

# Using capillary bridges to tune stability and flow behavior of food suspensions



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## ABSTRACT

Adding a small amount of an immiscible fluid to a particle suspension can lead to particle bridging and network formation. This effect occurs both if the secondary fluid wets the particles better or worse than the bulk fluid. The capillary bridging phenomenon can be used to stabilize particle suspensions and precisely tune their rheological properties. This allows stable food products to be created as shown here for starch and cocoa model suspensions. Adding small fractions of water to suspensions of starch or cocoa particles in oil increases the yield stress by several orders of magnitude. The yield stress and viscosity can be tuned in a wide range by changing the fraction of the secondary liquid or the wetting properties of the ternary particle/fluid/fluid system. The presence of aqueous capillary bridges between cocoa particles improves the heat stability of model chocolate systems. In suspensions of starch granules that have been conditioned over water, the network induced by capillary bridges forms spontaneously and results in the same yield stress as when the water is added to the suspension of dry particles. This demonstrates, that in contrast to Pickering emulsions, the formation of capillary suspensions is an energetically driven phenomenon. Water continuous suspensions can potentially be used to design novel low fat food products. We have modified suspensions of cocoa particles in water with trace amounts of appropriate oil to achieve texture and flow properties of regular fat continuous cocoa spreads.

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## 1. Introduction

Capillary suspensions, suspensions with a small amount of an added immiscible liquid, can be used in a wide range of applications. The addition of the secondary liquid can create a sample-spanning particle network due to capillary bridges formed between the particles. Accordingly, the rheological properties as well as the stability of the suspensions alter dramatically (Gögelein, Brinkmann, Schröter, & Herminghaus, 2010; Van Kao, Nielsen, & Hill, 1975; Koos, Dittmann, & Willenbacher, 2011; Koos, Johannsmeier, Schwebler, & Willenbacher, 2012; Koos & Willenbacher, 2011). Particles that are stabilized in a sample-spanning network due to capillary bridges do not sediment, even after long term storage (Koos & Willenbacher, 2011). Capillary suspensions can be created whether the secondary fluid preferentially wets the particles or not. Mixtures where the secondary fluid is the better wetting liquid (three phase contact angle is smaller than 90°) are referred to as pendular state suspensions. If

the bulk fluid is preferentially wetting, the contact angle is greater than 90° and the suspension is in the so-called capillary state.

Capillary suspensions are fundamentally different from particle-stabilized (Pickering) emulsions. In stable Pickering emulsions, the particle volume  $r^3$  is typically much smaller than the droplet volume  $V_1$ , so that  $V_1/r^3 \gg 1$  (Aveyard, Binks, & Clint, 2003; Binks, 2002), whereas in capillary suspensions the particle has a volume smaller or in the same range as the bridging volume  $V_1/r^3 \leq 1$  (Koos & Willenbacher, 2012). In Pickering emulsions, capillary forces are stabilizing the emulsion droplets from coalescing and gelation is caused primarily through the van der Waals force acting between adjacent particles (Akartuna, Studart, Tervoort, Gonzenbach, & Gauckler, 2008). In capillary suspensions, the gelation is caused directly by the capillary force, creating a sample spanning particle network.

The effect of water added to oil continuous suspensions for food applications has been previously discussed by Johansson and Bergenstahl for sugar (pendular state) and solid fat (capillary state) particles (Johansson & Bergenstahl, 1992a, 1992b, 1992c). There, particle agglomeration with the addition of water was reported resulting in faster sedimentation of the fat or sugar particles, but no sample-spanning network was observed. This is similar to the so-called spherical agglomeration technique used to separate solids

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in coal and ore preparations (Leonard, Greer, Markuszewski, & Wheelock, 1981; Puddington & Sparks, 1975). A focus on chocolate products can be found in literature, proposing that water can form capillary bridges between sugar particles and therefore a sugar network is created that prevents the fat phase from spreading while it melts (Killian & Coupland, 2012; Stortz & Marangoni, 2011). Several patents have been filed on that topic (Russel & Zenlea, 1948; Schubiger & Rostgno, 1965; Simbürger, 2009; Traitler, Windhab, & Wolf, 2000). Work has been done to investigate the rheological behavior of sugar networks or the effect of surfactant concentration in model chocolate dispersions when water is added to the suspensions (Garbolino, 2002; Ziegler, Garbolino, & Coupland, 2003). Corresponding preparation methods (Hugelshofer, 2000; Killian & Coupland, 2012) for chocolate products have been discussed. Other particle/liquid/liquid combinations that form sample-spanning networks remain unexplored as well as the influence of the wetting properties on the rheological behavior.

Both the capillary state and pendular state are controlled by the capillary force and are strongly influenced by changes in the amount of secondary fluid and the interfacial and wetting properties of the ternary system. The capillary force depends on the particle radii, the interfacial tension  $\gamma$  between the two fluids in contact with the particles, and the three-phase wetting angle  $\theta$  the secondary fluid forms against the solid surface in presence of the bulk fluid (Dittmann, Koos, & Willenbacher, 2012; Koos et al., 2011, 2012; Koos & Willenbacher, 2011, 2012). The force  $F_c$  between two equally-sized spheres of radius  $r$  connected by a pendular bridge is given by (Koos & Willenbacher, 2011; Pietsch, 1967; Schubert, 1984),

$$F_c = 2\pi r \gamma \cos \theta \quad (1)$$

It is assumed that the particles are in contact and that the pendular bridge is small compared to the particles (Pietsch, 1967; Schubert, 1984). For larger droplets, the force will depend on the volume of the secondary fluid, with various corrections given based on the filling angle and shape of the droplet. Additional corrections are available for surface roughness and particles that are not in contact (Butt, 2008; Pietsch, 1967). The yield stress  $\sigma_y$  of a pendular state suspension is related to the capillary force (Koos et al., 2012; Schubert, 1984),

$$\sigma_y = f(\phi) g(V_l, s) \frac{\gamma \cos \theta}{r} \quad (2)$$

where  $f(\phi)$  is a function of the volume fraction of the particles and depends on the number of contacts per particle. The volume of the bridge  $V_l$  and the distance between the two particles  $s$  are included in the function  $g(V_l, s)$ . For the capillary state, calculations and experiments have shown that clusters of different shapes are formed within the suspension. Cluster configuration is highly dependent on the amount of secondary liquid and its wetting behavior (Koos & Willenbacher, 2012). With higher amounts of secondary liquid particles tend to form octahedral clusters that have a stronger cohesion than tetrahedral clusters which are more favored for lower secondary liquid contents (Koos & Willenbacher, 2012). It has been shown before that the strength of a capillary suspension in the pendular as well as in the capillary state is proportional to the inverse of the particle size. Temperature can also alter the yielding and flow of capillary suspensions dramatically via its effect on interfacial tension and wetting properties. The addition of surfactant can prevent the formation of capillary bridges which results in a change in flow behavior of the capillary suspension (Koos et al., 2011, 2012).

In this study we discuss how capillary forces can be used to control the stability and flow behavior of food products. When

particles are dispersed in oil the capillary force may be used to stabilize the particles or to introduce a higher viscosity by simply mixing a small amount of a secondary liquid to the suspension instead of using other more complex rheology control agents.

Simple model systems of particles in oil suspensions were investigated to determine the parameters that affect the network formation and the resulting rheological properties. For this, two food model systems have been chosen: corn starch and cocoa particles in vegetable oil. Water is used as the secondary liquid in both admixtures. The effect of secondary phase viscosity and contact angle on suspension strength is systematically investigated. The influence of adsorption of water to the particles and the resulting flow properties will also be discussed. For the cocoa particles, the system was also inverted and cocoa particles were dispersed in water and a fatty acid was used as secondary liquid. This allows a first look at the use of the capillary suspension phenomenon for low fat food formulations.

## 2. Experimental methods

### 2.1. Sample preparation

Two particle systems were used in this study: native corn starch granules (G\*Gel 03401, donated by Cargill Deutschland GmbH, Krefeld) and cocoa particles (cocoa powder 10/12 SN, donated by ADM Schokinag GmbH Mannheim). The cocoa particles were non-alkalized and had a fat content of 10%. Commercial grade sunflower ("Ja!" Rewe Markt GmbH) oil ( $\eta = 39$  mPa s) for suspension preparation was purchased at a local supermarket and was used as provided. The cocoa particles were stored in airtight containers and used as provided. Glycerol as well as poly (ethylene oxide) (PEO,  $M_w = 10^6$  g/mol), used to adjust the viscosity of the aqueous secondary phase, were purchased from Carl Roth, Karlsruhe, Germany.

Starch granules were used as provided. For experiments regarding contact angle variation, the starch granules were treated with octenyl succinic anhydride (OSA) bought from Carl Roth to make the particles more hydrophobic (Bhosale & Singhal, 2006). For hydrophobization, the starch granules were dispersed in water and OSA was added in different concentrations (0%, 1%, 2% and 3 wt.% of the particle mass). Mixtures were stirred for 3 h and then centrifuged for 20 min at  $5000 \text{ min}^{-1}$ . The starch was washed three times by dispersing the particles in water and repeating the centrifugation step. Particles were then dried at  $40^\circ \text{C}$  for 72 h. Before dispersing the treated starch granules in oil for sample preparation, the powder was ground using a mortar and pestle.

The particle size was measured using a LALLS (Low Angle Laser Light Scattering, Sympatec HELOS H0309) while the particles were suspended in paraffin oil and subjected to ultrasonic dispersion using a Sympatec QUIXEL unit. Starch granules have a particle Sauter mean diameter of  $x_{3,2} = 8.4 \pm 0.1 \mu\text{m}$  and cocoa particles of  $x_{3,2} = 4.9 \pm 0.04 \mu\text{m}$  in oil.

Interfacial tension  $\gamma_{ow}$  was measured using the pendant drop method (Song & Springer, 1996) on an OCA 15 EC (Dataphysica, Germany). Contact angle was measured directly in the three phase system (Grundke, Bogumil, Werner, & Janke, 1996; Zhang & Hallström, 1990). Powder was pressed to a tablet using a hand press machine and soaked with the bulk fluid (sunflower oil) to ensure that no open pores are left in the pellet. The pressed pellet was placed in a glass container filled with oil and a drop of secondary fluid was placed onto the particle surface. Contact angle was measured immediately through the secondary phase droplet and calculated via image analysis (Hamilton, 1971).

Capillary suspensions were prepared as follows: particles were mixed into the bulk fluid using a turbulent beater blade (at 500–2000 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 air bubbles. The secondary fluid was added to the suspension and thoroughly mixed using a dispenser stirrer (at 1700 rpm for 5 min).

The samples were held in airtight containers until the measurements were completed. The secondary fluid content in a capillary suspension is characterized by the so-called saturation of the preferentially wetting fluid  $S$ ,

$$S = \frac{V_{\text{preferentially wetting fluid}}}{V_{\text{total fluid}}} \quad (3)$$

which is close to zero for the pendular state and approaches one for the capillary state (Koo & Willenbacher, 2011; Schubert, 1984). Saturation  $S$  is chosen in analogy to wet granular material, where saturations is described as the ratio between total pore volume (air) and the total volume between the particles (fluid filled and unfilled pores). In the present case, the fluid that wets the particles less well corresponds to the air in wet granular media. Since we defined saturation as the volume ratio dependant on wettability of the two fluids, mixtures where the secondary fluid is better wetting ( $\theta < 90^\circ$ ) have a saturation  $S$  close to 0, whereas in mixtures where the bulk fluid is the better wetting fluid ( $\theta > 90^\circ$ ) saturations close to 1 are obtained.

Additionally, it should be noted that the suspensions discussed here are not densely packed like in wet granular media.

Heat sensitivity measurements were performed by replacing the vegetable oil phase with cocoa butter (Dragonspice Naturwaren, Germany). The test for heat sensitivity was performed using the method of Schreiber (Killian & Coupland, 2012; Muthukumarappan, Wang, & Gunasekaran, 1999). Samples were prepared at 45 °C and cooled in cylindrical form (diameter: 2.5 cm, height: 2 cm) at 20 °C for 24 h and then placed in an oven at 50 °C while height and profile were detected over time via image analysis.

## 2.2. Rheological characterization

The strength of capillary suspensions is characterized here through the apparent yield stress (for brevity subsequently termed yield stress). Measurements were conducted using a rotational rheometer (MARS II, Thermo Fisher Scientific, Karlsruhe, Germany) with a sandblasted rough plate–plate geometry (35 mm diameter). The yield stress is defined as the stress at which the sample begins to flow irreversibly. These measurements were conducted using stress-steps, where the yield stress was found as the point at which the slope of the logarithmic deformation as a function of the logarithmic shear stress changes from a very low (nonzero) value to a high value. Measurements were done in triplicate and the calculated standard deviations are shown as error bars in the diagrams. In addition to yield stress measurements, 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 reached a steady state,  $(d\sigma/\sigma)/dt < 0.01 \text{ s}^{-1}$ , before recording the shear stress and corresponding viscosity. These experimental procedures have been described in more detail in previous papers on capillary suspensions (Koo et al., 2011, 2012; Koo & Willenbacher, 2011, 2012).

## 3. Results and discussion

### 3.1. Basic features of capillary food suspensions

Starch granules suspended in oil and a small fraction of water added can serve as a well defined model system for food capillary suspensions. Such a suspension was prepared by dispersing starch

granules in sunflower oil at a volume fraction of  $\phi = 0.33$ . The contact angle in the three phase system was measured to be  $\Theta = 129 \pm 14^\circ$  and the fraction of added water was varied between  $S = 1.0$  and  $S = 0.90$ . Although starch granules do have a hydrophilic nature, the direct measurement of the contact angle in the three-phase system shows a wetting angle greater than  $90^\circ$ . Since the angle is not measured using a single particle, we have to consider that tablet surface roughness and porosity could play a role. Corresponding calculations have been performed using a modified Cassie equation (Yan, Wang, Wu, & Ye, 2007) and the contact angle reduces to  $\Theta = 116^\circ$ . Since the calculated correction is small compared to the measured value, we use the observed value in the subsequent discussion.

In Fig. 1 starch granules in oil are shown to form a capillary network when water is added. The image has been created by overlaying the white light image with the fluorescence intensity image, for the latter the low intensity scattering has been removed and the higher intensity has been colored in yellow. The water is located between the particles, which indicate that a strong cohesion is created due to capillary forces.

The second model system investigated here are cocoa particles suspended in vegetable oil with water as secondary fluid. The suspension is presumably in the capillary state since oil as the bulk fluid is the better wetting liquid (Galet, Vu, Oulahna, & Fages, 2004). The three phase contact angle was measured to be  $148 \pm 4.5^\circ$ . The transition of such the cocoa suspension from a weakly elastic fluid to a gel upon addition of water is shown in Fig. 2. These images demonstrate that capillary suspensions can be created in cocoa suspensions even when no sugar is present. Cocoa particles form networks and maintain a smooth texture but do not cause large agglomerates as it has been reported for sugar particle suspensions (Stortz & Marangoni, 2011).

Stability against sedimentation of cocoa particles suspended in oil at a volume fraction of  $\phi = 0.35$  is demonstrated in Fig. 3. The pure suspension shows clear phase separation after 5 days resting (Fig. 3A), whereas the suspension with water added as secondary fluid ( $S = 0.90$ ) shows no settlement at all (Fig. 3B). This indicates that a sample spanning network is created, which prevents the particles from sedimenting.

In Fig. 4A the yield stress of starch granules in oil is shown as a function of saturation for volume fractions of  $\phi = 0.29$  and  $\phi = 0.33$ . Yield stress data are normalized to the respective value of the suspension where no water is added. The suspensions with water as secondary phase show a linear increase of yield stress in a semi-logarithmic plot and the absolute value of the slope is

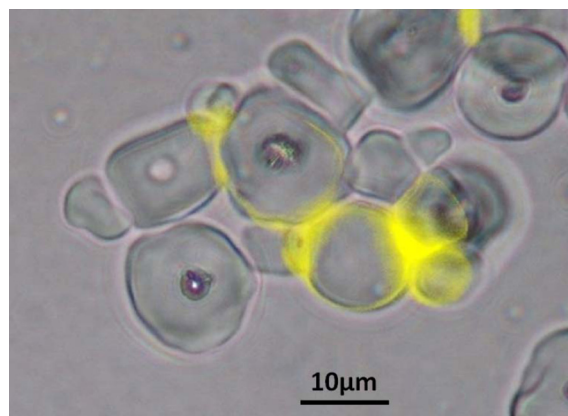


Fig. 1. Microscopic image, where the capillary suspension made from starch granules in oil with water as secondary phase. Water was colored with a fluorescent dye (PromoFluor-488 Premium, carboxylic acid), which appears yellow in the picture.

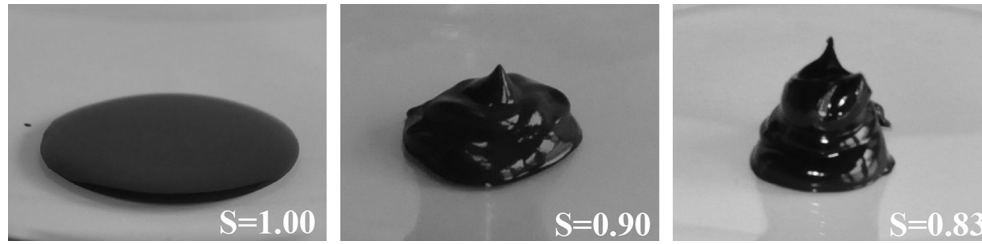


Fig. 2. Suspension of  $\phi = 0.35$  cocoa solids in oil suspension without added water ( $S = 1.0$ , left) and with added water in two different amounts ( $S = 0.90$ , middle and  $S = 0.83$ , right).

$|a| = 30.3 \pm 2.8$  for both concentrations. This results in an increase of  $\sigma_y$  by three orders of magnitude when  $S$  is decreased from 1.0 to 0.90. This confirms the formation of a sample spanning network when water is added to the starch in oil suspension since the yield stress is characteristic of the network strength. Starch suspensions with lower saturation exhibit a strong, inhomogeneous agglomeration, so reliable measurements could not be performed at saturations  $S < 0.90$ .

In Fig. 4B the yield stress for cocoa suspensions with different volume fractions of cocoa is plotted over a wide range of saturation  $S$ . Again, yield stress data are normalized to the corresponding value where no water is present ( $S = 1.00$ ). The normalized yield stress for different volume fractions follows a single master curve. Similar behavior has been observed for  $\text{CaCO}_3$  capillary suspensions (Koos & Willenbacher, 2011). The yield stress increases until a saturation of 0.7 is reached and then drops until a value close to the initial stress is obtained. This latter decrease is presumably due to spherical agglomeration (Leonard et al., 1981; Puddington & Sparks, 1975). In previous studies spherical agglomeration within capillary suspensions at elevated degrees of saturation was reported for oxide powders in oil (Dittmann et al., 2012). The process of wet granulation with water as bridging fluid is used to agglomerate dry cocoa powder (Vu, Galet, Fages, & Oulahna, 2003). The same granulation can also occur in suspension at high secondary liquid fractions during mixing. When the saturation exceeds 0.5, phase inversion is visible: water acts as the continuous phase and the suspension begins to phase separate. Again, a linear increase of the reduced yield stress as a function of saturation is found in semi-logarithmic representation for  $0.9 < S < 1.0$  with a slope of  $|a| = 14.4 \pm 1.0$ , which is half the value found for starch suspensions.



Fig. 3. Cocoa particles in oil  $\phi = 0.35$  after a storage time of 5 days, (A) no water added, (B) water added (saturation  $S = 0.90$ ).

This difference may be caused by several factors such as wetting angle, interfacial tension and, most relevant here, the fact that cocoa particles have a higher porosity and components like cellulose that can absorb water. This may lead to an uptake of water into the particles, which is then not available for capillary bridging.

Differences in wetting behavior and the resulting effect on the rheology of the admixture are discussed in the following sections.

If we have a look at the force of capillary bridges acting between two particles, a direct influence of secondary phase viscosity on capillary strength and therefore flow behavior of capillary suspensions is not expected (Schubert, 1984). But the preparation step of capillary suspensions can be seen as an emulsification of the secondary fluid in the bulk fluid. For emulsion preparation, it is known that droplet breakup is a function of the ratio of dispersed phase and continuous phase viscosity  $\eta = \eta_d/\eta_c$  (Grace, 1982). Therefore, we have investigated the influence of the viscosity ratio on secondary phase distribution and flow behavior. To modify the secondary phase viscosity, water was thickened with polyethylene oxide (PEO) varying in concentration from 0.1 wt.% to 2.5 wt.%. This increases the viscosity of the secondary phase by three orders of magnitude. But within experimental uncertainty all solutions show the same value of interfacial tension  $\gamma = 22 \pm 2$  mN/m.

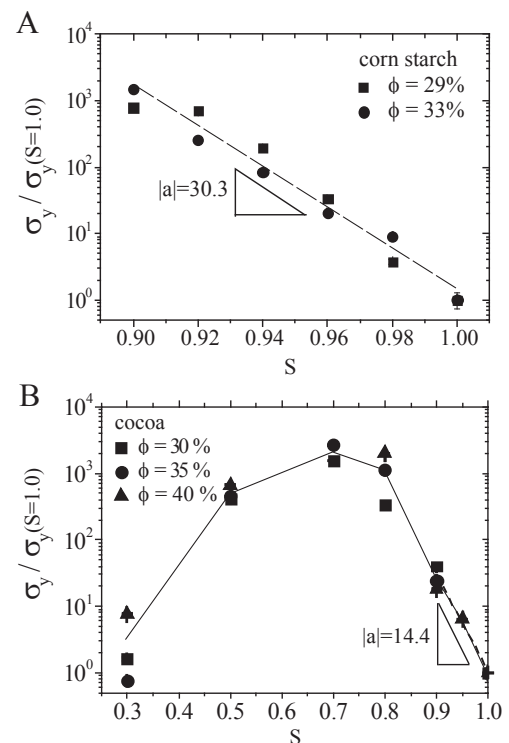


Fig. 4. Normalized yield stress as a function of saturation of the preferentially wetting fluid for (A) corn starch and (B) cocoa particles.

Fig. 5 shows corresponding yield stress for a cocoa and a starch suspension. The yield stress does not change significantly with increasing secondary phase viscosity, i.e. the droplet breakup conditions do not have an influence on network strength. The capillary bridging even occurs at ratios  $\eta_d/\eta_c \gg 1$  where shear induced droplet breakup should not appear (Grace, 1982). This suggests that the bridging phenomenon is not a just function of droplet breakup and emulsification of the secondary phase. Instead, we propose that the network state is energetically more favorable and the network formation also depends on the diffusion of the secondary fluid. This energetic favorability was previously demonstrated for small particle number clusters (Koo & Willenbacher, 2012).

Different wetting properties of the particles by the secondary fluid in the presence of the bulk fluid may affect not only the strength of the capillary bridges, but also the number of particle contacts and the particle configuration in the fractal network. Hence it may have a strong influence on yielding and flow of capillary suspensions. We have varied the contact angle between the two fluids and the particles using pure glycerol or glycerol/water mixtures instead of water as secondary phase in the starch suspension. The wetting angle decreases with increasing glycerol content, approaching  $90^\circ$  for pure glycerol. At the same time viscosity of the secondary fluid increases by three orders of magnitude, as shown in Table 1. Interfacial tension  $\gamma$  remains almost constant ( $24 \pm 2$  mN/m), variation among samples is within experimental error. Moreover, according to Grace droplet breakup is unlikely to occur for viscosity ratios  $\eta_d/\eta_c > 3$  in laminar flow (Grace, 1982). Assuming droplet breakup occurs at a Capillary Number

$$Ca = \frac{\eta \dot{\gamma} r}{\gamma} \approx 1, \quad (4)$$

a minimal attainable droplet size due to mixing can be estimated assuming  $\dot{\gamma} = 500 \text{ s}^{-1}$  (calculated from mixing conditions) and  $\eta = 0.5 \text{ Pa s}$ , which refers to the suspension where no water was added ( $S = 1.0$ ). This calculation results in a minimum droplet radius of  $r \approx 96 \text{ }\mu\text{m}$ , which is much larger than the typical size ( $< 5 \text{ }\mu\text{m}$ ) of a capillary bridge for the particle sizes used here. This is further evidence for a diffusion driven an energetically favored network formation.

Fig. 6 shows the yield stress of a corn starch in vegetable oil suspension ( $\phi = 0.33$ ) with water or glycerol/water mixtures added as secondary liquid at various degrees of saturation  $S$ . At given  $S$  the yield stress increases with increasing glycerol content. Samples

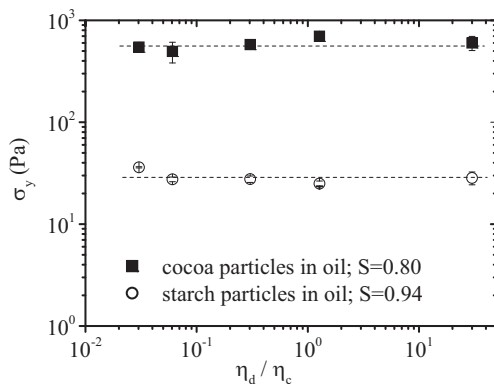


Fig. 5. Yield stress of corn starch ( $\phi = 0.33$ ) and cocoa ( $\phi = 0.35$ ) particles suspended in oil with aqueous PEO solutions of different viscosity as secondary phase versus the viscosity ratio of water to oil  $\eta_d/\eta_c$ .

Table 1

Contact angle between starch and various glycerol-water mixtures in the presence of sunflower oil as well as viscosity of these mixtures at  $20^\circ\text{C}$ .

	Viscosity in mPa s	Contact angle in $^\circ$
Water	1.0	$126 \pm 13.0$
25% Glycerol	2.5	$104 \pm 17.1$
50% Glycerol	8.5	$101 \pm 2.7$
75% Glycerol	53.3	$93 \pm 7.9$
100% Glycerol	1100.0	$92 \pm 9.0$

with pure glycerol as the secondary liquid show yield stresses up to one order of magnitude higher than samples made with pure water. The yield stress at  $S = 0.94$ , for example, is  $\sigma_y = 39 \pm 4.2 \text{ Pa}$  with water as the secondary phase, whereas with glycerol the yield stress is measured to be  $\sigma_y = 405 \pm 22.5 \text{ Pa}$  at the same saturation. This behavior fits the capillary bridging theory. Particles that are placed at an interface of two fluids are held with the energy  $E$  given by (Binks & Lumsdon, 2000),

$$E = \pi r^2 \gamma_{ow} (1 \pm \cos\theta)^2 \quad (5)$$

where the sign in the parentheses is negative for contact angles  $< 90^\circ$  and positive for angles  $> 90^\circ$ . The maximum energy  $E_{\text{max}}$  is therefore given at a contact angle of  $90^\circ$  and approaches zero for contact angles close to  $0^\circ$  and  $180^\circ$ . The energy gain coming with the formation of clusters varies with contact angle and degree of saturation (Koo & Willenbacher, 2012). In the aforementioned paper, it is described, that strongest clusters i.e. cluster structures with the lowest energy are formed at contact angles close to  $90^\circ$  and high saturations. Since glycerol and sunflower oil form a contact angle with starch granules closer to  $90^\circ$  than for water/sunflower oil (Table 1), the force for cluster breakup is higher and the corresponding clusters are more stable. This results in a more stable network and finally in a higher yield stress if glycerol is used as secondary fluid.

Uptake of secondary fluid by the starch granules could also be a reason for the variation of the yield stress with glycerol/water mixing ratio at constant  $S$ . Starch granules absorb water which can be incorporated into the amorphous parts of starch granule (French, 1984). Water that is trapped within the granules is not available to act as a bridging fluid. The strength of the network should decrease with increasing fraction of water in the secondary liquid since the effective saturation  $S_{\text{eff}}$  is lower than the nominal saturation  $S$  calculated from the amount of added fluid. In contrast, glycerol is not absorbed by the particles due to its higher molecular weight and therefore more secondary fluid is available for capillary

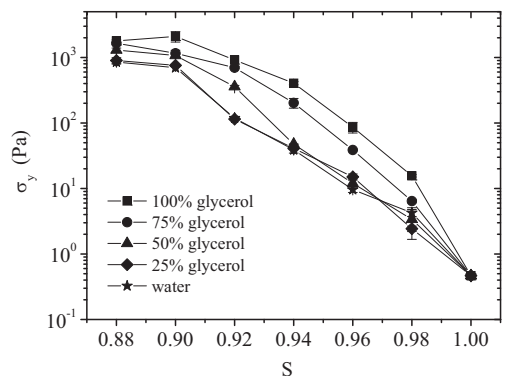


Fig. 6. Yield stress of a starch suspension in oil ( $\phi = 0.33$ ) vs. saturation for various glycerol/water mixtures as secondary fluid.

bridging. For the measured difference in yield stress due to water incorporation into the granules, about 0.8 g of water per 10 g of starch must be trapped in the granules. This is a reasonable number (French, 1984), so water uptake as well as variation of contact angle might contribute to the variation of yield stress in capillary starch suspension.

Swelling of starch granules, through the uptake of water, increases the granule volume by about 12% for the maximum water uptake calculated above (French, 1984). This small difference in volume fraction does not account for the overall increase in yield stress in capillary suspensions.

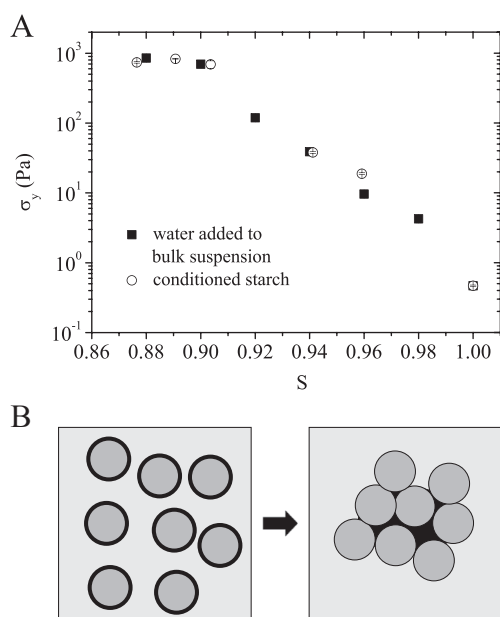
Since starch particles in air are hygroscopic, starch granules can also adsorb water in a single layer and, with higher relative pressure, multiple layers (Czepirski & Szymon, 2002; French, 1984; Peng, Chen, Wu, & Jiang, 2007). The uptake can even exceed a few molecular layers if the granule swells and thus incorporates water molecules. This allows for several weight percent water uptake as done in the conditioning experiment discussed below. Samples of 30 g of starch granules were stored over distilled water in a closed vessel for 2–21 days. Water uptake of conditioned granules in suspension was determined by the weight gain of granules during storage and the corresponding  $S$  value was calculated. Starch was then dispersed in the same amount of oil as was used for non-conditioned samples ( $\phi = 0.33$ ). For the non-conditioned starch suspension, water was added after granules were suspended in oil, whereas no additional water was added to suspension made from conditioned starch.

Fig. 7A shows the yield stress of conditioned and non-conditioned starch suspensions as a function of respective fraction of water  $S$ . Results from both preparation methods match within measurement error. Whether water is previously adsorbed to the dry granules or water is added after the bulk suspension is prepared, finally results in the same rheological behavior for these capillary starch suspensions.

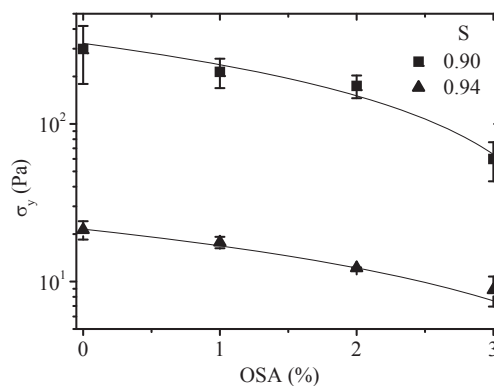
We assume that clusters are formed when the dispersed granules with adsorbed and absorbed water collide (Gögelein

et al., 2010) as depicted in Fig. 7B. If the starch granules come into contact, the system is not in an energetically favorable state since a sharp edge is created between the water layers (Herminghaus, 2005). The wetting liquid induces the formation of clusters which are energetically favorable and are held together due to the negative Laplace pressure across the curved surface (Herminghaus, 2005). The hygroscopic nature of the granules in air does not conflict with this structural change. The contact angle for water on starch in air is below  $90^\circ$  (Thielemans, Belgacem, & Dufresne, 2006), but the three phase contact angle for the system investigated here is above  $90^\circ$  (see Table 1) Similar observations have been made for cocoa particle suspensions where cocoa particles were conditioned over distilled water at  $20^\circ\text{C}$  for 21 days. The cocoa suspensions ( $\phi = 0.35$ ) also gelled during mixing, but exhibited a lower strength of  $\sigma_y = 70 \pm 9.1$  Pa than measured for suspension where the same amount of water was added during mixing ( $\sigma_y = 248 \pm 12.6$  Pa). This could be due to the more porous structure of cocoa, where absorbed water is not released for bridging, when particles come into contact. These findings for model starch and cocoa suspensions clearly demonstrate that the results shown in Fig. 6 are not due to absorption of water from capillary bridges. Instead water clearly diffuses from an adsorption layer into capillary bridges demonstrating that no mechanical energy input is required to create capillary suspensions. Furthermore, the phenomenon suggests a new preparation method for all hygroscopic particles that form capillary suspensions when oil is the bulk phase. So the described method may be a valuable tool for processing of new food products, but also points at a complication in existing processes where the product consistency may dramatically depend on the storage conditions for the solid particles.

Treating starch granules with OSA is supposed to make the surface more hydrophobic (Bhosale & Singhal, 2006) and should increase the wetting angle in the three phase system starch/vegetable oil/water. Nevertheless the three phase contact angles for all treatment levels investigated here were found to be  $\Theta = 130 \pm 7^\circ$  and no difference was detected with our setup. On the other hand, an increase in OSA concentration results in a reduction in the yield stress as shown in Fig. 8 for two saturation levels. It seems that subtle differences in surface properties not resolvable with conventional analytical methods still have a remarkable impact on the rheology of these capillary suspensions. At constant saturation a linear decrease of yield value is detected. This demonstrates that particle surface treatment is an additional option to tune the flow behavior of capillary suspension.



**Fig. 7.** Yield stress vs. saturation  $S$  for starch suspension in sunflower oil at  $\phi = 33\%$ , where granules have been conditioned over water at  $20^\circ\text{C}$  for 2–20 days compared with a non-conditioned starch suspensions where water was added while stirring the bulk suspension. (B) Spheres with adsorbed and absorbed water form an agglomerate caused by capillary forces upon contact.

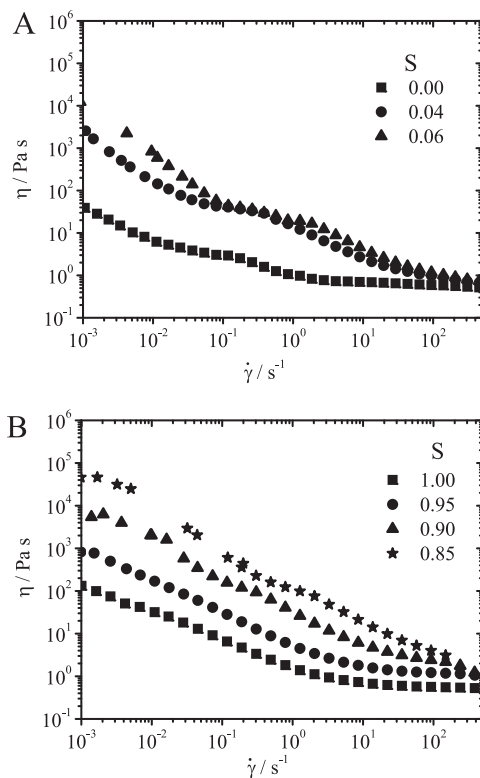


**Fig. 8.** Yield stress of suspensions ( $\phi = 0.33$ ) prepared from particles treated with OSA in oil for two saturations ( $S = 0.94$  and  $S = 0.90$ ) over OSA concentration.

### 3.2. Viscosity and processing

Viscosity curves for starch (A) and cocoa (B) suspensions in oil at different saturations are shown in Fig. 9. In both cases, the low shear viscosity increases with the addition of water by several orders of magnitude. At shear rates  $\dot{\gamma} > 500 \text{ s}^{-1}$  the curves approach each other, since capillary bridges are breaking and viscosity is then just a function of particle volume fraction. This strong degree of shear-thinning guarantees that capillary forces do not affect processing or application where high shear rates are involved (Steffe, 1992). For hard sphere suspensions with particle loadings between  $\phi = 0.33$  and  $\phi = 0.35$  and  $\eta_c = 34 \text{ mPa s}$ , we expect a high shear viscosity of 180–220 mPa s (Horn, Richtering, Bergenholtz, Willenbacher, & Wagner, 2000; Russel, 1989). The absolute values observed here for the cocoa and starch suspensions are about a factor of 2–3 times higher. This is due to the non-spherical shape of the particles or residual agglomerates in the suspension. For the starch suspensions, the high shear rate viscosity perfectly matches irrespective of the saturation. This confirms that granule swelling does not play a significant role in these capillary suspensions and bridges can be destroyed completely in high shear.

For the cocoa particles (Fig. 9B), the viscosity curve without added water ( $S = 1.0$ ) has a lower high shear viscosity value than samples where water was incorporated. This could be an evidence for water absorption by the particles (Svanberg, Lorén, & Ahrné, 2012). Since the amount of water that we add as the secondary liquid is small compared to the whole particle volume, we assume residual agglomerates to be responsible for the increased high shear viscosity and not only particle swelling. At intermediate shear rates, all viscosity curves for starch as well as cocoa suspensions exhibit a short plateau region where we assume structural changes to occur. Flow-induced break-up or reorganization of agglomerates might be involved there (Koo & Willenbacher, 2012).



**Fig. 9.** Viscosity vs. shear rate for suspension of starch granules ( $\phi = 33\%$ , A) and cocoa particles ( $\phi = 35\%$ , B) suspended in oil, at different saturation levels.

### 3.2. Heat stability

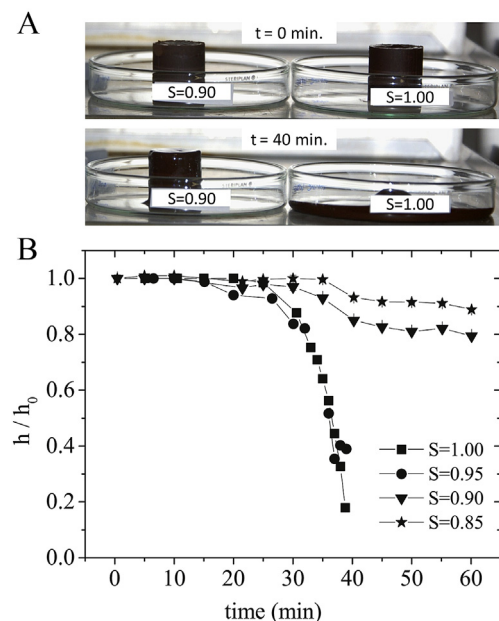
Since capillary forces in cocoa products are known to make chocolate more heat-stable (Stortz & Marangoni, 2011), tests have been performed to elucidate how the heat sensitivity of suspensions from cocoa particles ( $\phi = 0.35$ ) in cocoa butter is modified upon addition of water as a secondary phase. Samples were placed into an oven at  $50 \text{ }^\circ\text{C}$  and melting was documented via imaging as can be seen in Fig. 10A.

The height  $h$  of the samples was measured over time and normalized to the sample height  $h_0$  at the start of the test. In Fig. 10B this normalized height is plotted over time. For samples with saturation  $S \geq 0.90$ , a fast decrease in sample height can be detected, whereas samples with  $S \leq 0.90$  show an almost constant shape. Samples where water was added clearly melt slower than the samples where no water was added. We attributed this to the network formation that prevents the oil phase from spreading.

### 3.3. Water continuous capillary suspension

Preparing water continuous capillary suspensions could be a valuable route for ultra-low fat food suspensions such as low fat cocoa spreads.

In Fig. 11 the transition from a fluid-like suspension of cocoa in water (A) to a gel-like behavior (B) is seen when linoleic acid is added as secondary liquid. Fig. 11C shows a microscopic image of the diluted cocoa suspension in water. Linoleic acid is located between the particles as can be seen from the yellow spots inside the agglomerate. For network formation in water continuous suspensions, the secondary liquid must be able to rewet the particles, meaning it has to remove water from the particle surface. Thus, a slightly polar fluid that is immiscible with water must be found. Fatty acids like linoleic acid or oleic acid can be used for food applications. Cocoa in water with linoleic acid as secondary liquid is assumed to be in the pendular state, since linoleic acid wets the particles better than water.



**Fig. 10.** (A) Images of samples made from cocoa particles in cocoa butter ( $\phi = 0.35$ ) at the beginning and after 40 min of storage at a temperature of  $50 \text{ }^\circ\text{C}$ . (B) Sample height  $h$  normalized to the height at the beginning of the test  $h_0$  plotted over storage time at  $50 \text{ }^\circ\text{C}$  for various saturations.



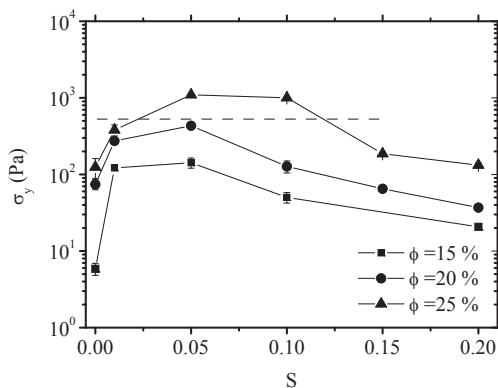
**Fig. 11.** Suspension of cocoa particles ( $\phi = 0.15$ ) in water without (A) and with (B) linoleic acid ( $S = 0.02$ ) added as secondary liquid. (C) Microscopic image of the diluted admixtures in B where linoleic acid is colored with a fluorescent dye (Nile Red, Sigma–Aldrich).

The increase in the yield stress due to the addition of oleic acid to the suspension of cocoa particles in water is shown in Fig. 12 for different volume fractions of cocoa particles. We do not observe an increase in the yield stress as high as in the oil continuous suspensions presented earlier, but up to one order of magnitude change can be measured and the attainable yield stress level is comparable to that of a commercial fat continuous chocolate spread. It should be noted, that in contrast to the oil continuous suspensions, the yield stress of water continuous cocoa suspensions reaches a maximum value at low fractions of secondary liquid. The reason for this is not yet clear and requires further investigation beyond the scope of this paper.

#### 4. Conclusion

Capillary suspensions offer new opportunities for the formulation of food products. We can see a clear transition from a liquid or very weak gel with no secondary phase added, to a strong gel-like state when water is added to the oil continuous suspensions made from cocoa or starch granules. This indicates that strong capillary forces act in this food model systems as has been reported earlier for suspensions of inorganic or synthetic polymer particles (Koo & Willenbacher, 2011).

Stability against sedimentation can be dramatically increased, texture can be modified and flow properties can be easily adjusted according to the demands of a broad variety of processing and application techniques. This can be done by adapting the amount of the secondary fluid and the wetting properties like the interfacial tension between the two fluids and the contact angle the fluids form with the particles. On the other hand, the secondary fluid viscosity has no influence on flow behavior like yield stress or viscosity of the investigated capillary suspensions. Furthermore,



**Fig. 12.** Yield stress over saturation of suspensions of cocoa particles in water for cocoa volume fractions of 15%, 20% and 25%. The saturation of secondary fluid (oleic acid) was varied from  $S = 0.0$  to  $S = 0.2$ . The dotted line represents the yield value of a commercial cocoa spread (Rewe “feine Welt”).

the adsorption of water by particles from natural sources during storage can dramatically influence the properties of oil continuous suspensions since capillary bridges form spontaneously from adsorbed water layers. Suspensions rheology is similar if the water is absorbed prior to suspension preparation or added to the suspension afterward. These findings lead to the conclusion that the formation of these capillary suspensions is energetically favorable and not controlled by mechanical energy input.

Capillary bridges offer an additional advantage to chocolate or other temperature sensitive systems by preserving shape stability even if the continuous phase of the suspension is molten. Finally, capillary suspensions can also be made using water as the primary fluid. This opens up a new pathway to create ultra low fat foods like, e.g. spreads.

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