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Rheological transition of concentrated emulsions during successive shearing cycles

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ABSTRACT

Rheological investigations have identified a shear viscosity transition from shear thinning to Newtonian at low to moderate shear rates for concentrated polydimethylsiloxane emulsions during successive shearing cycles. The viscosity "flattening" behavior is dependent on the maximum shear rate applied and on droplet deformation. Atomic force microscopy measurements indicate attraction between the "repulsive" emulsion droplets under deformation. The results suggest formation of stable droplet layers due to deformation under high shear hydrodynamic compression. Based on these findings, unique methods to control the post-shear rheology of concentrated emulsions can be envisaged.

1. Introduction

Emulsion rheology has been of great interest for decades for its high importance toward industrial applications [1,2]. Generally, the viscosity of concentrated emulsions decreases as the shear rate increases, i.e. shear thinning; while dilute emulsions exhibit constant viscosity over a wide shear rate range, i.e. Newtonian. Shear thinning behavior is considered due to perturbation and breakdown of the three-dimensional droplet structure formed in the emulsion [3]. Some shear thinning emulsions may exhibit a low shear viscosity plateau where perturbation of droplet structure caused by shear is instantly recovered by the Brownian forces and the droplet structure remains effectively constant. For dilute emulsions, the distance between droplets is relatively large and no distinct droplet structure can be formed, resulting in Newtonian behavior.

Breakdown of three-dimensional droplet structure leads to formation of ordered layer structure [3]. Once discrete droplet layer structure is established another shear viscosity plateau may be observed, where the layers slide and the layer structure essentially remains unchanged. In the case of suspensions of hard particles, higher shear then breaks the ordered layer structure into a disordered assemble of particle clusters, the so-called 'order–disorder' transition [3], resulting in shear thickening behavior. In the case of monodisperse emulsions, on the other hand, no apparent shear thickening behavior at high shear rates can be observed [4,5], indicating the droplet layer structure remains in the emulsions [5].

When the applied shear is removed, droplets restructure themselves into a thermodynamically preferred structure. For dilute emulsions, the main source of the restructuring will be the Brownian force. For highly concentrated emulsions, the Laplace pressure of droplets may also contribute toward the restructuring. The time required for restructuring, which is an essential factor in controlling the quality of emulsion products, may strongly depend on several system dependent factors, e.g. interdroplet interactions, physical rigidity of the droplet structure (especially when bulky stabilizers or flocculants are introduced), the viscosity of the medium, and the droplet deformability. Droplet interaction and droplet deformability are dependent on the system investigated. Systematic investigation using a model emulsion is therefore essential to clarify the effects of these factors on the post-shear restructuring and shearing history in emulsions.

In the present article we explore the effects of droplet deformability and interdroplet interactions on the post-shear rheological behavior in concentrated emulsions (a highly sensitive stress controlled rheometer is used). We incorporate polydimethylsiloxane (PDMS) emulsions as the model emulsion, whose droplet deformability is controllable without changing the droplet surface chemistry [6]. Sodium dodecyl sulfate (SDS) is used as a stabilizer, which is also applicable as an interfacial tension controller by changing the ionic strength of the medium [7,8]. Atomic force microscopy (AFM), which is known as a powerful tool to directly measure nano-scale forces of PDMS droplets [9,10], is utilized to characterize the interdroplet interactions.

2. Experimental

2.1. Materials

Diethoxydimethylsilane (DEDMS) and methyltriethoxysilane (MTES) were supplied by Aldrich (Milwaukee, USA). SDS and 25%

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ammonia solution were supplied by Merck (Darmstadt, Germany), and analytical grade sodium chloride by Chem-Supply (Gillman, Australia). The water used throughout the research was demineralized water further purified by a Milli-Q water filtration system provided by Millipore (Billerica, USA).

2.2. *Sample preparation*

PDMS emulsions were prepared by anion-catalyzed polymerization of DEDMS and MTES [6]; further detail of the procedure is given elsewhere [11,12]. The initial reactants for emulsion preparation were a DEDMS/MTES mixture (5 vol%), a 25% ammonia solution (10 vol%) and water (85 vol%). The fractions (by volume) of MTES in the DEDMS/MTES mixture were 0.30 and 0.45, described as PDMS(0.3) and PDMS(0.45), forming viscous and viscoelastic droplets, respectively [10,12]. The resultant emulsions were centrifuged (eppendorf centrifuge 5416) at 5000 rpm for 5 min and dispersed into 1 mM SDS (ionic strength, $I = 1$ mM) or 1 mM SDS + 99 mM NaCl ($I = 100$ mM) solutions to achieve the desired volume fractions. The SDS concentration of 1 mM is smaller than the critical micelle concentration of SDS (80 mM in water and 1.4 mM in 100 mM NaCl [11]), avoiding effects from creation of micelles. For both emulsions PDMS(0.3) and PDMS(0.45) the average droplet diameter was 1.7 ± 0.5 μm and the pH of the final emulsion was ~7. Bulk PDMS samples were prepared by placing centrifuged PDMS droplets on a watch glass and allowing the water to evaporate at room temperature over 2 days.

2.3. *Experimental methodology*

The volume fraction of PDMS emulsions was determined by centrifuging 1 mL of the emulsion in a tube with a 4 mm internal diameter at 10,000 rpm for 30 min and measuring the volume of the sedimentary fraction, which was then corrected by a drying method, described elsewhere [11,12]. The term “volume fraction” being used throughout this report is the effective volume fraction that includes the electrical double layer thickness.

All steady-mode rheological properties were collected by a stress-controlled rheometer (Rheometric Scientific SR-5000) using a 40-mm cone and plate geometry (cone angle: 0.0402 radians) in an air. The temperature was controlled at $25.0 \pm 0.1\,^{\circ}\mathrm{C}$ by a constant temperature bath. Preliminary experiments using various gap distances and geometry diameters indicated no apparent wall slip effect existent. No pre-shearing was implemented in the current study.

The droplet diameters were determined by laser diffraction (Malvern MasterSizer X) before and after rheological measurements, revealing no apparent coalescence of droplets. Interfacial tensions between bulk PDMS samples and a 1 mM SDS or 1 mM SDS + 99 mM NaCl solution were determined by the drop weight method [13]. Zeta potentials of emulsion droplets were determined by electroacoustics (Colloidal Dynamics AcoustoSizer II). Electroacoustic measurements were made over a range of frequencies between 300 kHz and 11 MHz and the electroacoustic sonic amplitude magnitude and phase angle spectrum determined; the zeta potential was then determined using the approach of Rowlands and O'Brien [14]. The viscosity, η, the density, ρ, and the interfacial tension, σ, of bulk PDMS samples and the zeta potential, ζ, of PDMS droplets are given in Table 1.

Forces between bulk PDMS samples and a borosilicate glass sphere were measured by an AFM apparatus (Asylum MFP-3D). A rectangular silicon nitride AFM cantilever (Olympus RC800PSA, 200 μm × 20 μm) was calibrated by the thermal noise method installed in the apparatus. A borosilicate glass sphere (radius, $R = 22$ μm) attached to the apex of the cantilever was immersed into a 1 mM SDS or 1 mM SDS + 99 mM NaCl solution which was gently dropped onto a bulk PDMS sample lying on a glass microscope slide. The aqueous solution formed a meniscus between the PDMS sample and the cantilever holder, completely engulfing the cantilever. The thickness of bulk PDMS samples was ~0.8 mm. Force versus distance curves were obtained at the approach and retract rate of 1 $\mu\mathrm{m\,s^{-1}}$. The nominal separation, i.e. the separation between the colloid probe and the undeformed bulk PDMS fluid surface, was determined by the method proposed by Gillies et al. [15].

Table 1
Physical properties of PDMS samples

Sample	Bulk			Droplet
	η ($\mathrm{N\,m^{-2}\,s}$)	ρ ($\mathrm{g\,cm^{-3}}$)	σ ($\mathrm{mN\,m^{-1}}$)[a]	ζ (mV)[a]
PDMS(0.3)	0.101	1.06	12.2, 1.8	−107.9, −93.1
PDMS(0.45)	3.90	1.11	17.2, 2.5	−98.4, −63.0

[a] In (left) a 1 mM SDS and (right) a 1 mM SDS + 99 mM NaCl solution at pH 7.

3. Results and discussion

3.1. *Rheological behavior during shear cycling*

Shear viscosity curves of PDMS emulsions for volume fractions, ϕ, of 0.6 and 0.7 at $I = 1$ mM during ten successive rheological measurements are shown in Fig. 1. The 1st, 3rd, 5th and 10th measurements are shown. Measurements were carried out immediately consecutive to the previous measurement (after ensuring that the rotor completely stopped) and the time interval between the commencements of each measurement was ~3 min. It can be clearly observed that the level of the shear thinning behavior gradually decreases as the shearing cycles are repeated and eventually the emulsion behaves as Newtonian for a PDMS(0.3) emulsion at $I = 1$ mM (Fig. 1a). A similar transition in the rheological behavior can be observed at $\phi = 0.7$, exhibiting identical rheological behavior at high shear rates (Fig. 1c). PDMS(0.45) emulsions at $\phi = 0.7$ also indicates the viscosity “flattening” behavior at low shear rates and identical behavior at high shear rates (Fig. 1d). PDMS(0.45) at $\phi = 0.6$ exhibits an increase in the degree of shear thinning behavior as the measurements are repeated (Fig. 1b). However, a general increase in the viscosity, which can be observed especially at the highest shear rate range for all samples, occurs due to an increase in the volume fraction where evaporation of water from the medium is inevitable even with application of a vapor trap. Therefore Fig. 1b is a combination of the viscosity “flattening” behavior and a small increase in the volume fraction; the viscosity “flattening” behavior is indicated at the lowest shear rate range ($<0.1\ \mathrm{s^{-1}}$).

At the volume fraction of 0.6 it is considered that PDMS(0.3) droplets experience a great level of deformation under the shear rate of 1000 $\mathrm{s^{-1}}$, while PDMS(0.45) droplets experience little deformation at the same shear rate [16]. Therefore, the difference in behavior during successive rheological measurements between PDMS(0.3) and PDMS(0.45) at $\phi = 0.6$ (Figs. 1a and 1b) indicates that droplet deformation promotes the viscosity “flattening” behavior. This point will be revisited later in this article.

A striking change in rheological behavior during ten successive shearing cycles is encountered when the ionic strength of the medium is increased to 100 mM, which is shown in Fig. 2. The most interesting result is that there is no sign of viscosity “flattening” behavior recognized for both PDMS emulsions. Instead, an apparent low shear viscosity plateau is observed for PDMS(0.45) (Fig. 2b). The low shear viscosity plateau is commonly observed for emulsions of attractive droplets (e.g. [17]), indicating attractive interactions between PDMS droplets at this ionic strength. DLVO simulation reveals a shallow potential well of neg-