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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.

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_l, so that $V_l/r^3 >> 1$ (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 $V_l/r^3 \leq 1$ (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 Bergenståhl for sugar (pendular state) and solid fat (capillary state) particles (Johansson & Bergenståhl, 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 γ between the two fluids in contact with the particles, and the three-phase wetting angle Θ 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),

$$F_c = 2\pi r\gamma \cos\theta \tag{1}$$

It is assumed that the particles are in contact and that the pendular bridge is small compared 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 σ_y of a pendular state suspension is related to the capillary force (Koos et al., 2012; Schubert, 1984),

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

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 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 °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 $x_{3,2} = 8.4 \pm 0.1$ μm and cocoa particles of $x_{3,2} = 4.9 \pm 0.04$ μm in oil.

Interfacial tension γ_{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