Droplet deformability and emulsion rheology: steady and dynamic behavior

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Abstract

The static and dynamic rheological behavior of concentrated sodium dodecylsulfate (SDS) stabilized, deformability controllable polydimethylsiloxane (PDMS) emulsions is reported and comparisons made with silica (hard sphere) suspensions. Steady-mode measurements indicate "hard" (viscoelastic) droplets behave as hard spheres, while "soft" (viscous) droplets induce structural flexibility of the emulsion against shear. Dynamic-mode measurements reveal that viscoelasticity of droplets provides the great magnitude of elasticity for the "hard" emulsion, while formation of planar films between droplets is the origin of the elasticity of "soft" emulsions. Combination of steady and dynamic rheological behavior has enabled depiction of droplet structure evolution in relation to the shear stress applied, especially by taking advantage of the normal force that reflects the transient deformation of droplets.

Keywords : emulsion rheology, droplet deformability, polydimethylsiloxane

1. Introduction

The rheological behavior of emulsions has been of great interest not only for fundamental scientific understanding but also for practical industrial applications (Barnes, 1994; Tadros, 1994). Emulsions exhibit contrasting rheological behavior to that of suspensions of hard spheres, due to the droplet deformation, the surface mobility and the internal fluid circulation.

At low volume fractions, the internal fluid circulation in droplets plays an important role in determining emulsion viscosity. Taylor (1932) derived an equation to predict the relative viscosity of emulsions using hydrodynamic theory. Unfortunately, applicability of the Taylor's equation is limited, because the internal fluid circulation in droplets can be easily interfered by surfactants that are normally used to stabilize emulsions (Nawab and Mason, 1958).

At high volume fractions, droplets deform due to an osmotic pressure and create a planar film of the continuous phase. The interface stores energy as a disjoining pressure, resulting in the elastic nature of emulsions even if the emulsion consists of two purely viscous liquids. Therefore the elastic modulus of an emulsion normalized by the Laplace pressure is equal to the osmotic pressure (Lacasse *et al.*, 1996). However, Dimitrova and Leal-Calderon (2004) reported that protein stabilized emulsions exhibited shear-induced droplet coalescence and relatively high val-

ues of the normalized elastic modulus in comparison to equivalent sodium dodecylsulfate (SDS) stabilized emulsions, indicating complex interdroplet interactions due to adsorbed proteins.

A major concern in advancing understanding of emulsion rheology is that droplet deformability is contingent upon the system investigated, i.e. when and how much the deformation occurs is specifically controlled by the oil type, stabilizer, droplet size, etc. To date it has not been possible to vary deformability of droplets without changing the emulsion system and therefore without changing the surface chemistry and physics of droplets, e.g. in aforementioned examples. Therefore, a direct and quantitative comparison of various emulsions is considered dubious and impractical. One decade ago, highly monodisperse polydimethylsiloxane (PDMS) emulsions were synthesized by Obey and Vincent (1994). The droplet deformability is controllable by introducing cross-linking agents (Goller *et al.*, 1997), and the surface chemistry of PDMS droplets is independent of the cross-linking level and similar to that of silica particles. Such PDMS emulsions have a high potential in systematically investigating the effects of droplet deformability on the various properties of droplets or emulsions, such as interdroplet interactions or nanorheology of droplets (Gillies *et al.*, 2002; Gillies and Prestidge, 2004), and emulsion viscosity (Saiki and Prestidge, 2005).

Our current study aims to elucidate the effects of droplet deformability on the rheological properties of the model concentrated emulsion, i.e. SDS stabilized PDMS emulsions with controlled deformability. In a previous report the

relative viscosity versus volume fraction curves of PDMS emulsions were successfully obtained for a wide volume fraction range, where droplet deformation was described in terms of hydrodynamic effects and geometrical argument (Saiki and Prestidge, 2005). The present paper explores the rheological behavior of concentrated PDMS emulsions under steady and oscillatory shear flow. Combination of steady and dynamic responses will provide a clear vision of the droplet structures evolving within the emulsion under shear and the role of droplet deformability.

2. Experimental

2.1. Materials

Diethoxydimethylsilane (DEDMS) and methyltriethoxysilane (MTES) were supplied by Aldrich (Milwaukee, USA). Sodium dodecylsulfate (SDS) and 25% ammonia solution were supplied by Merck (Darmstadt, Germany). 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 (Goller et al., 1997); further detail of the procedure is given elsewhere (Saiki and Prestidge, 2005). 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 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 (Gillies et al., 2002; Gillies and Prestidge, 2004). The resultant emulsions were centrifuged (eppendorf Centrifuge 5416) at 5000 rpm for 5 minutes and dispersed into 1 mM SDS solutions to achieve the desired volume fractions ($0.5 \leq \phi \leq 0.72$). 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.

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 screw-capped

vials. The dispersions were stirred for 24 hours using a magnetic stirrer, with occasional sonication to ensure there were no aggregated clusters of particles present. 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 centrifuging 1 mL of the emulsion in a tube with a 4 mm internal diameter at 10000 rpm for 30 minutes and measuring the volume of the sedimentary fraction, which was then corrected by a drying method, described elsewhere (Saiki and Prestidge, 2005). 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 rheological properties of emulsions and suspensions were investigated by a stress-controlled rheometer (Rheometric Scientific SR-5000). The temperature was controlled at $25.0 \pm 0.1°C$ by a constant temperature bath. A 40-mm cone and plate geometry (cone angle: 0.0402 radians) was used for all measurements. All dynamic-mode measurements were carried out at a frequency of 1.0 Hz.

The droplet or particle diameters were determined by laser diffraction (Malvern MasterSizer X) before and after rheological measurements, revealing that there was no apparent coalescence of droplets. Interfacial tensions between bulk PDMS samples and a 1 mM SDS solution were determined by the drop weight method (Harkins and Brown, 1919). Zeta potentials of droplets or particles were determined by electroacoustics (Colloidal Dynamics AcoustoSizer II) with application of the Smoluchowski equation. The viscosity, η, the density, ρ, and the interfacial tension, σ, of bulk PDMS samples and the diameter, d, and the zeta potential, ζ, of PDMS droplets and silica particles are given in Table 1. Due to the relatively high magnitude of the zeta potentials (~ -100 mV), PDMS droplets are considered highly repulsive.

3. Results and discussion

3.1. Steady rheological behavior

PDMS emulsions and silica suspensions have been shown to be Newtonian in the low volume fraction range

Table 1. Physical properties of PDMS and silica samples

Sample	Bulk			Droplet/Particle	
	$\eta/Nm^{-2}s$	$\rho/g\,cm^{-3}$	σ/mNm^{-1} [a]	$d/\mu m$	ζ/mV [b]
PDMS(0.3)	0.101 ± 0.004	1.06 ± 0.02	12.2 ± 0.7	1.7 ± 0.5	-107.9 ± 1.5
PDMS(0.45)	3.90 ± 0.06	1.11 ± 0.01	17.2 ± 0.9		-98.4 ± 1.0
Silica		2.0 [c]		1.2 ± 0.7	-57.2 ± 0.4

[a]Against a 1 mM SDS solution. [b]In a 1 mM SDS solution at pH 7. [c]Given by the supply company.
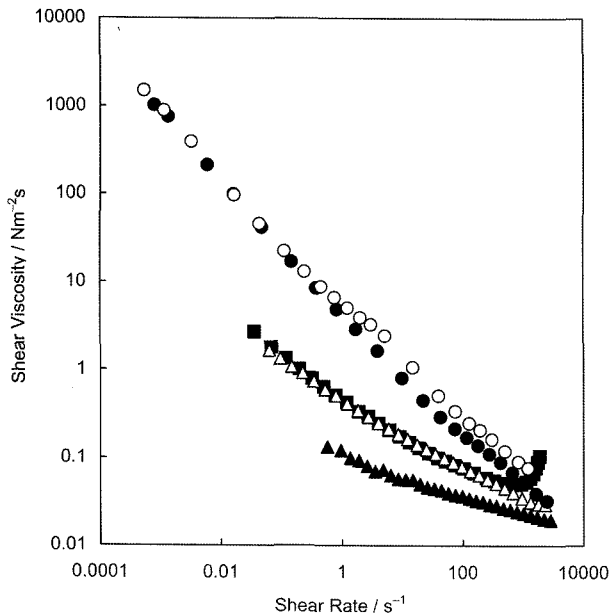
Fig. 1. Shear viscosity plotted against shear rate. Closed triangle: PDMS(0.3), $\phi = 0.60$. Open triangle: PDMS(0.45), $\phi = 0.62$. Closed square: silica, $\phi = 0.61$. Closed circle: PDMS(0.3), $\phi = 0.68$. Open circle: PDMS(0.45), $\phi = 0.68$.

Fig. 2. Power-law indices plotted against volume fraction. Closed circle: PDMS(0.3), closed triangle: PDMS(0.45), open square: silica. Lines are to guide the eye.

(e.g. $\phi < {\sim}0.4$) and show shear thinning behavior as the volume fraction increases. The shear viscosities plotted against the shear rate for PDMS emulsions and a silica suspension at $\phi = 0.61$ and 0.68 are shown in Fig. 1. For such colloidally stable systems, the shear thinning behavior originates from perturbation and breakdown of structures created among droplets or particles and formation of ordered layer structures (Tadros, 1994; Raghavan and Khan, 1997). The "ordered" particle layers then separate into clusters of particles, i.e. an 'order-disorder' transition (Raghavan and Khan, 1997), resulting in the shear thickening behavior (dilatancy) observed at the high shear rate range for the silica suspension. However, emulsions do not show apparent shear thickening behavior, indicating that the 'order-disorder' transition does not take place, which will be discussed later. Both emulsion types are more shear thinning at $\phi = 0.68$ than at $\phi = 0.61$.

The gradient of the shear viscosity versus shear rate curves denotes the magnitude of the structural change within concentrated dispersions. At high shear rates emulsions and suspensions are in a complex state as described above. In the case of the PDMS emulsions and silica suspensions investigated in this paper, there was no clear zero shear viscosity observed. This indicates that there is no state where the dispersion flows while sustaining the droplet or particle structure. Therefore, at the lowest shear rate range, the shear thinning behavior depicts the structural change from the state of rest. The shear viscosity curves of PDMS emulsions and silica suspensions at the lowest
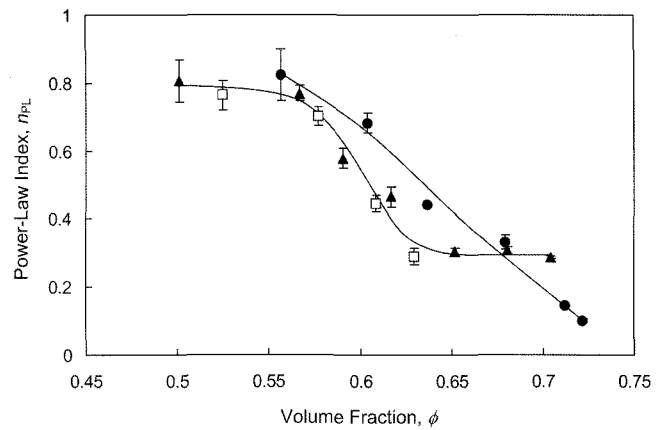
observable shear rate range were fitted by the power-law model:

$$\eta = A\dot{\gamma}^{n_{PL}-1}, \tag{1}$$

where A is a constant, $\dot{\gamma}$ the shear rate and n_{PL} the power-law index. Newtonian fluids give $n_{PL} = 1$ and shear thinning fluids $n_{PL} < 1$. The n_{PL} values for PDMS emulsions and silica suspensions plotted against the volume fraction, ϕ, are shown in Fig. 2. The n_{PL} of silica suspensions decreases as the volume fraction increases, with a noticeable sudden decrease at $\phi > 0.58$. The volume fraction of 0.58 is the colloidal glass transition volume fraction, ϕ_g (Götze and Sjogren, 1992), where particles are entrapped in a "cage" created by adjacent neighbors. When a suspension above the ϕ_g was sheared, significant breakdown of the particle "cage" structure is anticipated, resulting in high shear sensitivity, i.e. smaller n_{PL} values. Interestingly, PDMS(0.45) emulsions follow the trend of the silica suspension under these conditions, indicating that PDMS (0.45) droplets are effectively behaving as hard particles even though no dilatancy was observed. The n_{PL} of PDMS (0.45) reached a plateau value of ${\sim}0.3$ at $\phi = 0.65$, consistent with the value reported for avocado pulp in water emulsions (Freitas et al., 1996). On the other hand, the n_{PL} value of PDMS(0.3) emulsions does not sharply decrease at $\phi = 0.58$; this is as if the colloidal glass transition has no impact. The n_{PL} values of PDMS(0.3) gradually decreases as the volume fraction increases, eventuating significantly lower than the observed plateau value for PDMS(0.45). These results are due to the high deformability of PDMS (0.3) droplets. At moderate volume fractions deformation allows droplet encounters without significant changes to the structure. Whereas, at high volume fractions PDMS (0.3) droplets not only readily deform to form highly compressed layers, but also laterally distort resulting in extra
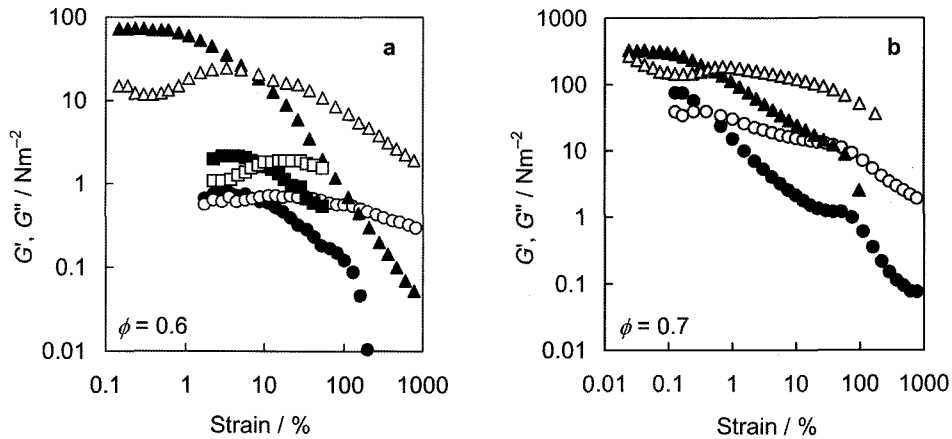
Fig. 3. Elastic modulus, G' (closed symbols), and viscous modulus, G'' (open symbols), plotted against shear strain. a: PDMS(0.3) $\phi = 0.60$ (circle), PDMS(0.45) $\phi = 0.61$ (triangle), silica $\phi = 0.61$ (square). b: PDMS(0.3) $\phi = 0.71$ (circle), PDMS(0.45) $\phi = 0.70$ (triangle). 1 Hz.

(extended) shear thinning behavior.

3.2. Dynamic rheological behavior

The elastic or storage modulus, G', and the viscous or loss modulus, G'', of PDMS emulsions and a silica suspension plotted against the shear strain are shown in Fig. 3. All data exhibit G' values higher than G'' in the low shear strain range, representing the elastic nature of emulsions and suspensions. While the elasticity of silica suspension originates from the network structure of particles (Tadros, 1994), the elasticity of emulsions may include other contributions, e.g. storage of energy at the interface, and the elastic or viscoelastic response of droplets. The G' values remain constant until the shear induces breakdown of particle or droplet structure (Tadros, 1994). The constant G' region is known as the linear viscoelastic region, which is normally used to non-destructively investigate the viscoelasticity by measuring G' and G'' as a function of frequency (Tadros, 1990; 1994). At $\phi = 0.6$, the critical strain, γ_{cr}, which is the onset of decrease in G', is ~8% for PDMS(0.3) and silica and ~0.8% for PDMS (0.45). At $\phi = 0.7$, both PDMS(0.3) and PDMS(0.45) exhibit similar γ_{cr} value at ~0.1%. After the linear viscoelastic region, decrease in G' and slight increase in G'' result in G'/G'' crossover.

The zero shear elastic modulus, G'_0, and the G'/G'' crossover strain, γ_{co}, are summarized in Table 2. The G'_0 values, which represent the elasticity of the system at a state of rest, were obtained from fitting the G' data plotted against the shear stress, τ, by a Carreau type model:

$$G' = G'_0(1+(A_1\tau)^{A_2})^{(A_3-1)/A_2}$$ (2)

where A_i ($1 \le i \le 3$) are constants. At $\phi = 0.6$, the G'_0 value of PDMS(0.45) is 100 times greater than that of PDMS (0.3) and 35 times greater than that of silica. At this vol-

Table 2. Dynamic rheological properties of PDMS emulsions and a silica suspension

Sample	ϕ	G'_0/Nm^{-2}	$\gamma_{co}/\%$
PDMS(0.3)	0.60	0.75	7.5
	0.71	76	0.40
PDMS(0.45)	0.61	73	6.8
	0.70	330	0.44
Silica	0.61	2.1	9.2

ume fraction, which is lower than the random close packing, ϕ_{rcp} (= 0.63), droplets retain their spherical shape and there will be no significant contribution from the storage of energy at the droplet interface. Therefore, the relatively high magnitude of G'_0 for the PDMS(0.45) emulsion is likely to originate from the viscoelasticity of PDMS(0.45) droplets. This indicates that the mechanism for structure breakdown of PDMS(0.45) emulsion is different from that of the PDMS(0.3) emulsion and silica suspension, which is reflected in the small γ_{cr} value. The G'_0 value of PDMS (0.3) being smaller than that of silica indicates flexibility and vulnerability of the droplet structure against shear due to the high magnitude of droplet deformability, which was also observed in the steady-mode measurements. However, at $\phi = 0.7$, PDMS(0.3) exhibits a G'_0 value that is 100 times greater than that of PDMS(0.3) at $\phi = 0.6$ and only 25% of that of PDMS(0.45) at $\phi = 0.7$. At volume fractions above ϕ_{rcp}, droplets are deformed and form planar films between them, resulting in the great magnitude of elasticity for both PDMS(0.3) and PDMS(0.45) emulsions, with PDMS(0.45) exerting extra elasticity due to the viscoelasticity of the droplets. Deformation of droplets at $\phi = 0.7$ leads to identical droplets structure and breakdown mechanisms for both PDMS(0.3) and PDMS(0.45), indicated by the identical γ_{cr} values.

The γ_{co} values of PDMS emulsions and silica suspensions at $\phi = 0.6$ were ~8%, consistent with the values obtained for silica suspensions in ethylene glycol at $\phi = 0.52$ and 0.56 (Mason and Weitz, 1995) and for SDS stabilized silicone oil in water emulsions at $\phi = 0.57$, 0.60 and 0.77 (Mason et al., 1997). Whereas, PDMS emulsions at $\phi = 0.7$ exhibited remarkably small γ_{co} values of ~0.4%, indicating the extensive shear vulnerability of the structure. Importantly, the obtained γ_{co} values were independent of the droplet deformability. This result puts forward a hypothesis: the droplet structure at $\phi = 0.7$ is in a mechanically and thermodynamically unstable geometrical condition.

3.3. Viscosity "Refrain" behavior

Some highly concentrated PDMS emulsions exhibited step-like shear thinning behavior during steady-mode rheological measurements, which is shown in Fig. 4. The normal force, F_N, simultaneously obtained in the steady-mode measurements, and the scaled elastic modulus, G'/ω, and the scaled viscous modulus, G''/ω, obtained by the dynamic-mode measurements are also shown. The scaled moduli G'/ω and G''/ω are imaginary and real components of the complex (dynamic) viscosity, η^*:

$$\eta^* = \frac{G^*}{i\omega} = \frac{G''}{\omega} - \frac{G'}{\omega}i,$$ (3)

where G^* is the complex modulus and ω the angular frequency. The viscosity of PDMS(0.45) emulsions exhibited creeping regions at small stresses (< 1 Nm^{-2}). The creep was not as evident for PDMS(0.3), which is representative of the high deformability of PDMS(0.3) droplets. The

shear thinning behavior following the creep was refrained at the intermediate stress range, and then recovered its magnitude at the high stress range. The G'/ω values diminished almost immediately after the "refrain" region, while G''/ω eventuated to η. The F_N values for PDMS(0.3) fluctuated in the negative range, whereas that of PDMS(0.45) first decreased until the beginning of the "refrain" region then increased returning to neutral at the end of the "refrain" region, and further increased as the stress increased.

Similar "constant" shear viscosity regions were reported for attractive water-in-oil emulsions at $\phi = 0.58$ using both concentric cylinders and parallel plates geometries (Montesi et al., 2004). The shear rate range the "constant" viscosity appeared was dependent on the gap thickness, i.e. a narrower gap thickness required a larger shear rate. Similar behavior for the first normal stress, N_1, which is proportional to F_N, was also observed, but the timing in relation to the behavior of the shear viscosity was different from the observations in the present paper, i.e.: N_1 decreased after the beginning of the "constant" viscosity region, the end of the "constant" viscosity region did not have an apparent influence on the behavior of N_1, and N_1 did not change its value from negative to positive until the shear rate increased close to 1000 s^{-1}. Based on the microscopic observations, Montesi et al. (2004) explained the "constant" shear viscosity by formation of cylindrical clusters of droplets, which rotate along the shear applied. However, there are several differences between (a) the observations in the present paper and (b) those reported by Montesi et al. (2004): the "constant" viscosity region is (a) oblique and (b) level, the volume fraction is (a) 0.7 and (b) 0.58,
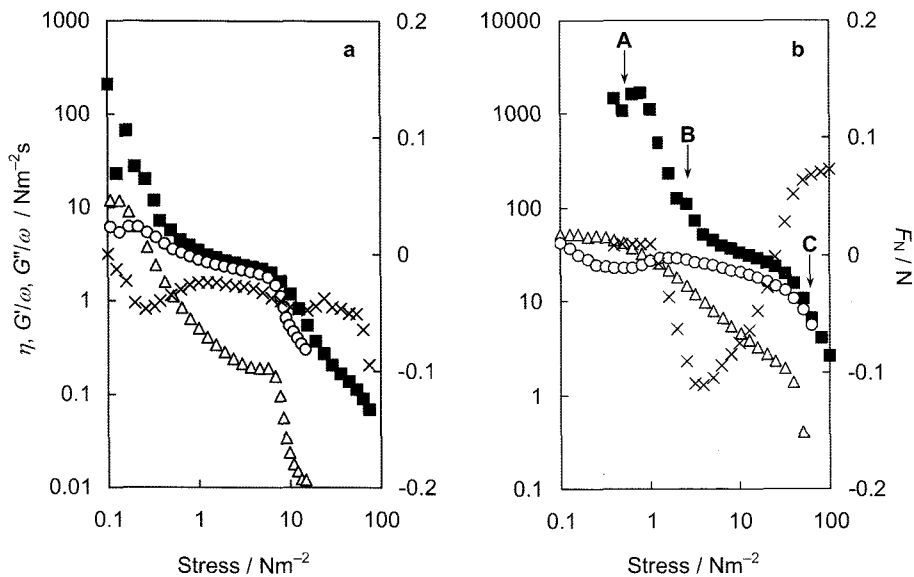

Fig. 4. Viscosity, η (closed square), scaled elastic modulus, G'/ω (open triangle), scaled viscous modulus, G''/ω (open circle), and normal force, F_N (cross), plotted against stress. a: PDMS(0.3) $\phi = 0.71$. b: PDMS(0.45) $\phi = 0.70$; A, B and C with arrows correspond to the states A, B and C shown in Fig. 5, respectively.
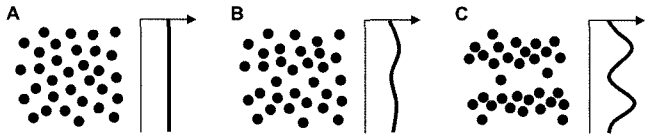
Fig. 5. Schematic illustration of droplet structures under shear. The direction of shear is either left to right or right to left. Droplet distribution profiles are also shown. A: at low shear, droplets are distributed homogenously. B: at moderate shear, ambiguous layers of droplets are formed causing slight segregation in droplet population. C: at high shear, discrete layers of droplets are formed.
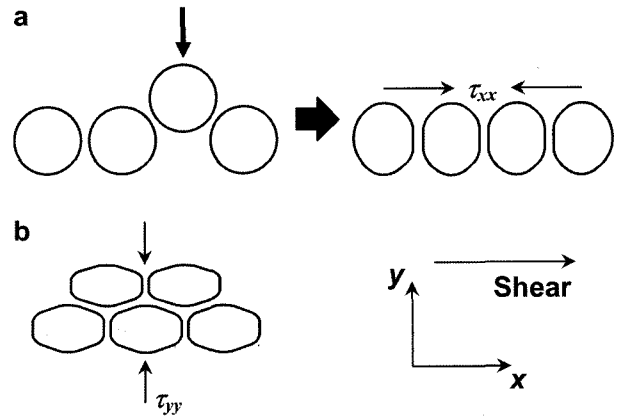

Fig. 6. Stress affecting on droplets under shear. a: a droplet is squeezed into a line of other droplets (left), inducing compressive stress in the direction of x-axis (right). b: droplets are compressed in the direction of y-axis due to hydrodynamic forces.

droplets are (a) repulsive and (b) attractive, and the behavior of the normal force contrasts as described above. Therefore, the currently investigated PDMS droplets are likely to be experiencing different structural evolution in comparison to those investigated by Montesi et al. (2004).

The "hesitation" of shear viscosity and anomalous behavior of N_1 seem to be common for polymer liquid crystals (e.g. Kiss and Porter, 1998). The anomalous behavior of N_1 is explained by formation of band structure perpendicular to the direction of shear, similar to that observed by Montesi et al. (2004). However, PDMS emulsions are unlikely to form liquid crystals, because of the isotropy and the surface fluidity of droplets.

3.4. Droplet structure evolution

By synthesizing the information extracted from Fig. 4, a mechanism for the shear-induced evolution of droplet structure is proposed, which is shown in Fig. 5. Here only centers of droplets are shown for clarity: each droplet is in contact with adjacent droplets with slight deformation in Fig. 5A. At the state of rest, droplets are randomly separated from each other and there is no macroscopic segregation in the droplet distribution (Fig. 5A). As the shear is applied, the droplets rearrange themselves into a geometrically preferred state, observed as the creeping behavior, then at a certain stress the droplet structure breaks down, which is represented by a decrease in G'/ω. The breakdown of droplet structure leads to formation of ambiguous layers (or clusters) of droplets (Fig. 5B), resulting in reduced viscosity. In order to form droplet layers, a droplet needs to be "squeezed in" to a line of other droplets, inducing a compression force within droplets stream-wise, i.e. in the x-axis direction (Fig. 6a). In this case $\tau_{xx} <$ 0 and $\tau_{yy} \approx 0$, therefore $\tau_{xx} - \tau_{yy} < 0$, where τ_{xx} and τ_{yy} are the stream-wise and transverse stress of droplets, respectively. Since the sign of F_N is the same as that of $\tau_{xx} - \tau_{yy}$ (Montesi et al., 2004), F_N exhibits a negative value for both PDMS (0.3) and PDMS(0.45). Once layers of droplets are formed, at the onset of the "refrain" region, the PDMS(0.3) droplets rearrange themselves within the layers to achieve a thermodynamically preferred geometry. Whereas, viscoelastic

PDMS(0.45) droplets may redistribute themselves within the layers in order to correct the stress imbalance, which was observed as recovery of F_N in Fig. 4b. If there is no redistribution of droplets within layers, there will be no "refrain": moderately concentrated emulsions form geometrically preferred droplet layers from the state of rest due to high flexibility of droplet structure and do not show the "refrain" behavior.

The end of the "refrain" region suggests that the rearrangement or the redistribution of droplets within layers has been completed, as was indicated by the F_N value for PMDS(0.45) returning to zero, and discrete layers of droplets are then formed (Fig. 5C). Formation of discrete layers eventually results in loss of elasticity, i.e. a sudden decrease in G'/ω, because there is no network of droplets remaining in the transverse direction. After this point, increased shear induces compression of droplet layers due to hydrodynamic interactions, enlarging the distance between layers and therefore resulting in the high magnitude of the shear thinning behavior. PDMS(0.3) droplets may readily comply with the compression force due to their high level of deformability, allowing further "squeeze in", maintaining negative F_N values. On the other hand, compression of firmly packed layers of PDMS(0.45) droplets requires transverse compression of droplets, i.e. $\tau_{yy} < 0$ (Fig. 6b). The stress acting on droplets stream-wise may be negligible, $\tau_{xx} \approx 0$. Therefore, at this state, $\tau_{xx} - \tau_{yy} > 0$ and the F_N values are positive. The layering and compression mechanism supports the observation that highly concentrated PDMS emulsions do not show shear thickening behavior at high shear rates (Fig. 1), because there will be no breakdown of layer structure.

It is worthy of note that PDMS(0.3) at $\phi = 0.722$ does not show the "refrain" behavior at all (data not included), indicating that the "refrain" behavior is highly sensitive to the

packing configuration of droplets, especially at volume fractions close to cubic or hexagonal close packing (= 0.74). This in return indicates that emulsions at a volume fraction of 0.7 have a droplet structure that is geometrically and thermodynamically unstable, resulting in the anomalously low γ_{co} values (Fig. 3b). This also indicates that the "refrain" behavior is not due to slip at the wall, which may result in double-sigmoidal shear viscosity curves (Barnes, 1995).

The shear rate range of the "refrain" region was $0.4\ \mathrm{s}^{-1} < \dot{\gamma} < 4\ \mathrm{s}^{-1}$ for PDMS(0.3) and $0.1\ \mathrm{s}^{-1} < \dot{\gamma} < 1\ \mathrm{s}^{-1}$ for PDMS (0.45), at the equivalent gap of 0.046 mm between the cone tip and the bottom plate (the gap is 0.85 mm at the edge). These shear rate ranges are consistent with the value observed for an emulsion of attractive droplets at a gap distance of 0.65 mm (Montesi *et al.*, 2004). Even though the mechanism of the "refrain" behavior is contrasting, the result indicates that breakdown and consecutive rearrangement of the droplet structure is a function of the shear rate and the gap distance, which may be determined by geometrical argument in relation to the droplet size. In the case of repulsive droplets it may be hypothesized that the gap distance affects the layer structure; this requires further investigation.

Despite the equivalent forms of the shear viscosity versus shear rate curves for emulsions of PDMS(0.3) and PDMS (0.45) at $\phi = 0.7$, the difference in droplet deformability resulted in differences in the normal force behavior. The normal force may be a useful measure in understanding the microscopic state of droplets in concentrated emulsions, especially for purely repulsive droplets where effects from aggregation or flocculation can be ignored.

4. Conclusion

Steady-mode rheological investigation on SDS stabilized PDMS emulsions revealed that droplet deformability plays an important role in controlling the shear thinning behavior. A "soft" emulsion was less shear thinning than a "hard" emulsion at low volume fractions, due to high level of structural flexibility. At high volume fractions, however, the "soft" emulsion exhibited "extra" shear thinning behavior, presumed due to lateral distortion of droplet structures. Dynamic rheological investigation has identified the elastic nature of both suspensions and emulsions of intermediate volume fractions at small strains, where "hard" (viscoelastic) droplets exhibited relatively high elasticity. At a high volume fraction, however, both "soft" and "hard" emulsions exhibited high elasticity due to formation of planar films between droplets. Combination of steady and dynamic rheological data enabled the depiction of the shear-induced evolution of droplet structure: perturbation and breakdown of droplet networks leads to formation of droplet layers, with rearrangement of droplets within the

layers at the intermediate stress range. Even though the shape of the shear viscosity curve of the "soft" emulsion was identical to that of the "hard" emulsion, difference in the state of droplet deformation was clearly observed as differences in the normal force behavior.

Acknowledgement

List of Symbols

d	: diameter
F_N	: normal force
G'	: elastic modulus
G'_0	: zero shear elastic modulus
G''	: viscous modulus
G^*	: complex modulus
M	: molarity (mol dm^{-3})
n_{PL}	: power-law index
N_1	: first normal stress
ϕ	: volume fraction
ϕ_g	: colloidal glass transition volume fraction
ϕ_{rcp}	: random close packing volume fraction
γ	: strain
γ_{co}	: G'/G'' crossover strain
γ_{cr}	: critical strain
$\dot{\gamma}$	: shear rate
ζ	: zeta potential
η	: viscosity
η^*	: complex viscosity
ρ	: density
σ	: interfacial tension
τ	: shear stress
τ_{xx}	: stream-wise stress
τ_{yy}	: transverse stress
ω	: angular frequency

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