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Droplet structure instability in concentrated emulsions

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Abstract

Dynamic rheological measurements are reported on concentrated emulsions of monodispersed sodium dodecyl sulfate-stabilized polydimethylsiloxane droplets with different cross-linking levels (i.e., controllable deformability and either viscous or viscoelastic) and over a volume fraction range 0.5 to 0.72. Emulsion structure instability is revealed at a volume fraction of 0.7 and is represented by an anomalously low G'/G'' crossover stain, γ_{co} (G', elastic modulus; G'', viscous modulus). This phenomenon is independent of the droplet cross-linking level and not observable for hard-sphere silica sols of volume fractions from 0.54 to 0.63. It is suggested that the structural instability arises from deformation-induced formation of "slip planes" between droplet layers specific to the repulsive droplets at the specific volume fraction, which may be dependent on the droplet packing configurations for the given polydispersity of the system. The γ_{co} value may be considered as an in situ index of the structural stability and interdroplet interaction balance in concentrated emulsions.

Keywords: Polydimethylsiloxane; Emulsions; Dynamic rheology; Droplet deformability; Packing configuration

1. Introduction

One of the interesting characteristics of concentrated emulsions is their elasticity, even when they comprise two purely viscous fluids. At high volume fractions, droplets deform and form interdroplet planar films, hence giving rise to the osmotic pressure. The elasticity basically originates from the energy stored at the planar films between droplets due to deformation. Therefore, an emulsion's elastic modulus scaled by the Laplace pressure of the droplets is proportional to the osmotic pressure [1].

Generally, concentrated emulsions are viscoelastic and the viscoelasticity is characterized by dynamic rheological measurements, where an oscillatory shear is applied. At low shear strains an emulsion's elastic modulus, G', is greater than the viscous modulus, G'', hence representative of the elastic nature. As the shear strain increases the value of G' decreases due to breakdown of the interdroplet structure; eventually a G'/G'' crossover phenomenon is observed and the emulsion shows viscosity-dominant behavior. Several reports have revealed that the G'/G'' crossover strain, γ_{co}, exhibits values of $\sim$10% for monodisperse emulsions [1,2] and suspensions [3,4], for a wide volume fraction range of $0.3 \leqslant \phi \leqslant 0.8$ depending on the interdroplet or interparticle interactions. In contrast, relatively polydisperse emulsions exhibit γ_{co} values of 1–2% [5,6], since their packing configurations are different from monodisperse dispersions [7]. These observations imply that the strain-dependent change of dispersions from elastic to viscous in nature is controlled by the packing structure, regardless of the volume fraction or deformability of the dispersed phase. Interestingly, however, for monodisperse polydimethylsiloxane (PDMS) emulsions, we have recently observed anomalously low γ_{co} values of $\sim$0.4% at $\phi = 0.7$ [8]. This result indicates that the PDMS emulsions at this volume fraction retain a unique droplet structure, which requires more detailed investigation.

Here, we demonstrate the nature of the anomalously low γ_{co} values in monodisperse concentrated emulsions. Stress-sweep and frequency-sweep dynamic rheological measurements are carried out on highly monodisperse sodium dodecyl sulfate (SDS)-stabilized PDMS emulsions of differ-

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ent droplet deformability (either viscous or viscoelastic) and silica suspensions for the volume fraction range of $0.50 \leqslant \phi \leqslant 0.72$. Furthermore, by changing the ionic strength of the PDMS emulsions' aqueous phase we have investigated the effects of the balance between attractive and repulsive interdroplet interactions in controlling droplet structure instability.

2. Experimental

2.1. Materials

Diethoxydimethylsilane (DEDMS) and methyltriethoxysilane (MTES) were supplied by Aldrich (Milwaukee, WI). SDS and 25% ammonia solution were supplied by Merck (Darmstadt, Germany), and analytical grade sodium chloride by Chem-Supply (Gillman, Australia). Spherical silica particles were supplied by Geltech Inc. (Alachua, USA). 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. Emulsion or suspension preparation

PDMS emulsions were prepared by anion-catalyzed polymerization of DEDMS and MTES [9]; further details of the procedure are given elsewhere [8,10]. The initial reactants for emulsion preparation were a DEDMS/MTES mixture (5 vol%), a 25% aqueous ammonia solution (10 vol%), and water (85 vol%). Two emulsions were prepared with a fraction of MTES in the DEDMS/MTES monomer mixture of either 0.30 or 0.45; these are referred to as PDMS(0.3) and PDMS(0.45) and are considered viscous and viscoelastic droplets, respectively [11]. The resultant emulsions were centrifuged (Eppendorf Centrifuge 5416) at 5000 rpm for 5 min and dispersed into 1 mM SDS solutions (or 1 mM SDS + 99 mM NaCl solutions for the higher ionic strength studies) to achieve the desired volume fractions ($0.50 \leqslant \phi \leqslant 0.72$). Size distribution measurements reveal no droplet coalescence during centrifugation (Table 1). The pH of the final emulsion was ~7. Bulk PDMS samples were prepared by placing precentrifuged pellets of PDMS droplets on a watch glass and allowing the water to evaporate at room temperature over 2 days.

Concentrated silica suspensions were prepared by dispersing the desired amount (0.52–0.63 volume fraction equivalent) of silica particles into 1 mM SDS solutions in sealed vials. The dispersions were stirred for 24 h using a magnetic stirrer, with occasional sonication to ensure there were no aggregated clusters of particles present, which was confirmed by laser diffraction. A 1 mM SDS solution was used as the continuous phase to achieve equivalence to the PDMS emulsions.

2.3. Experimental methodology

The volume fraction of PDMS emulsions was determined by centrifugation, which was then corrected by a drying method, described elsewhere [10]. The term "volume fraction" being used throughout this report is the effective volume fraction that includes the electrical double layer thickness, for both PDMS emulsions and silica suspensions.

The dynamic rheological properties of emulsions and suspensions were determined using a stress-controlled rheometer (Rheometric Scientific SR-5000). The temperature was controlled at 25.0 ± 0.1 °C by a constant temperature bath. A 40-mm cone and plate geometry (cone angle: 0.0402 rad) was used for all measurements. Stress-sweep measurements were carried out at a frequency of 1.0 Hz and frequency-sweep measurements at a stress of $1.0\ \mathrm{N\,m^{-2}}$. Preliminary experiments using various gap distances and geometry diameters indicated no apparent wall-slip effects.

The size distributions of droplets or particles were determined by laser diffraction (Malvern MasterSizer X). Size distribution data both before and after rheological measurements revealed no apparent coalescence of droplets or aggregation of particles. Interfacial tensions between bulk PDMS samples and aqueous solutions were determined by the drop weight method [12]. Zeta potentials of droplets or particles were determined by electroacoustics (Colloidal Dynamics AcoustoSizer II) with application of the Smoluchowski equation. The interfacial tension, Γ, of bulk PDMS samples and the diameter, d, and the zeta potential, ζ, of PDMS droplets and silica particles are given in Table 1. Nano-rheological parameters (short time elasticity limit, E_0 [$\mathrm{mN\,m^{-2}}$], long time elasticity limit, E_∞ [$\mathrm{mN\,m^{-2}}$], characteristic relaxation time, τ [s]) and the spring constant, k, of PDMS droplets obtained by AFM [11] are also shown. For silica, the elastic modulus for fumed silica [13] is reported as E_0 in Table 1. Due to the relatively high magnitude of the zeta potentials (~ −100 mV), PDMS droplets in 1 mM SDS solutions are considered highly repulsive.

Table 1
Physical properties of PDMS and silica samples

Sample	Bulk	Droplet/particle			
	Γ [$\mathrm{mN\,m^{-1}}$][a]	E_0, E_∞, τ	k [$\mathrm{mN\,m^{-1}}$]	d [μm]	ζ [mV][a]
PDMS(0.3)	12.2/1.8	–	47[b]	1.7	−107.9/−93.1
PDMS(0.45)	17.2/2.5	0.55, 0.4, 0.07[b]	140[b]		−98.4/−63.0
Silica	–	72×10^3,[c] –, –	–	1.2	−57.2/−23.6

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

[b] For bare droplets of $d \sim 0.5$ μm from [11].

[c] For fused silica from [13].