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SHORT COMMUNICATION

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Yield stress and viscoelastic properties of high internal phase ratio emulsions

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Abstract The rheology of high internal phase ratio oil-in-water emulsions was investigated using a controlled-stress rheometer. The dispersed-phase (oil) concentration was varied from 71.24 to 89.61% by volume. Three different types of rheological experiments were conducted for each emulsion, namely: steady shear, oscillatory shear, and creep/recovery experiments. All the emulsions investigated in this study possess a yield stress. The yield-stress values obtained from different rheological experiments for the same emulsion show good agreement with each other. The yield-stress value increases exponentially with an increase in the dispersed-phase concentration. The yield-stress data of this study can be described quite well with the Princen and Kiss equation for high internal phase ratio emulsions provided that the thickness of the interdroplet films is taken into account. For any given emulsion, the storage modulus, measured in the linear viscoelastic region, is found to be constant, independent of the frequency, indicating a solid-like behaviour. The value of the storage modulus increases with an increase in the dispersed-phase concentration. The storage modulus data are interpreted in terms of the Princen and Kiss equation.

Key words Emulsion – Rheology – Viscoelastic – Yield stress – Concentrated emulsions

Introduction

Emulsions are dispersions of two immiscible liquids, such as oil and water. Emulsions also contain a third component, called the emulsifying agent or emulsifier, which has two principal functions:

1. To decrease the interfacial tension between oil and water.
2. To stabilize the droplet against coalescence once it is formed.

When the volume fraction of the dispersed phase (ϕ) of the emulsion exceeds the maximum packing volume fraction ($\phi_{\max}$, where the droplets just touch each other), the emulsion is referred to as a high internal phase ratio emulsion (HIPRE).

The dispersed droplets of the emulsions are generally of spherical shape when ϕ is less than $\phi_{\max.}$ When ϕ is greater than $\phi_{\max}$, the droplets are no longer spherical; they are deformed against their neighbors and take the shape of a polyhedron. The rheological properties of the HIPREs are governed by a three-dimensional interconnected network structure of thin liquid films of continuous phase. When such highly concentrated emulsions are subjected to small shear deformation, they exhibit a strong elastic response (characterized by a high value of the storage modulus); they also exhibit a yield stress.

While a substantial amount of literature has been published on the rheology of dilute and moderately concentrated emulsions [1–9], little attention has been given to HIPREs. Princen [10] carried out a theoretical analysis of the rheology of model emulsions of high internal phase ratio. He assumed the emulsion to be composed of long cylindrical drops of uniform size. For such two-dimensional cylindrical systems, he developed the following relations for the yield stress (τ_0) and the static shear modulus (G):

$$\tau_0 = 1.05 \frac{\sigma \cos\theta}{R} \phi^{1/2} F \tag{1}$$

$$G = 0.525 \frac{\sigma \cos\theta}{R} \phi^{1/2} \ , \tag{2}$$

where σ is the interfacial tension, θ is the contact angle associated with the thin films separating adjacent droplets, R is the radius of undeformed cylindrical droplets, ϕ is the volume fraction of the dispersed phase, and F is a dimensionless parameter that depends on both ϕ and θ. In deriving Eqs. (1) and (2) the thickness of the interdroplet films was considered to be negligible. The equations indicate that both the yield stress and the static shear modulus increase with a decrease in the droplet radius. Also, the yield stress and the static shear modulus are both proportional to the interfacial tension and they both increase with an increase in the dispersed-phase concentration (ϕ).

For real emulsions of polyhedral droplets, Princen and Kiss [11–12] proposed the following empirical relations for the yield stress and the static shear modulus:

$$\tau_0/(\sigma/R) = \phi^{1/3}[-0.08 - 0.114 \log_{10}(1-\phi)] \tag{3}$$

$$G/(\sigma/R) = 1.769 \phi^{1/3}(\phi - 0.712) \ , \tag{4}$$

where R is the Sauter mean radius of an emulsion. As the thickness of the films separating individual droplets was negligible in the case of the emulsions investigated by Princen and Kiss [11–12], the above equations are valid for emulsions with negligible interdroplet film thickness. According to Princen [10], the effect of a finite film thickness can be taken into account by using the effective volume fraction (ϕ_{eff}) of the dispersed phase (instead of the true volume fraction ϕ) in the above equations. The relationship between ϕ_{eff} and ϕ is given by [11]

$$\phi_{\mathrm{eff}}^{-1/3} = \phi^{-1/3} - 1.105 \frac{h}{D} \ , \tag{5}$$

where h is the film thickness and D is the average droplet diameter.

Princen and Kiss [11–12] developed their empirical equations, Eqs. (3) and (4), on the basis of a limited amount of experimental data. For example, the yield-stress equation (Eq. 3) was developed on the basis of only seven data points involving oil-in-water (O/W) emulsions. The shear modulus equation, Eq. (4), was developed on the basis of eight data points. Thus, it is not clear if these equations have broad applicability.

This article reports new results on the rheology of HIPREs. Steady shear, oscillatory shear and creep/recovery measurements are carried out on a series of highly concentrated O/W emulsions. The yield stress is determined from and compared for different measurements. The experimental data for yield stress and storage modulus are interpreted in terms of the Princen and Kiss equations (Eqs. 3, 4).

Experimental

Materials

The O/W emulsions were prepared using odourless kerosene supplied by Fisher Scientific. The viscosity of the kerosene batch used in the present study was 1.5 mPa s at 25 °C. The surfactant used for the preparation of emulsions was Triton X-100, a commercially available nonionic surfactant manufactured by Union Carbide Chemicals & Plastics Technology Corporation, USA. Triton X-100 is an octylphenol ethoxylate with an average of 9–10 molecules of ethylene oxide. It is water-soluble and has a high hydrophile–lipophile balance value of 13.5. The water used throughout the experiments was deionoized.

Methods

A series of eight O/W emulsions of identical droplet size but varying dispersed-phase concentration (ϕ) was prepared by dilution of a parent emulsion ($\phi = 0.8961$) with a continuous phase. The parent emulsion was prepared by shearing together known amounts of the continuous and dispersed phases in a homogenizer (Gifford Wood, model 1-L) at room temperature. The continuous phase was an aqueous solution of 5.58 wt% Triton X-100.

All the rheological measurements were carried out at 25 °C in a Bohlin controlled-stress rheometer (Bohlin CS-50). For any given emulsion, the steady shear, oscillatory shear and creep/recovery data were collected. The data were collected using a serrated parallel-plate geometry. The serrated parallel-plate geometry consisted of a stainless steel upper plate (diameter 25 mm) and an aluminium lower plate (diameter 40 mm). The gap width between the plates was 1 mm.

The droplet size of the parent emulsion was determined from photomicrographs. The sample was diluted with the same continuous phase before taking the photomicrographs. The photomicrographs were taken with a Zeiss optical microscope equipped with a camera. About 1000 droplets were counted to determine the droplet size distribution and mean droplet size. The droplet size distribution of the emulsion is shown in Fig. 1: the Sauter mean diameter was 2.83 μm. The interfacial tension between the oil and surfactant solutions (5.58 wt% Triton X-100) was measured using the drop-volume (drop-weight) method: its value was 0.77 mN/m.

Results and discussion

Steady shear results

When HIPREs are subjected to a shear stress below a certain critical value (yield stress), they exhibit very small deformation rates indicating creeping behavior. Upon increasing the shear stress above the critical value, a large increase in shear rate is observed indicating fracturing of the material. The typical shear rate versus shear stress behavior of a highly concentrated O/W emulsion is shown in Fig. 2a. The yield stress is indicated by a vertical segment of the shear rate versus shear stress plot.

The effect of the dispersed-phase concentration (volume fraction of dispersed phase, ϕ) on the shear rate–shear stress behaviour of HIPREs is shown in Fig. 2b. For the sake of clarity, the creeping portion of the data is not shown. Clearly, the yield stress increases with an increase in the dispersed-phase concentration.

The effect of aging (storage time) on the steady shear data of emulsions was also examined by collecting data after about 24 days. The emulsions were found to exhibit a negligible change in the rheological properties over a storage period of 24 days.

Oscillatory shear results

The stress sweep data for fresh O/W emulsions at different dispersed-phase concentrations are shown in Fig. 3. The stress sweep data were collected at a frequency of 0.1 Hz. The storage modulus versus stress plots exhibit a linear response (constant value of the storage modulus independent of the stress) up to a certain critical shear stress (yield stress). With further increase in shear stress, the storage modulus drops sharply. The yield stress where a sharp reduction in storage modulus occurs, increases with an increase in the volume fraction of the dispersed phase (ϕ).

The effect of storage time (aging) on the stress sweep response of emulsions was also examined. The emulsions exhibited negligible deterioration (aging) over a storage period of about 24 days.

The frequency sweep data, that is, storage modulus versus frequency, are shown in Fig. 4 for differently concentrated O/W emulsions. These data were collected at a shear stress well within the linear viscoelastic region. The storage modulus is constant independent of the frequency indicating a solid-like behavior of the emulsions. The magnitude of the storage modulus increases with an increase in the volume fraction of the dispersed phase. Like other rheological data (steady shear, stress sweep), the frequency sweep data undergo negligible change over a storage period of 24 days.

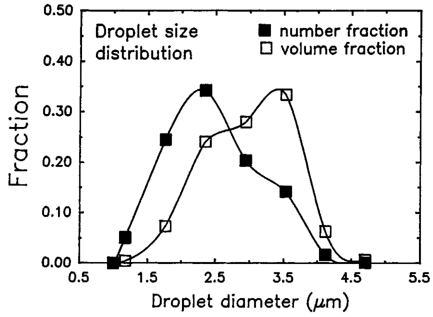

Fig. 1 Droplet size distribution of the emulsion

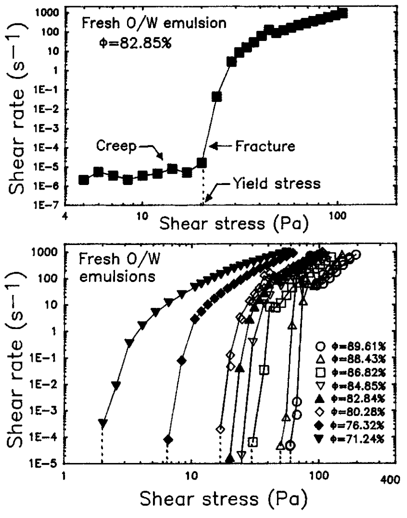

Fig. 2 Shear rate versus shear stress data for differently concentrated oil-in-water (O/W) emulsions

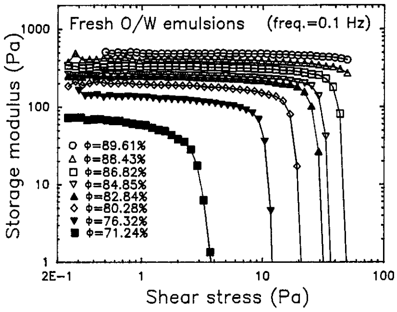

Fig. 3 Stress sweep oscillatory data for fresh O/W emulsions at different dispersed-phase concentrations

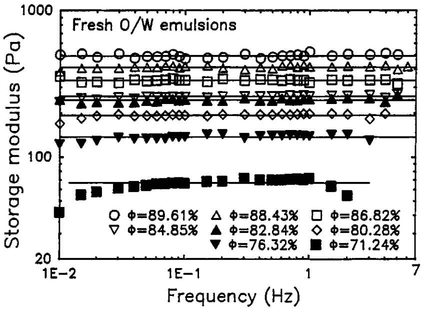

Fig. 4 Storage modulus versus frequency data for differently concentrated O/W emulsions (in the linear viscoelastic region)

Creep/recovery results

The creep/recovery behavior of fresh emulsions at different oil concentrations (ϕ) is shown in Fig. 5. The compliance, defined as the ratio of strain to stress, is plotted as a function of time. The creep/recovery experiments were conducted as follows. A constant shear stress of 2 Pa was applied to the emulsion sample and the resulting strain was monitored as a function of time. The imposed stress was suddenly removed after 500 s and recovery, on release of the stress was monitored for another 500 s. Figure 5 indicates that emulsions are highly elastic in nature. They all exhibit an instantaneous elastic compliance and a recoverable compliance. The value of the creep compliance decreases with an increase in the volume fraction (ϕ) of the dispersed phase. The percentage recovery in compliance, upon removal of the stress, increases with an increase in ϕ.

The effect of stress on the creep/recovery behavior of a highly concentrated emulsion ($\phi = 0.8961$) is shown in Fig. 6. At low stresses (2, 10 Pa), the emulsion exhibits a fixed creep compliance and when the stress is removed, the recovery is nearly complete. At intermediate stresses ($20\ \text{Pa} \leq \tau \leq 60\ \text{Pa}$), the emulsion exhibits a fixed creep compliance but the recovery in compliance upon the removal of the stress is partial. Note that creep compliance increases whereas recovery decreases with an increase in shear stress. At a shear stress of 70 Pa, the compliance increases dramatically with time indicating fracture or breakdown of the emulsion microstructure. Thus, the yield stress for this emulsion is close to 70 Pa, which is approximately the same as that obtained by steady shear data (see Fig. 2).

Yield stress and storage modulus correlations

The yield stress of emulsions is determined from and compared for different experiments such as steady shear, stress sweep and creep experiments. The yield stress data as a function of dispersed-phase concentration (volume percent of oil) are shown in Fig. 7. The yield-stress values obtained from different experiments for the same emulsion show good agreement with each other. Also, the yield stress increases exponentially with an increase in the dispersed-phase concentration.

Figure 7 also compares our yield stress data with the Princen and Kiss [12] equation (Eq. 3). The dimensionless group $\tau_0/(\sigma/R)$ is plotted as a function of volume fraction of the dispersed phase (ϕ). The Princen and Kiss equation underpredicts the yield-stress values; one

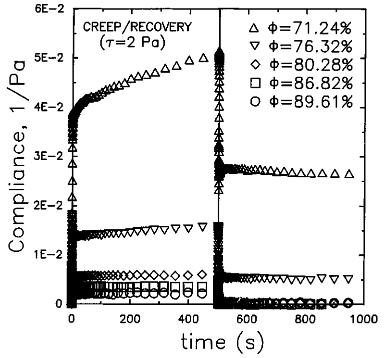

Fig. 5 Creep/recovery behavior of fresh emulsions at different dispersed-phase concentrations (ϕ)

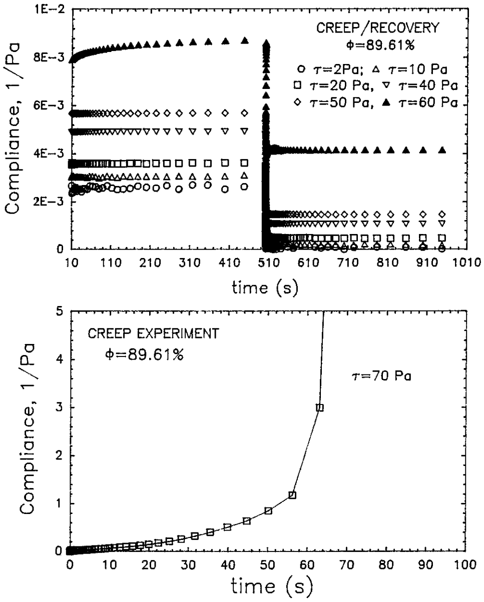

Fig. 6 Effect of shear stress on the creep/recovery behavior of a highly concentrated emulsion ($\phi = 0.8961$)

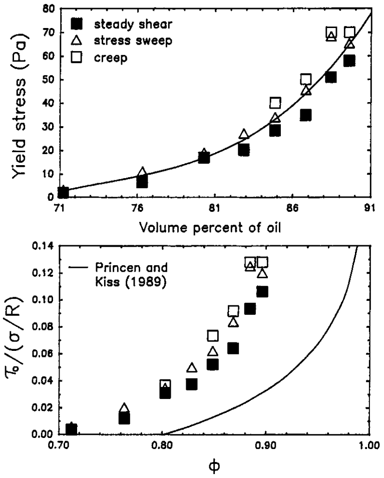

Fig. 7 Yield stress data of emulsions

possible reason for this discrepancy is that the effective volume fraction of the dispersed phase may be significantly higher than the actual volume fraction of our emulsions because of the finite interdroplet film thickness. Note that the Sauter mean diameter of the emulsions investigated in the present work (2.83 μm) is much smaller than the Sauter mean diameter of the emulsions investigated by Princen and Kiss (20.55 μm). According to Eq. (5), a smaller droplet diameter results in a larger effective volume fraction for the same ϕ and film thickness. Plots of $\tau_o/(\sigma/R)$ versus ϕ predicted from Eq. (3) using the effective volume fraction, ϕ_{eff} (Eq. 5) are shown in Fig. 8. As can be seen, our experimental data show excellent agreement with Eq. (3) provided that the interdroplet film thickness is taken to be 0.09 μm.

The storage modulus data of the emulsions as a function of the dispersed-phase concentration are shown in Fig. 9. As expected, the storage modulus increases with an increase in the volume fraction of the dispersed phase. Figure 9 also compares our storage modulus data with the Princen and Kiss equation (Eq. 4). The dimensionless group $G'/(\sigma/R)$ is plotted as a function of ϕ. The Princen and Kiss equation underpredicts the modulus values. The same situation was encountered in the case of yield-stress prediction. The underprediction of modulus values is again due to the fact that the effective volume fraction of the dispersed phase may be significantly higher than the actual volume fraction because of the finite interdroplet film thickness. A comparison between our experimental data and the curves predicted from Eq. (4) using the effective volume fraction (Eq. 5) is shown in Fig. 10. Clearly, the agreement between our data and Eq. (4) improves substantially when the film thickness is increased from 0 to 0.09 μm, the value determined from the analysis of the yield-stress data; however, at high values of ϕ, the experiment data still fall somewhat above the values predicted by Eq. (4) with $h = 0.09$ μm. One possible reason for this deviation is that the constants in Eq. (4) (1.769, 0.712) are not universal constants: they may vary from one system to another.

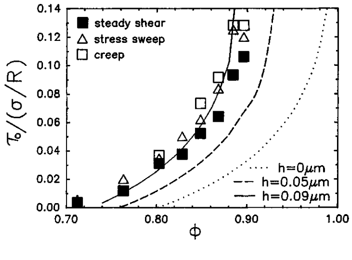

Fig. 8 Yield stress predicted from the Princen and Kiss equation using the effective volume fraction

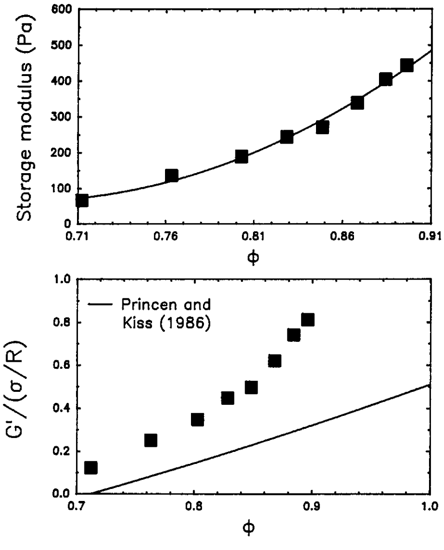

Fig. 9 Storage modulus data of emulsions

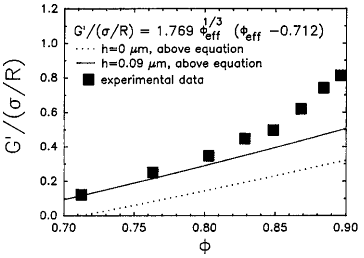

Fig. 10 Storage modulus predicted from the Princen and Kiss equation using the effective volume fraction

Conclusions

Based on the experimental results and analysis, the following conclusions can be made:

1. The steady shear results indicate that up to a certain critical shear stress (i.e. yield stress), the HIPREs exhibit a creeping behavior with negligibly small shear rates. Upon increasing the shear stress slightly above the yield stress, a large increase in the shear rate is observed, indicating fracturing of the material.
2. With an increase in the shear stress during oscillatory shear measurements, the storage modulus initially remains constant up to a certain critical shear stress (yield stress). With further increase in shear stress, a dramatic decrease in the storage modulus occurs.
3. The storage modulus of HIPREs, measured in the linear viscoelastic region, is constant independent of the frequency, indicating a solid-like behavior; however, the storage modulus increases with an increase in the volume fraction of the dispersed phase.
4. Creep/recovery experiments indicate that the emulsions are highly elastic in nature at shear stresses

below the yield value. At low shear stresses, emulsions exhibit a significant recovery in compliance upon the removal of shear stress. At shear stresses above the yield value, the creep compliance exhibits a dramatic increase with the duration of the application of stress. Also, the recovery in compliance upon the removal of stress is zero.

5. The rheological properties of HIPREs investigated in the present study show negligible aging effects over a storage period of about 24 days.
6. The yield-stress values obtained from different rheological experiments (steady shear, oscillatory shear, creep) for the same emulsion show good agreement with each other. The yield stress increases exponentially with the increase in the dispersed-phase concentration.
7. The Princen and Kiss equations are found to underpredict the yield-stress and storage modulus values of our emulsions. This deviation is believed to be due to the finite interdroplet film thickness. The modified Princen and Kiss equations where an effective volume fraction of the dispersed phase is used instead of an actual volume fraction are found to describe our experimental data reasonably well.

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