Comments

Comment on "Preparation and Enhanced Electrorheological Activity of TiO_2 Doped with Chromium Ion"

Recently, Yin and Zhao[1] reported a novel system with a chromium (Cr) ion doped TiO_2 particle that exhibited enhanced electrorheological (ER) activity. They showed that the yield stress (τ_y) of a 10 mol % Cr doped TiO_2 suspension was about 2.3 kPa at the electric field strength of 4 kV/mm and the volume fraction was 18%. The ER efficiency [$((\tau_y - \tau_0)/\tau_0)$; τ_0 is shear stress when the electric field strength is 0 kV/mm] of this Cr doped TiO_2 suspension was also reported to be 280 at the shear rate of 10.55 s^{-1} with 3 kV/mm, which is 18 times greater than that for a pure TiO_2 suspension. The yield stress depends strongly on the doping degree of Cr, and the ER activity tends to decrease with phase separation when the doping degree becomes higher than 10 mol %. Generally, ER fluids are suspensions of polarizable particles in a nonconducting liquid, exhibiting drastic changes in rheological properties under an applied electric field.[2−8] Despite numerous reports on ER fluids, further investigations are still required for rheological behaviors of the ER fluids with complex flow curves.[9−11]

In this comment, we examine the flow properties of the ER suspension by reanalyzing the shear stress of a 10 mol % Cr doped TiO_2 ER suspension under three different electric field strengths (2.0, 3.0, and 4.0 kV/mm)[1] using our recently proposed rheological equation of state.[12] Flow curves of semiconducting poly(naphthalene quinone) (PNQR) particle based ER fluids under several applied electric field strengths and particle concentrations were constructed, and their flow characteristics were examined via three different constitutive equations, the Bingham model, the De Kee−Turcotte model, and our proposed model.[12] Our proposed equation fits the data very well.

The Bingham fluid model has been widely used to describe the rheological response of various suspension systems including ER fluids. The Bingham flow exhibits a nonvanishing yield stress (τ_y), which is defined as a stress where the suspension behavior changes from solidlike to fluidlike at a zero shear rate limit. The Bingham fluid equation, the simplest model with two parameters, is given as follows:

$$\begin{aligned} \tau &= \tau_y + \eta_0\dot{\gamma} \qquad \tau \geq \tau_y \\ \dot{\gamma} &= 0 \qquad \tau < \tau_y \end{aligned} \tag{1}$$

Here, τ_y is specifically a function of electric field strength, $\dot{\gamma}$ is the shear rate, and η_0 is the zero shear viscosity. The relationship between the shear stress (τ) and the suspension microstructure has been studied via examining the behavior of particle chain or aggregate structures under the shear deformation. The Bingham fluid model consists of two flow regimes: a rigid pre-yield behavior for shear stress less than the yield stress and Newtonian or non-Newtonian flow response beyond the yield stress τ_y (post-yield region).[13] However, deviations from the Bingham fluid model have been observed for several ER systems. Kim et al.[14] reported the existence of critical shear rate in the flow curve of styrene−acrylonitrile copolymer/clay nanocomposite based ER fluid; below the critical shear rate the shear stress decreased as a function of shear rate, and then above the critical shear rate the fluid exhibited pseudo-Newtonian behavior. Even though there have been extensive studies of quantitative analysis on both yield stress and shear stress behaviors,[15,16] surprisingly only a few reports on the constitutive equation can be found.[16,17] Furthermore, it has been recently reported that the complex shear stress behaviors such as the plateau region over a broad shear rate range, the existence of minimum shear stress at a relatively low shear rate region,[18,19] and the coexistence region of liquid−solid-like system[20] are often observed.

To examine such a complex flow curve, recently we proposed the following model constitutive rheological equation of state for the ER fluids under an applied electric field.[12]

$$\tau = \frac{\tau_y}{1 + (t_2\dot{\gamma})^{\alpha}} + \eta_\infty\left(1 + \frac{1}{(t_3\dot{\gamma})^{\beta}}\right)\dot{\gamma} \quad \text{(our proposed model)} \tag{2}$$

Here, α and β are related to the decrease in the stress, t_2 and t_3 are time constants, and η_∞ is the viscosity at a high shear rate. To satisfy $d\tau/d\dot{\gamma} \geq 0$, the exponent β has the range $0 < \beta \leq 1$. It is found that the above six-parameter model can describe the stress decrease phenomena in the low shear rate region as well as provide an accurate estimate for the yield stress (τ_y) when we plot the original Figure 8a of ref 1 for the Cr doped TiO_2 based ER fluids. The first term in eq 2 describes the decrease of shear stress with increase in shear rate at a low shear rate region, and the second term is responsible primarily for the contribution of the shear stress at a high shear rate region. Note that the shear stress depends directly on either the particle

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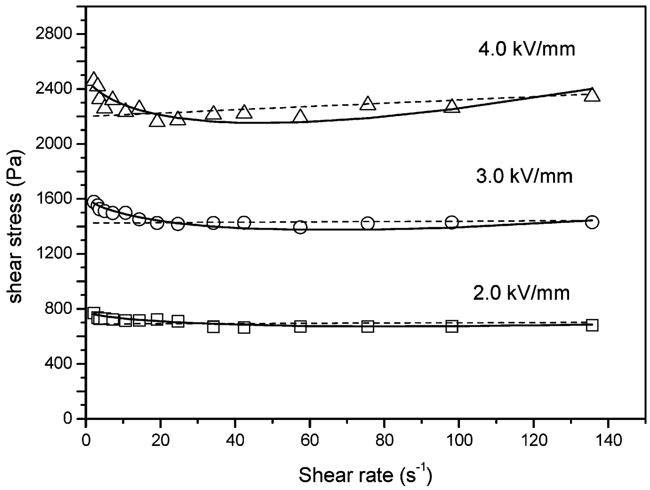

Figure 1. Flow curves for 10 mol % Cr doped TiO_2 ER fluid (symbols are data from ref 1, dashed line is for the Bingham model, and solid line is for our model).

interactions[13] or the derivative of the electrostatic energy with respect to the shear strain.

The Bingham fluid model (eq 1) and our proposed model given in eq 2 are used to analyze the shear stress versus shear rate data as shown in Figure 1.

The dotted lines in Figure 1 are obtained from the Bingham fluid model equation, and the solid lines represent our proposed model. The optimal parameters used to fit the data to these two models are summarized in Table 1.

The coefficient, α, depends on the particle concentration in the case of PNQR based ER fluids,[12] while independent of electric field strength. The β values are 0.23, 0.03, and 0.01 for the electric field strengths of 2, 3, and 4 kV/mm, respectively, for Cr doped TiO_2 suspensions. From these results, we found that Cr doped TiO_2 is found to become a Newtonian fluid in the high shear rate region under 4 kV/mm. Furthermore, it was found that the yield stresses obtained from the Bingham fluid model are much lower than that from our model for Cr doped TiO_2. This can be explained from the fact that our proposed model accurately fits the decrease in shear stress for the region of shear rate from 0 to 40 (1/s), while the Bingham model does not fit the data accurately, as shown in Figure 1. The large deviation between two models is observed especially at the low shear rate.

Table 1. Optimal Parameters in Each Model Equation Obtained from the Flow Curve of Cr Doped TiO_2 Based ER Fluids at Various Electric Field Strengths

model	parameter	2 kV/mm	3 kV/mm	4 kV/mm
Bingham	τ_y	690	1425	2200
	η_0	0.09	0.12	1.2
eq 2	τ_y	780	1620	2500
	t_2	0.004	0.005	0.006
	α	0.72	0.72	0.72
	η_∞	0.90	1.90	3.90
	t_3	0.03	0.004	0.0005
	β	0.23	0.03	0.01

In conclusion, it was found that our proposed model was able to not only fit the flow curves more accurately than the Bingham fluid model but also deduce achievable shear stress by explaining the decreases in shear stress with increasing shear rate at low shear rate for Cr doped TiO_2 based ER fluid in ref 1.

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