

RHEOLOGY AND MICROSTRUCTURE OF SHEAR THICKENING FLUID SUSPOEMULSIONS

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ABSTRACT:

A novel shear thickening suspoemulsion is formulated and studied with a new rheo-microscope instrument. The experimental fluid system is comprised of a immiscible blend of Newtonian, low molecular weight poly(dimethylsiloxane) and a shear thickening suspension of colloidal silica in poly(ethylene glycol). The blend is studied as a function of composition where phase inversion is evident at low shear rates and is found to be shear rate dependent. A shear thickening viscosity curve is observed when blends comprised of shear thickening fluid dispersed as droplets are subjected to high shear rates. Dispersing a continuously shear thickening fluid, $\phi_{silica} = 0.42$, results in continuously shear thickening response from the blend. Dispersing a discontinuously shear thickening fluid, $\phi_{silica} = 0.51$, results in bulk shear thickening that can also be discontinuous. Shear thickening in the final suspoemulsion is consistently first detected at $\phi_{STF} = 0.2$, with the magnitude of shear thickening being dependent on the particle concentration in the STF phase. The onset of shear thickening also corresponds with the formation of extended droplet structures in the fluid. The complex properties of these suspoemulsions and the ability to formulate dispersed droplet morphologies in this mixture are shown to result from the underlying shear thickening rheology of the dispersed phase.

KEY WORDS:

shear thickening, suspensions, emulsions, suspoemulsions, rheo-microscopy, thixotropy

1 INTRODUCTION

Suspension emulsions, or suspoemulsions, are mixtures of two fluids where the dispersed phase is a suspension of solid particles in a suspending medium. Suspoemulsions are industrially relevant as they are used by the agricultural, personal care, and pharmaceutical industries [1, 2]. Many of these formulations use high concentration colloidal suspensions so it is important to understand how mixtures of Newtonian and non-Newtonian fluids behave under flow. The goal of this work is to examine the rheological behavior of a novel suspoemulsion comprised of a Newtonian poly(dimethyl siloxane) (PDMS) fluid melt blended with a non-Newtonian shear thickening fluid (STF). This is achieved by performing stress controlled rheological measurements simultaneous with measurements of the blend microstructure during shear using a novel rheo-microscope. The use of simultaneous microstructure and rheology measurements is necessary as the properties of the STF suspoemulsion depend strongly on the dispersion morpholo-

gy, which is in turn greatly affected by preparation and flow history. This study seeks to qualitatively and quantitatively describe these relationships to develop a better understanding of the fundamental physics required to effectively formulate complex fluid suspoemulsions for targeted applications.

The shear thickening response of colloidal dispersions has been a topic of considerable recent interest in both industrial and academic research. The shear thickening behavior of concentrated particle suspensions and the underlying microstructural mechanisms for the shear thickening have been studied extensively using simulations, [3–5] optical techniques, [6, 7] and neutron scattering techniques, [8–14] as well as rheo-microscopy [15]. The history of and underlying mechanisms for shear thickening in concentrated suspensions has been recently reviewed [16, 17]. The viscosity of shear thickening fluids (STFs) do not monotonically increase with shear stress or shear rate, as the name would superficially suggest. Rather, the viscosity of a STF decreases throughout the low shear stress regime

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tonian homopolymer can exhibit significant bulk shear thickening at volume fractions as low as $\phi_{STF} = 0.3$, whereas suspoemulsions made from the weakly continuous shear thickening fluid do not show significant shear thickening. Thus, the presence of a strong shear thickening response in the STF is necessary for observed a shear thickening response in the suspoemulsion.

For the suspoemulsion blended with the discontinuously shear thickening fluid, below $\phi_{STF} = 0.3$ three regimes are observed in the rheology: a viscosity plateau in the limit of low shear stress, a shear thinning regime, and a shear thickening regime at stresses above the critical shear stress of the pure STF. The rheo-microscopy shows that for all STF suspoemulsions tested, coalescence is significant system wide during the shear-thinning regime. At low to moderate STF content, a thread-like phase was observed under flow near the viscosity minimum. These threads break-up in to droplets in the thickening regime with increasing applied shear stress increases. The implication of this is that a well dispersed droplet morphology can be restored for these suspoemulsions by imposing a shear stress sufficiently high so as to be in the shear thickening regime of the STF dispersed phase (on the order of 1000 Pa for the suspoemulsions discussed here). For blends with $\phi_{STF} > 0.4$ behavior closer to that of the pure STF is observed at all shear rates.

The limited modeling analysis shows that simple, phenomenological viscosity models can qualitatively describe the behavior of the shear thickening suspoemulsion. The modified polymer emulsions model captures the qualitative behavior for the dilute suspoemulsions, providing a reasonable prediction of the stress necessary to achieve shear thickening in the suspoemulsion. For STF loadings above $\phi_{STF} = 0.3$ volume fraction, the fluidity-additivity model describes the qualitative features of the viscosity vs. shear stress curve between 0.1 and 1000 Pa. However, this model incorrectly predicts a viscosity plateau below 0.1 Pa for suspoemulsions with $\phi_{STF} = 0.4$ to 0.7 STF as it does not account for the co-continuous microstructure observed in the rheo-microscope. These approaches are useful for guiding formulations of novel STF suspoemulsions for specific applications.

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