

STRUCTURE FORMATION IN MICRO-CONFINED POLYMERIC EMULSIONS

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Introduction

Application of a shear field to a concentrated emulsion induces a complex spatial and temporal response (1-3). Typically, the behavior of these materials under shear is considered as a problem in emulsion rheology, and the behavior of a concentrated system is treated as an extrapolation of the well-understood behavior of isolated droplets (or of the behavior of two droplets). However, in order to fully understand the behavior of a concentrated system (many droplets) it may be necessary to invoke concepts from other fields, in particular non-equilibrium pattern formation in dissipative systems that are driven far from equilibrium.

In the present work, we present results of concentrated solutions under shear, with particular emphasis on the case that the emulsion is micro-confined. When the size of a typical droplet is comparable to the gap width between the shearing plates, we observe interesting non-equilibrium pattern formation of the collective behavior. We present three results in which spontaneous structures emerge in the system; string formation, the pearl necklace structure and droplet layering.

Background. The size and morphology of the dispersed component is determined during material processing and is crucial to the final physical properties; for example fibers can provide great enhancements in unidirectional strength, sheet structures can possess ultra-low permeability and spherical inclusions provide impact resistance. The fundamental understanding of the dispersion mechanism comes from the works of Taylor and others who have shown the ratio of the viscous to interfacial stresses on a droplet, i.e. the capillary number (Ca), determines its stability in a shear field (1-3). For the case considered here of (roughly) equal viscosity between droplet and matrix, there is a critical capillary number; droplets in a shear field with $Ca < 0.5$ will remain stable whereas those with $Ca > 0.5$ will elongate and break up.

Experimental

The shear-induced structures are generated by placing the sample in between two parallel quartz disks (Figure 1) and rotating one at a controlled rate. Stroboscopic optical microscopy is utilized to visualize the structures and the data is recorded onto videotape for subsequent analysis. The minority component is Polydimethylsiloxane (PDMS), used at a mass ratio typical of industrial polymer processing, and the majority component is Polyisobutylene (PIB). Both components are fairly Newtonian (constant viscosity) for the shear rates used here and are nearly matched in viscosity; and at room temperature. The materials are weighed, blended, and loaded into the quartz shear cell.

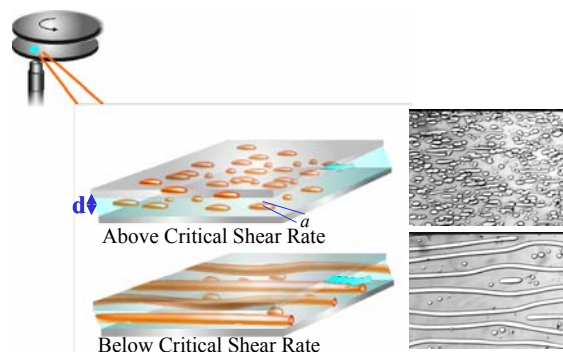


Figure 1. Typical structure of the droplets in the shear field for the cases above and below the critical shear rate. Left side is artist's rendition; right side is video-micrographs.

A summary of the observed structures as a function of shear rate and mass fraction of the dispersed component is shown as a "morphology diagram" in Figure 2. This plot shows four distinct morphologies that have been observed. In the upper right quadrant is the two layer structure, in which two planes of droplets exist that slide over each other. In the lower right section is the string structure, in which a massive coalescence of droplets creates string-like structures. In the left side of the diagram (low mass fraction), the mass fraction is so low that only a single layer of disordered droplets is observed. At intermediate shear rate and composition, the pearl

necklace state is observed.

String Structures. The typical experimental procedure is to decrement the shear rate in 20% (or less) intervals and wait for system equilibration (minimum wait time is two hours). For sufficiently high shear, approximately three layers of droplets exist between the disks, (as determined by monitoring the velocity of the droplets in the video image.) As the shear rate is decreased, the size of the droplets increases so that only two layers of droplets fits between the disks; then only one layer fits. We observe the unexpected droplet-string transition upon further decrease of the shear rate. Figure 1 shows that the droplets have coalesced into very long strings.

The kinetics of the droplet-string transition upon reduction of shear proceeds in four stages. In the first stage, the shear is reduced from a point just above the transition to a point below it. In the first regime, there is an increase in the average droplet size. In the second regime, the large droplets self organize into pearl necklace like chains. Eventually, the aligned droplets coalesce with each other to form strings. The strings then coalesce with each other. In the rotating disk geometry, the strings are concentric arches about the axis of rotation. In some cases, they actually form into closed ring structures. In summary, this four stage process transforms droplets with typical volume $\sim (30 \mu\text{m})^3$ into strings with typical dimensions $(30 \mu\text{m} \times 125 \mu\text{m} \times 75,000 \mu\text{m})$, an increase by 4 orders of magnitude.

We measure the sharpness of the transition by taking advantage of the linear increase in shear-rate as a function of radial distance from the axis of rotation. Thus, eight hours after applying a shear rate known to be near the transition, we quickly translate the objective lens in the radial direction. Subsequently, we seamlessly link together images taken at different radial positions. We observe droplets at higher shear towards the top of the image and strings at lower shear towards the bottom. This way we find the width of the transition region between droplets and strings. We find that the width of the transition region is as small as 2% in shear rate. The sharpness of the transition indicates that it is useful to consider the steady state structure diagram as roughly analogous to an equilibrium phase diagram.

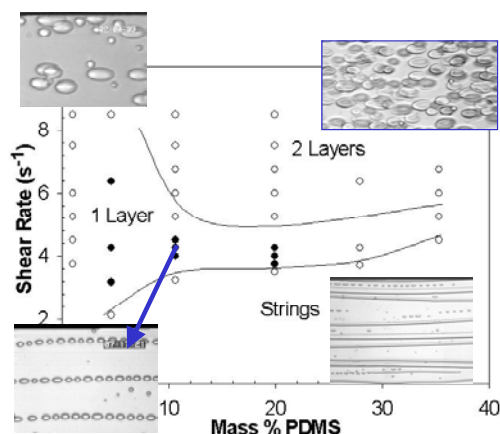


Figure 2. Morphology diagram showing the four steady state morphologies that have been observed as a function of shear rate and composition. In the one layer state, the open circles correspond to a disordered (in-plane) structure and the closed circles correspond to the pearl necklace structure.

Pearl Necklace. A key step in the kinetics of the transformation from dispersed droplets to strings is the transient pearl necklace structure. Chaining of solid particles has been observed in sedimentation and shear flow but has not been reported previously when the dispersed phase is a fluid. In the case of shear and sedimentation, chaining is only observed when the suspending fluid is visco-elastic, i.e. it generates large normal forces under shear. It was shown that the strong viscosity redistributions that occur for a sphere moving in a non-Newtonian fluid relative to a Newtonian one cause an attractive interaction between spheres that can cause them to line up. In our case, both fluids are Newtonian and clearly there is no attractive interaction when the droplets are much smaller than the gap width. We speculate that the walls distort the velocity fields when the droplet size is comparable to the wall dimension enough to cause an attractive interaction.

The formation of highly ordered pearl necklace-like chains of particles (shaded data points in Fig. 6) is observed in the one layer state for emulsions containing 5 % to 20 % PDMS. Other data points in the one layer state (e.g., for 1 % PDMS and 35 % PDMS, which have not been shaded in Fig. 6), correspond to a disordered one-layer microstructure. Data on the 5 % PDMS emulsion at higher shear rates ($\dot{\gamma} = 8.5, 10.8, 13.3, 15.0$ and 17.0 s^{-1} ; some data not shown in Figure 2), show a one layer disordered microstructure – this system does not show a two-layer state at any of the shear rates investigated.

Optical micrographs of a 5 % PDMS emulsion showing disordered microstructure at $\dot{\gamma} = 8.5 \text{ s}^{-1}$ and pearl necklace arrangement at $\dot{\gamma} = 4.25 \text{ s}^{-1}$. While at a 28% mass fraction of PDMS, the formation of the necklace structures was only seen as a transient state during a study of the droplet-string transition kinetics, we find that at lower mass fraction the pearl-necklace morphology is a stable (non-transient) steady state, persisting for timescales on the order of several days without showing a transition to any other state. Although this is the first reported observation of pearl-necklace formation in suspensions where the dispersed phase is made of deformable fluid droplets, there have been related observations (discussed above). In hard-sphere suspensions necklace formation has been observed when the matrix fluid is viscoelastic. In our system, the component fluids are Newtonian, with no measurable normal stresses. Further, while interfacial elasticity certainly contributes to normal stresses in an emulsion, our steady shear rheology experiments detect no measurable first normal stress difference in our emulsions.

Finally, at the lowest shear rates, droplets in the one layer state coalesce to form strings. Strings and droplets co-exist at the lowest shear rate studied for each composition. A “dilute” (1% PDMS) emulsion did not form strings and only showed a single layer disordered microstructure, due to the low concentration of droplets. The threshold shear rate at which strings first form in the system increases somewhat with increasing composition. This result may be understood qualitatively on the basis of an increase in droplet size and also in the increase in the number density of droplets with composition. As the concentration of the droplet phase in the emulsion increases, this limiting r/d is attained at higher shear rates, leading to an increase in the threshold shear rate with composition.

Layering. A qualitative observation of the video of the droplets under flow indicated that the droplets may be layered, i.e., it appeared that their could be two or three layers of droplets and that the layers were effectively sliding over each other. In order to quantitative this observation, we present results from droplet velocimetry measurements. If the droplets were uniformly dispersed in the matrix, then a histogram of the velocities would be a flat. However, if the droplets were layered, then the velocity histogram would have peaks.

Figure 3 shows the results for two different shear rates; the higher shear rate being the two-layer structure (also see Fig. 2) and the lower shear rate is the one layer structure. The presence of a bimodal structure is clearly observed in the histogram. The layered structure (and the transitions) occurs due to an interplay of three considerations. First, there is a force on the droplets which causes them to migrate towards the center plane (4). Second, as droplets collide, they tend to drive each other away from the center plane (5). Third, as the droplets become larger (upon lowering of the shear rate) there are packing consideration. Only a finite number of droplets can fit into a given plane.

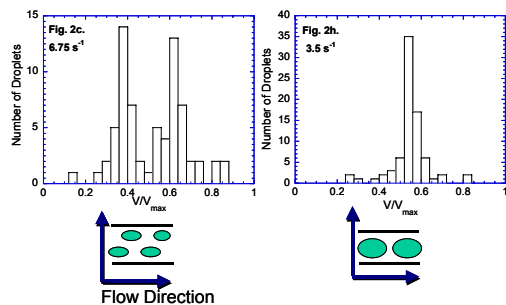


Figure 3 Histograms of the velocity distribution in the two-layer state (left) and the one-layer state (right).

Conclusions

We have observed a number of new structures upon shearing of concentrated emulsions in the case where the typical droplet size is comparable to the gap width. These non-equilibrium structures emerge as a result of hydrodynamic interactions between droplets coupled with the fact that the droplets can coalesce and break up.

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