Tailoring flow behavior and texture of water based cocoa suspensions

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1. Introduction

The texture of low-fat food products must be adjusted to mimic regular full fat products in order to gain consumer acceptance (Le Révérend, Norton, Cox, and Spyropoulos., Apr. 2010). For chocolate products fat reduction can be achieved by minimize trapped fat in the cocoa particles (Do, Vieira, Hargreaves, Mitchell, and Wolf., May 2011) or by incorporating water into the product (Skelhon, Olsson, Morgan, & Bon, 2013), (Norton, 2009), (Norton & Fryer, Nov. 2012). A similar mouthfeel and the stability of regular fat products can be achieved by producing emulsions with similar droplet size as full fat products (Le Révérend et al., Apr. 2010), (Cain et al., 1990), (Norton, Brown, & Underdown, 1996). Particle stabilized emulsions have been widely studied as a pathway for making low calorie food products. Especially fat particles and crystals are known to form stable Pickering emulsions (Ghosh & Rousseau, Oct. 2011; Rousseau & Hodge, Jun. 2005; Rousseau, Jan. 2000). Chocolate products using cocoa particles as emulsion stabilizers have also been used to incorporate water in chocolate products (Skelhon, Grossiord, Morgan, & Bon, 2012), (Gould, Vieira, and Wolf., Sep. 2013). The stability of Pickering emulsions is influenced by particle shape and size, and especially by surface properties like the wettability of the particles by the surrounding fluids (Binks & Lumsdon, Nov. 2000). Natural organic particles are often used as

stabilizers for food products but the wetting behavior seems to be ambiguous. For cocoa particles it was found that higher surface energy fluids like water exhibit higher contact angles than hydrophobic substances with a lower surface energy (Galet, Vu, Oulahna, and Fages., Dec. 2004).

Recently, we have studied the behavior of suspensions of cocoa particles in water stabilized by a secondary immiscible fluid (Hoffmann, Koos, and Willenbacher., Feb. 2014). It was stated that capillary bridges are formed between the particles and a sample spanning network is created resulting in a transformation from a fluid like suspension to a particulate gel (Koos & Willenbacher, 2011). This capillary bridging phenomenon has already been studied for various food particle/fluid/fluid combinations like starch, cocoa or sugar particles in oil (Hoffmann et al., Feb. 2014), (Killian & Coupland, Feb. 2012), but for cocoa particles dispersed in water the gelling mechanism induced by the addition of a secondary fluid is not yet fully understood (Hoffmann et al., Feb. 2014). The addition of a fatty acid to the water continuous suspension of cocoa particles may result in capillary bridging or lead to the adsorption of the fatty acid to the surface then causing hydrophobic interactions between the particles. The latter were found to lead to spherical agglomeration in $CaCO_2$ suspensions (Kawashima, Handa, Takeuchi, & Takenaka, 1986). The combination of both mechanisms could also be possible (Koh, Uhlherr, & Andrews, 1985). Capillary bridges can be induced by addition of a secondary fluid, but may also be created using already incorporated fat in the food particles. It has been reported that food particles like ground seeds with an oil content form agglomerates during, e.g., roasting due to the oil released. Particles stick together since oily capillary bridges are formed between them (Takenaka, Ogata, Yabe, Yamauchi, and Kato., Aug. 2006). These investigations were restricted to dry granular matter and no work has been done yet regarding the behavior of such particles upon heating in suspension. In this research paper, we focus on the flow behavior of aqueous cocoa suspensions and how this can be adjusted by temperature or addition of a secondary liquid. This research should encourage the development of low fat cocoa spreads that are not based on gums, hydrogels or other polysaccharides, but provide structural stability through a particle network formed within the suspension, resulting in a creamy texture. This research paper first provides a thorough rheological characterization of the cocoa suspensions exposed to different temperature treatment or upon addition of non-polar organic

liquids. Potential mechanisms causing particle network formation are discussed based on various supplementary experiments for physico-chemical characterization of suspensions made from extracted and non-treated cocoa particles including microscopy, solubility, dynamic mechanical and SANS measurements.

2. Materials and methods

2.1. Materials

Cocoa powder 10712 SN donated from ADM Schokinag GmbH, Mannheim was used to prepare cocoa suspensions. Non-alkalized cocoa powder with a residual fat content of 11% were used as a standard. They were used as provided, but also extracted with ethanol and n-hexane. Extraction solvents were purchased from Carl Roth, Karlsruhe. For comparison, cocoa powder with a fat content of 22% were processed. These particles were donated from Storck GmbH, Halle, Germany. Pure cocoa butter was purchased from Spiceworld GmbH, Salzburg, Austria. All other fluids used for the experiments were purchased from VWR international and were used as provided if not stated otherwise.

2.2. Methods

2.2.1. Extraction
Particle extraction was done by washing with the extraction solvent. For this, 6 g of cocoa particles were mixed with 40 ml of extraction solvent in a centrifugation tube for 10 min at room temperature. The suspension was then centrifuged for 10 min at 8980 g and residual cocoa particles were suspended again with fresh solvent. This procedure was done in triplicate. The particles were then dried over silica gel at 20 °C for two days before they were used for experiments.

2.2.2. Particle size of cocoa
The particle size was measured using LALLS (Low Angle Laser Light Scattering, Sympatec HELOS H0309) while the particles were suspended in distilled water and subjected to ultrasonic dispersion using a Sympatec QUIXEL unit. Particle size distributions of extracted and non extracted particles can be found in Fig. 1.

2.2.3. Solubility of cocoa butter
The solubility of cocoa butter in the relevant solvents was characterized by adding 1.5 g solid cocoa butter (disc of radius 22.5 mm and 4.25 mm in height) to 10 ml of various fluids. Samples were placed on a shaking table at 250 rpm and the time for complete dissolution as observed by eye was documented.

2.2.4. Sample preparation
The suspensions were prepared as follows: particles were mixed into the bulk fluid using a turbulent beater blade (at 500 rpm for 20 min) until a uniform suspension was created. This mixture was then held under vacuum (100 mbar) for a few minutes to remove residual air bubbles. The samples were then held in airtight containers and stored for 24 h at different temperatures in a heating oven. Viscosity measurements were performed immediately after storage. A secondary liquid was added to the primary suspension and thoroughly mixed using a dispensing stirrer (at 1700 rpm for 5 min) in order to prepare water continuous capillary cocoa suspensions.

The secondary fluid content in a capillary suspension is characterized by the saturation of the preferentially wetting fluid S,
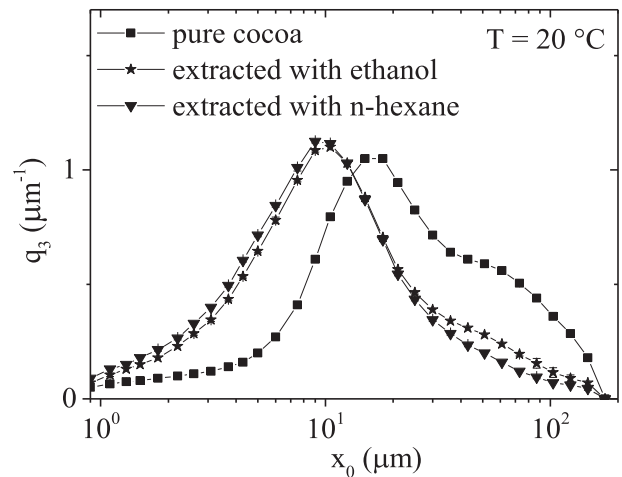

Fig. 1. Particle size distribution of extracted and non extracted cocoa particles.

$$S = \frac{V_{preferentially\ wetting\ fluid}}{V_{total\ fluid}}$$

which is close to zero for the pendular state and approaches one for the capillary state (Koos & Willenbacher, 2011). The quantity S is chosen in analogy to wet granular materials where the saturation is described as the ratio between liquid bridge volume and the total pore volume available between the particles.

2.2.5. Rheological measurements
The rheological properties of suspensions are characterized here through the apparent yield stress (for brevity subsequently termed yield stress), the shear rate dependent viscosity as well as the storage and loss modulus as a function of oscillatory frequency. Measurements were conducted using a rotational rheometer (MARS II, Thermo Fisher Scientific, Karlsruhe, Germany) with a sandblasted rough plate–plate geometry (35 mm diameter, 1 mm gap height). The sample viscosity was measured using shear rate steps. The shear rate was increased incrementally and held at a constant value, for at least 10 s and for a maximum of 100 s, until the stress σ reached a steady state, $(d\sigma/\sigma)/dt < 0.01$ s^{-1}, before recording the shear stress and corresponding viscosity. The yield stress, i.e. the stress at which the sample begins to flow irreversibly, was obtained from measurements in the stress-step mode, where every stress-step was held to equilibrate for 10s. The yield stress was found as the point at which the slope Δ of the logarithmic deformation as a function of the logarithmic shear stress changes from $\Delta \approx 1$ to $\Delta \gg 1$. Measurements where done in triplicate and the calculated standard deviations are shown as error bars in the diagrams. Transient viscosity measurements were performed by applying a constant shear rate of $\dot{\gamma} = 0.1$ s^{-1} for an extended period of time (24 h). Oscillatory measurements were performed using the standard plate–plate geometry as described above. Frequency sweeps were performed in the linear viscoelastic regime by maintaining a constant stress $\sigma = 10$ Pa.

2.2.6. Confocal microscopy
An inverse Leica TCS SP8 confocal laser scanning microscope (Leica Microsystems, Mannheim, Germany) was used for microscopic imaging. The microscope is equipped with lasers of 488 nm and 552 nm wavelength. Cocoa particles were dyed using Toluidine Blue to suppress the autofluorescence of the particles (Kadow, 2010). For this, 0.5 g of Toluidine Blue was dispersed in 180 ml of

water and 30 g of cocoa particles were added. The suspension was stored overnight on a shaking table and then centrifuged for 20 min at 5000 min^{-1}. The cocoa particles were washed by dispersing them in water and repeating the centrifugation step three times. Particles were then dried at 20 °C over silica gel for two days. Suspensions were prepared as described above and Nile Red was added to the suspension to dye the residual cocoa butter within particles.

2.2.7. SANS

Small angle neutron scattering (SANS) experiments were performed at the KWS-1 instrument of the Jülich center for neutron sciences (JCNS) outstation at the FRM II, Garching, Germany. For the experiments, a wavelength of $\lambda = 0.7$ nm ($\Delta\lambda/\lambda = 20\%$) and sample-detector distances of 1.4, 8 and 20 m were used thus covering the q-range from 0.0012 Å^{-1} to 0.23 Å^{-1}. The samples were mounted in standard glass cuvettes with a light path of 0.5 mm in an double-walled aluminum sample holder. Data reduction was done using the software QtiKWS provided by JCNS. SANS curves were fitted with a Gaussian model to analyze the peak shift at large q values. Suspensions were prepared in D$_2$O instead of H$_2$O for these experiments in order to increase the scattering contrast between the organic particles and the surrounding fluid. For the scattering length density calculation, the cocoa particles are treated as cellulose.

3. Results and discussion

3.1. Effect of temperature on flow behavior of pure aqueous cocoa suspensions

Suspensions of $\phi = 15$vol% cocoa particles in water were stored at three different temperatures T_s for 24 h in sealed containers. After that, the viscosity function was immediately measured at a temperature $T_m = 20$ °C. Samples were placed into the rheometer and rested for 1 min to adjust temperature. Corresponding viscosity functions are plotted in Fig. 2. Storage at 30 °C results in a three decades higher low shear viscosity than storage at 20 °C, whereas the suspension stored at 40 °C exhibits a viscosity level even lower than that of the sample stored at 20 °C. The high shear data for 20 °C and 30 °C samples was taken using a capillary rheometer as described in (Pahl, Gleißle, & Laun, 1995). At shear rates $\dot{\gamma} > 10000$ s^{-1}, the viscosity data of samples stored at different temperatures superimpose.

Obviously, storing water continuous suspensions of cocoa powder at different temperatures has an enormous effect on the flow behavior of these suspensions. One might assume that the viscosity increase results from a swelling of the particles, however, the strong increase observed here cannot be due to swelling and must be due to the formation of a particle network. This is confirmed by the convergence of the high shear viscosity data. Inter-particle bonds are broken and viscosity is just a function of particle volume fraction under the influence of high shear rates. Particle swelling would result in an increased effective solid phase volume fraction and correspondingly in an increase of high shear viscosity. Network formation can be deduced from comparing sedimentation behavior of samples stored at different temperatures. Those stored at 20 °C and 40 °C show slow sedimentation as a supernatant can be detected after 24 h storage in quiescent. Samples stored at 30 °C do not show sedimentation behavior on that time scale. In all cases sedimentation is so slow that it does not affect rheological measurements on a time scale of several minutes.

Bridging between the particles at elevated temperatures can be induced by molten or softened cocoa butter on the particle surfaces. Crystal forms I–V of the cocoa butter start to melt at 30 °C (Norton
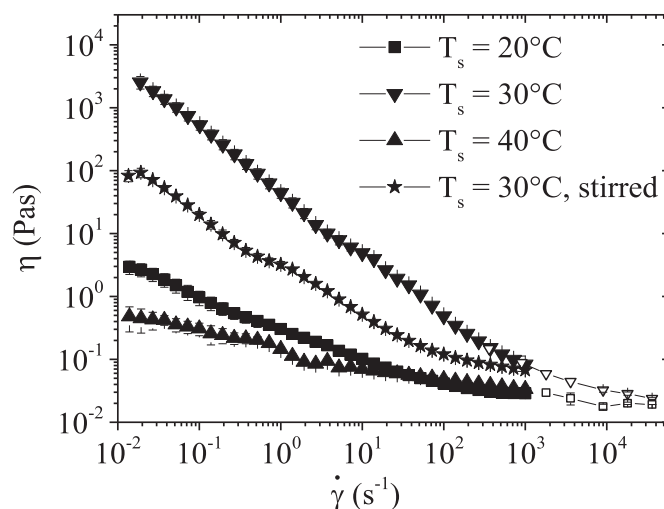

Fig. 2. Viscosity function of cocoa samples ($\phi = 15\%$) stored at 20 °C, 30 °C and 40 °C for 24 h. Measurements plotted with an open symbol were completed using a capillary rheometer. Stirred sample was prepared by mixing the sample during storage using a magnetic stirrer.

et al., Nov. 2009), (Beckett, 2000), but the cocoa butter is not in a completely liquid form. To confirm this, cocoa butter flakes were placed in water and stored for 24 h at 20 °C, 30 °C and 40 °C. At 20 °C and 30 °C the cocoa butter flakes maintained their shape, whereas the cocoa butter stored at 40 °C became liquid and completely phase separated from the water. The melting behavior is also documented in Fig. 3, where the frequency dependent storage and loss moduli G' and G'' of pure cocoa butter are plotted for different temperatures. At temperatures $T < 35$ °C, the cocoa butter behaves like a predominantly elastic solid where G' dominates over G'' in the whole frequency range. At 40 °C, the cocoa butter is in a fluid-like weakly viscoelastic state with $G'' > G'$ at low frequencies.

Two different mechanisms that can account for the temperature sensitive behavior of the cocoa suspensions can be proposed. One hypothesis is for a sintering process to occur. Sintering typically sets in when the material is heated above 60% of its melting point and solid bridges are formed via diffusion of the particle material. Higher temperatures increase the speed of the diffusion process. Sintering reduces the internal surface of the system and leads to an energetically more favorable state (Salmang & Scholze, 2007). For cocoa particles, cocoa butter would be the diffusing material and particle bridging could therefore be a function of the diffusion properties of cocoa butter when the particles are in contact. The other option is for the cocoa butter to be in a semi-crystalline state at 30 °C. This may correspond to an increased tackiness compared to the liquid state at 40 °C or the solid, fully crystalline state at 20 °C (Adhikari, Howes, Bhandari, and Truong., Mar. 2001), (Adams, 2005).

The stickiness, or self-adhesion, of the cocoa butter can be correlated to the storage modulus G' of the butter at given temperature. Modulus values $G \approx 10^5$ Pa correspond to a pronounced tackiness of soft polymers as pointed out by Dahlquist (Dahlquist, 1969) who quoted that good tack for pressure sensitive adhesives is achieved for $G' < 3.3 \cdot 10^5$ Pa at low frequency. According to Fig. 3, the modulus G' of cocoa butter at 30 °C and 35 °C is in the range of 10^5 Pa, so a good tack or stickiness should be provided. Values for cocoa butter at 20 °C exceed this range ($G' \approx 10^8$ Pa) and no stickiness can be expected anymore. At 40 °C, cocoa butter is liquid and accordingly does not provide any tackiness. Therefore particles that come into contact at 30 °C will stick together due to adhesive
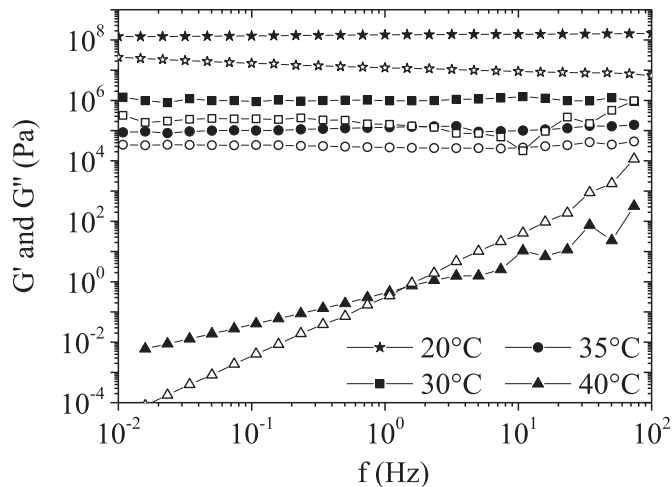
Fig. 3. G' (closed symbols) and G" (open symbols) vs. frequency for cocoa butter at 20 °C, 30 °C, 35 °C and 40 °C.

forces when cocoa butter is located at the surface. Moreover, we like to emphasize that our standard system is in quiescence during the tempering process, so shear-induced agglomeration can be excluded.

As proposed earlier (Hoffmann et al., Feb. 2014), capillary bridges may form from liquid cocoa butter spread over the particles surface, when particles come in contact, but this is not evident here. At 40 °C, the suspension behaves similarly to the suspension stored at 20 °C. For visual analysis of the samples at different temperatures, cocoa suspensions where diluted and corresponding images are shown in Fig. 4. It is confirmed that no agglomerates are formed at 40 °C as well as at 20 °C, whereas at 30 °C a clear floc formation is visible in the diluted samples. It has been reported earlier that the addition or the presence of too much secondary fluid may lead to spherical agglomeration (Dittmann & Willenbacher, Aug. 2014), but as shown here this seems not to be the reason for the reduced viscosity at 40 °C. Confocal images of cocoa particles dispersed in water were taken to show the cocoa butter distribution for suspensions stored at different temperatures. At 40 °C cocoa butter is in a fluid state and the confocal microscope images (Fig. 5, right) show that the liquid cocoa butter is at least partly removed from the particles surface appearing as separate emulsion droplets. These droplets apparently cannot form capillary bridges to create a sample-spanning network and rather remain emulsified in the suspension, which explains the fluid-like flow behavior. Images of the 30 °C sample, however, show a blurry distribution of the cocoa butter which is presumably at the particles surfaces or located between them thus enabling a network formation but with a bridge size too small to be distinguished individually. At 20 °C, the signal of the cocoa butter is much weaker than the residual signal of the
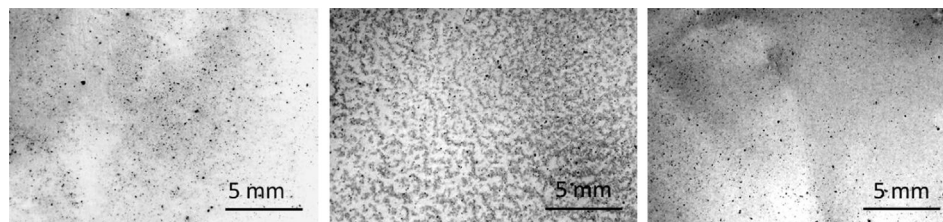
particles indicating that the butter remains inside.

In order to probe the resistance of the network against shear, one sample stored at 30 °C was continuously stirred during storage time using a magnetic stirrer bar at 200 rpm. In Fig. 2, the viscosity of the stirred sample is plotted in comparison to the sample left in quiescence at the same temperature. The low shear viscosity of the stirred sample is clearly lower than that of the sample stored at rest. Continuous shearing either diminishes the formation of bridges between the particles or larger capillary agglomerates are formed resulting in a weaker network (Koos, Johannsmeier, Schwebler, & Willenbacher, 2012), (Domenech & Velankar, 2014).

Fig. 6 shows the viscosity of a cocoa sample measured at $\dot{\gamma} = 0.1 \text{ s}^{-1}$ during a temperature ramp from 40 °C down to 20 °C. It is demonstrated that the viscosity of the sample once heated to 40 °C will not go to the level found for the sample stored at 20 °C for 24 h. Instead, the viscosity increases to the value found for the sample stirred during storage at 30 °C (30 Pa s) and remains at this high level even upon further reducing the temperature to 20 °C. Once the cocoa butter is released from the particle interiors, bridges will be liquid and unstable at 40 °C, stable and viscoelastic at 30 °C and solid at 20 °C. We must assume that not all of the cocoa butter is removed from the particles and forms emulsion droplets in the suspension during the storage period at 40 °C, but some residual butter must remain at the particle surface to induce the network formation when the suspension is cooled to 20 °C. As we have a continuous shearing process while measuring, the viscosity is comparable to the "30 °C stirred" level and not the standard 30 °C sample stored at rest.

The influence of cocoa butter included in the particles was further investigated by preparing suspensions of particles with the cocoa butter extracted. Particle extraction was performed using ethanol and n-hexane. N-hexane removes the fatty phase whereas ethanol is also capable of removing polar substances from the particles. In Fig. 7, the flow behavior of suspensions made from differently treated particles is displayed. Particles extracted with n-hexane and ethanol do not show an increase in low shear viscosity when stored at 30 °C while the untreated system clearly exhibits an increased low shear viscosity as was previously discussed. These findings demonstrate that the residual cocoa butter is critical for the structure formation and unusually high viscosity of the suspension stored at 30 °C. At 20 °C and 40 °C storage temperatures, viscosity curves for suspensions of extracted and non-extracted particles superpose. In summary, the storage temperature does not affect the flow behavior of suspensions made from n-hexane or ethanol extracted cocoa particles due to the absence of the cocoa butter.

Cocoa particles with different amounts of remaining cocoa butter are commercially used. Here we have investigated suspensions of cocoa particles with 11% residual cocoa butter as standard and also cocoa particles with 22% remaining butter for comparison. In Fig. 8 the yield stresses of cocoa suspensions with varied particle volume fractions and the two different cocoa butter contents stored at 30 °C are plotted. The yield stress characterizes the strength of

Fig. 4. Photographic images of diluted cocoa suspensions stored at 20 °C (left), 30 °C (middle) and 40 °C (right).
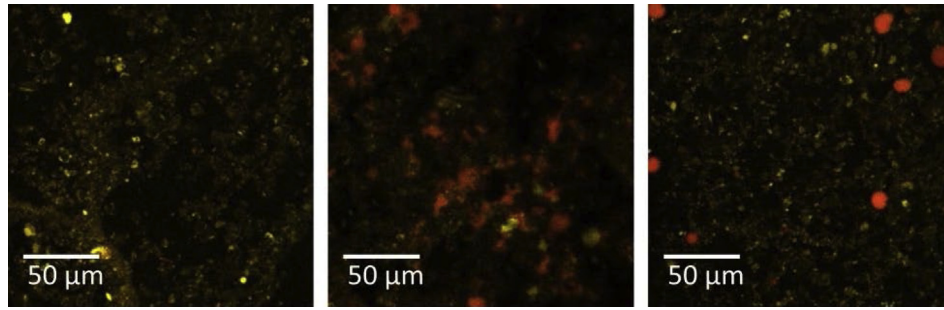
Fig. 5. Confocal microscopy images of cocoa particles suspended in water $\phi = 15\%$, for storage temperatures of 20 °C (left), 30 °C (middle) and 40 °C (right). The yellow signal is generated by the cocoa particles and the red channel denotes to the cocoa butter. The fluorescence of cocoa particles has been suppressed by washing them in Toluidene Blue and the cocoa butter has been stained with Nile Red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
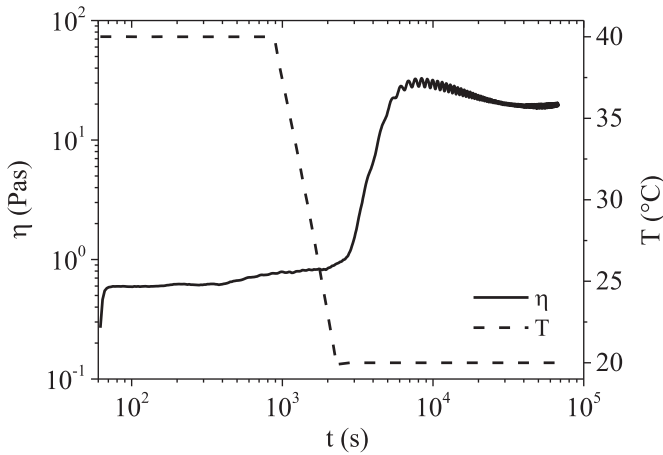
Fig. 6. Continuous shearing of a cocoa suspension ($\phi = 15\%$) at $\dot{\gamma} = 0.1$ s^{-1} during cooling from 40 °C to 20 °C.

the particle network within the suspension similar as the low shear viscosity of the samples. The yield stress increases with increasing particle loading, but below $\phi = 5\%$, no yield stress can be detected. Samples made from cocoa with 22% of residual cocoa butter exhibit a higher yield value throughout the whole concentration range.

More cocoa butter obviously leads to a stronger network and we attribute this to the formation of more and larger cocoa butter bridges between the particles.

3.2. Effect of secondary fluids on flow behavior of aqueous cocoa suspensions

In a previous study we stated that the formation of a capillary network in water continuous cocoa suspensions can be achieved by adding a secondary immiscible liquid (Hoffmann et al., Feb. 2014). In this previous work we used fatty acids as a secondary phase to create a particle network. Here, we discuss how temperature affects network formation if a secondary fluid is added and if the presence of cocoa butter is necessary for the formation of capillary bridges. In Fig. 9 the viscosity curves of suspensions with and without added oleic acid obtained at different storage temperatures are shown. A strong effect of oleic acid added to the suspension is visible for the suspension stored at 20 °C. The suspension with added oleic acid shows a low shear viscosity almost two orders of magnitude higher than that of the pure suspension. For 30 °C, the curves superpose at an even higher level than the 20 °C curve with secondary fluid. Suspensions stored at 40 °C do not show an increase of low shear viscosity upon the addition of oleic acid.

Different hypotheses can now be proposed regarding the effect of adding oleic acid to a cocoa suspension. First, the adsorption of oleic acid to the particle surface may render the surface of the cocoa
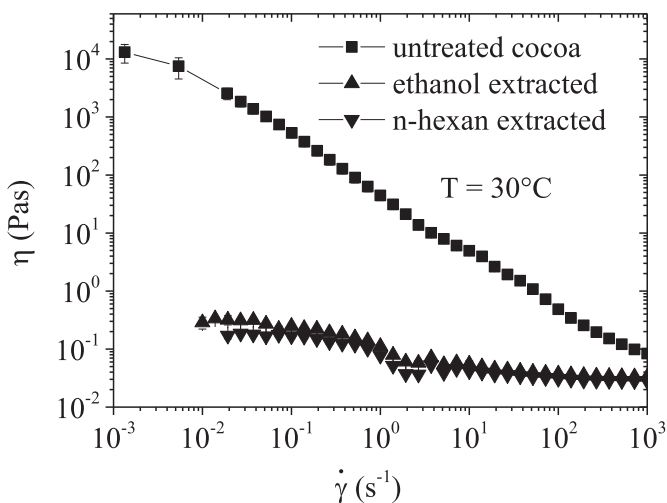
Fig. 7. Viscosity curves of suspensions ($\phi = 15\%$) prepared with untreated particles and particles extracted with n-hexane and ethanol stored at 30 °C.
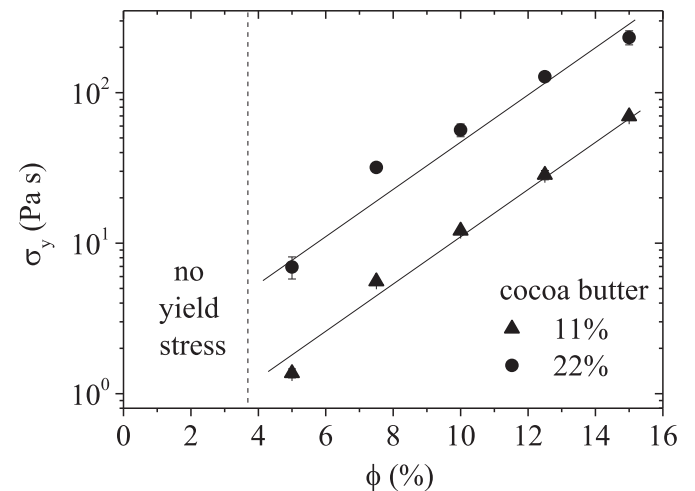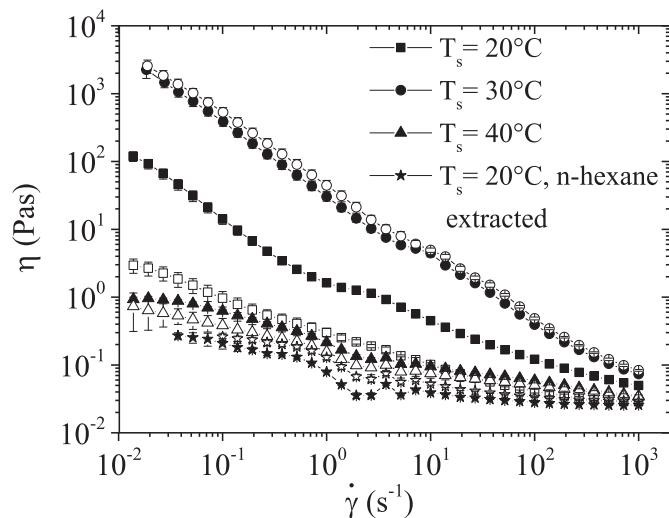

Fig. 8. Yield stress plotted over particle volume fraction of water continuous cocoa suspensions stored at 30 °C for 12 h. Particles with a cocoa butter content of 11% and 22% were used.

particles more hydrophobic as reported for other particle systems (Koh et al., 1985), (Sadowski & Smith, Jan. 1989), (Wu, Robbins, Winschel, & Burke, 1988). According to Koh et al. (Koh et al., 1985), oleic acid added to a water based sheelite suspension absorbs to the particle surface inducing a hydrophobic attraction that causes particle agglomeration. Furthermore, they propose that simultaneously oleic acid can form liquid bridges between particles, holding them together. These two, probably interfering processes, may also occur for the cocoa particle system described here. The second possible mechanism is the dissolution and extraction of the cocoa butter distributed inside the cocoa particles by the oleic acid. Solving cocoa butter in oleic acid could result in a waxy, sticky surface around the particles gluing them together upon contact. Oleic acid may act as a plasticizer for cocoa butter having a similar effect on mobility and stickiness as increasing the temperature.

It is possible to investigate the effect of added oleic acid on suspensions of cocoa particles from which cocoa butter was extracted using n-hexane. The corresponding viscosity data also shown in Fig. 9, clearly demonstrates that the addition of oleic acid does not change the rheology of cocoa suspensions when cocoa butter is removed. This result leads to the conclusion that the high low shear viscosity achieved upon adding oleic acid is a result of particle bridges formed from cocoa butter/oleic acid mixtures and cocoa butter is the key parameter controlling the flow behavior of aqueous cocoa suspensions.

To further understand the network formation process, the viscosity of suspensions with and without added oleic acid stored at 20 °C was measured over time of storage, starting right after sample preparation and continuing with discrete steps using a new sample for every measurement point. Corresponding viscosity data taken at $\dot{\gamma} = 0.1 \ s^{-1}$ is plotted in Fig. 10. Viscosity increases in all cases but with different slopes. Samples with added secondary fluid exhibit higher initial viscosities, but the viscosity values match after 7 h for the samples stored at 30 °C as already shown in Fig. 9. The sample with oleic acid stored at 20 °C needs longer time for network formation, but after 10 h it reaches a similar viscosity level as those stored at 30 °C. This further supports the hypothesis that cocoa butter is dissolved by the secondary fluid as already described in the previous section, where the process of melting the cocoa butter at 30 °C is faster than dissolving it in oleic acid at 20 °C.

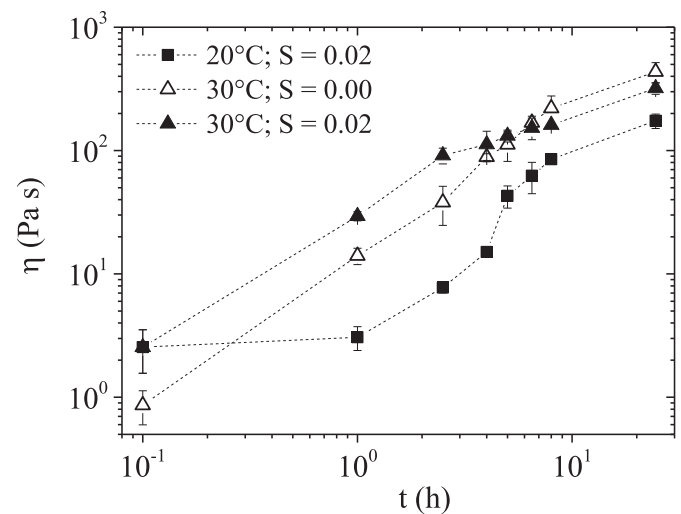The effect of adding oleic acid to cocoa suspensions has been discussed so far. We will now compare different fluids immiscible with water but comprising different functional groups, varied hydrocarbon chain lengths and entirely unpolar oils. These substances and their characteristic features are listed in Table 1. For these water continuous suspensions interfacial tension is not the decisive factor for thickening as has been reported for capillary food suspensions with oil as the bulk phase (Hoffmann et al., Feb. 2014), since sunflower oil and oleic acid show similar equilibrium interfacial tensions against water at 20 °C, but a change in viscosity can only be detected when oleic acid is added.

Yield stress values obtained at different times after preparation of the two-fluid cocoa suspensions ($S = 0.01$) are plotted in Fig. 11. Obviously, secondary fluids exhibiting a shorter chain length (C8 vs. C18) induce faster increase of yield stress than fluids with longer chains like oleic acid. After a storage time of 100 h suspensions prepared with secondary fluids of different chain length show the same yield value. Therefore, the chain length of the secondary fluid determines the kinetics of network formation in these suspensions, but does not affect the final network strength despite the different interfacial tension. Different functional groups also does not result in a measureable difference with respect to the yield stress or gel strength of the suspension. Suspensions with added sunflower oil or silicon oil do not show any measurable effect on flow behavior compared to the regular bulk suspension. We attribute these findings to a different solubility of cocoa butter in the different secondary fluids. Cocoa butter did not completely dissolve in sunflower oil or silicone oil even after 58 h. In contrast, cocoa butter dissolved completely in octanoic acid within 2 h and in oleic acid within 8 h. Mixtures of cocoa butter with these organic acids form wax-like, soft, sticky fluids at the concentration ratios present in the cocoa suspensions ($\phi = 15\%$, residual cocoa butter within particles 11%, $S = 0.02$) and this seems to be the prerequisite for the formation of network structures similar to those developing when pure aqueous cocoa suspensions are heated to T = 30 °C.

3.3. Structural information about cocoa particles from SANS experiments

Small angle neutron scattering experiments were used to identify structural changes upon heating or addition of secondary

Fig. 9. Viscosity functions of cocoa suspensions ($\phi = 15\%$) made from original cocoa particles stored at 20 °C, 30 °C and 40 °C with (filled symbols, $S = 0.02$) and without (open symbols) the addition of oleic acid.

Fig. 10. Time dependent network formation for pure cocoa samples ($\phi = 15\%$) stored at 20 °C and 30 °C with and without added secondary fluid. Viscosity data was measured at shear rate $\dot{\gamma} = 0.1 \ s^{-1}$. The rheometer was filled with a fresh sample for each measurement point.

Table 1
Characteristics and solubility of immiscible liquids added as secondary fluids to cocoa suspensions.

	Octyl acetate	Octanoic acid	Oleic acid	Octanol	Sunflower oil	Silicon oil AK10
Functional group	−OCOOH	−COOH	−COOH	−OH	−	−
Interfacial tension against water (20 °C)	20 mN/m	8 mN/m	14 mN/m	8 mN/m	22 mN/m	39 mN/m
Chain length	8C	8C	18C	8C	16C–20C	−
Thickening effect	✓	✓	✓	✓	X	X
Solubility of cocoa butter (20 °C)	<1 h	1:42 h	8 h	8:15 h	>58 h	insoluble
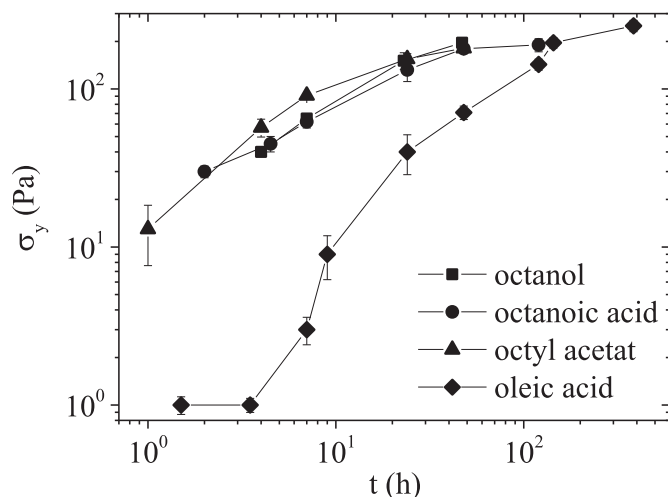
Fig. 11. Yield stress over time for aqueous cocoa suspensions ($\phi = 15\%$) with different secondary fluids ($S = 0.01$). The rheometer was filled with a fresh sample for every measurement point.
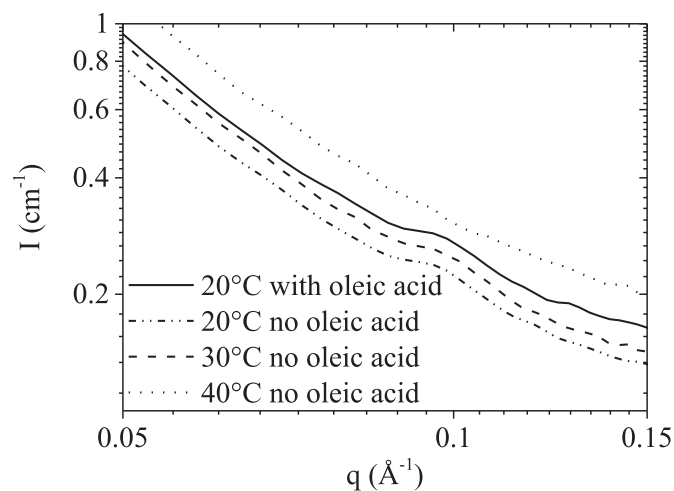
Fig. 12. Scattering intensity I vs. scattering vector q for cocoa in water samples ($\phi = 15\%$) at temperatures of 20 °C, 30 °C and 40 °C and 20 °C with added oleic acid ($S = 0.02$).

fluid. In Fig. 12, the scattering curves of samples made from $\phi = 15\%$ cocoa powder in water at 20 °C with and without secondary fluid and at 30 °C as well as 40 °C without secondary fluid are shown. The scattering intensity strongly decreases with increasing q-value in all cases. The samples stored at 20 °C and 30 °C exhibit a characteristic peak in the high q-rage. For the pure cocoa suspensions at 20 °C this peak occurs at $q = 0.173$ Å^{-1} corresponding to a characteristic length of 36 Å. We can interpret this as a bilayer of triglyceride molecules. For the samples with added oleic acid this length increases to 51 Å and a characteristic length is 53 Å is found for the pure suspension heated to 30 °C. This would then correspond to a triple layer of triglyceride. The peak width is similar in all cases, so it does not include additional information about the structural changes induced by heat treatment or addition of a secondary liquid. No peak is found for the sample stored at 40 °C.

The characteristic length in the suspensions revealed by the peak in the scattering intensity is interpreted as a surface layer covering the cocoa particles. The thickness of this layer is increased when cocoa butter leaks to the particle surface at elevated temperatures or when oleic acid is added. No surface layer of cocoa butter exists at 40 °C. As already shown in Fig. 5, the cocoa butter separates from the particles at this temperature and forms large droplets which do not contribute to the scattering intensity in the q-range investigated here. The surface layer observed in SANS experiments may not be sufficient to facilitate bridging between particles considering their irregular shape but its change is another indicant for the leaking of the butter from the particle interior at elevated temperatures or upon addition of a secondary fluid. The stickiness of the surface layer provided either by the mixture of cocoa butter and oleic acid or by the pure cocoa butter at elevated temperature is decisive for the formation of a sample spanning network structure and a distinct rheological behavior

corresponding to a creamy texture.

4. Summary

The rheological behavior of aqueous cocoa particle suspensions stored at different temperatures or modified by the addition of a secondary fluid has been investigated in this paper. When cocoa particles are dispersed in water and stored at a temperature of 30 °C, a network of particles is formed which leads to an increase in low shear viscosity and a gel-like, creamy texture. Heating the sample further up to 40 °C or above results in a network collapse and the suspension behaves fluid-like again. The critical factor controlling this behavior is the residual cocoa butter in the particles. At 30 °C, the cocoa butter is in a semicrystalline state and bridges of this cocoa butter between the particles are formed via a diffusion process (similar to sintering) or just by sticking together upon contact due to cocoa butter that has leaked to the surface. The cocoa butter is completely liquid at 40 °C and partly forms emulsion droplets in the water phase that are not connected to the particles as shown via confocal imaging. The key role of cocoa butter for network formation, texture and flow of the aqueous suspensions has been proven by extracting it from the particles as well as increasing the amount of cocoa butter. Particles, where the fat has been removed show no temperature dependent change in flow behavior. Particles with higher butter content form stronger networks as proven for a wide range of particle loadings. Samples, once heated above 30 °C, will not go back to their initial state at 20 °C and remain in a gelled state. High network strength is obtained upon storage over extended periods of time at rest (>24 h).

Adding a secondary fluid to the cocoa suspension results also in an increased yield stress attributed to the formation of a network of particles even at room temperature. This bridging phenomenon

only appears for particles with residual cocoa butter content. This leads to the assumption that the secondary fluid dissolves the cocoa butter and, similar to the heated particles a soft and sticky semi-crystalline fluid is created that glues the particles together. This process is faster for short chain solvents with a polar end-group compared to longer chain fatty acids and can be correlated to the speed at which the respective fluid dissolves the cocoa butter. Less polar substances like silicone oil or sunflower oil do not induce a particle network formation, which is attributed to the poor and slow solubility of cocoa butter in these fluids.

SANS experiments also revealed structural differences between samples stored at different temperatures. Samples stored at 30 °C or at 20 °C, but with added oleic acid exhibit a scattering peak corresponding to a characteristic length scale of about 50 Å whereas the characteristic length reduces to about 35 Å for a pure cocoa suspension stored at 20 °C. This length scale is attributed to the cocoa butter layer on the particle surface and completely vanishes upon storage at 40 °C.

Finally, we have shown how the flow behavior of water continuous cocoa suspensions and correspondingly their creaminess and texture can be tuned in a wide range via appropriate heat treatment or addition of an adequate, immiscible secondary fluid. This may open up a new pathway for the formulation of low fat food products based on cocoa or other finely dispersed particles.

Acknowledgments

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