



Research paper

# Time-dependent rheology of clay particle-stabilised emulsions

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## ABSTRACT

We have studied the thixotropic behaviour of clay particle-stabilised emulsions using a combination of rheology and confocal fluorescence microscopy. Oil drops were stabilised by laponite particles attached to their surfaces and incorporated into a three dimensional super-aggregate structure of laponite particles that formed in the water. The self-supporting, three-dimensional network of drops and laponite particles gives the emulsions pronounced gel-like properties. The transient flow behaviour of the emulsions depends on the mechanical properties of the laponite dispersions and the oil drop volume fraction.

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## 1. Introduction

Clay particles are added to emulsions to modify and control their flow behaviour (Viseras et al., 2007). The time-dependent rheology of emulsions is important in food products, cosmetics, paints and concrete (Barnes, 1997; Mewis and Wagner, 2009). Recently it was shown that the thixotropic response of surfactant-stabilised emulsions can be controlled by loading the emulsions with clay particles (Ragouilliaux et al., 2007). The addition of colloidal particles confers gel-like properties which disappear on shaking, but reappear on allowing the emulsions to rest. In this work, we instead investigate the thixotropic behaviour of emulsions stabilised by particles alone (Binks, 2002; Dickinson, 2010; Leal-Calderon and Schmitt, 2008). The aim is to understand how the time-dependent rheology of clay dispersions is incorporated into particle-stabilised (or Pickering) emulsions. In particular, the focus is to relate the time scales of structure breakdown and recovery in the emulsion and particle dispersions.

A clay dispersion is defined as thixotropic (de Kretser et al., 1998) if, starting from rest, its viscosity decreases with time when a constant shear is applied (breakdown). When the shear ceases, the dispersion gradually recovers its consistency and the structure it had at rest (recovery). For example, laponite particles, a synthetic hectorite, cluster reversibly into dense micrometre-sized aggregates (Pignon et al., 1998; van Duijneveldt et al., 2005; Willenbacher, 1996). Dispersion flow behaviour is determined by the competition between the spontaneous build-up of the laponite aggregates at rest and their breakdown under shear. Typically, the evolution of the linear viscoelastic response (the storage and loss moduli) with time is used as a measure of the rebuilding structure in thixotropic materials.

The literature describing the structure and rheology of emulsions containing clay particles can be divided into studies of mixtures of surfactant-stabilised emulsions and clay (suspoemulsions) and studies of clay-stabilised emulsions. Pal et al. (1992) showed that mixtures of water drops and kaolinite particles in oil flow like bimodal dispersions. Lagaly et al. (1999) found that emulsions stabilised by montmorillonites showed slightly pseudoplastic behaviour, with shear stresses and viscosities higher than those of the dispersions, due to the presence of the oil drops. The viscoelasticity of clay-particle stabilised emulsions (Binks et al., 2005; Torres et al., 2007) and the elastic properties of clay particle-coated interfaces (Nciri et al., 2010; Tan et al., 2012) have been linked to the kinetic stability of the emulsions. Examination of emulsion structures revealed that significant fractions of the particles remain in the continuous phase (Cui et al., 2011; Guillot et al., 2009; Thieme et al., 1999; Zhang et al., 2008). Abend et al. (1998) found that paraffin-in-water emulsions stabilised by mixtures of a layered double hydroxide particle and montmorillonite were highly elastic. Abend et al. (1998) argued that the positively charged hydroxide particles form a network with the negatively charged montmorillonite particles in the water that enhances drop stability. Few studies have considered the time-dependent rheology of emulsions containing clay (Abend et al., 1998).

This work examines the thixotropy of emulsions of oil drops in laponite gels. The emulsion microstructure was investigated using confocal fluorescence microscopy. Transient rheology was used to probe the time scales of emulsion breakdown and recovery. This combination of techniques shows how particle aggregation causes thixotropy in Pickering emulsions. We show that incorporating oil drops into the laponite gels forms a stress-bearing, interconnected network. The emulsions behave like jammed solids at small stresses. Emulsion breakdown and recovery are determined by the flow behaviour of the laponite gel.

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## 2. Experimental section

### 2.1. Dispersion and emulsion preparation

Laponite RD particles (Rockwood Additives Limited) are disc shaped, 1 nm thick and 30 nm in diameter. Dispersions of laponite in solutions of sodium chloride (Chem Supply, 99%) in water (resistivity  $\geq 18.2$  M $\Omega$  cm) were prepared using a rotor–stator mixer (Ingenieurbüro CAT X1030D, M. Zipperer GmbH) with a 19 mm head operated at 11,000 revolutions per minute for 2 min to form transparent gels. The pH value of the dispersions was adjusted to 9.5 with concentrated solutions of NaOH.

Emulsions were prepared by homogenising 1-bromohexadecane (Sigma Aldrich, 99%, passed through chromatographic alumina twice to remove polar impurities) with the aqueous laponite dispersions using the rotor–stator mixer operated at 13,000 rpm. Emulsification times were set to obtain similar drop size distributions (number average radius  $\sim 20$   $\mu\text{m}$ ). The mechanical state of the laponite dispersions used to stabilise the emulsions was fixed by adjusting the laponite concentration relative to that required for gelation (Mourchid et al., 1998). This parameter depends only on the salt concentration in the dispersion. Typically the particle concentration was chosen to be close to that required for gelation. Emulsions prepared at oil volume fractions,  $\phi_o \leq 0.4$ , and laponite concentrations in the aqueous phase,  $C_p > 1.0$  wt.%, did not coalesce for several weeks. The emulsions were diluted at constant particle and salt concentration to investigate the effect of oil volume fraction on the elasticity.

### 2.2. Dispersion and emulsion rheology

Viscous flow and oscillatory measurements were made using a Rheometric Scientific Dynamic Stress Rheometer SR2000 in the controlled rate mode with a cone and plate geometry at a fixed temperature of  $25 \pm 0.1$  °C. Geometries with either smooth hydrophobic surfaces or roughened (by sand blasting) steel surfaces were used to minimise wall slip effects. A solvent trap was used to prevent evaporation. Samples were typically stirred by hand for 30 s, loaded into the rheometer and then left to rest for 180 s prior to measurements.

The viscous flow and oscillatory response of the laponite dispersions are reproducible after about 24 h, indicating that the fast ageing processes in the dispersions were completed. Slower ageing processes occur over a time period of several weeks (Bhatia et al., 2003). All the results shown here were obtained within 72 h of preparation to avoid any effect of the slow ageing dynamics of the laponite dispersions.

Breakdown tests involved measuring the stress response while applying a jump in the shear rate from an initial value (typically  $0 \text{ s}^{-1}$ ) to a final value (typically  $5 \text{ s}^{-1}$ ). Recovery tests involved applying a fixed small sinusoidal strain (corresponding to the linear viscoelastic region) after breakdown. The change in the viscoelastic moduli over time was measured.

### 2.3. Confocal fluorescence microscopy

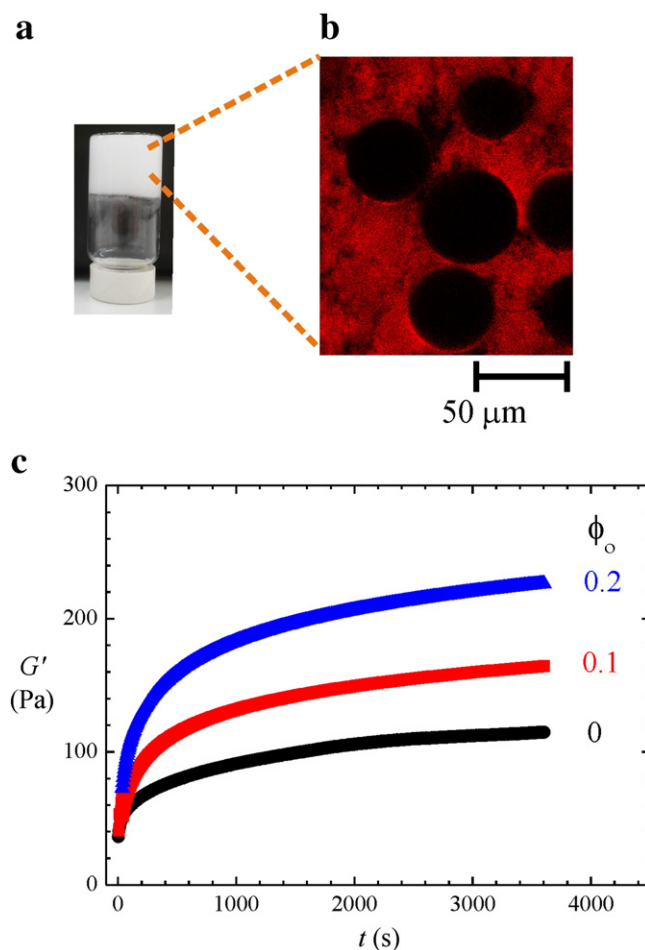
Confocal fluorescence microscopy (CFM, Leica SP5 spectra scanning confocal microscope) was used to visualise both dispersions and emulsions containing Rhodamine B (Sigma, 97%). At the low concentration used ( $\sim 0.3$   $\mu\text{M}$ ) the dye adsorbs completely onto the laponite particles. The samples were excited at a wavelength of 514 nm and the fluorescence emission intensity was collected over 555 to 655 nm. The particles appeared bright, while the aqueous and oil phases were black. The mean droplet size was calculated from at least 50 individual measurements of drop diameters in the confocal images.

## 3. Results and discussion

Laponite-stabilised emulsions are solid-like materials that resist flowing, as shown in Fig. 1a. Coagulation of the laponite particles leads to complex structures in the emulsions as the interactions between the particles cause rapid growth of large particle clusters. The oil droplets are trapped within these super-aggregate particulate structures. The resulting structure is a network of interconnected drops and particles that spans the whole emulsion volume (Fig. 1b). This drop-particle heteroaggregate structure has a critical influence on the emulsion breakdown and recovery behaviour.

The dynamic rheological behaviour of the laponite dispersions and emulsions in the linear viscoelastic regime was used to characterize the dispersions and emulsions at rest. The gelled laponite dispersions exhibit a yield stress and an elastic storage modulus,  $G'$ , which is much higher than their viscous loss modulus,  $G''$ .  $G'$  shows limited dependence on the frequency of the oscillatory stress being applied, as shown in Fig. 2 ( $\phi_o = 0$ , black symbols). A low-frequency plateau in  $G'$  indicates that the particle network structure can bear stress (Trappe and Weitz, 2000).

The emulsions exhibit enhanced viscosity and yield stresses compared to the clay dispersions alone. Fig. 2 shows that the emulsion elasticity increases with  $\phi_o$ . The elastic storage modulus is independent of



**Fig. 1.** (a) Photo of an emulsion in an inverted tube. The emulsion is highly viscous and does not flow readily. It has a drop volume fraction of 20 vol.% and is stabilised by 2 wt.% particles in 0.01 M NaCl. (b) Confocal fluorescence image of the interconnected network of drops and particles in the emulsion. Shearing disrupts this structure, causing the emulsion viscoelasticity to decrease. (c) Recovery of the elastic storage moduli ( $G'$ ) of emulsions with time ( $t$ ) after shearing is halted. Data is shown for emulsions formed at different drop volume fractions ( $\phi_o$ ). The emulsions were stabilised by 2 wt.% particles and the salt concentration in the aqueous phase was 0.002 M NaCl.

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