FUNDAMENTAL CHARACTERIZATION OF "STRUCTURED" FIBRID SUSPENSIONS

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ABSTRACT

Aramid fibrids are believed to form microstructures in suspensions at very low loading levels (~0.5%) because of the "space-filling" nature of their shapes and thus provide a convenient means of introducing yield stress behavior for various commercial applications. The effect of fibrid shape, concentration and medium (corn syrup/water) viscosity on the dynamic, steady and transient shear responses was determined using a parallel plate geometry.

KEYWORDS: NOMEX® FIBRIDS, STRUCTURED SUSPENSIONS, DYNAMIC YIELD STRESS, THIXOTROPY

INTRODUCTION

Nomex® aramid particulates like fibrids induce yield stresses in various suspensions by the addition of very small amounts (~0.5%) for potential applications such as sealants, adhesives, roofing and roof coatings, thick film coatings, aqueous latex paints and caulks; fumed silica behaves similarly. The desired properties for these applications include a high viscosity (or yield stress behavior) at low shear rates for sag or slump resistance and a low viscosity at high shear rates for good processability in operations like mixing, pumping, painting and spraying. These characteristics are a result of the rectangular platelet shape of these fibrids (~100x100x0.1 μm) which is rarely approached in most situations because of their tendency to form coils (see Figure 1). In addition, these additives also impart other properties like reinforcement, chipping resistance and surface finish because of the chemical nature of the Nomex® polymer (poly(isophthaloyl-chloride/meta-phenylene-diamine)).

Fibrids with three different morphologies were used to prepare "structured" suspensions and dynamic, steady shear and transient responses of these suspensions were investigated comprehensively. The roles of fibrid properties, fibrid concentration and the dispersion medium viscosity were evaluated. The results were correlated with suspension microstructure and dispersability which are critical aspects in their commercialization.

EXPERIMENTAL DETAILS

Three Nomex® fibrids with different morphology were used in this work which are referred to as F10, F20 and F25 as per DuPont terminology; the increasing number reflects increasing levels of mechanical work done on the fibrids in a refining process. The fibrids were provided in wet form with varying water content which were then suspended in a commercial grade corn syrup; the corn syrup was diluted with different levels of water to obtain varying levels of Newtonian behavior (7.4, 2.45 and 0.70 P for water concentrations of 7.1, 13.8 and 23.9 % respectively at 25 C). Three weight concentrations (0.18%, 0.54% and 0.80%) were considered for each fibrid shape and viscosity level so that a total of 27 formulations were studied.

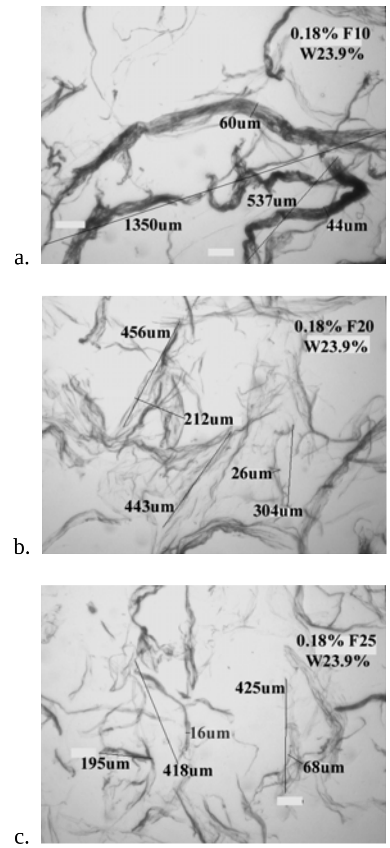

Figure 1. Typical images of 0.18% fibrids dispersed in corn syrup with 23.9% water ; a: F10, b: F20, c: F25.

To facilitate dispersion, the fibrids were separated by hand and then dispersed at high concentration (1.2%) in pure corn syrup (with a viscosity of 39.1 P) for 3 minutes using an Arrow 1750 motorized stirrer to form a master solution. The dispersion quality was verified by visual inspection under a microscope. A masterbatch of 1400 gm was prepared for each type of fibrid from which the various test solutions were prepared in 150 gm quantities by thinning down with water by high shear stirring for 2 minutes. The prepared suspensions were allowed to sit for one week to eliminate air bubbles. Typical pictures of the three fibrids at one concentration are shown in Figure 1. The F20 fibrids are seen to be more uniformly distributed and "space-filling" than the other types.

Dynamic, transient and steady shear data were obtained on a Rheometrics RMS 800 instrument using parallel plate fixtures at 25 C. Normal stresses were not considered in view of their arbitrary behavior and a failure to reflect any clear trends. Slip effects were effectively eliminated by moving to large gaps (a 1.5 mm gap was used). Evaporation effects were minimized by using a thin coating of low viscosity vegetable oil. Loading and initial structure effects were eliminated by subjecting the sample to multiple strain sweeps (2 - 200%) at a fixed frequency of 1 rad/s. In steady shearing experiments, pre-shearing at 0.5 1/s for 1 minute was found to be essential to provide reproducible results.

Essentially constant stress values were obtained after two strain sweeps; a three-run consecutive strain sweep was therefore adopted for all samples to eliminate residual structure effects and to get reproducible results. The dynamic moduli did not attain a constant value even at strains as low as 2% indicating non-linear viscoelasticity (or possibly a linear viscoelastic region only at vanishing low strains); the loss modulus had a weaker strain dependence than the storage modulus for all the suspensions studied. To minimize this non-linear effect, a fixed strain of 5% was used in the frequency sweep for all the suspensions studied (this also satisfied torque limitations for the low viscosity samples). Only limited ultra-low frequency data at 0.001 rad/s were obtained for comparison purposes (in view of the inordinately long times (~18 hours) required).

Only data (figures) for suspensions of all three fibrid types at 0.54% loading in a suspending medium of viscosity 2.45 P are reported in interests of clarity and space. Data for the other concentrations and viscosities are mentioned only where appropriate. Intrinsic viscosity and extensional viscosity results will be reported later.

RESULTS AND DISCUSSIONS

Dynamic storage and loss moduli

Figure 2 indicates that the loss modulus is much lower than the storage modulus until very high frequencies are achieved after which it has the higher value; this indicates the presence of a microstructure with an associated yield stress behavior. The F20 suspension has both the largest storage modulus and loss modulus, followed by the F25 suspension and then the F10 suspension; this indicates that the microstructure formed in the F20 suspension has the highest strength. The F20 data also indicate a frequency-independence at low frequencies, implying that the sample is far away from the yielding point and behaves as an elastic solid.

The dynamic moduli were observed to increase significantly with fibrids concentration. For the suspension containing 0.80% fibrids, the storage modulus remained unchanged over the entire range of frequency. Increasing the matrix viscosity was found to result in little change in the dynamic moduli at low frequencies but resulted in a larger loss modulus at high frequencies.

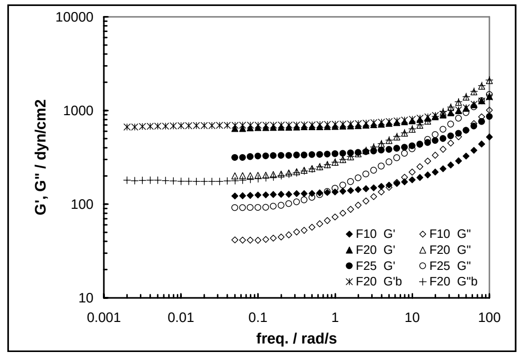

Figure 2. Dynamic moduli vs. frequency (strain = 5%).

Steady shear viscosity

A three decade change in shear viscosity between the low shear rate region and the high shear rate region is seen for all three suspension types in Figure 3. This demonstrates the enormous influence of the addition of a tiny amount of fibrid particulates. The F20 suspension has the highest shear viscosity followed by the F25 and the F10 suspensions and is consistent with the dynamic data. However, these suspensions do not exhibit a yield-stress-type behavior other than high zero-shear viscosities at low shear rates, which deviates from the dynamic data. For comparison, complex viscosity data are also plotted as a function of frequency in Figure 3 for these suspensions, and it is seen that the Cox-Merz rule is not valid. The slope of complex viscosity vs. frequency at low frequencies equals -1, indicating a constant stress which may be called the “dynamic yield stress”.

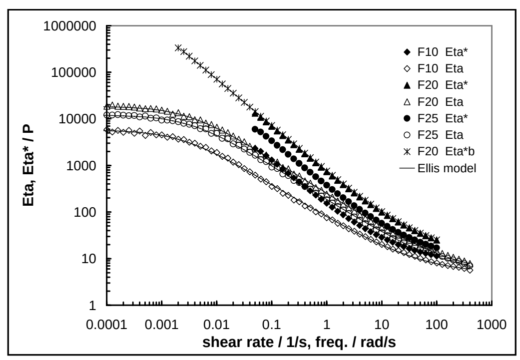

Figure 3. Shear viscosity and complex viscosity vs. shear rate or frequency; solid lines are Ellis model fits.

Figure 4 indicates that the zero-shear viscosities of the suspensions of all fibrid types are effectively independent of the suspending medium viscosity and determined only by the morphology and concentration of the fibrids. The matrix viscosity only affects the flow behavior in the shear thinning region and at very high shear rates. This behavior is also reflected in the complex viscosity data shown in Figure 4. These results indicate that the microstructure at low shear rates is governed only by the unique morphology and adjustable concentration of the fibrids; at high shear rates the microstructure might be expected to be disrupted because of the higher stresses imparted.

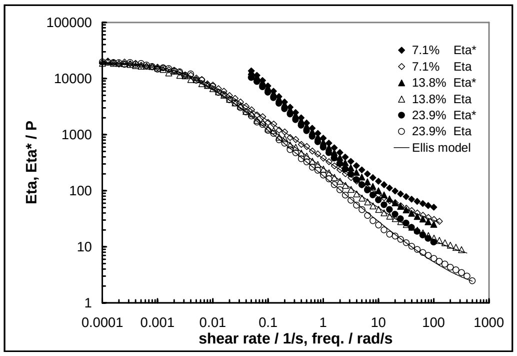

Figure 4. Effect of dispersion medium viscosity on shear viscosity and complex viscosity vs. shear rate or frequency for 0.54%F20 suspensions; solid lines are Ellis model fits.

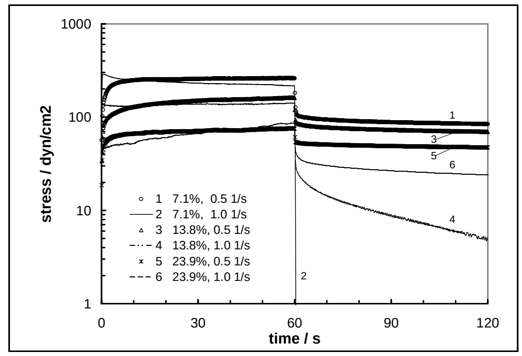

Figure 5. Stress growth and decay curves from step shear rate tests at 0.5 and 1.0 s^{-1} in three dispersion media for 0.54% F20 suspensions.

Figures 3 and 4 clearly indicate a high zero-shear viscosity region at low shear rates, followed by a shear thinning region, and eventually a low infinite-shear viscosity region at high shear rates. The Ellis model was used to describe the viscosity behavior and the Ellis model fits are shown by the solid lines in the Figures 3 and 4.

<u>Stress growth and decay</u>

Step rate experiments were used to identify microstructure evolution in the fibrid suspensions. A step shear rate of 0.5 or 1.0 1/s was applied for the first 60 s to observe stress growth and then stepped down to zero shear rate to observe stress decay for another 60 s.

Typical stress growth and decay curves are shown for three suspending liquid viscosity levels in Figure 5. For step shear rate increases to the lower final shear rate (0 -> 0.5 1/s) the suspensions show stress growth curves that reach equilibrium with the equilibrium stress increasing with the matrix viscosity. In the subsequent stress decay experiment (0.5 -> 0) there is an instant small initial drop after which the stress stays at a constant high level which increases with increasing matrix viscosity. This response is quite unlike that of a Newtonian or typical viscoelastic fluid. It was observed that the residual stress level depends on the morphology of the fibrids and their concentration.

In the higher shear rate experiments at 1.0 1/s, during the step increase phase from 0 to 1.0 1/s, the suspensions first show a weak stress overshoot before attaining an equilibrium stress value. However, in the subsequent step decrease phase from 1.0 to 0 1/s, the material response again strongly depends on the composition.

These results indicate the presence of a microstructure which is destroyed by shearing. At low stress levels (corresponding to low shear rate and/or low medium viscosity) the microstructure is weakened but not completely destroyed which results in a lower level residual stress. At high stress levels, the microstructure is destroyed and there is no residual stress. Finally, at intermediate stress levels the microstructure undergoes gradual destruction resulting in a stress decay.

The strength of the microstructure as reflected in the residual stresses depended on the fibrid type and concentration. At the same concentration, F20 samples gave stronger structures than F25 and F10 samples as also reflected in the steady shear and dynamic data.

<u>Thixotropic loops</u>

Thixotropy describes a time dependent material response (typically viscosity) associated with reversible changes in the microstructure of fluids. Thixotropy was measured by ramping up the shear rate from zero to 20 1/s and then ramping down from 20 1/s to zero for another 60 seconds and determining the area inside the envelope.

The F10 suspensions were found to exhibit more thixotropy (as compared to the F20 sample) in spite of the lowest values of the dynamic moduli and viscosity; no obvious thixotropy was observed for the F25 samples. This result can be ascribed to the different morphology and dispersability of the fibrids. Poorly dispersed F10 samples take relatively longer time to build up the microstructure destroyed by shearing. It is also concluded from experimental data that thixotropy increases with fibrids concentration; increasing the matrix viscosity has little effect on thixotropy and at very high levels can depress it because of the larger disruptive stresses imparted to the microstructure.

CONCUSIONS

Dynamic yield behaviors at low frequency but high zero-shear viscosity plateaus at low shear rates were observed. The shear viscosity was dominated by fibrid properties at low shear rates and by suspending medium properties at high shear rates which is consistent with a microstructure whose strength depends on the stress level imparted by the medium. The viscosity-shear rate behavior was best described by the Ellis model. The fibrid with the most space-filling geometry (F20) had the highest values of the dynamic moduli and zero-shear viscosity. The instantaneous strength of the microstructure was found to depend on the “space-filling” ability of the fibrids (as determined by shape and concentration) as well as the stress level (shear rate and medium viscosity).

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