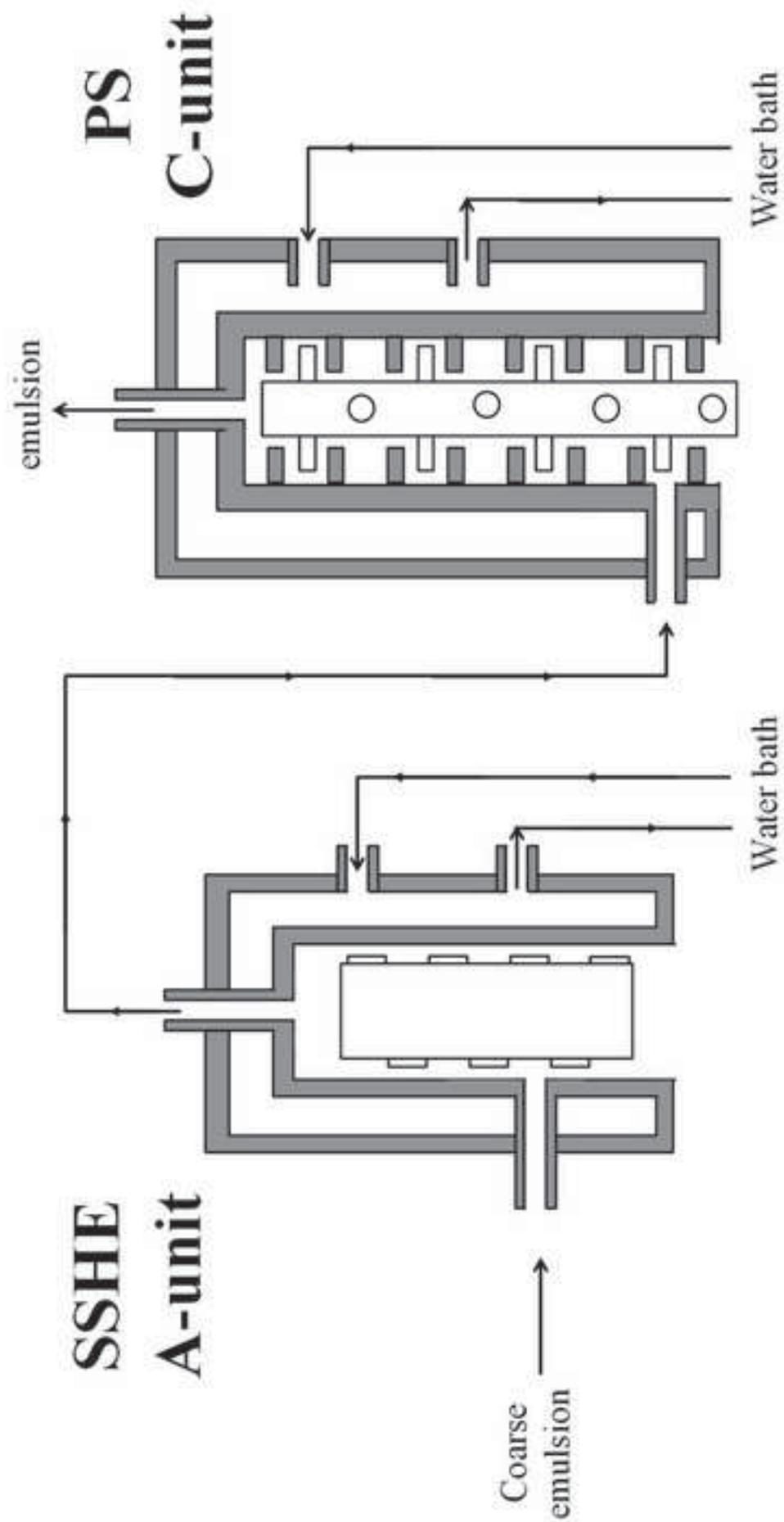
Tab. 1. Melting parameters for water in oil CB emulsion with different formulation

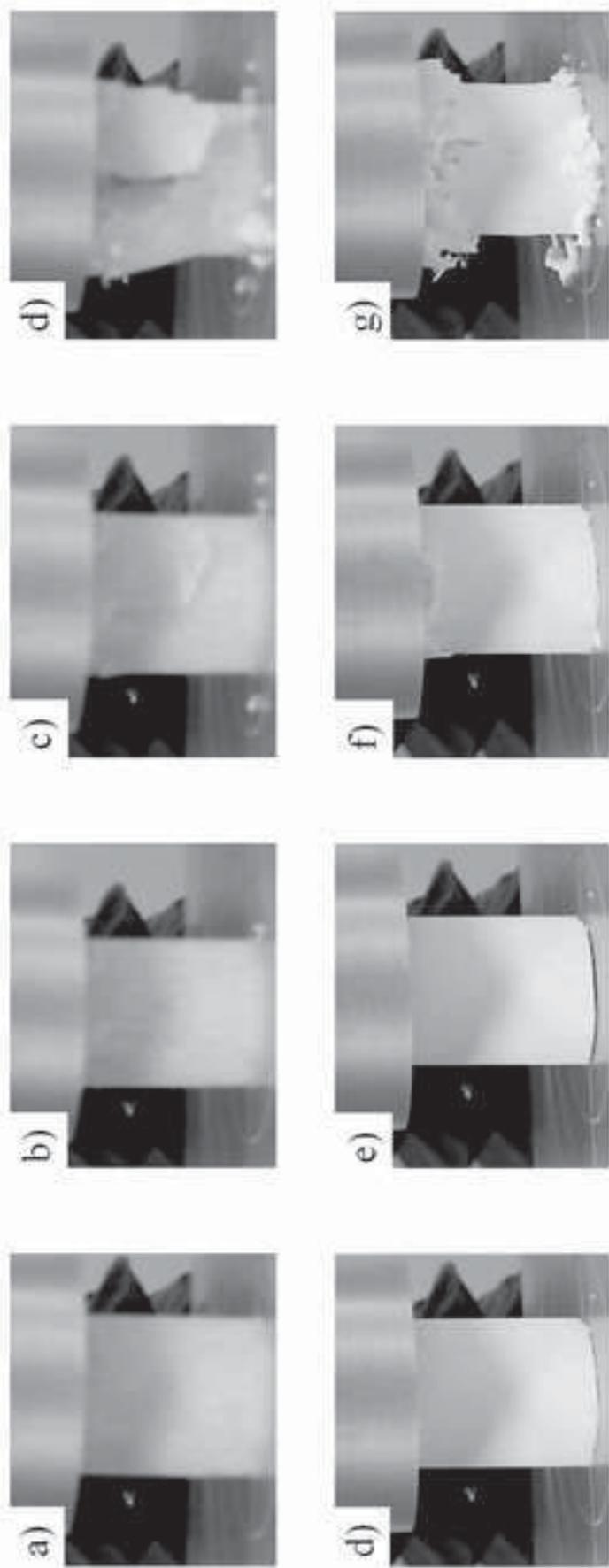
Tab. 2. Droplet volume change parameter (K_v) and surfacial layer thickness (h) for the emulsion studied

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Highlights

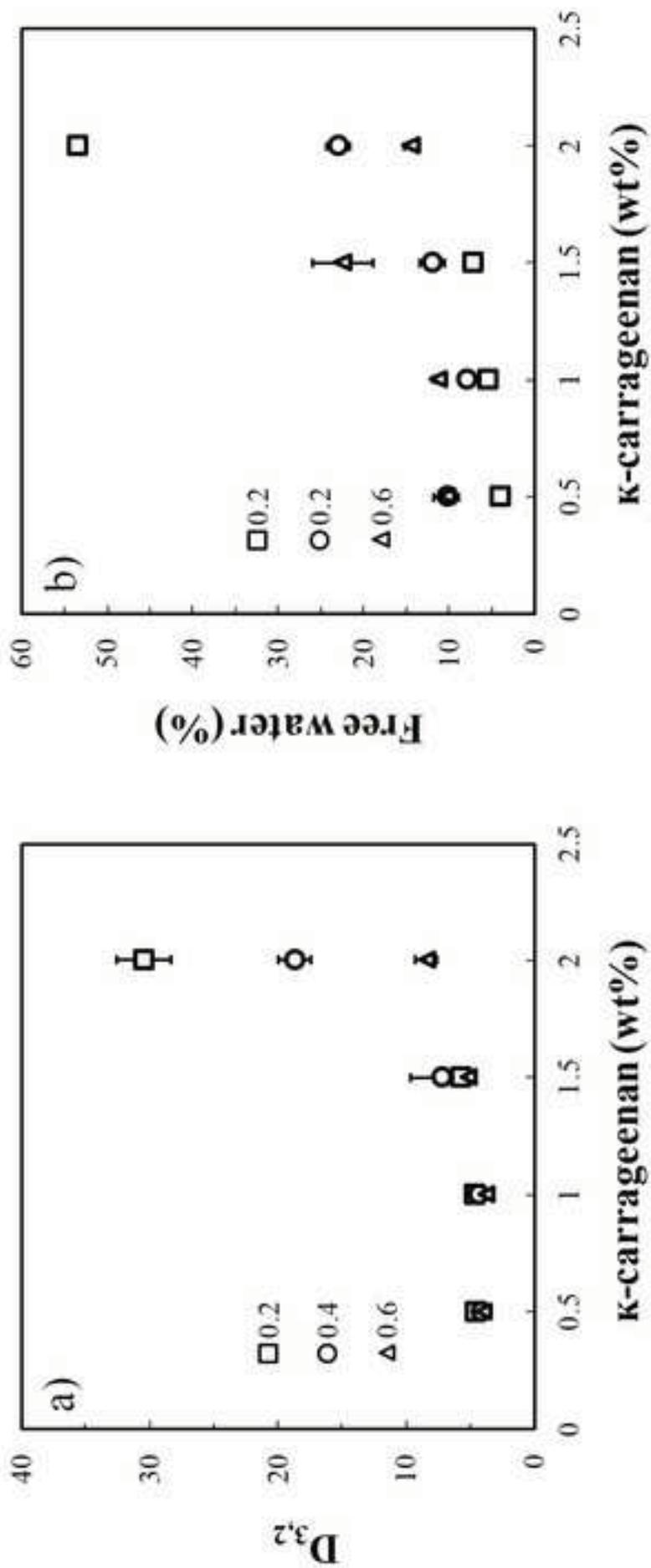
- Water in cocoa butter emulsions were prepared using a bench scale scraped surface heat exchanger followed by a pin stirrer.
- The effects of κ -carrageenan concentration and mix emulsifiers on properties of the emulsions were investigated.
- Droplet size and polymorphic form are determined by the rate of hydrocolloid gelation and the presence of lecithin.
- Overall, the incorporation of water droplets resulted in a monotonic decrease of the stress to fracture of the emulsions.
- The presence of lecithin favours droplets flocculation and as consequence the viscosity of the emulsions increases.

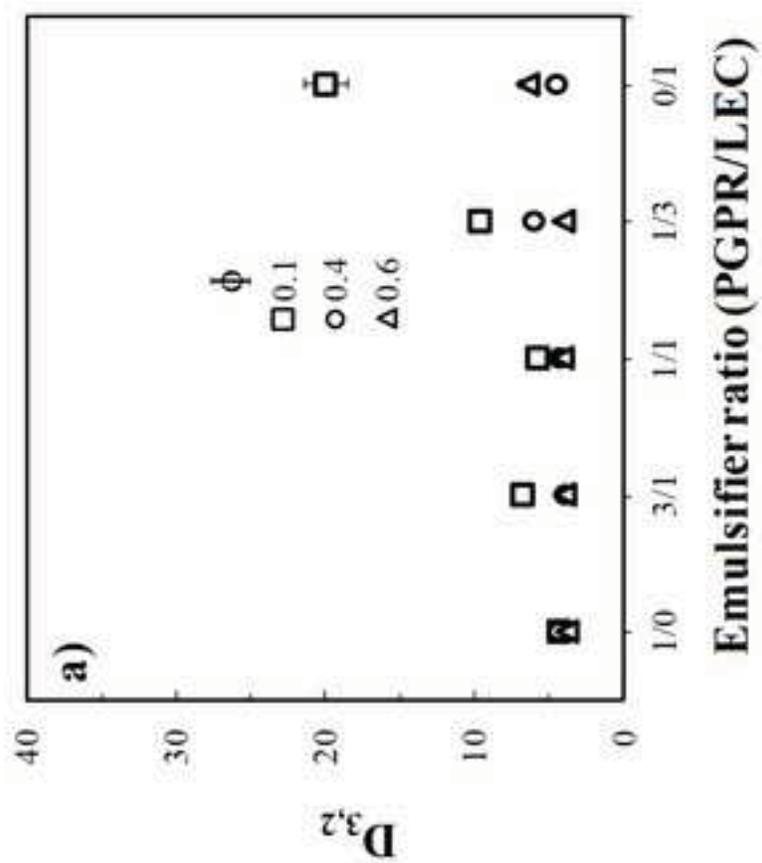
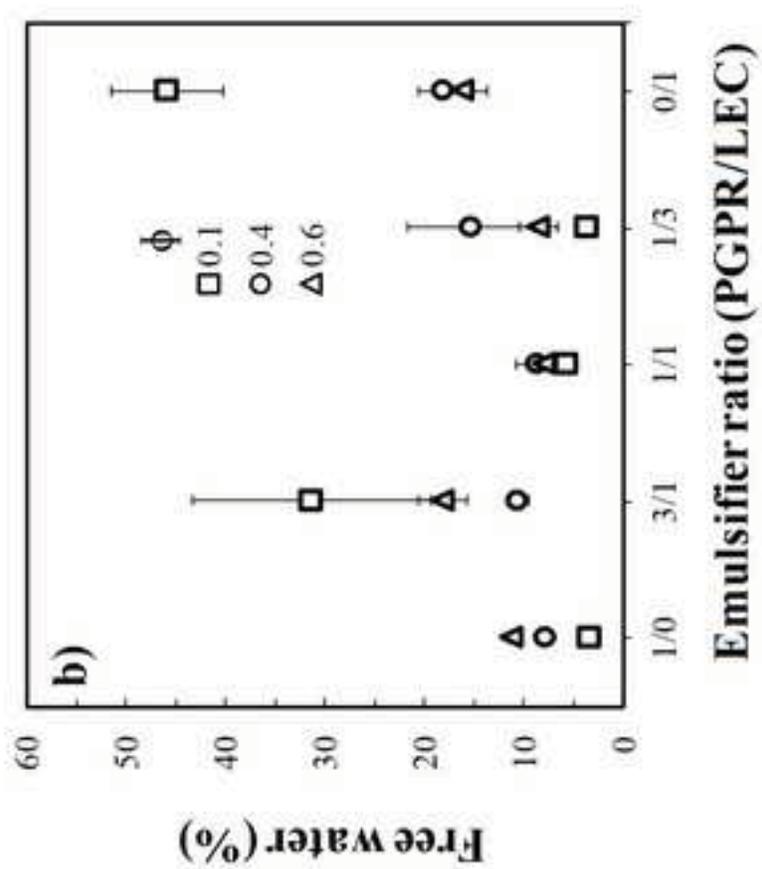




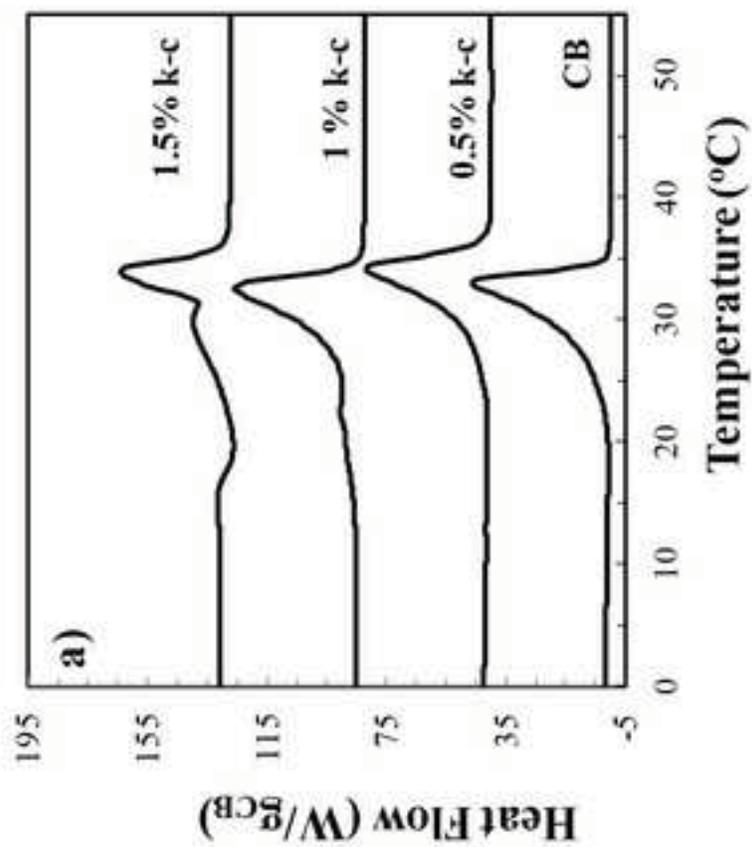
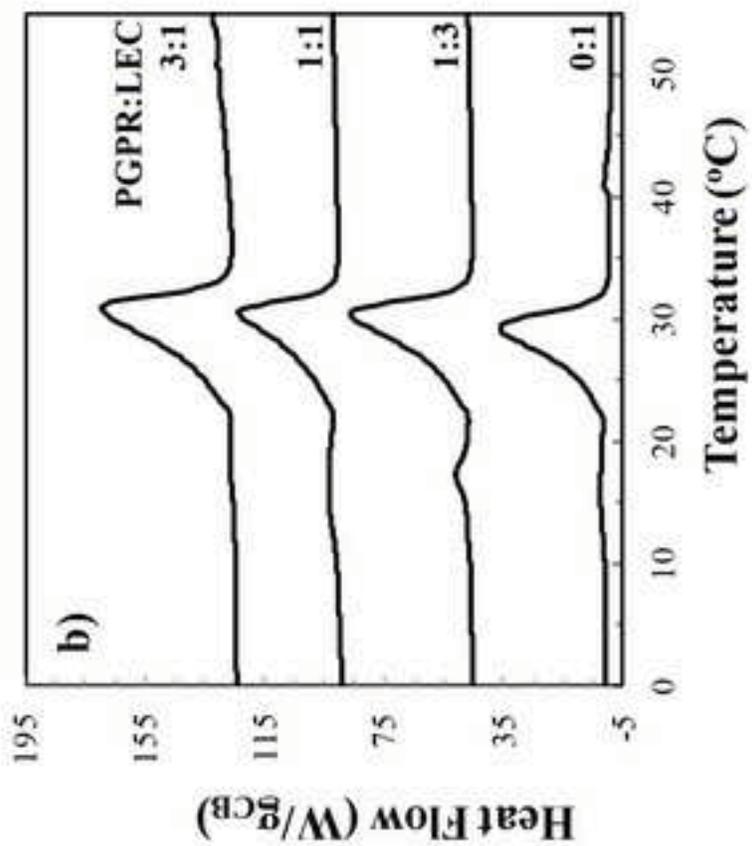
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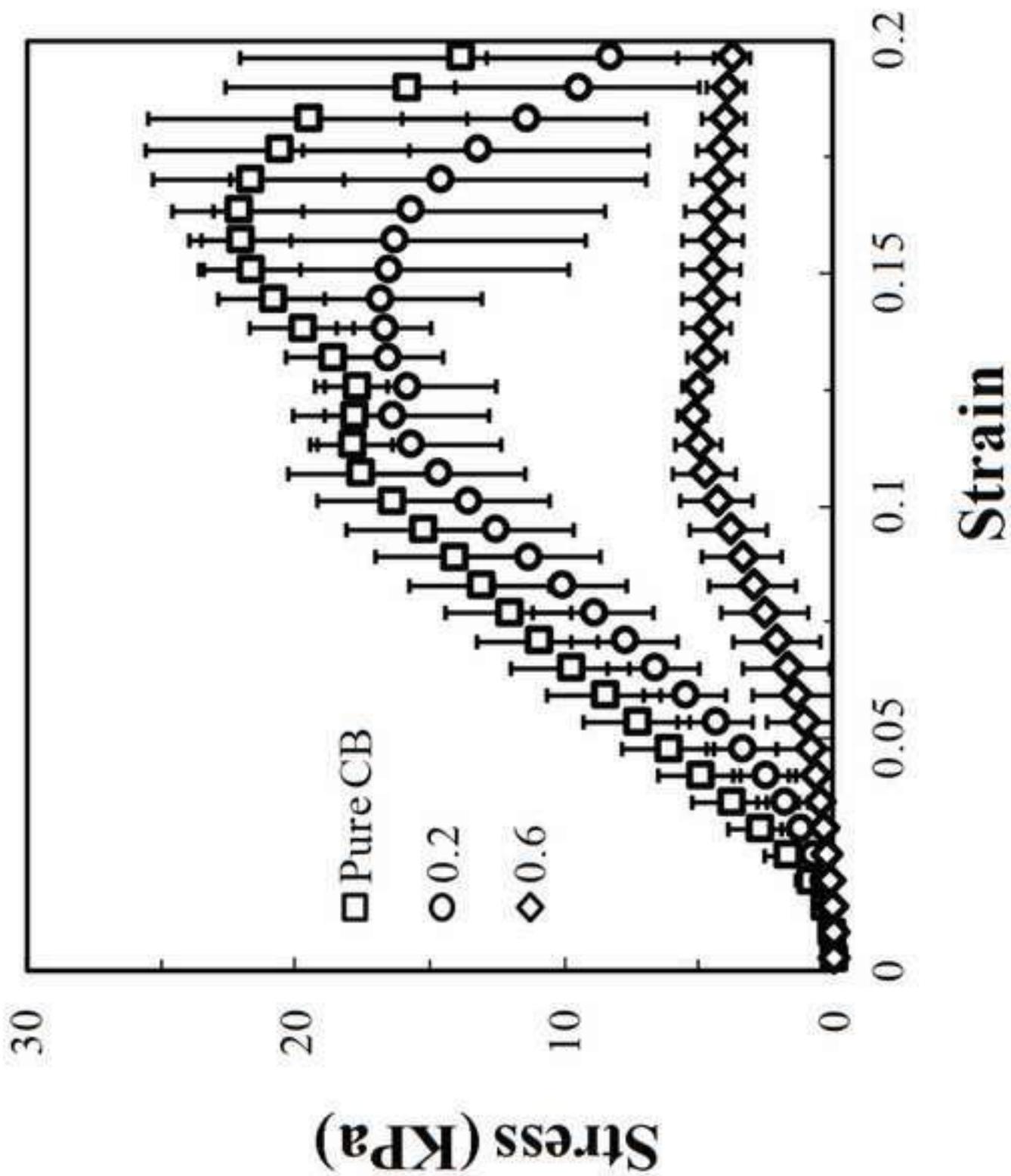
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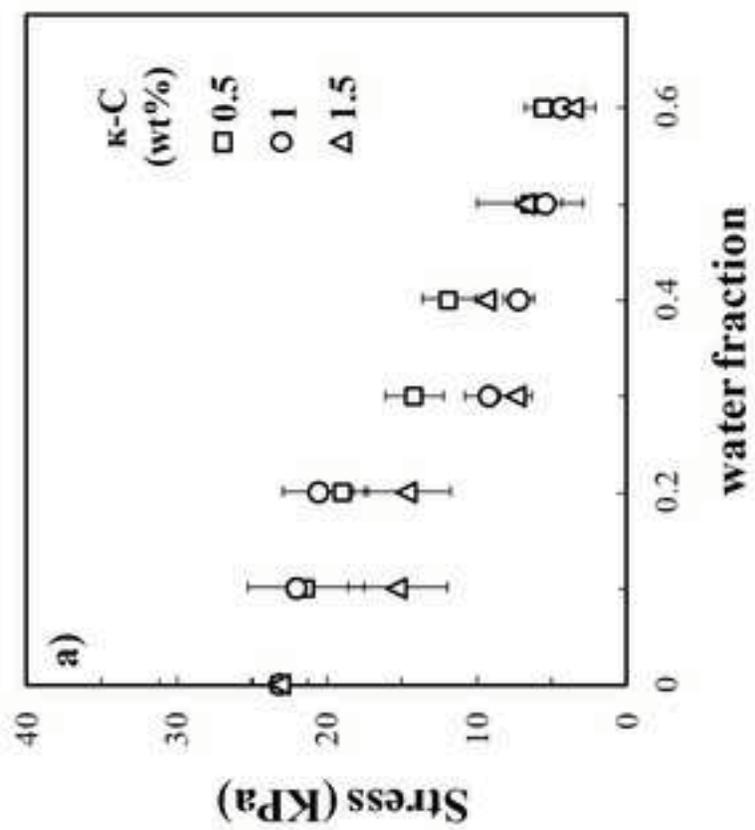
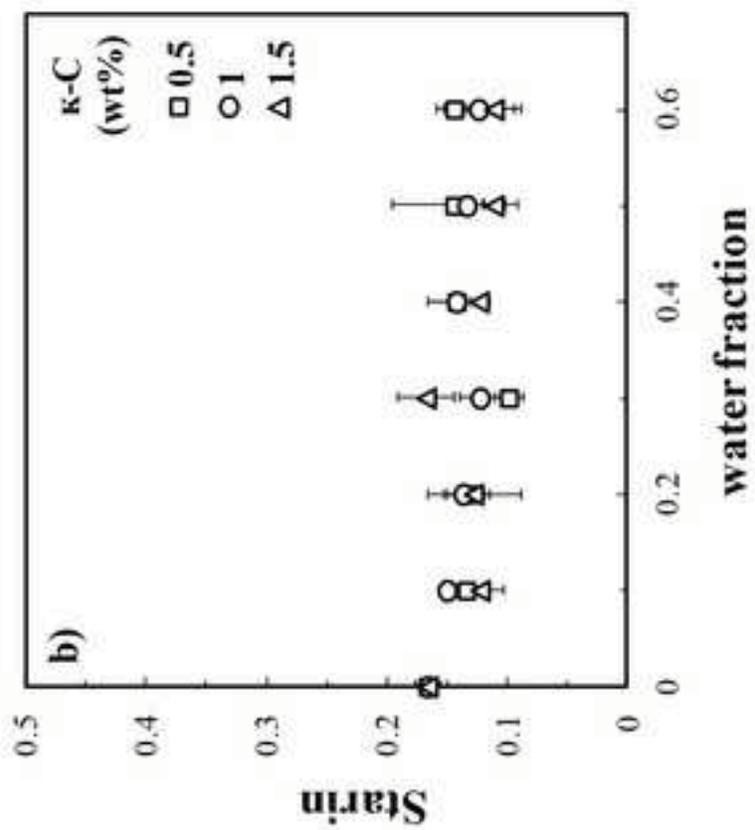


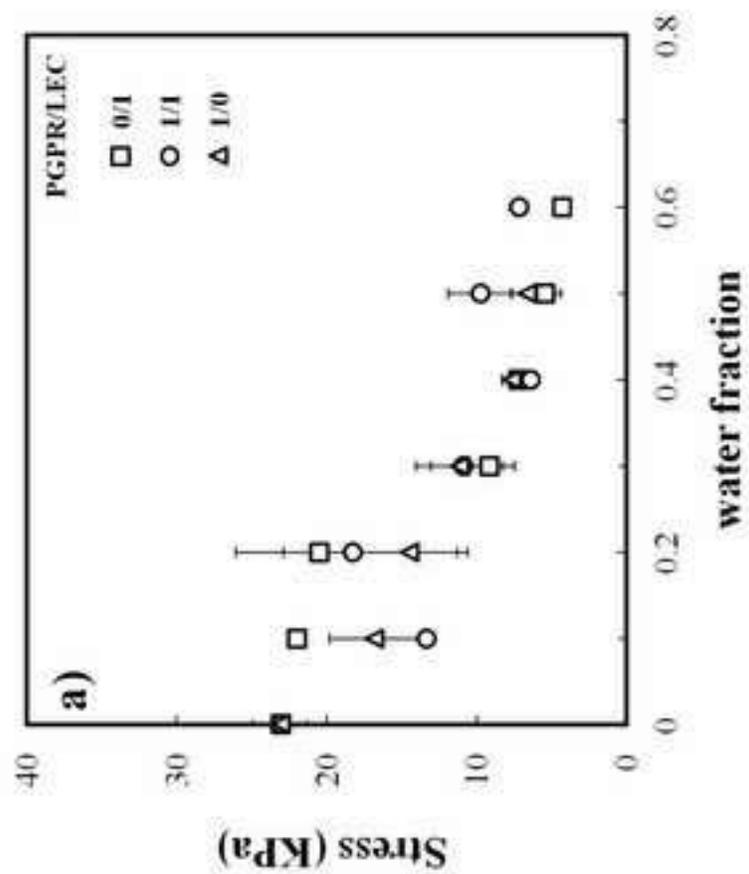
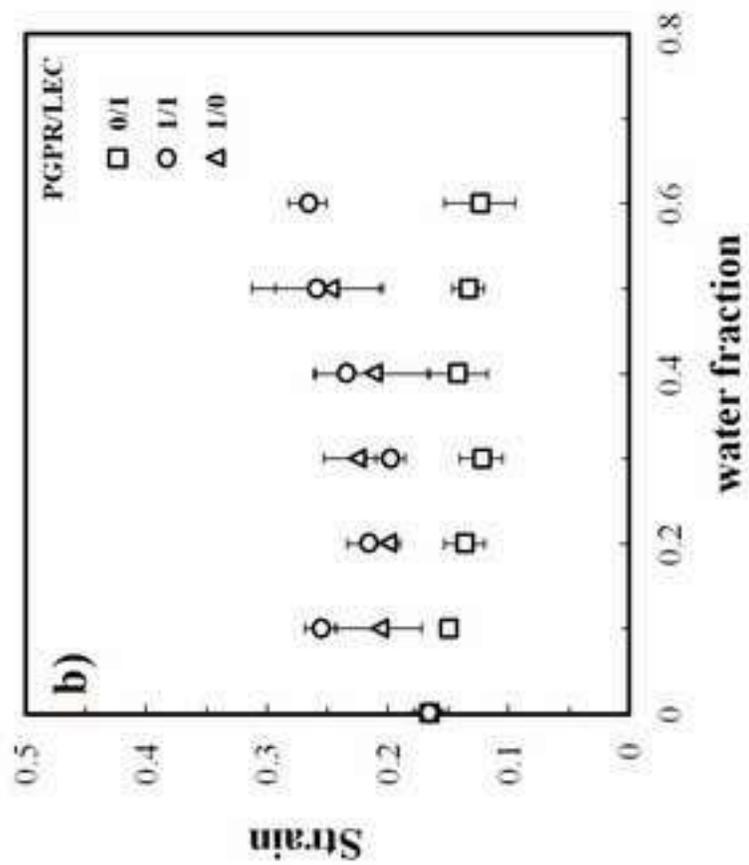


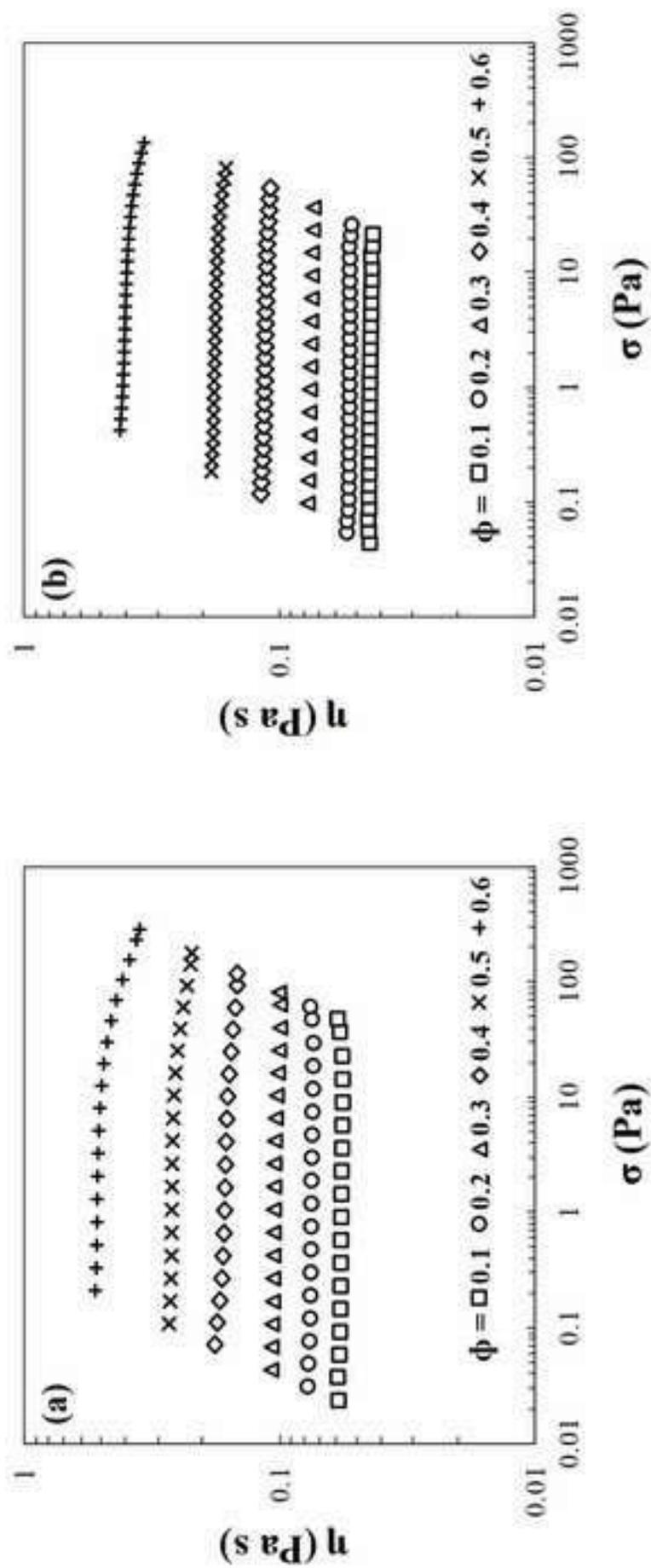
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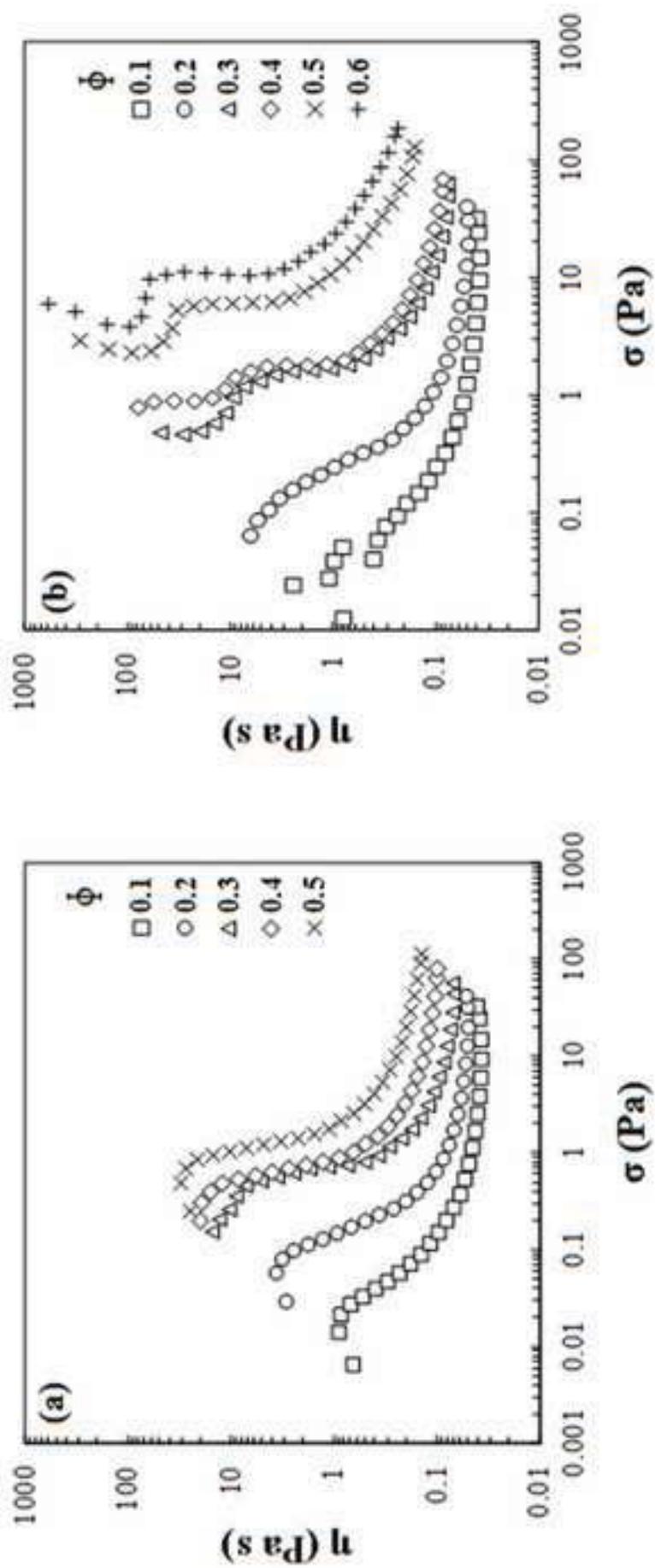


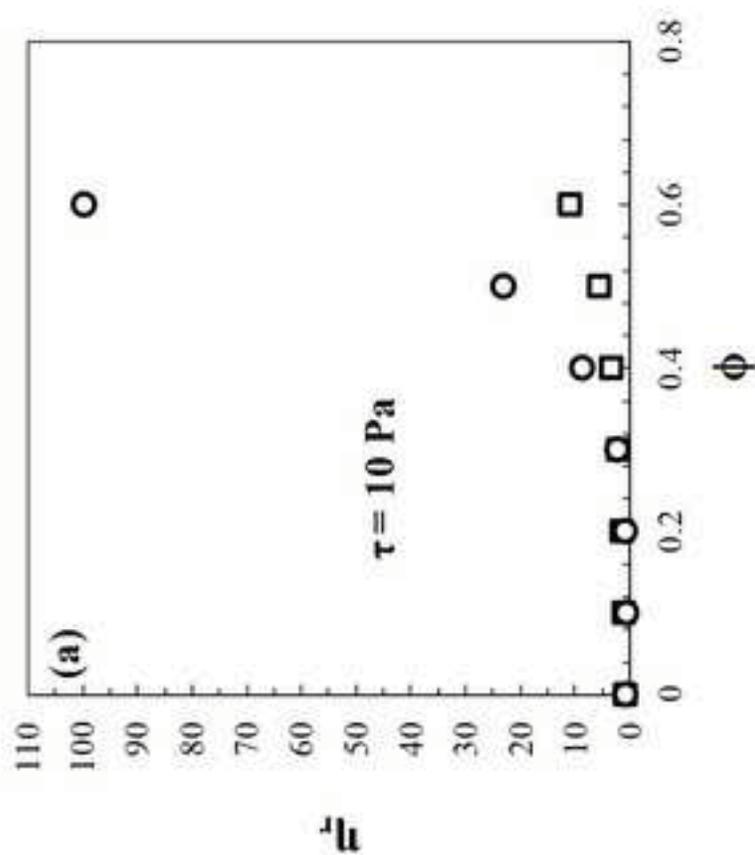
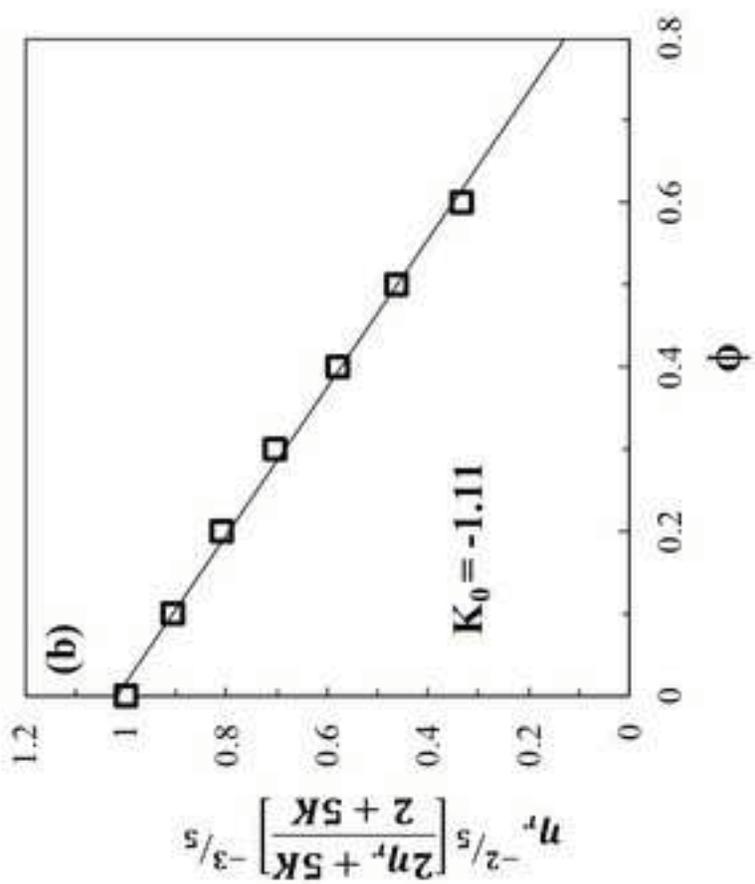












Sample	water fraction	Tp		$\Delta H(J/g \text{ CB})$	
		Peak 1	Peak 2		
Pure CB		n.a	32.8 ± 0.9	132 ± 2.4	
K-carrageenan (wt%)	0.5	0.2	33.1 ± 0	134.2 ± 2.3	
		0.4	32.8 ± 0.7	133.9 ± 14.1	
		0.6	33.8 ± 0.8	136.5 ± 6.2	
	1	n.a	34 ± 1	132.5 ± 4.1	
		0.4	34.2 ± 0.5	131.7 ± 2.7	
		0.6	32.9 ± 0.5	134.3 ± 9.2	
	1.5	0.2	35.6 ± 0.6	113.9 ± 1.8	
		0.4	34.5 ± 0.7	114.4 ± 3	
		0.6	34.6 ± 0.6	115 ± 1.4	
	PGPR:LEC	3/1	0.2	31.0 ± 0.4	129.0 ± 3.4
			0.4	31.1 ± 0.9	125.0 ± 5.3
			0.6	31.1 ± 0.4	131.2 ± 10.6
1/1		n.a	30.6 ± 0.1	112.0 ± 4.0	
		0.4	30.7 ± 0.9	113.3 ± 4.1	
		0.6	30.6 ± 0.4	110.0 ± 2.4	
1/3		0.2	18.0 ± 0.1	30.8 ± 1.1	126.0 ± 2.4
		0.4	17.7 ± 0.3	30.8 ± 0.2	128.0 ± 2.3
		0.6	17.8 ± 0.1	30.5 ± 0.7	138.0 ± 6.8
1/0		0.2		29.2 ± 1.1	105.0 ± 1.5
		0.4	n.a	29.5 ± 0.2	102.0 ± 5.4
		0.6		28.9 ± 0.7	104.0 ± 9.0

sample	λ_0	ϕ_m	h^a (μm)
κ-carrageenan (wt%)			
0.50	1.1	0.90	0.08
1.00	1.1	0.92	0.07
1.50	1.1	0.91	0.09
LEC/PGPR			
1/3	1.3	0.76	0.26
1/1	1.8	0.57	0.59
3/1	na	na	na

$$\phi_{eff} = \phi \left[1 + \left(\frac{h}{r} \right)^2 \right] \quad (\text{Tadros, 1994})$$