Supporting Information

Stability of Laponite-stabilized high internal phase Pickering emulsions under shear

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1. Experimental details

1.1 Sample preparation

As in previous works on Laponite-stabilized emulsions[1], the continuous aqueous phase is first prepared by suspending 2wt% Laponite® RD in a 0.1M Sodium Chloride (NaCl, Ultrapure, from Sigma Aldrich) solution in ultra-pure water (Millipore Milli-Q). To disperse the particles, we use a high intensity ultrasonic disperser (Branson solifier 250, tip diameter 5mm), operating at 20kHz and 100W for 30 minutes. For optical microscopy observations, we prepare transparent emulsions in which the continuous phase is refractive index matched to the oil phase (Silicone oil Rhodorsil ®47 V 500) by adding glycerol (99% GC, from Sigma-Aldrich) to the aqueous phase. For both the silicone oil and the castor oil, the oil is gradually added to the aqueous phase when stirring with a Silverson l5m- emulsifier at 10,000 rpm for 2 minutes[2]. During emulsification the sample is cooled in an ice bath to prevent heating of the sample. Emulsions with different volume fractions ϕ are prepared by diluting the original emulsion (ϕ=0.70) with 2wt% Laponite in 0.1M NaCl.
Immediately after preparation of the silicone oil-in-water emulsions, a layer of oil is formed at the surface, similarly to the observations for Toluene-in-water emulsions of Ashby and Binks[1]. This layer of oil is not observed in the castor oil emulsions. The oily layer for the silicone oil emulsions does not grow significantly in time after preparation, and both types of emulsions are stable to coalescence for at least several months when stored in a properly closed bottle. The emulsions do evaporate rather quickly; if evaporation is not prevented, within 30 minute coalescence of droplets is observed by confocal microscopy.

1.2 Rheological measurements

The rheology of these emulsions was studied on an Anton Paar MCR302 rheometer equipped with a cone plate geometry of 50mm radius and with a cone angle of 1° with roughened surfaces to avoid wall slip[3]. To prevent this a vapor trap is used during all the rheological tests. An up-and-down shear rate sweeps performed repeatedly (three times consecutively) to study the stability of the samples.

1.3 Confocal fluorescent microscopy

Confocal fluorescent microscopy is used to image the internal structure of the emulsions and Laponite suspensions. As a fluorescent dye we use Rhodamine G6 (from Sigma), a hydrophilic fluorescent molecule. At low concentrations (~$5*10^{-6}$M) the dye is completely adsorbed onto the Laponite particles and no free dye is left in the aqueous phase[4]. The behavior of the transparent silicone oil-in-water emulsions, before, during and after shearing, is observed with the confocal microscope in combination with a rheometer (Anton Paar DSR 301) with a cone-plate geometry; the bottom plate is transparent and the visualization is done through this bottom plate.

2. Results for silicone oil-in-water emulsions

Silicone oil in water emulsions show similar behavior to the castor oil emulsions. Figure S1 shows the flow curves of silicone oil-in-water. Clearly, the rheological test shows that the emulsion gets destroyed when shearing. Figure S2 shows a photo of the castor oil-in-water emulsion before and after shear on the rheometer. In addition a microscopic confocal image is added of the transparent silicone oil-in-water emulsion.

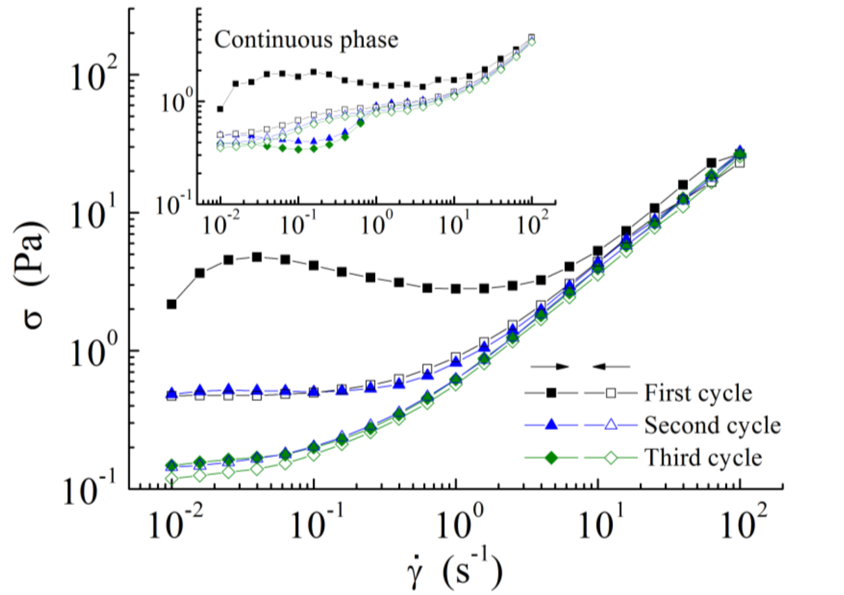

Figure S1. Flow curves of silicone oil-in-water (ϕ_{oil} = 0.7) with 2wt% Laponite in 0.1M NaCl. Directly after samples are prepared the stress is measured by applying increasing (filled symbols) and decreasing (empty symbols) shear rate. Three increasing/decreasing sweeps are done, in the following order (from top to bottom in graph) black, blue and green. (Inset) Same measurement for 2wt% Laponite in 0,1M NaCl, sample has left to rest for 2 hours before the first shear rate sweep starts.

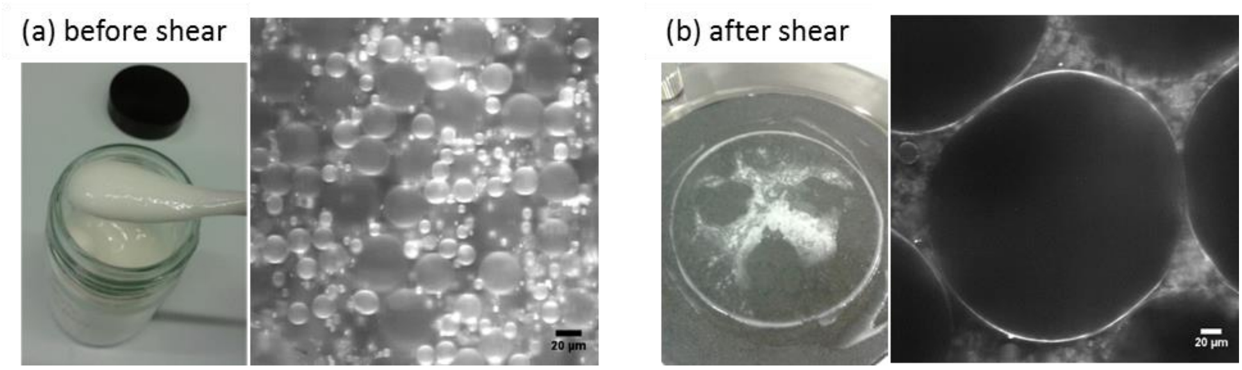

Figure S2. 'Pickering' emulsion (ϕ_{oil} = 0.7) oil-in-water stabilized by 2wt% Laponite in 0.1M NaCl Laponite. Before (a) and after (b) shear, showing a macroscopic (Castor oil-in-water) and microscopic (Silicone oil-in-water) image. The microscopic images obtained by confocal fluorescence microscopy (oil is dyed with Nile Red).

3. References

[1] N.P. Ashby, B.P. Binks, *PCCP*, 2000, **2**, 5640-5646.

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[3] A. Fall, J. Paredes, D. Bonn, *Physical review letters*, 2010, **105**, 225502.

[4] F. Lopez Arbeloa, M. J. Tapia Estevez, T. Lopez Arbeloa, I. Lopez Arbeloa, *Clay Minerals*, 1997, **32**, 97-106.