Dielectric RheoSANS for the simultaneous interrogation of rheology, microstructure, and electronic properties of complex fluids

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In situ measurements are an increasingly important tool to elucidate the complex relationship between nanoscale properties and macroscopic measurements. One important example is the electrical and mechanical properties of carbon black slurries. While carbon based nanocomposites have been studied for decades, an emerging application is their use as an electrically percolating network in semi-solid flow battery electrodes [1]. In this application, electrical conductivity must be maintained while the electrode is continuously pumped through an electrochemical flow cell. Under these conditions, it is highly desirable to maximize the conductivity of these suspensions while reducing their viscosity in order to minimize pumping losses. Our hypothesis is that the relationship between viscosity and conductivity is a direct product of material microstructure and colloidal interactions. To test this hypothesis, we seek a way to measure the electrical, mechanical, and microstructural response of carbon particles under arbitrarily complex deformations. To accomplish this, we have developed a new Dielectric RheoSANS environment.

The instrument consists of a Couette geometry mounted on an ARES G2 strain controlled rheometer enclosed in a modified Forced Convection Oven (FCO) shown Figure 1a. The carbon black slurry is confined between concentric titanium cylinders that are nearly transparent to neutrons. Both cylinders are electrically isolated from the rheometer. In a Dielectric RheoSANS experiment, the impedance response is measured by an impedance-capacitance (LCR) meter and stress response is measured by the rheometer. The control scheme for this procedure is shown in Figure 1b. and is made possible through a programmable Labview interface that measures signals from the LCR meter and the rheometer. An analog triggering protocol synchronizes those measurements to the SANS event mode acquisition. At the end of a preprogrammed set of shear conditions, the entire rheological, electrical and microstructural characteristics of the sample can be reconstructed and time binned in order to quantify changes in microstructure as a function of both the shear conditions and time.

An example raw data output from Dielectric RheoSANS experiment from a 3 % by mass Vulcan XC72 sample dispersed in hydrogenated propylene carbonate is shown in Figure 1c. From top to bottom Fig. 1c shows the rheological, electrical, and microstructural response of a single sample throughout the course of an acquisition. Using this approach, we are able to capture the liquid to gel transition that takes place as shear stress imposed on the carbon black suspension drops below the yield stress of the bulk gel. The instrument design and findings resulting from initial testing will appear in forthcoming publications [2, 3]. While the Dielectric RheoSANS instrument was developed to answer important questions related to flowability of carbon black suspensions, it has the potential to expand the study of other complex suspension behavior, and will soon be available for use within the user program.

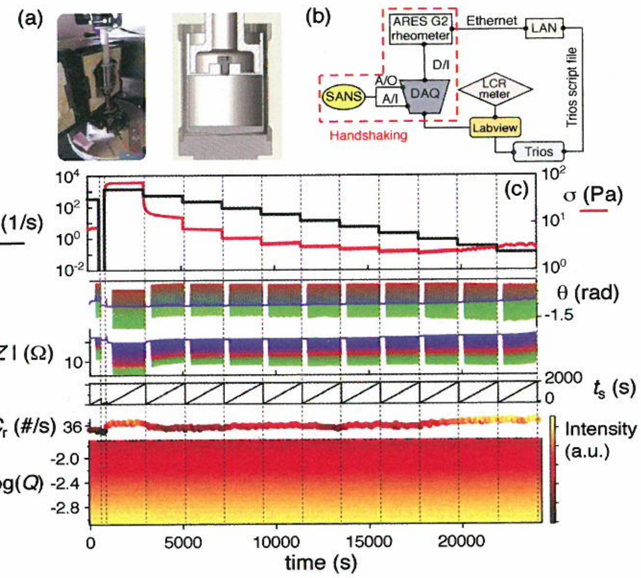

FIGURE 1: (a) (left) Picture of the dielectric Couette geometry contained within the FCO accessory and mounted onto an ARES G2 rheometer, (right) Schematic radial cross-section of dielectric Couette geometry. (b) Control scheme for Dielectric RheoSANS experiment detailing how synchronization of the three measurements is accomplished. (c) (top) shear rate, $\dot{\gamma}$, and shear stress, σ; (middle) impedance magnitude, $|Z|$, and phase shift, θ; (bottom) neutron arrival time, t_s, detector count rate, C_r, and intensity (a. u.) vs. log(Q); all as a function of measurement time throughout the acquisition of a single Dielectric RheoSANS experiment. Shown here is a flow sweep experiment consisting of a 600 s preshear and 300 s delay and then 11 logarithmically spaced programmed shear rates ranging from 1000 (1/s) to 0.1 (1/s), each 2100 s long. From the neutron time plot the synchronization scheme is evident as the detector clock was reset between each specified shear rate resulting in a hedgehog pattern emphasized here by vertical dotted lines through the plots.

References

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