

Particle configurations and gelation in capillary suspensions

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When a small amount (less than 1%) of a second immiscible liquid is added to the continuous phase of a suspension, the rheological properties of the mixture are dramatically altered from a fluid-like to a gel-like state (Figure 1). The yield stress and viscosity increase by several orders of magnitude as the volume of the second fluid increases (Figure 2). This transition is attributed to the capillary forces of the two fluids on the solid particles, and in an analogy to wet granular materials, two distinct states are defined: the "pendular state" where the secondary fluid preferentially wets the particles; and the "capillary state" where the secondary fluid wets the particles less well than the primary fluid. We find that both states are associated with a transition in the suspension from a fluid-like to gel-like state [1].

Capillary suspensions, suspensions with the addition of a small amount of a second immiscible liquid, are a new class of materials that can be used to create tunable fluids, stabilize mixtures which would otherwise sediment, and to create new materials such as low-fat foods or microporous foams. Capillary suspensions have even recently been used to create porous ceramics with unprecedentedly high porosity and small pore sizes [2]. Previous investigations have shown that capillary suspensions transition to a gel-like state in micron-sized particles at volume fractions as low as $\phi = 0.10$ – well below the limit of dense packing – increasing the yield stress and viscosity by several orders of magnitude as the volume of the second fluid increases. In the pendular state, the secondary fluid preferentially wets the particles and pendular bridges form between particles. The capillary force associated with such bridges is usually much stronger and dominates over other forces, such as the van der Waals force, leading to the formation of a sample-spanning network of particles bridged by the secondary fluid. In the capillary state, the volume between particles is filled with the secondary liquid. The typical size of these droplets is close to the particle size, such that that normalized volume $V_d/r^3 \approx 1$. This differs from Pickering emulsions where the droplet volume is typically much larger than the particle size, $V_d/r^3 \gg 1$. In the capillary state, macroscopic observations show that a sample-spanning network has formed, but the underlying mechanism for such a network is not straightforward.

This current research investigates the capillary state suspensions in more detail using a computational model to evaluate the lowest energy states of small particle number clusters. These clusters are used as building blocks for the formation of sample-spanning networks within the admixture, where the constituent structures have limited regions of stability based on the wetting angle and volume of the secondary fluid leading to changes in the strength of the network. The influence of the capillary force in the formation of these networks is further substantiated using rheological measurements. The strength of these mixtures demonstrate a dependence on the reciprocal particle radius, reduce in strength with increasing temperature (trending with interfacial tension), and are completely reversible if the secondary fluid is removed.

References

[1] E. Koos and N. Willenbacher, *Science* **331** (2011) 897.

[2] J. Dittmann, E. Koos, N. Willenbacher and B. Hochstein, German Patent DE 10 2011 106 834.5 (2011).

Figures

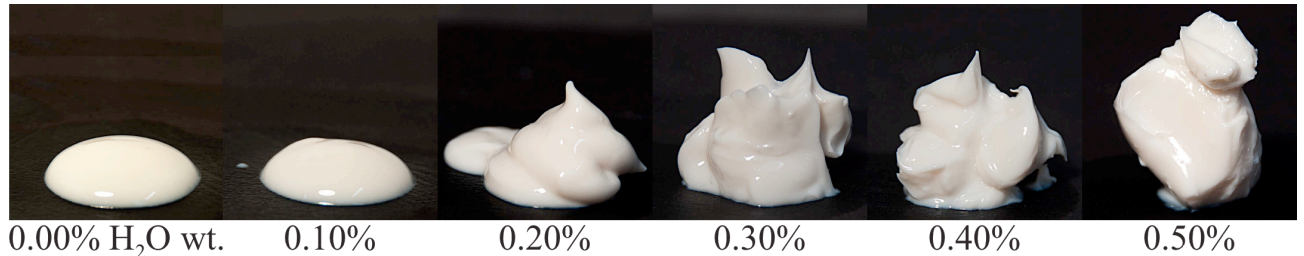


Figure 1: Transition from weakly elastic, fluid-like to highly elastic, gel-like state with the addition of small amounts of a second immiscible fluid as shown for hydrophobic calcium carbonate ($\phi = 0.111$) in diisononyl phthalate with less than 0.50% wt. distilled water.

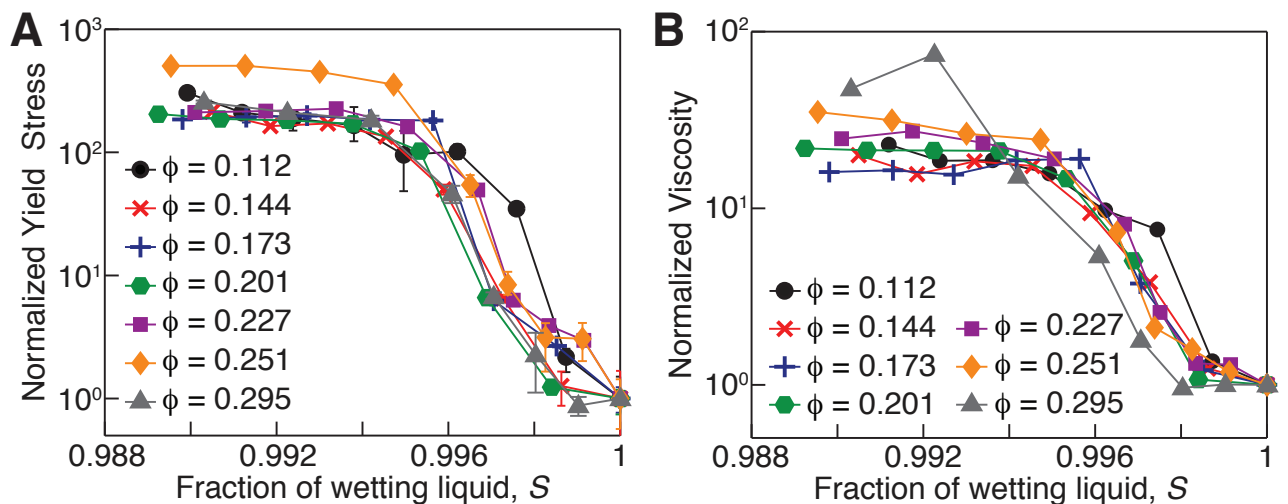


Figure 2: Effect of added water on the yield stress and viscosity. (A) Normalized yield stress and (B) normalized viscosity at a single shear rate of $\dot{\gamma} = 1 \text{ s}^{-1}$, for various volume fractions of hydrophobic calcium carbonate in diisononyl phthalate. The yield stress in (B) and viscosity in (C) are normalized by the value at $S = 1$, where no water is present.