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Comment on: Preparation, microstructure, and electrorheological property of nano-sized TiO_2 particle materials doped with metal oxides

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Abstract We comment on the shear stresses of recently reported Na-doped, Zr-doped, Al-doped, and Ce-doped TiO_2-based electrorheological (ER) suspensions under applied electric strengths. Using deduced critical electric-field strength and additional scaled parameter, we found that the shear stresses could be analyzed using the universal yield stress equation, collapsing the data of Na-doped, Zr-doped, Al-doped, and Ce-doped TiO_2 ER fluids onto a single curve

Recently, Shang et al. [1] reported electrorheological (ER) systems using Na_2O-, ZrO_2-, Al_2O_3-, and CeO_2-doped nano-sized TiO_2 with enhanced ER activity, in which the shear stresses increased with different metal oxides doping such as Na, Zr, Al, and Ce on TiO_2-based ER fluids under an applied electric field. The ER fluid, typically a suspension of semiconducting or dielectric solid particles in electrically nonconducting liquid media, exhibits rapid and reversible change in shear viscosity under imposed electric fields. This phenomenon is known to originate from the aggregation of the solid particles due to attractive forces, induced by the external electric field. The reversible behavior in the order of millisecond is related to dielectric properties of the ER particles via polarization mechanisms of both orientational polarization (Debye polarization) and interfacial polarization (Wagner polarization). The field-induced dipoles with dipolar moments attract each other and cause the particles to form chains or fibrillar structures in the direction of the electric field. These chains are thus formed by interparticle forces which exhibit sufficient strength to inhibit fluid flow, i.e., these colloidal suspensions with high electric-field strength and particle concentration, demonstrate strong resistance against a shear deformation.

Among their results in [1], Fig. 1, which provided high shear stresses as a function of the applied electric-field strength at a given shear rate, drew our attention since our previously reported universal yield stress equation has been applied to either yield stress or shear stress at a low shear rate of ER fluids. Thereby, in this comment, we expanded applicability of the universal yield stress to certain shear stress with ER performance by reanalyzing their ER data of Na-doped, Zr-doped, Al-doped, and Ce-doped TiO_2 [1] via both polarization and conductivity models, and found that not only is the shear stress strongly affected by the modification with different dopant, but also our universal yield stress equation collapses their data onto a single curve.

Note that the yield stress is a critical design parameter in the ER devices along with shear stress, and has attracted considerable attention both experimentally and theoretically [2]. Theoretical models for the yield stress have been proposed to describe the ER phenomena, and the polarization model, in general, relates material parameters of the ER fluids such as dielectric response of both liquid media and solid particles and electric-field strength to the rheological properties. Using an idealized ER system, in which uniform dielectric hard spheres are dispersed in a Newtonian fluid medium, the derived electrostatic force was found to be dependent on the dielectric constant mismatch

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between the particle and the continuous media [2, 3]. Based on these assumptions, the yield stress τ_y is known to be proportional to the square of the applied electric-field strength, E_0, as follows:

$$\tau_y = \varphi K_f E_0^2 f(\beta), \tag{1}$$

where φ is the volume fraction of the particles and $\beta = (K_p - K_f)/(K_p + 2K_f)$ is the dimensionless dielectric mismatch parameter. Here, K_p and K_f are the dielectric permittivities of the particles and the fluid, respectively. This polarization model demonstrates excellent agreement with the data for small φ and low E_0 [4]. However, the yield stress data deviate significantly from Eq. 1 at high E_0 and are better represented by the power law relationship in E_0 such that $\tau_y \propto E_0^m$, in which $m = 2$ for the polarization model and $m = 1.5$ for the conduction model.

Concurrently, the conduction model takes into account the particle interaction only and does not consider the microstructural changes that occur after imposition of an electric field. As the gap between the conducting particles in the fluid decreases, the electric response of the fluid becomes nonlinear, e.g., electrical breakdown or particle discharge at high electric-field strength occurs. In this case, the ER effect is caused by the fluid-induced conductivity enhancement among particles that are nearly in contact. Therefore, the conductivity mismatch between particles and liquid media, rather than the dielectric constant mismatch, is considered to be a dominant factor for the dc and low-frequency ac excitation [5].

Meanwhile, the critical electric-field strength, E_c, was introduced via the universal scaling function to interpret the deviation of the yield stress from both the polarization model and the conductivity model. The simple hybrid yield stress equation for a broad electric-field strength range is proposed as [6]

$$\tau_y(E_0) = \alpha E_0^2 \left(\frac{\tanh \sqrt{E_0/E_c}}{\sqrt{E_0/E_c}} \right) \tag{2}$$

Here, the parameter α depends on the dielectric property of the fluid, the particle volume fraction, and the critical electric field. E_c, originated from the nonlinear conductivity effect, can be obtained by the crossover point of the slopes for all ranges of the electric-field strengths. Equation 2 has the following asymptotic characteristics at both low and high electric-field strengths:

$$\tau_y(E_0) = \alpha E_0^2 \quad \text{for} \quad E_0 \ll E_c \tag{3}$$

and

$$\tau_y(E_0) = \alpha \sqrt{E_c} E_0^{3/2} \quad \text{for} \quad E_0 \gg E_c \tag{4}$$

Equations 3 and 4 indicate that τ_y is proportional to E_0^2 at low E_0, as expected from the polarization model, and to $E_0^{3/2}$ at high E_0, as predicted from the conductivity model. The results of both electric field ranges, good for the polarization model and the conductivity model, explain well the data for various ER fluids, representing that the yield stress is proportional to E_0^2 at low fields and approaches $E_0^{3/2}$ at high fields. Recently, several research groups reported such behavior of yield stress as a function of an electric field for emulsion-based ER fluid [7] and conducting polypyrrole in mesoporous silica-based ER fluid [8].

We replotted the shear stresses of Fig. 1 reported in [1] as a function of the applied electric-field strengths in a log–log scale as given in Fig. 1, and estimated E_c for Na-doped, Zr-doped, Al-doped, and Ce-doped TiO_2. E_c is given by the crossover of two slopes, i.e., the slope of the polarization model (slope = 2) and that of the conductivity model (slope = 1.5). E_c was also found to depend on the volume fraction of particles in several ER fluids [9, 10]. The estimated $\tau_y(E_c)$, based on the slope change from slope = 2.0 to slope = 1.5 (as indicated by dotted line) from Fig. 1, is 2.21 kPa at 3.92 kV in the case of the Na-doped TiO_2 ER fluid.

To correlate of the data into a single universal curve, we normalized Eq. 2 using E_c and $\tau_y(E_c) = 0.762\alpha E_0^2$ as [6]

$$\hat{\tau} = 1.313\hat{E}^{3/2} \tanh \sqrt{\hat{E}}, \tag{5}$$

where $\hat{E} \equiv E_o/E_c$ and $\hat{\tau} \equiv \tau_y(E_o)/\tau_y(E_c)$. Various ER fluids [11–14] were found to fit well with this universal yield stress equation.

Figure 2 shows the universal plot of $\hat{\tau}$ vs. $\hat{E}$ for the four samples of different metal oxides-doped TiO_2 in dimethyl silicone oil, indicating that the data from Fig. 1 of [1] follow the solid curve pertaining to the normalized universal yield stress equation (Eq. 5).

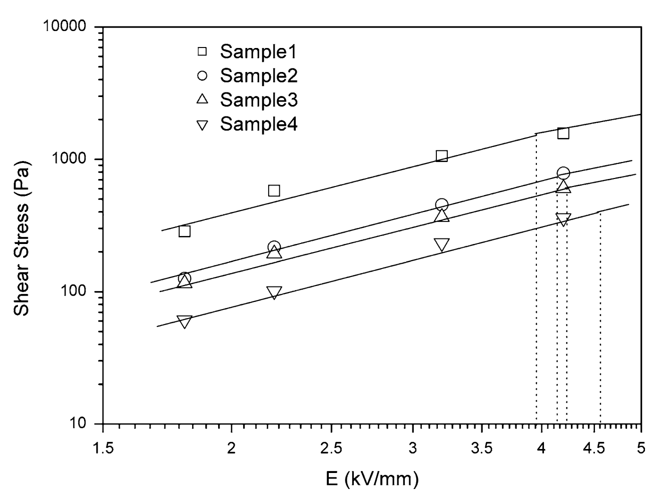

Fig. 1 Replotted shear stress vs. electric-field strength for suspensions of the samples 1–4 from Fig. 1 in [1]

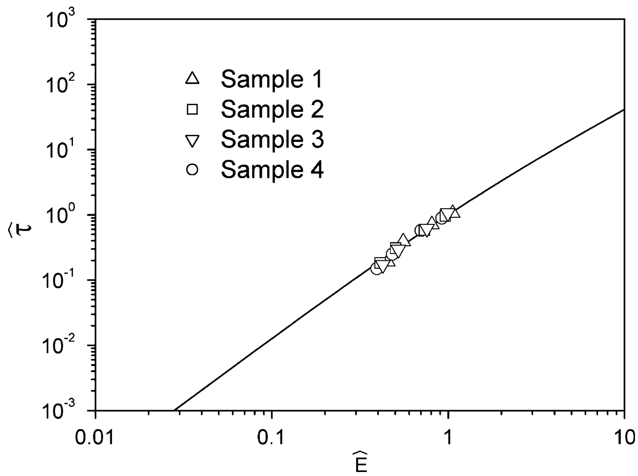

Fig. 2 Universal curve of suspensions of the samples 1–4 (symbols from [1] and solid lines from Eq. 5)

In conclusion, the universal yield stress equation was found to fit shear stresses of four differently doped ER fluids well into a single universal curve, implying the universal scaling behavior of the shear stress of the experimental data obtained from [1].

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