International Journal of Modern Physics B
Vol. 19, Nos. 7, 8 & 9 (2005) 1065–1070
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THE ELECTRORHEOLOGICAL FLUIDS WITH HIGH SHEAR STRESS

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A series of high performance ER fluids newly manufactured in our laboratory are presented. The yield stress of those ER fluids can reach several tens of kPa, 100 kPa and even 200 kPa, respectively. For understanding the high shear stress effect a model is proposed base on the electric field induced molecular bounding effect. The main effective factors in fabricating the high performance ER are discussed.

The electrorheological (ER) fluid which was discovered half century ago has attracted much attention because of its wide potential applications in the technology. However, the fact that the shear stress of available ER fluids was not high enough for the practical requirement is the main obstacle for its application.

According to the conventional dielectric theory, the attractive force of the particles in ER fluids is $f \propto \varepsilon_f \beta^2 E^2$, where β is dielectric mismatch factor and equals to $(\varepsilon_p - \varepsilon_f)/(2\varepsilon_p + \varepsilon_f)$. E is the applied electric field. ε_p and ε_f are the permittivities of the particles and the liquid respectively. The β is higher, the interaction of the particles should be higher. Nevertheless, by using the particle with high permittivity in ER fluids the dielectric mismatch factor β tends to a saturated value and a little increase can be achieved in the shear stress as declared by many measurements. Even for the ER fluids containing ferroelectric $BaTiO_3$ and TGS ($(NH_2CH_2COOH)_3 \cdot H_2SO_4$) particles with very high dielectric constant the ER response is quite low, usually less than 1kPa [1-3]. On the other hand, the ER response should increase by using the oil with high ε_f due to $f \propto \varepsilon_f$. However, it's hard to find such suitable oils in practice because the high dielectric liquids usually go with high conductivity, which must result in a high current density and may cause electrical breakdown of ER fluid.

Based on a first-principle calculation with dielectric theory Ma et al [4] concluded that the physical upper bound in the yield stress is about 10kPa/kV/mm. A similar result was also predicted by Conrad [5]. All the studies based on the ordinary dielectric principle demonstrate that it is not able to obtain high performance ER fluids by only using either the particles or the oil with intrinsic high permittivity.

Although there was a despondence for the situation of the low shear stress in ER fluids as described above, many efforts still have been made in last decade to find new ER fluids for the goal of enhancing the shear stress.

An arisen approach was that the yield stress could be significantly enhanced by using the thin dielectric layer coated conducting particles in the ER fluids [6-10]. Wu and Conrad [8, 9] proposed a model and pointed that the shear strength could be as high as tens of kPa by using the coated particles with their recommended parameters in the preparation of ER fluid. In practice, with Ni inner and TiO_2 outer coating on glass spheres [7] or TiO_2 coating on graphite spheres [10] an order of magnitude enhancement in the yield stress was obtained compared to that of bare particles. Despite the complication of the coating technique and the obdurability of the coating layer, the enhancement in the shear stress by using such coated particles, typically several kPa, is still not satisfied for a broad application.

It's known for a long time that by adding small amount water in the particle the ER response can be substantially improved. However, there are some shortcomings for such ER fluids: the water evaporation at high temperatures, high current density and device erosion caused by water. Therefore the ER fluids containing water are not suitable for the application. The active mechanism of the water on the ER response is still an open problem up to now, though there were some explanations such as the water bridge model [11-13] which was equivocal and lack of sufficient experimental evidence. It's a reasonable illation that the role of water in enhancing the interaction of the particles must come from the comparatively high dipole moment of H_2O molecule (1.85 Debye [14]). This effect of H_2O molecule inspires us to improve ER materials by trying to add some other dipole molecules with high dipole moment, but with higher boiling point than that of water to avoid the evaporation at high temperature. For instance, acetamide and urea molecules are optional ones, of which the dipole moments are 3.76 and 4.56 Debye [14], the boiling or decomposing temperatures are 221°C and 133°C, respectively. Based on the consideration described above, we reported a surface modified complex strontium titanate (STO) ER fluid, of which the yield stress of ~30 kPa (at 3 kV/mm) was achieved [15-17]. Wen et al [18,19] created a giant electrorheological (GER) fluid with the urea coated Ba-Ti-O (BTO) nano-particles dispersed in oil. The yield stress can reach 130 kPa and even 250 kPa (at 5kV/mm). In those ER fluids the dependence of yield stress on the electric field shows a near-linear behavior instead of the quadratic behavior in ordinary ER fluids. A simulation based on the model of saturation surface polarization was performed and the calculated results were consisted with experimental ones [18, 20]. It can be concluded that the mechanism for those newly developed ER materials is different *from the traditional dielectric theory.*

In this paper some high-performance ER fluids newly manufactured in our laboratory are presented. A model for understanding the effect is proposed and a discussion about the main effective factors for achieving high-performance ER is made.

Several TiO_2, Ca-Ti-O etc based nano-particles with doping or without designed doping were synthesized by wet chemical techniques. The detailed procedures of the material preparation are described elsewhere [21, 22]. The sizes of the particles are in the range of 50-70nm. The ER fluids were made by suspending the particles in silicon oil and the suspensions were blended sufficiently. The yield stress τ_y of those ER fluids can reach as high as several tens of kPa, 100 kPa and even 200 kPa, respectively, for different samples prepared with various processes.

It is well known that the shear stress for an ER fluid consisted of dry TiO_2 particles is quite low. Fig.1 plots the relations of shear stress versus E for the pure TiO_2/silicon oil ER fluid, in which the TiO_2 are in the shape of crystalline powder with size about 10μm. The frequency dependence of the shear stress and the quadratic dependence of the shear stress on field strength E show a typical dielectric interaction between the particles.

For the purpose to improve the ER response we tested many kinds of TiO_2 particles prepared with various wet chemical methods (sol-gel, hydrothermal and co-deposition) and doped with different molecules. Fig.2 plots the shear stress versus electric field of some of those ER fluids, in which the curve numbers represent different doping molecules and quantities contained in the samples. It can be seen that the shear stresses of the samples are much higher than that of dry TiO_2 ER fluids but still less than 10 kPa. The dependence of the shear stress on the electric field shows a linear behavior in stead of the quadratic one as in ordinary dry TiO_2 ER fluids. These results encouraged us to change the experimental condition for screening out higher performance ER fluids. By improving

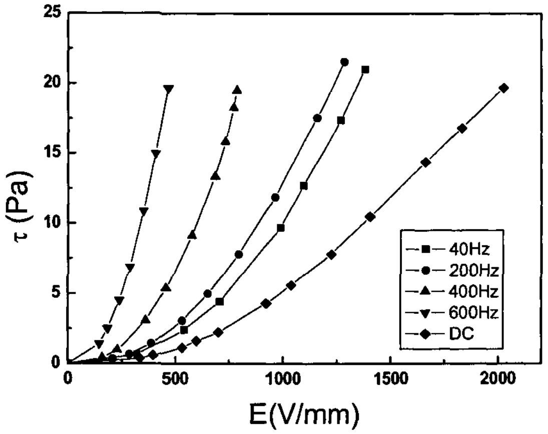


Fig.1 The yield stress vs. electric field strength for pure TiO_2 /silicon oil ER fluids (volume fraction ϕ= 15%)

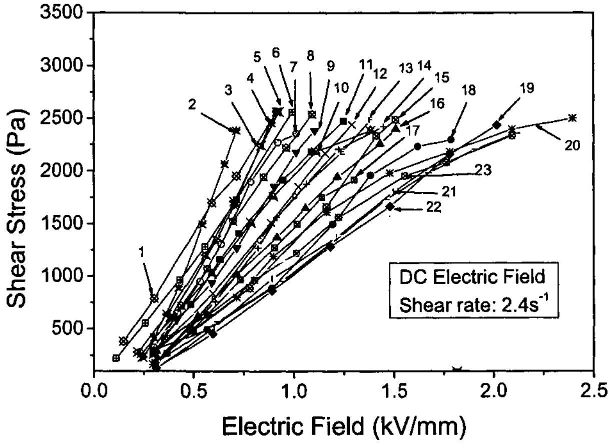
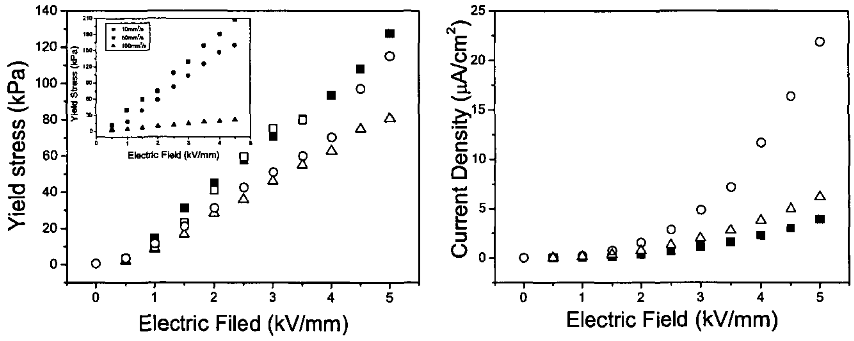


Fig.2 The shear stress vs. electric field strength for some ER fluids containing TiO_2 particles prepared with various wet chemical methods and doped with different molecules (volume fraction $\phi \approx$ 15%)

manufacture process of TiO_2 particles, quite a few high shear stress ER fluids were obtained. Even if there were no designedly doping molecules in the particles we could still get the high performance ER fluids. Also Ca-Ti-O particles synthesized without any designedly doping could possess good ER response up to ~100 kPa [22]. The relations of yield stress vs. electric fields of some those ER fluids are shown in Fig. 3(a) and their current densities are quite low as shown in Fig.3 (b). From the chemical analysis we knew that there were some C-H, O-H, chloride et al. group and molecules remained in the particles. When the particles were sintered at high temperature (~700^{o} C) and the doped or remained molecules were removed, then the ER fluids consisted of the sintered particles lost their high shear stress character. In addition it is found that the shear stress



(a) (b)

Fig.3 Yield stress (a) and current density (b) as functions of field strength for different ER fluids. Symbols indicate different ER fluids: filled square — urea doped TiO_2 ER fluid (30vol%) ; triangle — acetamide doped TiO_2 ER fluid (30vol%); square — undoped TiO_2 ER fluid; circle — undoped Ca-Ti-O ER fluid. Inset in Fig.3 (a) shows the effect of oil viscosity on ER response for TiO_2 ER fluid (40vol%).

is sensitive to the viscosity of the silicon oil. Sometimes the significant differences can be observed on the yield stresses when the same particles are respectively dispersed in various silicon oils with different viscosities. As shown in the inset of Fig.3 (a) there is more than ten times of difference in the yield stress by using the silicon oils of 10 mm^2/s and 100 mm^2/s. Another advantage of those ER fluids consisted of nano-particles is that there is no obvious sedimentation happened within a few months.

In previous model [18] the GER effect was ascribed to the polarization saturation layers in between two neighboring coated particles. In our case, however, either the coated molecules or remained trace molecules on the particles can play important role on the GER effect. It indicates that the coated layers on the particles are not necessary at all time for the GER effect. We have proposed a model to explain the origin of the effect which is described briefly as follows. Our experimental results indicate that the high ER response is dominated by the small amount of dipole molecules contained in the suspended particles. From the traditional dielectric theory it is known that the local electric field E_{loc} in the region between two neighboring particles is much higher than applied field and its magnitude depends on the particle properties as well as the gap size between the particles. If E_{loc} is high enough the molecules absorbed on the particle surface in the region can be aligned to the direction of the field. In the case of the two particles nearly contact, the molecules from two neighboring particles can attract and bound each other when the electric field is applied. The interaction energy between two dipole molecules is $U_d = \frac{\mu^2}{4\pi\varepsilon_0 d^3}$ (for same molecules), where μ is the dipole moment of the molecule and d is the distance between them. When we assume typically $\mu \approx 2$ Debye and $d \approx 0.4$ nm, this interaction energy is larger than KT. The interaction force between such two molecules is about the same as that between two particles of 50 nm in diameter, which can be calculated with the dielectric theory [23, 24]. Accompanying with the increase of the electric field more molecules in the gap between the particles can be turned to the electric direction and attract each other. When the electric field is switched off, the aligned molecules will then return back to disordered state due to the thermal motion and their interactions will disappear. Since there must be a large number of dipole molecules remained in the interface region of nearly contacted particles, consequently the total attractive force of all those molecules will be much larger than that of field induced interaction from particles themselves. The increase of the applied field, together with the local field, mainly causes the number of interactive molecules increasing and affects not much on the dipole moment of the molecules. This fact results in the linear behavior on the relation of the interaction force versus the field strength in the ER fluids. Above analysis can give us a better understanding on the observed phenomenon for both high shear stress and its linear dependence on field strength. In conclusion, the GER phenomenon can be attributed to the electric field induced molecular bounding effect. Because of this molecular bonding happened on the interface, therefore the surface tension, viscosity of oil as well as the electric-wetting effect [20] may play a role and cause different ER responses. A rigorous calculation and detailed discussion will be published elsewhere.

For achieving high shear stress ER fluids, in our experience, several effective factors should be taken into account in the manufacture of ER samples. i) The ER fluids ought to be consisted of nano-size particles with relatively high dielectric constant. The particles with high dielectric constant can induce high local electric field in the region between particles, which is in favor of rearranging the molecules on the particle surface turned to the direction of the field. ii) The nano-particles usually can be prepared with wet chemical method with doping or without doping purposely, where must be some dipole molecules with high dipole moment remained in the particles. iii) In the undoping case a suited amount of the dipole molecules should be kept on the particles during the procedures such as washing, drying etc. iv) Dipole molecules contained in the particles should not be disengaged in the temperature range for application. v) It is necessary to test different oils for matching the particles because the ER response is sensitive to the viscosity of the silicon oil.

In summary we have manufactured several high performance ER fluids with the yield stress up to 100 kPa and even higher, which also show other advantages such as low current density and anti-sedimentation. A model for explaining the mechanism is proposed and described briefly based on the electric field induced molecular bounding effect. A discussion about the main effective factors in preparing high performance ER fluids is also presented.

Acknowledgement

This work is supported by The Outstanding Overseas Chinese Scholars Fund of Chinese Academy of Sciences. The authors would thank Prof. J. X. Liu, W. Y. Lai for helpful discussion.

References

1. Lan Y., Men S., Zhao X. and Lu K., The dependence of particle permittivity on the shear stress of electrorheological fluids, *Appl. Phys. Lett.*, **72**(1998)pp.653-655
2. Lan Y. C., Men S. Q., Xu X. Y. and Lu K. Q., Experimental study of dielectric constant influence on electrorheological effect, *J. Phys. D: Appl. Phys.*, **33**(2000) pp. 1239-1243

3. Lan Y. C., Huang C. K., Men S. Q. and Lu K. Q., Experimental investigation of the frequency dependence of the electrorheological effect, *Phys. Rev. E*, **70** (2004) 021507
4. Ma H. R., Wen W. J., Tam W. Y., and Sheng P., Frequency dependent electrorheological properties: origin and bounds, *Phys. Rev. Lett.*, **77** (1996) pp.2499-2502
5. Conrad H., Chen Y. and Sprecher A. F., The strength of electrorheological (ER) fluids, *Intern. J. Mod. Phys. B*, **6** (1992) pp.2575-2594
6. L. C. Davis, The metal-particle/insulating oil system: An ideal electrorheological fluid, *J. Appl. Phys.* **73** (1993) pp.680-683
7. Tam Y., Yi G. H., Wen W. J., Ma H. R., Loy M. M. T., and Sheng P., New electrorheological fluid: theory and experiment, *Phys. Rev. Lett.*, **78**(1997)pp. 2987-2990
8. C. W. Wu and H. Conrad, Influence of a surface film on the particles on the electrorheological response, *J. Appl. Phys.*, **81**(1997) pp.383-389
9. Wu C. W. and Conrad H., Multi-coated spheres: recommended electrorheological particles, *J. Phys. D: Appl. Phys.*, **31** (1998) pp.3312-3315
10. Xu S. J., Men S. Q., Wang B. and Lu K. Q., Study of an electrorheological fluid: TiO_2 coating graphite/silicone oil, *Acta Physica Sinica*, 49(2000)pp.2176-2179
11. J.E. Stangroom, Phys. Techn. **14** (1983) 290.
12. Kim Y. D. and Klingenberg D. J., Two Roles of Nonionic Surfactants on the Electrorheological Response, *J. Colloid Interface Sci.*, **183** (1996) pp.568-578.
13. See H., Tamura H. and Doi M., The role of water capillary forces in electro-rheological fluids, *J. Phys. D: Appl. Phys.*, **26** (1993)pp.746-753.
14. Handbook of Chemistry and Physics, 61st. 1980-1981 edition, edited by R. C. Weast (CRC Press).
15. Zhang Y., Ma Y., Lan Y., Lu K. and Liu W., The electrorheological behavior of complex strontium titanate suspensions, *Appl. Phys. Lett.*, **73**(1998)pp.1326-1328
16. Zhang Y. L., Zhang S. H. and Lu K. Q., The ER behavior of surface modified complex strontium titanate suspensions, *Intern. J. Mod. Phys. B*, **15**(2001) pp.596-598
17. Zhang Y., Lu K., Rao G., Tian Y., Zhang S. and Liang J., Electrorheological fluid with an extraordinarily high yield stress, Appl. Phys. Lett.,80(2002)888-890
18. Wen W., Huang X., Yang S., Lu K. and Sheng P., The giant electrorheological effect in suspensions of nanoparticles, *Nature Materials*, **2**(2003)pp.727-730
19. Wen W., Huang X., and Sheng P., Particles size scaling of the giant electrorheological effect, *Appl. Phys. Lett.*, **85**(2004)pp.299-301
20. Sheng P., in this proceedings.
21. Shen R., Lu K., Wang X. and Wen W., in this proceedings. And also: Shen R., Lu K., Wang X. et al., Chinese Patent.
22. Wang X. Z, Shen R., Wen W. J. and Lu K. Q., in this proceedings. And also: Wang X., Shen R., Lu K., et al., Chinese Patent.
23. Davis L. C., Polarization forces and conductivity effects in electrorheological fluids, *J. Appl. Phys.* **72** (1992)pp.1334-1340.
24. Tao R., Jiang Q. and Sim H. K., Finite-element analysis of electrostatic interactions in electrorheological fluids, *Phys. Rev. E*, **52** (1995) pp.2727-2735.

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1. Ning Ma, Xufeng Dong. 2015. Diammonium phosphate modified titanium dioxide suspensions with improved ER efficiency. *Smart Materials and Structures* **24**, 065009. [CrossRef]
2. Jianbo Yin, Xiaopeng ZhaoPolyaniline Nanocomposites for Smart Electrorheological Fluid Applications 731-758. [CrossRef]
3. Ludan Li, Jianbo Yin, Yang Liu, Xiaopeng Zhao. 2015. Graphene oxide vs. reduced graphene oxide as core substrate for core/shell-structured dielectric nanoplates with different electro-responsive characteristics. *J. Mater. Chem. C* . [CrossRef]
4. Zhenhua Li, Fenghua Liu, Gaojie Xu, Jialiang Zhang, Chengyi Chu. 2014. A kinetics-controlled coating method to construct 1D attapulgite @ amorphous titanium oxide nanocomposite with high electrorheological activity. *Colloid and Polymer Science* **292**, 3327-3335. [CrossRef]
5. Jianbo Yin, Runtian Chang, Yan Kai, Xiaopeng Zhao. 2013. Highly stable and AC electric field-activated electrorheological fluid based on mesoporous silica-coated graphene nanosheets. *Soft Matter* **9**, 3910. [CrossRef]
6. Jianbo Yin, Xiaoxiao Wang, Runtian Chang, Xiaopeng Zhao. 2012. Polyaniline decorated graphene sheet suspension with enhanced electrorheology. *Soft Matter* **8**, 294. [CrossRef]
7. Jianbo Yin, Xiaoxiao Wang, Runtian Chang, Xiaopeng Zhao. 2012. Polyaniline decorated graphene sheet suspension with enhanced electrorheology. *Soft Matter* **8**, 294-297. [CrossRef]
8. KUNQUAN LU, RONG SHEN, XUEZHAO WANG, DE WANG, GANG SUN. 2011. POLAR-MOLECULE-DOMINATED ELECTRORHEOLOGICAL (PM-ER) FLUIDS: THE PROPERTIES AND EVALUATIONS. *International Journal of Modern Physics B* **25**:07, 957-962. [Abstract] [References] [PDF] [PDF Plus]
9. Jianbo Yin, Xiaopeng Zhao. 2011. Electrorheology of nanofiber suspensions. *Nanoscale Research Letters* **6**, 256. [CrossRef]
10. Jianbo Yin, Xiang Xia, Xiaoxiao Wang, Xiaopeng Zhao. 2011. The electrorheological effect and dielectric properties of suspensions containing polyaniline@titania nanocable-like particles. *Soft Matter* **7**, 10978. [CrossRef]
11. Jianbo Yin, Xiang Xia, Liqin Xiang, Xiaopeng Zhao. 2010. Coaxial cable-like polyaniline@titania nanofibers: facile synthesis and low power electrorheological fluid application. *Journal of Materials Chemistry* **20**, 7096. [CrossRef]
12. Rong Shen, Xuezhao Wang, Yang Lu, De Wang, Gang Sun, Zexian Cao, Kunquan Lu. 2009. Polar-Molecule-Dominated Electrorheological Fluids Featuring High Yield Stresses. *Advanced Materials* **21**:10.1002/adma.v21:45, 4631-4635. [CrossRef]
13. Y Lu, R Shen, X Z Wang, G Sun, K Q Lu. 2009. The synthesis and electrorheological effect of a strontium titanyl oxalate suspension. *Smart Materials and Structures* **18**, 025012. [CrossRef]
14. Jianbo Yin, Xiaopeng Zhao, Liqin Xiang, Xiang Xia, Zhanshu Zhang. 2009. Enhanced electrorheology of suspensions containing sea-urchin-like hierarchical Cr-doped titania particles. *Soft Matter* **5**, 4687. [CrossRef]
15. Frank FiliskoCurrent Developments in Electrorheological Materials . [CrossRef]
16. Jianbo Yin, Xiaopeng Zhao. 2008. Electrorheological properties of titanate nanotube suspensions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **329**, 153-160. [CrossRef]
17. RONG SHEN, XUEZHAO WANG, YANG LU, GANG SUN, WEIJIA WEN, KUNQUAN LU. 2007. THE METHODS FOR MEASURING SHEAR STRESS OF POLAR MOLECULE DOMINATED ER FLUIDS. *International Journal of Modern Physics B* **21**:28n29, 4813-4818. [Abstract] [References] [PDF] [PDF Plus]

18. KUNQUAN LU, RONG SHEN, XUEZHAO WANG, GANG SUN, WEIJIA WEN, JIXING LIU. 2007. POLAR MOLECULE TYPE ELECTRORHEOLOGICAL FLUIDS. *International Journal of Modern Physics B* **21**:28n29, 4798-4805. [Abstract] [References] [PDF] [PDF Plus]

19. R. Shen, X. Z. Wang, Y. Lu, W. J. Wen, G. Sun, K. Q. Lu. 2007. The methods for measuring shear stress of polar molecule dominated electrorheological fluids. *Journal of Applied Physics* **102**, 024106. [CrossRef]

20. Lu Kun-Quan, Shen Rong, Wang Xue-Zhao, Sun Gang, Wen Wei-Jia, Liu Ji-Xing. 2006. Polar molecule dominated electrorheological effect. *Chinese Physics* **15**, 2476-2480. [CrossRef]