Capillary force-induced tuning of suspension rheology

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Suspension rheology or flow behaviour plays a critical role in coatings such as paint which is a suspension of pigment and polymer dispersed in a liquid. The rheology of suspensions can be usually controlled by various interactive forces such as attractive van der Waals forces, repulsive electrostatic forces and Brownian forces[1–3]. Interactive forces among particles in a suspension affect the viscosity in addition to the size and shape of the dispersed particles. The forces between the particles are generally controlled by the addition of surfactants which can adjust the surface properties of the dispersed particles. Recently, Koos and Willenbacher[4] from Germany have made a breakthrough on controlling the rheology of suspensions. They found that addition of small amounts of an immiscible liquid to another liquid can cause transition from the viscous state to an elastic state[4].

They first dispersed hydrophilic glass beads in a primary liquid diisononyl phthalate (DINP) and then added 1 wt% of water as a secondary liquid to it with stirring. During the process, the suspension changed from a viscous fluid to an elastic or gel-like state. It is important to mention here that there is already a report in the literature on the transition from a viscous to elastic state by the addition of trace amounts of a secondary liquid, when the added liquid wets the particles[5]. Figure 1 shows the stabilization of the dispersed phases by the addition of a third phase. Figure 1 *a* shows the formation of a pendular water meniscus by the dispersed particles in a primary liquid, if the contact angle is low and the added secondary liquid (water) wets the dispersed particles. The particles tend to aggregate and form a network due to the interfacial tension. These are capillary forces, which are much stronger than the van der Waals forces. Capillary forces play an important role in wet granular materials, where the addition of water and wetting of the grains cause the creation of a network of grains connected by pendular bridges. Complex structures such as sandcastles are formed due to this mechanism. It was earlier considered that capillary forces do not work under non-wetting conditions with high contact angles. However, the experimental observation of Koos and Willenbacher[4] proved this wrong, when they reported the existence of capillary force with hydrophobic glass beads. In their case, drops of the secondary liquid form the centre of the particle aggregates (Figure 1 *b*), when the secondary liquid does not wet the particles with high contact angle. Figure 2 illustrates the transition from a weakly elastic behaviour to highly elastic, gel-like behaviour by the addition of a small amount of water to a suspension of hydrophobically modified calcium carbonate in DINP. In this case, several particles gather around a droplet of water and protect it from the formation of large interfacial area with the bulk non-polar liquids. The contact angles are around or above 90°. Koos and Willenbacher[4] studied many different combinations of immiscible liquids and solid particles while observing similar changes in their rheological properties. This suggests that the effect can be observed in many other suspensions.

A similar effect has been used for more than a century for the stabilization of emulsions which are a mixture of two immiscible liquids such as oil in water or water in oil. A pickering emulsion is stabilized by the addition of colloidal particles which move the oil–water interface. This prevents droplets in the emulsion

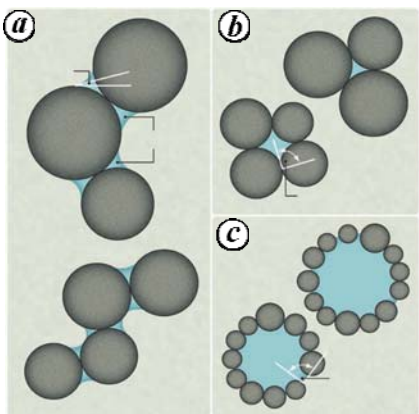

Figure 1. Schematic representation showing the stabilization of suspensions and emulsions with a third added phase. ***a***, Pendular state; ***b***, Capillary state; ***c***, Pickering emulsion. (From Butt[6], reprinted with permission from AAAS.)

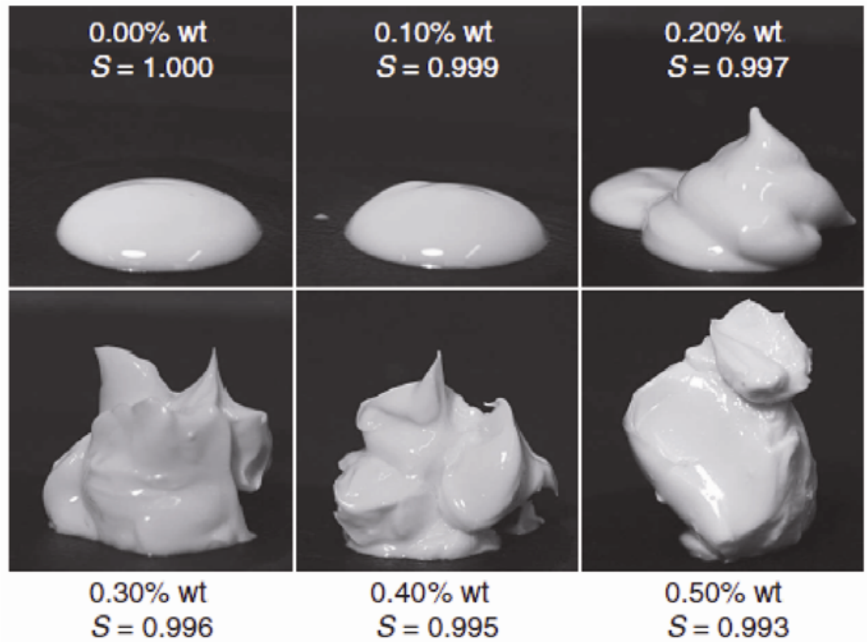

Figure 2. Photograph illustrating the transition from a weakly elastic behaviour to highly elastic gel-like behaviour by the addition of small amounts of water to a suspension of hydrophobically modified calcium carbonate in DINP. (From Koos and Willenbacher[4], reprinted with permission from AAAS.)

from merging into larger droplets (Figure 1 *c*). In contrast to the capillary state in suspensions, the amount of secondary liquid in a pickering emulsion is comparable to that of the primary liquid and drops are much larger than the particles[6]. It is important to note here, that the well-known Young's equation has been used to determine whether a suspension enters the pendular or the capillary state. Young's equation correlates the interfacial tension to the contact angle:

$$\cos\theta = \gamma_{SA} - \gamma_{SB}/\gamma_{AB},$$

where γ_{SA} is the interfacial tension of a solid particle with a primary liquid *A*, γ_{SB} the interfacial tension of a solid particle with a secondary liquid *B* and γ_{AB} the interfacial tension of the liquid–liquid interface. If the secondary liquid wets the particles better than the primary liquid then, $\gamma_{SA} > \gamma_{SB}$. The contact angle is low and a pendular state will form. On the other hand, if the secondary liquid wets the particles less than the primary liquid, then $\gamma_{SA} < \gamma_{SB}$. The contact angle will be high (more than 90°) and the capillary state will form.

The discovery of Koos and Willenbacher[4] will have considerable technological impact. One can tune the flow properties of suspensions in a simple, environmentally friendly and inexpensive way without the addition of surfactants or polymers. However, the discovery seems to serve as a warning to avoid the contamination of a suspension with an immiscible liquid. Further work needs to be carried out to understand some of the fundamental questions such as influence of polydispersity, particle size and surface roughness on the capillary state.

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