THE GIANT ELECTRORHEOLOGICAL EFFECT IN SUSPENSIONS OF NANOPARTICLES

Weijia Wen[1], Xianxiang Huang[1], Shihe Yang[2], Kunquan Lu[3], Ping Sheng[1]

[1]*Department of Physics and Institute of Nano Science and Technology, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China*
[2]*Department of Chemistry and Institute of Nano Science and Technology, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China*
[3]*Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

Summary We have prepared suspensions of coated nanoparticles which exhibit electrically controllable, reversible liquid-solid transitions on a time scale of 1 to 10 msec. The solid state exhibits maximum yield stress on the order of 130 kPa, breaking the theoretical upper bound derived on the general assumption of linear electrical response of the component materials. Predictions based on the model of surface saturation polarization in the contact region of neighboring particles are in excellent agreement with the experiments.

A transmission electron microscope (TEM) image of the GER particles is shown in Fig. 1 (A). They have an average size of 50-70 nm, each with a surface coating of ~3-10 nm. Under an applied electric field, induced polarization in the particles causes their aggregation into columns aligned along the field direction (Fig. 1(B)). These columns are responsible for the solid yield stress when sheared along the transverse direction. A closer look at one of the columns is shown by the TEM image in Fig. 1(C), where it is seen that the particles' contact areas are somewhat flattened, indicating a degree of softness in the coatings.

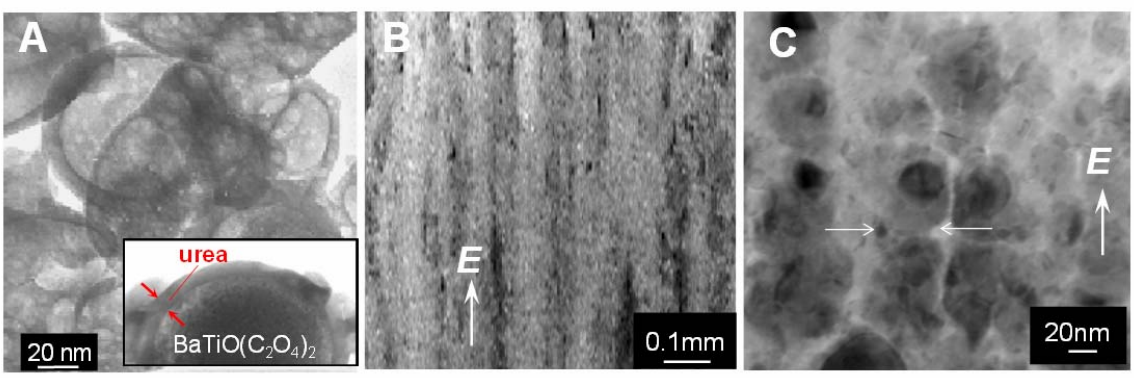

Figure 1 Images of nanoparticles in GER suspensions. (A) TEM image of coated nanoparticles. Urea coatings are clearly seen. (B) Optical microscope image of a sample prepared in epoxy, solidified under an applied field of 2000 V/mm. Aligned columns along the field direction are visible. (C) TEM image of a section of the column shown in (B). The arrows indicate one of the flattened interfaces [1].

The static yield stress curves for two volume fractions, measured under DC electric fields, are shown in Fig. 2. The corresponding current densities are shown in the inset. The current density J is below 4 μ A/cm^2 for E<2 kV/mm for the 30% sample. The yield stress varies as a function of temperature from 10 to 120 ^{o}C to within 30%. A similar temperature variation in current density was observed. At 1000 V/mm and 30% volume concentration, our GER has a measured Young's modulus $Y \approx 6$ Mpa under pulling. At concentrations <15%, both the onset and decay times of the yield stress are on the order of 10 ms. However, at high concentrations the initial fast decay of the yield stress is usually accompanied by a long time tail (extending to ~ 1 sec) that is small in magnitude, implying a degree of metastability.

The magnitude of GER's static yield stress, reaching 130 kPa at 5 kV/mm, sets it apart from the conventional ER fluids because it exceeds the theoretical upper bound, $(138\sqrt{R})(\varepsilon_\ell E^2/8\pi)$ (with R in units of microns), derived on the general assumption of linear dielectric and electrical conductive response of the component materials. With ε_ℓ =2 for the silicone oil dielectric constant, R=0.04 (micron) and E=5000 V/mm, the upper bound is 6.1 kPa, ~20 times smaller than the observed value. Another characteristic of GER is its near-linear field dependence of the yield stress. In general, the static yield stress is proportional to the energy density

$-\vec{P}\cdot\vec{E}$, where $\vec{P}$ is the polarization density. A linear dependence of $\vec{P}$ on $\vec{E}$, i.e., $\vec{P}=\chi\vec{E}$, implies a quadratic field dependence of the yield stress. The observed near-linear field dependence suggests the GER mechanism to involve a constant $\vec{P}_o$, i.e., a saturation polarization.

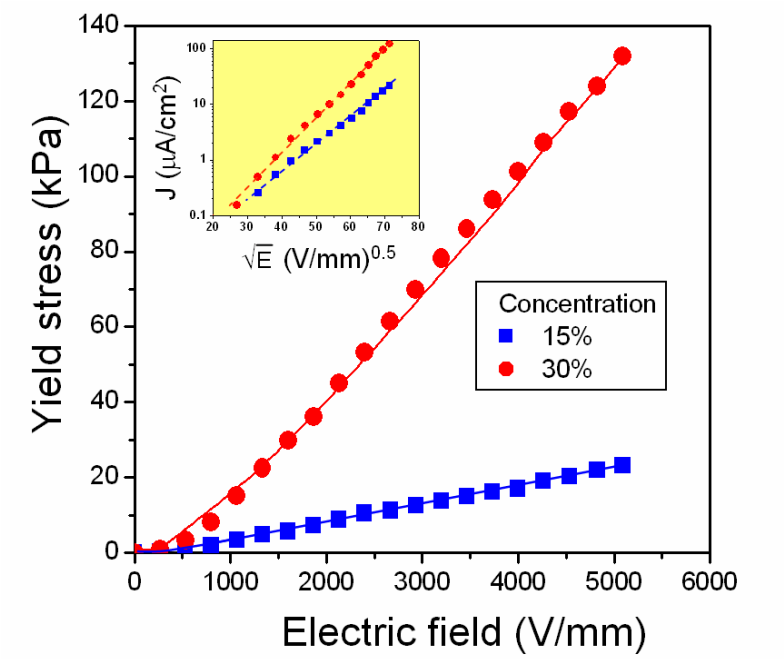

Figure 2 Static yield stress variation plotted as a function of applied electric field for two solid concentrations. Symbols denote experiment; solid lines are theory. Inset: logarithm of the current density *J* plotted as a function of $\sqrt{E}$. The dashed straight lines serve to delineate the $\ell nJ \propto \sqrt{E}$ relationship, indicating the mechanism of activation over the Coulomb barrier [1].

We propose the mechanism of saturation surface polarization, in the contact region of the neighboring spheres, to be responsible for the GER effect. The contact region is modeled by a 2Å gap separating the two surfaces, with an area determined by the Hertzian solution of two elastic spheres pulled together by a force F[21]: $\pi F^{2/3}[\kappa R/2]^{2/3}$, where R denotes the coated sphere radius and κ^{-1}, the deformation modulus of the coating, is the only adjustable parameter of our model. In the contact region the surface dipoles form two aligned layers, in contrast to other areas where such a configuration represents a higher energy state. The aligned configuration is possible due to (1) the high dielectric constant of the coating, which reduces the repulsive interaction between the aligned dipoles, (2) the favorable attractive interaction across the gap that considerably lowers the overall energy, and (3) the magnitude of the favorable interaction energy, which is sufficient to overcome the entropy effect. To buttress our argument, we have used finite element approach to calculate the interaction energy for two (nearest neighbor) pairs of dipoles. The result shows that the interaction energy at the gap separation of 2 Å is ~ -7 *kT*, sufficient to overcome the entropy effect and to induce a localized collective transition to the aligned state.

The predicted yield stress as a function of *E* is shown in Fig. 2 as the solid lines. Excellent agreement between theory and experiment is seen. In particular, the discernable deviation from linearity is well-captured by the elastic component of the model. However, for the 15% concentration, our model (by using a larger average volume per particle) obtains agreement only by using a solid concentration of 5%. This is plausible because the theory concentration is that of the network backbone responsible for the overall rigidity; at lower concentrations the probability increases that a solid particle in the actual (random) system does not belong to the backbone. With no adjustable parameter, the Young's modulus was calculated to be 5 MPa at 1000 V/mm for a concentration of 30%, in good agreement with the experiment (6 Mpa).

Reference

[1] W. Wen, X. Huang, S. Yang, K. Lu, Ping Sheng, *Nature Materials* **2**, 727-730 (2003).