Polar-Molecule-Dominated Electrorheological Fluids Featuring High Yield Stresses

By *Rong Shen, Xuezhao Wang, Yang Lu, De Wang, Gang Sun, Zexian Cao*, and *Kunquan Lu**

Recent works on the development of various electrorheological (ER) fluids composed of TiO_2, Sr—Ti—O, and Ca—Ti—O particles coated with C—O/H—O polar groups are summarized, in which an extremely large yield stress up to 200 kPa is measured and the dynamical yield stress reaches 117 kPa at a shear rate of 775 s^{-1}. Moreover, unlike that of traditional dielectric ER fluids, the yield stress displays a linear dependence on electric field strength. Experimental results reveal that it is the polar molecules adsorbed onto the dielectric particles that play the decisive role: the polar-molecule-dominated ER effect arises from the alignment of polar molecules by the enhanced local electric field in the gap between neighboring particles. The pretreatment of electrodes and the contrivance of new measuring procedures, which are desirable for the characterization and practical implementation of this material, are also discussed. The successful synthesis of these fluids has made many of the long since conceived applications of the ER effect available.

1. Introduction

Electrorheological (ER) fluids are referred to as a kind of colloids consisting of dielectric particles suspended in a non-conducting carrier liquid. By applying an electric field the rheological properties of ER fluids can be changed immediately, typically in a few milliseconds, as a response to the transition between the liquid and the solid-like phases, and in a reversible manner. An obvious advantage of ER devices is that they can control considerably more mechanical power than the electrical power used to control the effect, i.e., it can act as a power amplifier. Consequently, ER fluids can have a broad range of applications in various industries. The very common applications for ER fluids include fast acting valves, clutches, brakes and shock absorbers, and many novel uses such as in accurate polishing, robotics, haptic controllers, tactile displays, and making of bulletproof vests are also under test.

The research over ER fluids has gone through three successive stages when viewed with regard to the dispersed particles and the additives used. At the initial stage immediately following the discovery of ER effect by Winslow in 1949,[1] water was usually added into the carrier fluid to active the ER effect. The hydrated ER fluids are unfortunately inapplicable because the ER effect in such a fluid decays rapidly following the evaporation of water, and the leakage current is unacceptably high due to the presence of water. Then it followed a long drowsy period for the study of ER fluids till 1985 when Block succeeded in making a water-free ER fluid.[2] This sparked a wave of research enthusiasm towards anhydrous ER fluids in the world. In the following decade or so, water-free ER fluids had been thoroughly investigated, and the underlying physical mechanism became well understood from the dielectric theory.[3–5] It is established that the ER effect arises from the interaction of the polarized particles which form chains and columns along the direction of the external electric field, and the yield stress displays a quadratic dependence on the field strength. This type of ER fluids is conventionally termed as dielectric ER fluid. Although much research efforts had been made to improve the performance of ER fluids, however, the yield stresses available were still generally less than 5 kPa, too low to meet the requirements for practical applications. More frustration came in 1996 when a first-principles calculation based on the dielectric theory claimed an upper bound of only about 10 kPa for the yield stress of the dielectric ER fluids.[3] Clearly, the mechanical performance of the dielectric ER fluids is uncompetitive in comparison with the magneto-rheological fluids, of which the yield stress usually can be 50–100 kPa, though the former may possess some complementary advantages.

The last decade has witnessed a favorable turn for the research over ER fluids. In 1998, our research group reported an ER fluid composed of strontium titanate (Sr—Ti—O) particles, of which the yield stress measures 28 kPa under a field of 3 kV mm^{-1},[6] already exceeding the measure range of rheometers available at that time. The reason for such a high yield stress value lies in the usage of particles of a high dielectric constant, and the presence of polar molecules in the carrier fluid. This recipe originates in the consideration that, since water can significantly enhance ER

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[*] Prof. K. Lu, Dr. R. Shen, Dr. X. Wang, Y. Lu, D. Wang, Prof. G. Sun, Prof. Z. Cao
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics
Chinese Academy of Sciences, Beijing 100190 (P. R. China)
E-mail: lukq@aphy.iphy.ac.cn

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effect but spoils the fluid due to its evaporation, the substitution of water by other polar molecules that are less volatile might do the work better.

In 2003, with the ER fluid composed of $BaTiO(C_2O_4)_2$ nanoparticles coated with urea (NH_2CONH_2) a yield stress up to 130 kPa was measured.[7] Up to now, we have fabricated several high-yield stress ER fluids with titanium oxide (TiO_2),[8] calcium titanate (Ca–Ti–O)[9] and strontium titanate (Sr–Ti–O)[10] nano-particles which are coated with deliberately chosen polar molecules, and the yield stress even reaches as high as over 200 kPa. Other new ER fluids of this type that display very high yield stressed have been synthesized in recent years by other researchers.[11–13] A notable character of these ER fluids is the linear dependence of yield stress upon the electric field, rather than quadratic as for the dielectric ER fluids. Obviously a different physical mechanism is in action in these new ER fluids which are now termed by us as the polar-molecule dominated electrorheological (PM-ER) fluids.[14] The current review article will provide a brief line of thought and practice for the synthesis of PM-ER fluids and for the establishment of the underlying physical mechanism. Also the improved measuring methods for the high yield stresses, only becoming desirable recently with the advent of our PM-ER fluids, and the possible implementation of PM-ER fluids for some applications are discussed.

2. Synthesis of PM-ER Fluids

Polar molecules or polar groups are added to the nanoparticles of TiO_2, Ca–Ti–O, and Sr–Ti–O in the due course of particle synthesis. By adding urea molecules or C=O and O–H polar groups to the TiO_2 nanoparticles, and adding C=O and O–H polar groups to the nanoparticles of Ca–Ti–O as well as Sr–Ti–O, the ER fluids thus obtained exhibit a very high yield stress. The dipole moments of urea, C=O and O–H are 4.56, 2.3–2.7, and 1.51 Debye ($1\ \text{Debye} = 3.3564 \times 10^{-30}\ \text{C} \cdot \text{m}$), respectively. Analysis of the IR spectroscopic data confirms the adsorption of the polar molecules or polar groups onto the particles in the fluid. For the preparation of PM-ER fluids concerned here, TiO_2 and Ca–Ti–O particles of 50–100 nm[8,9] in diameter, and Sr–Ti–O particles of 2–6 μm in dimension,[10] are suspended in silicone oil with volume fractions of about 35%. The yield stresses of such ER fluids measured under various field strengths are shown in Figure 1a, which display a roughly linear dependence upon the field strength. The current densities measured exclusively less than 20 $\mu A\ cm^{-2}$. Figure 1b plots the shear stress versus shear rate curve for the ER fluid composed of TiO_2 nanoparticles, which was measured with a custom-designed sealed cylindrical rheometer shown in the inset of Figure 1b (for details, see Ref. [14]). To prevent the sliding of ER fluid on the electrodes, the surface of the electrodes was coated with a layer of diamond grains. It can be seen that the shear stress amounts to about 60 kPa at 3 kV mm^{-1}. For the ER fluid composed of Ca-Ti-O particles, with a volume fraction of 40%, the nominal shear stress was measured to be 117 kPa at a shear rate of 775 s^{-1} under the electric field of 4 kV/mm, while the nominal shear stress at zero field is only about 10 kPa. This appreciably large shear stress at zero field is mainly owing to the friction caused by the sealing ring enclosing the rotary cylinder. Obviously, the yield strength of the PM-ER fluids is much higher than that obtained in the traditional dielectric ER fluids.

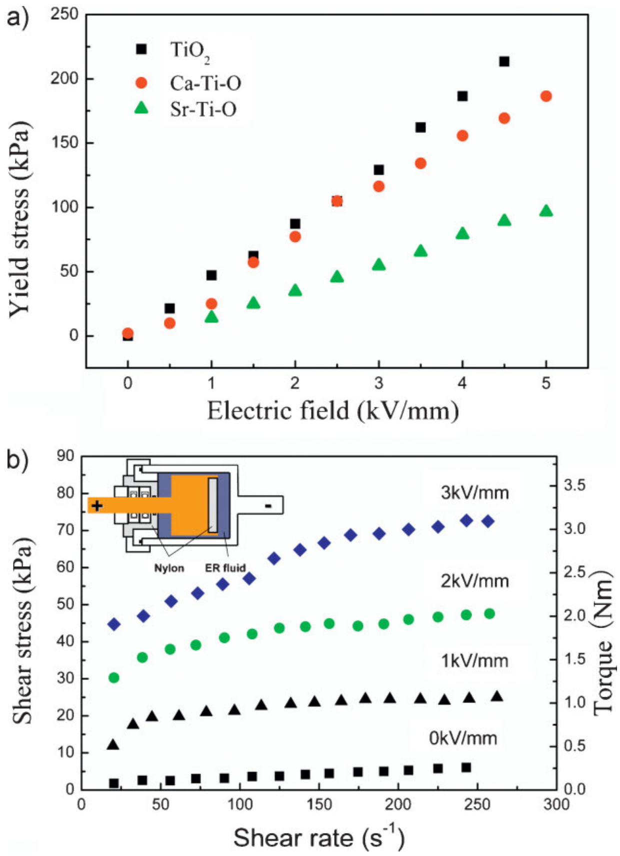

Figure 1. a) Yield stress versus electric field strength for three ER fluids composed of TiO_2, Ca–Ti–O, and Sr–Ti–O nanoparticles coated with C=O and O–H groups. b) Shear stress versus shear rate under various field strengths for the ER fluid composed of TiO_2 nanoparticles. The data were obtained with a sealed cylindrical rheometer shown in the inset to (b).

3. Physical Mechanism of PM-ER Fluids

That it is the polar molecules that give effect to the high yield stress in these newly developed ER fluids can be verified by the following observation. In an ER fluid made with the particles that have been heated at high temperature (500–800 °C) for a sufficiently long time to completely release the adsorbed polar groups, as confirmed by IR and differential scanning calorimeter measurements, the large yield stress is simply diminished and the suspension behaves as an ordinary dielectric ER fluid. This observation is valid for all the aforementioned three types of particles,[8–10] and it justifies the nomenclature of PM-ER fluids. Therefore a pertinent model for the PM-ER fluids must cope with the behavior of the polar molecules in determining the ER effect of the fluid.

Although a preliminary model based on the concept of polarization saturation layer has been proposed to explain the giant ER phenomenon in the urea-coated particle system,[8] our further experiments indicate that this model needs to be improved. Based on our experimental observation, a more reasonable model for the explanation of the PM-ER effect can be formulated,[14] which is sketched as follows. When an electric field E is applied, the polarized particles in the fluid attract each other and align along the field direction to form chains. The local electric field E_{loc} in the gap between two particles is much higher than E,[4,5] and the value of E_{loc}/E depends on δ/r and $\varepsilon_p/\varepsilon_f$, where δ is the separation of particles, r the particle radius, ε_p and ε_f the dielectric constants of the particles and the carrier fluid, respectively. According to Davis,[5] E_{loc}/E is about 10^3 for the case of $\delta/r \approx 10^{-3}$ and $\varepsilon_p/\varepsilon_f \approx 100$. The reliability of Davis's calculation has been demonstrated by measuring the attractive force between two spheres subjected to an electric field.[15] Although the local field is so high in between the particles, electrical breakdown rarely occurs at such a narrow and small region in oil. The polar molecules on the surface of the particles are weakly bonded to the particles with an adsorption energy of U_{ad}, usually slightly greater than kT. We suppose that the molecules are still free to rotate; thus they can be reoriented in the direction of a strong electric field,[16] i.e., the magnitude of μE_{loc} is comparable with U_{ad} and larger than kT.

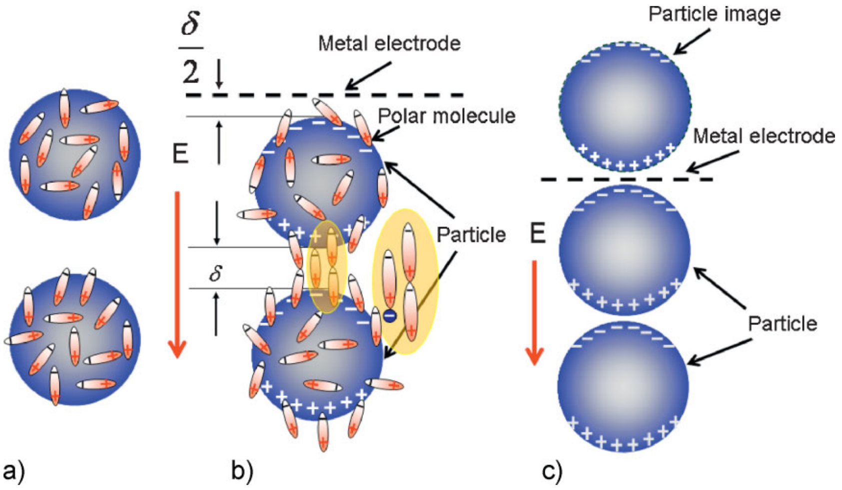

Figure 2. Schematic illustration of the polar-molecule alignment by external electric field. (a) $E=0$, polar molecules adopt a random distribution on the particle surface; b) polar molecules in the gap of two particles turn aligned along the field when E is sufficiently large. Two possible interactions, the dipole-dipole interaction and dipole-polarization charge interaction, are shown. The nearest separation of the particles from the electrode may be half of the particle gap due to the image charge effect. c) depicts the corresponding situation for conventional ER fluids under an applied field.

Figure 2 schematically illustrates the rearrangement of polar molecules on the particle surface induced by the applied field. Under zero field, the polar molecules lie randomly scattered on the particle surface (Fig. 2a). A sufficiently strong electric field can effectively bring the particles together, thus the E_{loc} are capable of aligning the polar molecules in the gap of two adjacent particles along the field direction. Two types of interactions are to be considered: dipole-dipole interaction among the molecules, f_{m-m}, and dipole-charge interaction among the polar molecule and the polarization charge from the particle, f_{m-e} (Fig. 2b). Calculation concludes that the force f_{m-m} is much weaker, therefore the PM-ER effect comes mostly from the attractive force f_{m-e}. The total attractive force F_{m-e} of molecule-charge in a unit area perpendicular to the external field can be approximated by

$$F_{m-e} = \frac{3\phi}{2\pi r^2} N f_{m-e} = A\frac{3\phi\rho_m e\mu^2 E}{\pi r\varepsilon_0\varepsilon_f d^2} \tag{1}$$

in which[17]

$$f_{m-e} = \frac{e\mu}{2\pi\varepsilon_0\varepsilon_f d^3_{m-e}} \tag{2}$$

the factor A is related to the properties of the particle and the oil, geometry of the particles as well as the adsorption energy U_{ad}, ϕ is the volume fraction of the particles in suspension, ρ_m is the area density of the polar molecules adsorbed on the particles, e is the fundamental charge, μ and d are the dipole moment and the size of the polar molecule, r is the radius of the particle, and ε_o and ε_f are the dielectric constant of vacuum and the dispersing phase, respectively.

From Equation 1, some relevant conclusions can be drawn:

(1) F_{m-e} increases linearly with E following $N(E) \propto \mu E$, i.e., the yield stress depends nearly linearly on the applied electric field (cf. Fig. 1a).
(2) $F_{m-e} \propto r^{-1}$ means that PM-ER fluids composed of smaller particles have a higher yield stress, as confirmed by the experiment.[18] This also differs from the conventional ER fluids for which the yield stress usually becomes larger with increasing particle size.[4]
(3) Nanoparticles are not only favorable for obtaining ER fluids of high shear stresses, but also advantageous when particle sedimentation is of concern. This, however, has to be taken at the cost of increased viscosity at zero field. Note also that larger particles are beneficial for getting a higher local electric field, and for small particles this can be compensated by choosing materials of very large dielectric constant.[4]
(4) $F_{m-e} \propto \mu^2 d^{-2}$ indicates that choosing smaller polar molecules yet with a larger dipole moment is mostly favorable. Also polar molecules with larger μ can be easily aligned at a lower E.

Equation 1 helps us to estimate the yield stress in PM-ER fluids. As an example, let's consider a system of $r = 30$ nm, $\delta = 0.2$ nm, $d_{m-e} = 0.2$ nm, $\mu = 2$ Debye, $\phi = 35\%$ and $N = 1$, then an $F_{m-e} = 180$ kPa can be achieved. In contrast, for a traditional ER fluid composed pure TiO_2 particle, only an $F_{p-p} = 0.6$ kPa is obtainable at $E = 3 \times 10^6$ V m^{-1}.[4] It can be seen that $F_{m-e}/F_{p-p} \approx 3 \times 10^2$, assuming even in average there is only one polar molecule active on each particle. Therefore a yield stress 2–3 orders of magnitude higher than the conventional ER fluids is expected for PM-ER fluids. We expect even a yield stress in MPa is realizable when the material parameters are appropriately optimized.

4. Electrode Pretreatment

The yield stress of conventional ER fluids is usually less than 10 kPa. In the strength measurement for or application of such ER fluids, the boundary condition at the interface of ER fluid and electrode is comparable to that inside the fluid (Fig. 2c). Therefore the measured values of yield stress can be taken as the true rheological property of the conventional ER fluids. However, for PM-ER fluids it differs a lot at the fluid-electrode interface and inside the fluid. By virtue of the image effect, the separation of the electrode from the nearest particles is roughly half the gaps between particles in the fluid, therefore it is hardly likely for the adsorbed polar groups to align along the direction of the electric field (Fig. 2b). Consequently the interaction at the fluid-electrode interface is usually much weaker. When determining the shear stress by using the conventional rheometer, yield starts at the interface and the ER fluid slides along the electrodes at a large enough field strength, consequently the nominal value is much lower than the intrinsic value of the fluid. The situation is even worse in dynamic measurement.

Roughening the surface of electrodes should be a straightforward way to prevent sliding of PM-ER fluids on electrodes.[19] Three groups of electrodes at largely differing roughness levels are applied: A) Polished electrodes; B) Rough electrodes ground by coarse sand paper (about 200 mesh); C) Electrodes with a filed surface with grooves of a typical depth in a few tens of micrometer, for which the protuberant tips were coated with epoxy resin to prevent point discharge. The effect of electrode surface roughness on the measurement of yield stress can be immediately recognized from the corresponding curves shown in Figure 3, where the measurement obtained with a new device contrived by us is also displayed for comparison (curve D, to be discussed below). With the smooth electrodes, the sliding of ER fluids leads to a seriously underestimated yield stress (curve A) that at 5.0 kV mm^{-1} it only measures 30 kPa, roughly one sixth of the value in curve D. With the ground electrodes the sliding of ER fluid can be suppressed to some extent that the measured values roughly doubled (curve B), yet even with the filed electrodes it still gives an underestimated value for the yield stresses. Clearly, the large yield stress in the PM-ER fluids calls for an innovated measuring procedure and appropriate device design. The photographs in Figure 3 help the readers to gain an intuitive appreciation of the improved conglutination of ER fluids on the electrodes with increasing roughness (from top to bottom).

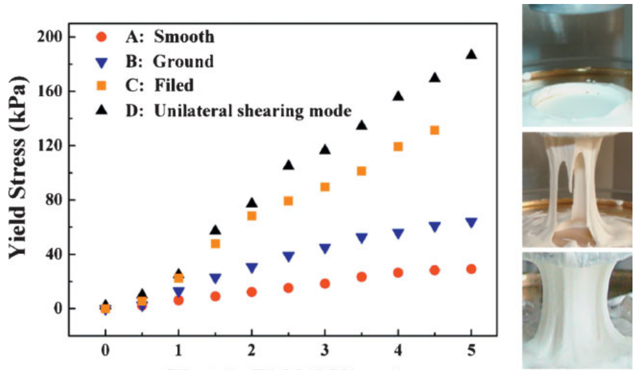

Figure 3. Variation of yield stress versus electric field measured with different electrodes. Curves A, B, and C represent the data measured with smooth, ground and filed electrodes, respectively. Curve D illustrates the values obtained with the unilateral shearing mode, which can be taken as the intrinsic property for the material. The photographs at right, from top to bottom, display the conglutination of ER fluids on the electrodes referred to curves A, B, and C, respectively. Electrical field strength: 2 kV mm^{-1}.

The undesirable drawback of using a roughened electrode is the markedly raised current density, sometimes even breakdown occurs. We proposed and have tried various methods, including mechanical processing, spraying, chemical vapor deposition, adhesive bonding, plating, sintering and infiltrating, to prepare electrodes that are rough yet will not lead to point discharge. We found that electrodes coated with diamond and alumina grains (≈150 mesh) can best meet the above requirements. Moreover, such coated electrodes are also favorable for shear stress measurement at high shear rates since the superhard diamond and alumina grains are exceptionally wear-resistant.

5. New Measuring Methods

Although the measured strength of the PM-ER fluids has been raised by a few times with the pretreated rough electrodes, yet we know it has not reached its intrinsic value since the weak bonding to the electrodes remains an unavoidable disturbing factor. In order to circumvent such a problem, we devised two measuring procedures inspired by the shear stress measuring equipments for solids, which are named as unilateral shearing mode and slice shearing mode by us. Detailed information over the measuring setups can be found in Ref. [20]. Briefly, two metallic electrodes are embedded into two separated grooves of insulating blocks which are filled and connected by ER fluid. A step motor is used to drive the upper insulating block in the unilateral shearing mode or to push the central, exposed part of the ER fluid in the slice shearing mode, and a force sensor is attached to detect the shear force F. Shear stress can then be calculated from $\tau = F/S$, where S is the cross sectional area of the ER fluid. With these measuring procedures the effect of fluid sliding on the electrode can be eliminated that the measured yield stresses can be taken as the intrinsic character of the ER-fluids. Of course, the values thus measured should be higher than those obtained with the parallel plate rheometer, as confirmed by curve D in Figure 3.

6. Conclusions and Outlook

In summary, yield stresses in the order of hundreds of kPa can be obtained in the PM-ER fluids wherein the interaction between the adsorbed polar molecules and polarization charge on the particles plays the decisive role in determining the rheological properties of this type of new materials. Based on the model calculation, even yield stresses up to MPa are anticipated if the effecting material parameters can be reasonably optimized. The very high yield stresses obtained in the new ER fluids have opened the door to the practical implementation of this fantastic material, of course some limiting factors such as the somewhat high viscosity at zero field have yet to be fixed in the near future.

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