J Mater Sci (2009) 44:2999–3001
DOI 10.1007/s10853-009-3404-0

LETTER

Comment on "preparation and electrorheology of new mesoporous polypyrrole/MCM-41 suspensions"

Ying Dan Liu · Hyoung Jin Choi

Received: 14 February 2009 / Accepted: 16 March 2009 / Published online: 2 April 2009

Electrorheological (ER) fluid, typically composed of polarizable particles and an insulating liquid, is a kind of smart materials which can be characterized by a reversible change from a liquid-like to a solid-like state without or with an electric field, [1–9] along with its magnetically analogous magnetorheological suspensions under an external magnetic field [10–12]. Rheological properties of this ER material such as shear stress and shear viscosity are also altered and tuned according to the electric field. Therefore, many investigators put a focus on this material and dedicate to their potential applications [13, 14].

Recently, Cheng et al. [15] reported a new type of anhydrous ER fluid prepared by dispersing nanocomposite particles (PPy/MCM-41) of conducting polypyrrole (PPy) confined in mesoporous silica (MCM-41) in silicone oil. This ER material was synthesized via a polymerization of pyrrole, which was introduced to the MCM-41 channels prior to the reaction [16, 17], in an aqueous solution of $FeCl_3 \cdot H_2O$. The PPy/MCM-41 nanocomposite based ER fluid showed Newtonian behavior in the absence of an electric field. However, when an electric field was applied, it was reported to behave like a Bingham fluid with a nonvanishing yield stress (τ_y) owing to the formation of fibrillar structures [18, 19] of the dispersed particles caused by the inter-particle forces (polarization forces) [20–22].

In this letter, we replotted an original flow curve of the ER fluid based on the PPy/MCM-41 under different electric fields as shown in Fig. 4 of Ref. [8], and then analyzed it using Bingham fluid and De Kee–Turcotte models [23] as well as recently proposed Cho–Choi–Jhon model [24, 25], aiming to have better explanation on flow properties of the novel ER fluid. Compared to the Bingham fluid and De Kee–Turcotte models, the Cho–Choi–Jhon model was found to fit the flow curves much better. Although several reports have focused on this study, it still needs further detailed investigations.

A Bingham fluid equation is the simplest model which can be applied to analyze flow behaviors of non-Newtonian fluids, taking the ER fluid as an example here. It is characterized by a yield stress followed by Newtonian behavior, and its relation between shear stress (τ) and shear rate ($\dot{\gamma}$) is as follows:

$$\dot{\gamma} = 0, \quad \tau \leq \tau_0$$
$$\tau = \tau_0 + \eta\dot{\gamma}, \quad \tau \geq \tau_0 \tag{1}$$

herein, η is a shear viscosity, and τ_0 is a yield stress which is the minimum stress rendering the ER fluid flow under an electric field, and its magnitude is related to the applied electric field strength. Initial studies on the ER fluids usually have adopted this simple model to describe the steady shear response as a function of shear rate. However, more interesting but complicated flow phenomena which generally deviate from the Bingham fluid model, are discovered [26], including both decrease of shear stress along with increase of shear rate at low shear rate region [27, 28] and trembling shear behavior which has been recently reported for modified chitosan based ER fluid [29].

Furthermore, De Kee–Turcotte model given in the following Eq. (2) was introduced to offer some advantages [30] over the Bingham model by modifying Eq. (1).

$$\tau = \tau_0 + \eta_1\dot{\gamma}e^{-t_1\dot{\gamma}} \tag{2}$$

where t_1 is a time constant, and η_1 is a shear viscosity. Based on its mathematical analysis, the second term was

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

found to be much affected by a high shear rate, in which many non-Newtonian fluids demonstrate shear thinning behavior. Nonetheless, a model which gives a better explanation for complex flow behaviors especially at a low shear rate region is still lacking.

Based on these backgrounds, Cho et al. [24] proposed a new constitutive rheological equation of state, named Cho–Choi–Jhon model, especially for the ER fluids under an applied electric field. It is a six-parameter modified equation shown as follows:

$$\tau = \frac{\tau_0}{1 + (t_1\dot{\gamma})^{\alpha}} + \eta_{\infty}\left(1 + \frac{1}{(t_2\dot{\gamma})^{\beta}}\right)\dot{\gamma} \tag{3}$$

where t_1 and t_2 are time constants, η_∞ is the shear viscosity at an infinite shear rate and is also considered as the shear viscosity in the absence of electric field at an infinite shear rate because the shear viscosity of both with and without an electric field is same at an infinite shear rate. The α is related to the decrease of shear stress at low shear rate region, while β is in the range of zero to 1 since $d\tau/d\dot{\gamma} \geq 0$ above the critical shear rate ($\dot{\gamma}_{crit}$) [31, 32] at which point the shear stress becomes a minimum. The two terms in the right-hand side of the equation represent the shear stresses in different shear rate regions. The first term describes the flow behavior of ER fluid at low shear rate region, indicating the decrease of shear stress as a function of shear rate. The second term covers the high shear rate region where all the shear stresses increase and then converge to a single line as the shear rate reaches to an extremely high value [33].

For the new ER material of PPy/MCM-41 nanocomposite which was prepared by introducing conductive PPy to the channels of MCM-41 [15] dispersed in silicone oil (10 wt%), it was observed that all the shear stresses under applied electric fields (1, 2 and 3 kV/mm) i.e., flow curves according to different electric field strengths, decrease slightly in the low shear rate region. The similar or more distinctive phenomena [34] were observed for various ER fluids. Thus, in order to analyze this flow behavior, we replotted the flow curve of Fig. 4 from Ref. [15] and fitted them using three different rheological models described above. The fitting parameters were summarized in Table 1.

All the yield stresses (τ_0) and viscosities (η_0, η_1, η_∞) for the different models increased with electric field strengths. The yield stresses estimated from the Cho–Choi–Jhon model, (17, 48, and 80 Pa for 1.0, 2.0 and 3.0 kV/mm, respectively) were observed to be a little bit higher than those from other two models. This can be explained by the introduction of the factor regarding the shear stress decrease as the first term of Eq. (3). In addition, the exponents, α and β also played important roles for the better fittings.

Table 1 The optimal parameters appeared in each model equation obtained from the flow curves of PPy/MCM-41 based ER fluid at various electric field strengths

Model	Parameter	Electric field strength		
		1 kV/mm	2 kV/mm	3 kV/mm
Bingham	τ_0	14	45	78
	η_0	0.18	0.20	0.26
De Kee–Turcotte	τ_0	15	43	74
	η_1	0.15	0.21	0.26
	t_1	0.0003	0.0002	0.0001
Cho–Choi–Jhon	τ_0	17	48	75
	η_∞	0.12	0.18	0.29
	α	0.20	0.21	0.38
	β	0.30	0.60	0.80
	t_1	5.00	2.00	1.00
	t_2	0.01	0.007	0.007

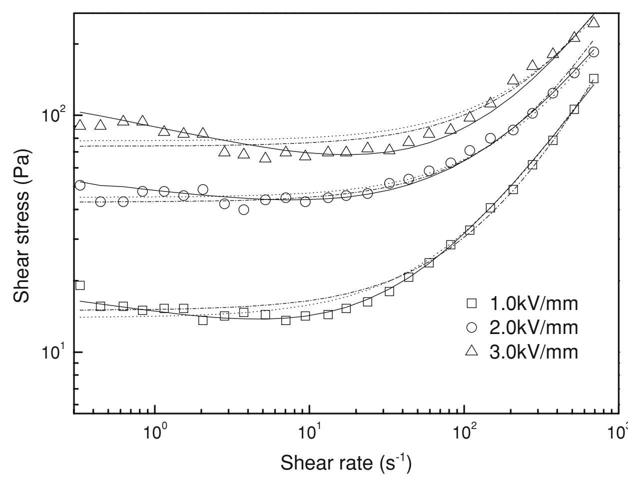

Fig. 1 Flow curves of PPy/MCM-41 based ER fluid (symbols for Ref. [15], *dot line* for the Bingham fluid model, *dash-dot line* for the De Kee–Turcotte model, and the *solid line* for the Cho–Choi–Jhon model)

The flow curves as well as the fitting lines are displayed in Fig. 1. Neither Bingham fluid model nor De Kee–Turcotte model could fit the flow curves well especially in the low shear rate region, while the Cho–Choi–Jhon model fits the flow curve better.

The flow curves of Fig. 1 under different electric field resulted different $\dot{\gamma}_{crit}$ values, 14.9 s^{-1} for 1 kV/mm, 15.7 s^{-1} for 2 kV/mm and 16.4 s^{-1} for 3 kV/mm. This upward trend was determined by the increased polarization forces affected by electric field strengths. In the low shear rate region (before $\dot{\gamma}_{crit}$), this force dominated compared to the hydrodynamic force in controlling the flow behaviors of the ER fluid. Note that well confirmed formation of the ER fluid under an electric field is the chain-like or columnar structure. Under applied shear, these structures tend to be destroyed and reformed by an external electric field. However, for the particles do not have enough time to form new chains after destruction by shear, their destruction rate of fibrillar structure becomes faster than the reformation rate as the shear rate increases [35]. When it reaches the high shear rate region, the hydrodynamic force rather than polarization force will be dominant so that no fibril structures exist and the ER fluid acts as like a Newtonian fluid.

Conclusion

In conclusion, the flow curves of the PPy/MCM-41 based ER fluid were adopted and analyzed using three different models, and then it was found that the Cho–Choi–Jhon model exhibits not only better fittings but also better understandings than two other Bingham fluid model and De Kee–Turcotte model, suitably explaining the decrease of shear stress in a low shear rate region well.

Acknowledgement This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Korea.

References

1. Fang FF, Choi HJ, Joo J (2008) J Nanosci Nanotech 8:1559
2. Choi HJ, Jhon MS (2009) Soft Matter. doi:10.1039/b818368f
3. Kim DH, Kim YD (2007) J Ind Eng Chem 13:879
4. Hong CH, Choi HJ, Kim JH (2008) J Mater Sci 43:5702. doi:10.1007/s10853-008-2915-4
5. Oz K, Yavuz M, Yilmaz H, Unal HI, Sari B (2008) J Mater Sci 43:1451. doi:10.1007/s10853-007-2319-x
6. Li GF, Wang ZQ, Wang NH (2007) J Mater Sci 42:8242. doi:10.1007/s10853-007-1733-4
7. Yoon DJ, Kim YD (2007) J Mater Sci 42:5534. doi:10.1007/s10853-006-1026-3
8. 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
9. Yavuz M, Cabuk M (2007) J Mater Sci 42:2132. doi:10.1007/s10853-006-1296-9
10. Bica I (2007) J Ind Eng Chem 13:299
11. Bica I, Choi HJ (2008) Int J Modern Phys B 22:5041
12. Fang FF, Choi HJ (2008) J Appl Phys 103:07A301
13. Liu L, Cao W, Wu J, Wen W, Chang DC, Sheng P (2008) Biomicrofluids 2:034103
14. Belza T, Pavlinek V, Saha P, Quadrat O (2008) Colloid Surf A 316:89
15. Cheng QL, He Y, Pavlinek V, Lengalova A, Li CZ, Saha P (2006) J Mater Sci 41:5047. doi:10.1007/s10853-006-0126-4
16. Cho MS, Choi HJ, Ahn WS (2004) Langmuir 20:202
17. Cho MS, Choi HJ, Kim KY, Ahn WS (2002) Macromol Rapid Commun 23:713
18. Liu ZP, Lin YB, Wen XH, Su Q (2005) Colloid Surf A 264:55
19. Hiamtup P, Sirivat A, Jamieson M (2006) J Colloid Interface Sci 295:270
20. Xiao JJ, Huang JP, Yu KW (2008) J Phys Chem B 112:6767
21. Hong CH, Choi HJ, Seo Y (2008) Synth Met 158:72
22. Kim YD, Kim JH (2008) Synth Met 158:479
23. De Kee D, Turcotte G (1980) Chem Eng Commun 6:273
24. Cho MS, Choi HJ, Jhon MS (2005) Polymer 46:11484
25. Kim SG, Lim JY, Sung JH, Choi HJ, Seo Y (2007) Polymer 48:6622
26. Espin MJ, Delgado AV, Plocharski JZ (2006) Rheol Acta 45:865
27. Hong CH, Choi HJ, Jhon MS (2006) Chem Mater 18:2771
28. Yin J, Zhao X, Xia X, Xiang L, Qiao Y (2008) Polymer 49:4413
29. Ko YG, Choi US, Chun YJ (2008) Macromol Chem Phys 209:890
30. Zhu H, Kim YD, De Kee D (2005) J Non-Newtonian Fluid Mech 129:177
31. Hong CH, Choi HJ (2006) Scripta Mater 55:415
32. Ryu JC, Kim JW, Choi HJ, Choi SB, Kim JH (2003) J Mater Sci Lett 22:807
33. Hong CH, Choi HJ (2007) Colloid Surf A 295:288
34. Fang FF, Kim JH, Choi HJ, Seo YS (2007) J Appl Polym Sci 105:1853
35. Chin BD, Winter HH (2002) Rheol Acta 41:265