J Mater Sci (2009) 44:4503–4506
DOI 10.1007/s10853-009-3688-0

LETTER

Comment on “study on electrorheological properties of novel polymer-Ce^{4+} complex”

Seung Woo Ko · Hyoung Jin Choi

Received: 7 April 2009 / Accepted: 15 June 2009 / Published online: 27 June 2009

Recently, Song and Lin [1] reported electrorheological (ER) fluids based on the synthesized bithiazole ring and *p*-aminobenzoic acid containing new polymer system, and $CeCl_4$ mixed polymer-Ce^{4+} complex. Two different ER fluids systems were prepared and their electrical properties were compared each other. It was observed that the cerium ion (Ce^{4+}) enhanced ER activity, in which the yield stresses increased compared with pure polymer based ER fluid under an applied electric field.

The typical ER fluid implies a suspension of semiconducting or dielectric solid particles in non-conducting liquid media [2–7], exhibiting reversible and drastic changes in their rheological properties which include a large increase in apparent viscosity and the formation of reversible suspension microstructures under an applied electric field [8, 9] along with its magnetically analogous magnetorheological suspensions under an external magnetic field [10–12]. The reversible behavior on the order of millisecond is related with dielectric properties including interfacial polarization, and this phenomenon results from the aggregation of the solid particles due to attractive forces induced by the external electric field among the dipolar moments. The induced dipoles by electric field attract each other and cause the particles to form chains structures by interparticle forces in the direction of the electric field. These colloidal suspensions with high electric field strength and particle concentration exhibit strong resistance against a shear deformation. Clearly, the ER performance depends on the electrical properties of the suspended particles [13].

In this comment, we replotted the original yield stress curves of ER fluids based on the polymer or polymer-Ce^{4+} under different electric field as shown in [1], which provided high yield stress as a function of the applied electric field strength with increased polymer or polymer-Ce^{4+} contents in a log–log plot. Then, we analyzed it using our previously reported universal yield stress equation [8, 14]. Generally, the universal yield stress equation has been applied for either yield stress or shear stress at a low shear rate of ER fluids. Therefore, we expanded the adoptability of universal yield stress to certain yield stress with ER fluid performance by reanalyzing their ER behaviors [1] via polarization and conduction models in this comment. We found not only the yield stress strongly affected by the modification with different contents, but also our universal yield stress equation collapses their data onto a single curve. Moreover, pure polymer and polymer-Ce^{4+} complex systems were observed to follow polarization model and deviated from the single curve at some points of low electric field strength. It is noted that yield stress is a critical parameter in designing ER devices, thus it has attracted both experimental and theoretical attentions [15]. Based on both the polarization and conduction models, it shows that the yield stress is strongly correlated with the universal yield stress equation. Generally, in the ER phenomenon, the polarization model is related to the dielectric response of both liquid and solid particles under the electric field strength. Using idealized ER fluids, 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 [16]. In these assumptions, the yield stress (τ_y) is proportional to the square of the applied electric field strength, E_0, as follows:

S. W. Ko · H. J. Choi (✉)
Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea
e-mail: hjchoi@inha.ac.kr

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

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 permittivity of the particles and the fluid, respectively. This polarization model is known to fit the data very well for small ϕ and low E_0 [17]. However, the yield stress data often deviate significantly from Eq. 1 in many cases such as at high values of E_0 and at high volume fraction. Therefore, they are better represented by the power law relationship in $\tau_y \propto E_0^m$. Note that $m = 2$ for the polarization model, while $m = 1.5$ for the conduction model.

The yield stress data of ER fluids have been widely tested for a broad range of electrical field strength and Sim et al. [18] introduced the critical electric field strength (E_c) via the universal scaling function to bridge the deviation of the yield stress from both the polarization model and the conduction model. The simple hybrid yield stress equation for a broad electric field strength range is proposed as:

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

where the parameter κ is known to depend on the dielectric property of the ER fluid, the particle volume fraction, and the critical electric field (E_c). The critical electric field (E_c) originated from the non-linear conductivity effect, can be mainly obtained by the crossover point of the slopes for all ranges of the electric field strengths. However it can be also extrapolated if it is out of measurement range. Equation 2 has the following asymptotic characteristics at both low and high electric field strengths:

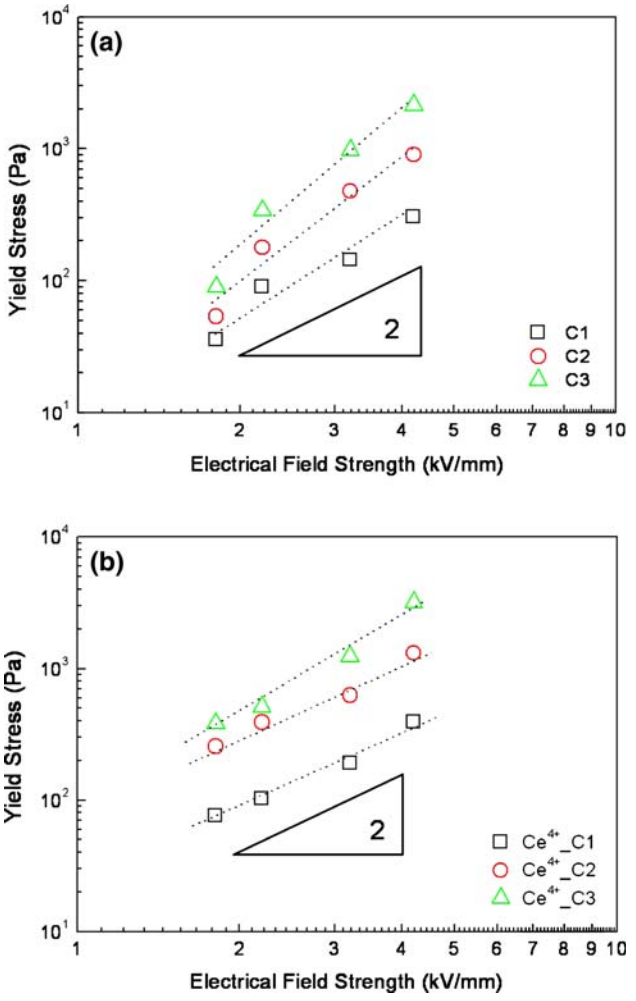

Fig. 1 Yield stress replotted as a function of electric field strength for ER fluids from Figs. 1 and 3 in [1], **a** pure polymer ER fluid and **b** polymer-Ce^{4+} complex ER fluid

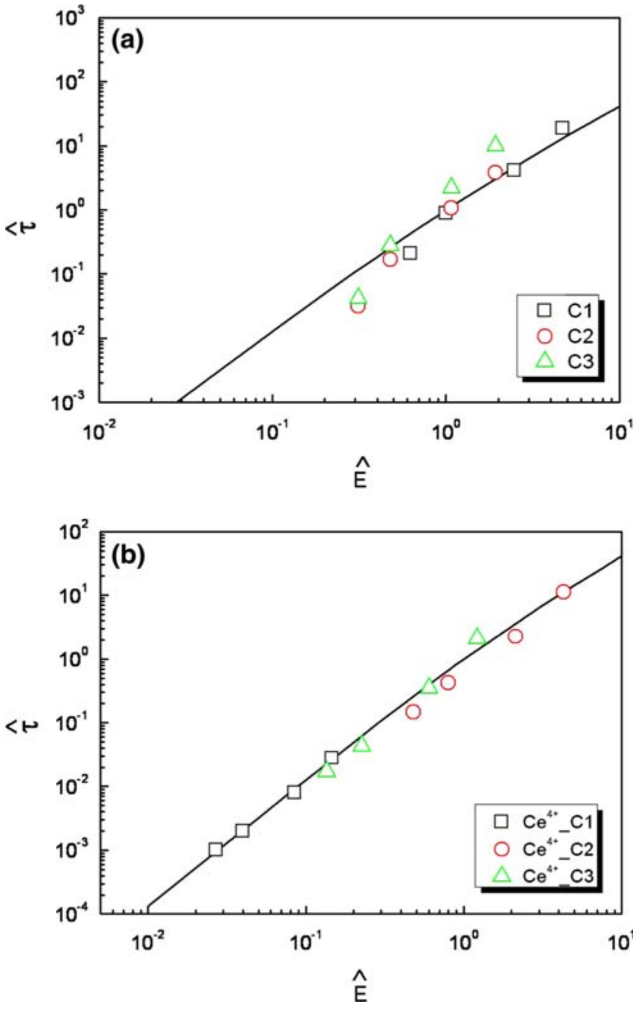

Fig. 2 Universal curve of ER fluids **a** pure polymer ER fluid and **b** polymer-Ce^{4+} complex ER fluid (symbols from [1] and solid lines from Eq. 5)

$$\tau_y(E_0) = \kappa E_0^2 \left(\frac{\tanh\sqrt{E_0/E_c}}{\sqrt{E_0/E_c}}\right) \propto E_0^2 \quad \text{for } E_0 \ll E_c \qquad (3)$$

$$\tau_y(E_0) = \kappa E_0^2 \sqrt{(E_0/E_c)^{-1}} = \kappa\sqrt{E_0^2}E_0^{3/2} \propto E_0^{3/2} \quad \text{for } E_0 \gg E_c \qquad (4)$$

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 conduction model. The results of both electric field ranges for the polarization model and the conduction model correspond well with the data for various ER fluids, indicating that the yield stress is in proportional to E_0^2 at low fields and approaches $E_0^{3/2}$ at high fields.

In Fig. 1, we replotted the yield stresses of Figs. 1 and 3 originated from [1] as a function of the applied electric field strengths in a log–log scale for pure polymer and polymer-Ce^{4+} complex. Deviation from the polarization model (slope = 2) is observed.

In order to examine the correlation of the data with a single, universal curve, we normalized Eq. 2 using E_c and $\tau_y(E_c) = 0.762\alpha E_0^2$ as:

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

where $\hat{E} \equiv E_o/E_c$ and $\hat{\tau} \equiv \tau_y(E_o)/\tau_y(E_c)$. Various ER fluids [19–21] were found to being fitted well with this universal yield stress equation.

Figure 2 shows a plot of $\hat{\tau}$ vs. $\hat{E}$ for pure polymer and polymer-Ce^{4+} complex in bromodiphenylmethane medium, indicating that the data from Figs. 1 and 3 of [1] follow the solid curve pertaining to the normalized universal yield stress equation (Eq. 5).

Figure 3 is a re-plot of the yield stresses of Fig. 4 originated from [1] as a function of the applied electric field strengths in a log–log scale to obtain E_c for 15 wt% polymer-Ce^{4+} complex at different temperature, showing that they follow the polarization model (slope value = 2) quite well.

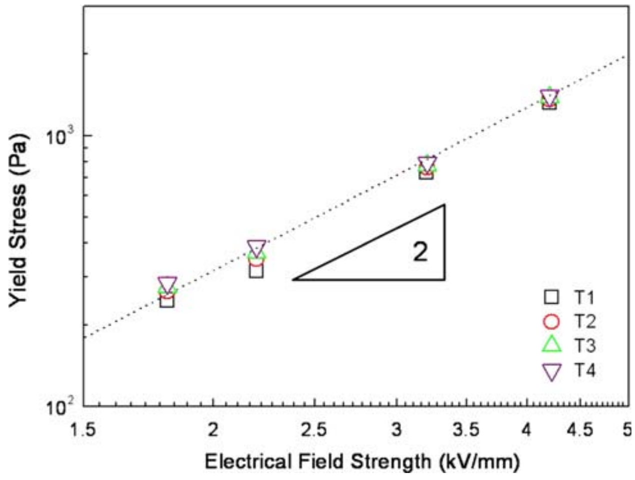

Fig. 3 Yield stress replotted as a function of electric field strength for ER fluids from Fig. 4 in [1]

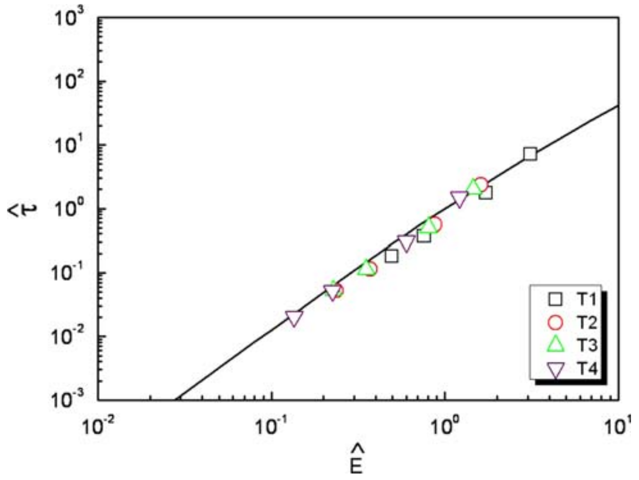

Fig. 4 Universal curve of ER fluids of 15 wt% polymer-Ce^{4+} complex ER fluid at different temperature (symbols from [1] and solid lines from Eq. 5)

Nonetheless we represent a plot of $\hat{\tau}$ vs. $\hat{E}$ for 15 wt% polymer-Ce^{4+} complex in bromodiphenylmethane medium at different temperature conditions as shown in Fig. 4. It indicates that the data from Fig. 4 of [1] follow the solid curve pertaining to the normalized universal yield stress equation (Eq. 5).

In conclusion, the universal yield stress equation incorporating both polarization model and conduction model was found to fit the yield stresses of both ER fluids from pure polymer and polymer-Ce^{4+} complex in bromodiphenylmethane medium onto a single universal curve quite well.

Acknowledgements This study was supported by Inha University (2009).

References

1. Song X, Lin Y (2006) J Mater Sci 41:2055. doi:10.1007/s10853-006-4505-7
2. Hong CH, Choi HJ, Kim JH (2008) J Mater Sci 43:5702. doi:10.1007/s10853-008-2915-4
3. Oz K, Yavuz M, Yilmaz H, Unal HI, Sari B (2008) J Mater Sci 43:1451. doi:10.1007/s10853-007-2319-x
4. Li GF, Wang ZQ, Wang NH (2007) J Mater Sci 42:8242. doi:10.1007/s10853-007-1733-4
5. Yoon DJ, Kim YD (2007) J Mater Sci 42:5534. doi:10.1007/s10853-006-1026-3
6. Shang YL, Jia YL, Liao FH, Li JR, Li MX, Wang J, Zhang SH (2007) J Mater Sci 42:2586. doi:10.1007/s10853-006-1336-5
7. Yavuz M, Cabuk M (2007) J Mater Sci 42:2132. doi:10.1007/s10853-006-1296-9

8. Choi HJ, Cho MS, Kim JW, Kim CA, Jhon MS (2001) Appl Phys Lett 78:3806
9. Yin J, Zhao X, Xia X, Xiang L, Qiao Y (2008) Polymer 49:4413
10. Bica I, Choi HJ (2008) Int J Modern Phys B 22:5041
11. Fang FF, Choi HJ (2008) J Appl Phys 103:07A301
12. Kim JH, Fang FF, Choi HJ, Seo Y (2008) Mater Lett 62:2897
13. Boissy C, Atten P, Foulc JN (1996) J Intell Mater Sys Struct 7:599
14. Lee KH, Park BJ, Choi HJ (2006) Eur Phys J E21:387
15. Kim DH, Kim YD (2007) J Ind Eng Chem 13:879
16. Stenicka M, Pavlinek V, Saha P, Blinova NV, Stejskal J, Quadrat O (2008) Colloid Polym Sci 286:1404
17. Duan X, Chen H, He Y, Luo W (2000) J Phys D: Appl Phys B 13:696
18. Sim IS, Kim JW, Choi HJ, Kim CA, Jhon MS (2001) Chem Mater 13:1243
19. Kim SG, Lim JY, Sung JH, Choi HJ, Seo Y (2007) Polymer 48:6622
20. Choi HJ, Lee IS, Sung JH, Park BJ, Jhon MS (2006) J Colloid Interface Sci 295:291
21. Choi HJ, Jhon MS (2009) Soft Matter 5:1562