

Comment on ‘Two roles of guest and crosslinked degree on hydrosoluble β -cyclodextrin polymer electrorheological fluids’ by Z. Gao and X. Zhao

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Abstract

Comments on the recent studies of electrorheological (ER) properties of hydrosoluble β -cyclodextrin polymer based ER fluids are given based on the analysis of their yield stress data as a function of applied electric field strengths. Using our previously reported universal yield stress equation and critical electric field strengths deduced, it is found that we can collapse their data into a single curve.

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Recently, Gao and Zhao [1] reported that supramolecular complexes of 5' based ER fluid which consists of β -cyclodextrin polymer and 3-hydroxy-2-naphthoic acid showed a notable ER effect. The ER fluids, in general, typical suspensions formed by dispersion polarizable particles in insulating oil, could respond rapidly and reversibly to external electrical fields, leading to a sharp increase in the shear viscosity with yield stresses [2–4]. They [1] used hydrosoluble β -cyclodextrin polymer as a host to build supramolecular complex and then prepared the ER fluid by dispersing these particles in silicone oil, being attributed to the enhancement of dielectric properties under the structural change. It was observed that the molar crosslinking degree plays a significant role to control the supramolecular complex ER behavior. Among their results reported, we reanalyzed their yield stress in Fig. 7 of Ref. [1], and found that our universal yield stress equation collapsed their data into a single curve.

The polarization model attributes the attractive force between the particles to Maxwell–Wagner’s interfacial polarization and employs the point-dipole approximation. 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 between the particles and the continuous media [5]. With these assumptions, the yield stress (τ_y) [6] is proportional to the square of applied electric field strength, E_0 , as follows:

$$\tau_y \propto \phi K_f E_0^2 f(\beta), \quad (1)$$

where ϕ is the volume fraction of the dispersed particles and $\beta = (K_p - K_f)/(K_p + 2K_f)$ is the dimensionless dielectric mismatch parameter, with K_p and K_f the dielectric permittivities of the particles and the fluid, respectively. This polarization model has been observed to fit the data well for small ϕ and low E_0 [7,8]. However, the nonlinear conductivity effect becomes dominant in the bulk conducting particle model and yield stress data deviate from Eq. (1) at high E_0 and are better represented by the power law relationship in E_0 ; $\tau_y \propto E_0^m$ (m appears to be smaller than 2), implying that the electric response of the fluid becomes nonlinear. In this case, the ER effect is caused by the fluid-induced conductivity enhancement among nearly touching particles. The conductivity mismatch between particles and liquid media, rather than the dielectric

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constant mismatch, was considered to be a dominant factor for the dc and low frequency ac excitation [9]. The conduction model considers the particle interaction only and does not take into account the microstructural changes which occur after the application of an electric field. Note that $m = 2$ for the polarization model, while $m = 1.5$ for the conduction model.

To correlate the yield stress data for a broad range of electric field strengths, Choi et al. [10] introduced the critical electric field strength, E_c . The critical electric field strength was introduced via the universal scaling function to interpret the deviation of the yield stress from both the polarization model [7] and the conduction model [9]. The simple hybrid yield stress equation for a broad electric field strength range is proposed as [10]:

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

where the parameter α depends on the dielectric property of the fluid and the particle volume fraction. E_c stems from the nonlinear conduction model, and represents the crossover behavior. It appears to be proportional to the particles conductivity and separates the two different slopes for E_0 vs. yield stress plot, that is, Eq. (2) clearly processes the following asymptotic characteristics at both low and high electric field strengths:

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

and

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

Eqs. (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 conduction model [11]. We replotted the original Fig. 7 of Ref. [1] in a log–log plot as given in Fig. 1 as a function of applied electric field strengths, and obtained the E_c for the three different samples which resulted from the

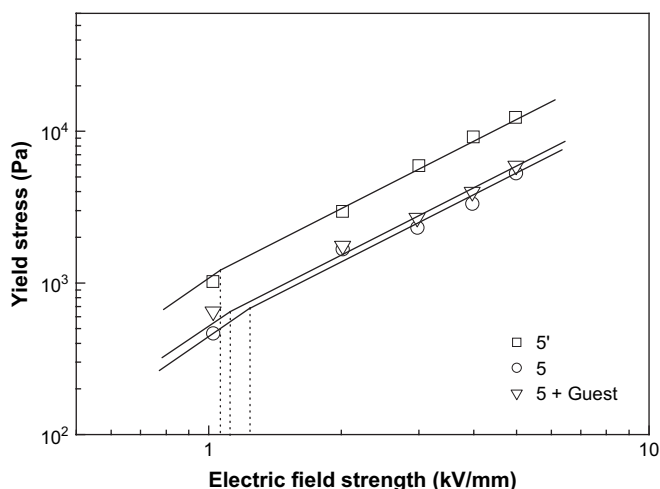


Fig. 1. The replotted yield stress vs. electric field strengths for 5', 5 and 5 + Guest dispersed in silicone oil.

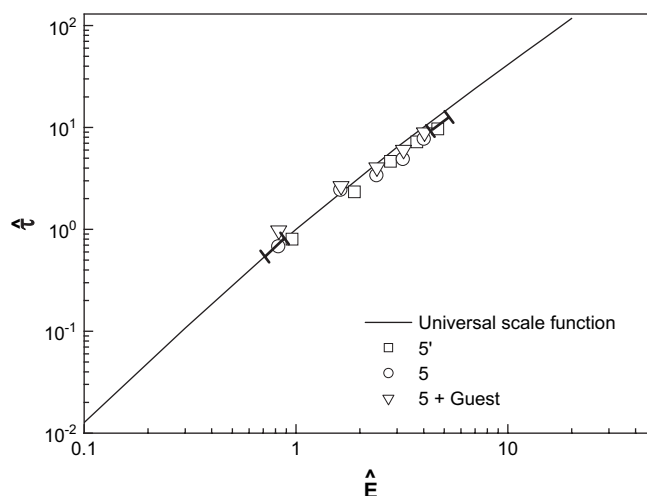


Fig. 2. $\hat{\tau}$ vs. \hat{E} for 5', 5 and 5 + Guest dispersed in silicone oil. The error bars show the sensitivity of numerical value of E_c and for clarity only two points are applied.

crossover of two slopes, corresponding to the polarization model (slope = 2) and conduction model (slope = 1.5), respectively. The E_c was found to depend on the molar crosslinked degree of β -cyclodextrin polymer in ER fluids. The estimated E_c s are 1.07 ± 0.05 kV/mm for 5', 1.24 ± 0.05 kV/mm for 5 and 1.23 ± 0.05 kV/mm for 5 + Guest dispersed in silicone oil.

In order to collapse the data into a single curve, we normalized Eq. (2) using E_c and $\tau_y(E_c) = \alpha E_c^2 \tanh(1) = 0.762 \alpha E_c^2$

$$\hat{\tau} = 1.313 \hat{E}^{3/2} \tanh \sqrt{\hat{E}} \quad (5)$$

where $\hat{E} \equiv E_0/E_c$ and $\hat{\tau} \equiv \tau_y(E_0)/\tau_y(E_c)$. Various ER fluids [11–17] were found to fit very well with this universal yield stress equation. The data shown in Fig. 1 collapsed into a single curve by using Eq. (5), as shown in Fig. 2. Fig. 2 represents the universal curve for $\hat{\tau}$ vs. \hat{E} for 5', 5 and 5 + Guest dispersed in silicone oil. In addition, the error bars of two data points in both ends show the sensitivity of the numerical value of E_c . The deviations of the E_c do not change the scaled universal yield stress equation itself but the point moves following the universal yield stress equation, moving up for the higher E_c and moving down for the lower E_c [18].

Therefore, we found that the data from Fig. 7 of Ref. [1] collapsed into to a single curve via normalized universal yield stress equation (Eq. (5)).

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