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Rapid Communication

Polar molecule dominated electrorheological effect*

Lu Kun-Quan(陆坤权)[a)†], Shen Rong(沈 容)[a)], Wang Xue-Zhao(王学昭)[a)], Sun Gang(孙 刚)[a)], Wen Wei-Jia(温维佳)[a)b)], and Liu Ji-Xing(刘寄星)[a)c)]

[a)] *Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing* 100080, *China*

[b)] *Department of Physics, Hong Kong University of Science and Technology, Hong Kong, China*

[c)] *Institute of Theoretical Physics, Chinese Academy of Sciences, Beijing* 100080, *China*

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The yield stress of our newly developed electrorheological (ER) fluids consisting of dielectric nano-particles suspended in silicone oil reaches hundreds of kPa, which is orders of magnitude higher than that of conventional ones. We found that the polar molecules adsorbed on the particles play a decisive role in such new ER fluids. To explain this polar molecule dominated ER (PM-ER) effect a model is proposed based on the interaction of polar molecule-charge between the particles, where the local electric field is significantly enhanced and results in the polar molecules aligning in the direction of the electric field. The model can well explain the giant ER effect and a near-linear dependence of the yield stress on the electric field. The main effective factors for achieving high-performance PM-ER fluids are discussed. The PM-ER fluids with the yield stress higher than one MPa can be expected.

Keywords: electrorheological fluid, polar molecule, polarization, shear stress
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The electrorheological (ER) fluids consisting of dielectric particles suspended in insulating oil possess the character of electrically controllable liquid–solid transition, that comes from the interaction between the polarized particles aligned in the electric field.[1−3] The peculiar property of such novel materials, that the shear stress or the hardness is continuously, rapidly and reversibly tunable by applying an electric field, has attracted much attention. The physical mechanism of dielectric ER fluids has been well established,[1,3,4] of which the upper limit of the yield stress predicted by traditional dielectric theory is about 10 kPa.[5] The low yield stress of the available ordinary ER fluids, usually a few kPa, has been hindering their applications for half a century.

In recent years several ER fluids, of which the yield stress can much exceed the predicted upper bound and even reach 200 kPa, has been fabricated.[6−10] Although a model based on the polarization saturation layers has been proposed to explain the giant ER effect in a urea coated particle system,[7] yet we find that it is the polar molecules adsorbed on the particles that play the decisive role in the high performance of such new ER fluids.

We have fabricated a series of ER fluids with high yield stress, in which the particles are synthesized with absorbed polar molecules or polar groups. By adding urea, or C=O and O–H polar groups *et al* to TiO_2 nano-particles and C=O and O–H polar groups to Ca–Ti–O nano-particles, respectively, all the ER fluids exhibit the characteristic of high yield stress. The dipole moments of urea, C=O and O–H are 4.56, 2.3−2.7 and 1.51 (1deb = 3.3564×10^{-30} C·m), respectively. The presence of polar molecules or polar groups adsorbed on the particles of those ER fluids was confirmed by chemical analysis and infrared spectroscopy. The particles were prepared in spheral shape with diameter range of $50 - 100$ nm[9,10] and were suspended in silicone oil with volume fractions about 35%. In Fig.1(a) the dependences of the yield stress on the electric field of such two ER fluids are presented. The yield stresses of the ER fluids were measured by using an apparatus as schemed in the inset of Fig.1(a), which ensures to reveal the intrinsic character of those new ER fluids. The yield stresses of those ER fluids can reach about 200 kPa. Another characteristic of them is the near linear dependence of the yield stress on electric field in contrast to the quadratic one in ordinary ER flu-

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†E-mail: lukq@aphy.iphy.ac.cn

ids. The current densities of those ER fluids are less than 20 μA/cm^2. Figure 1(b) plots the dynamic shear stress of the ER fluid consisting of TiO_2 nano-particles with $(NH_2)_2CO$ adsorbed, which was measured with a sealed cylindrical rheometer as shown in inset of Fig.1(b). The surfaces of the electrodes were coated with special layer for reducing the slide of ER fluid on the electrodes. It can be seen that the dynamic shear stress is about 60 kPa at 3 kV/mm. Some high shear stress at zero field mainly comes from the friction of the seal ring assembly of the rheometer. The characteristics of the high static and dynamic shear stress, low current density and anti-sedimentation of those new ER fluids are very attractive for the applications.

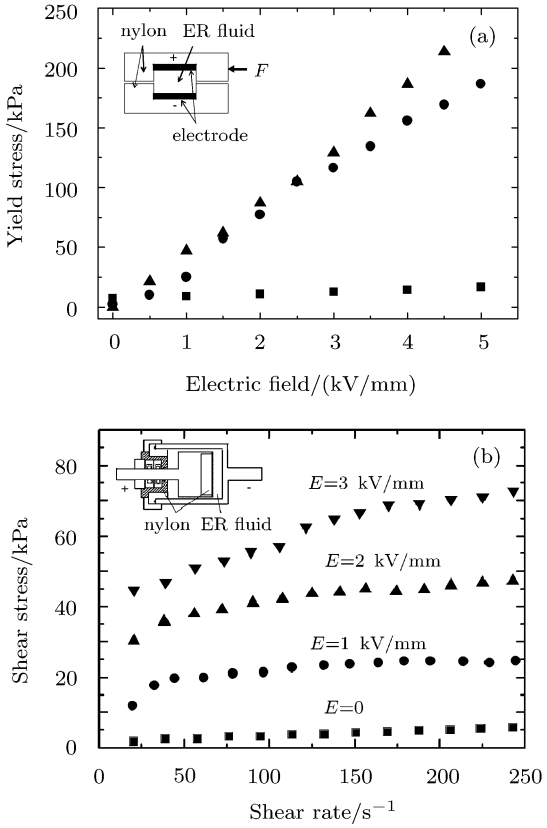


Fig.1. (a) Yield stress versus electric field for ER fluids consisting of TiO_2 nano-particle with $(NH_2)_2CO$ (triangles) and Ca–Ti–O nano-particle with C=O, O–H groups (dots). The yield stress of the ER fluid consisting of sintered Ca–Ti–O particles only is denoted by squares. Inset shows schematic drawing of the apparatus for yield stress measurement. (b) The dynamic shear stress versus shear rate at different field strength for the ER fluid of TiO_2 with $(NH_2)_2CO$. Inset is the sketch of the rheometer for measuring dynamic shear stress.

By heating the particles to high temperature (500–800°C) all the adsorbed polar groups are desorbed, that has been validated with infrared absorption spectrum and differential scanning calorimeter measurement. Then the ER fluids consisting of the sintered particles lose their characteristic of high yield stress and behave as ordinary ER fluids. As an example, as shown in Fig.1(a) the yield stress of ER fluid consisting of the sintered Ca–Ti–O particles is very low as the C=O, O–H polar groups are all removed by heating the particles at 500°C.

The aforementioned facts demonstrate that the polar molecules or polar groups contained in the particles play a crucial role for the high yield stress in the newly developed ER fluids. Therefore we designate those new ER fluids as polar molecule dominated ER (PM-ER) fluids. The high yield stress and a near-linear dependence of yield stress on electric field in PM-ER fluids indicate that the mechanism of PM-ER fluids must be different from the conventional ER fluids and can not be explained by the traditional dielectric theory. We propose a reasonable model to describe the PM-ER effect as follows.

When an electric field E is applied the polarized particles in the ER fluids attract each other and align along the field direction to form chains. The local electric field $E_{\rm loc}$ in the gap between the particles is much higher than E.[11−14] The value of $E_{\rm loc}/E$ depends on δ/r and $\varepsilon_{\rm p}/\varepsilon_{\rm f}$, where δ is the gap width between particles, r is the radius of particle, $\varepsilon_{\rm p}$ and $\varepsilon_{\rm f}$ are the dielectric constants of the particles and oil, respectively. According to Davis's calculation[11] $E_{\rm loc}/E$ is about 10^3 when $\delta/r \approx 10^{-3}$ and $\varepsilon_{\rm p}/\varepsilon_{\rm f} \approx 100$. The reliability of Davis's calculation has been demonstrated by measuring the attractive force of two spheres in an electric field.[15,16] As an example, we consider our TiO_2 nano-particle ER fluid. The dielectric constant $\varepsilon_{\rm p}$ of the TiO_2 nano-particles is much higher than that of the bulk materials.[17,18] $E_{\rm loc}$ in between TiO_2 particles should be about 10^9 V/m when $E \approx 10^6$ V/m, $r = 30$ nm, $\delta \approx 0.2$ nm. Even if the local field is very high in between the particles the possibility of electrical breakdown is scarce at such narrow and small region in an oil medium.

The polar molecules adsorbed on the surfaces of the particles with adsorption energy $U_{\rm ad}$, which is usually slightly larger than kT, are weakly bonded to the particles other than in the bulk state. They are relatively free for rotation and potentially to be oriented in the direction of a strong electric field.[19,20] Thus polar molecules in the gap between the particles are able to turn to the electric direction as the magnitude of $\mu E_{\rm loc}$ is comparable with $U_{\rm ad}$ or larger than about

kT. For example, to align a molecule with μ =2 deb, the local field $E_{\rm loc}$ has to be higher than 6.4×10^8 V/m, which can be achieved in our case as described above.

Figure 2 schematically illustrates the orientating behaviour of the polar molecules on the particle surfaces without and with field applied, respectively. In the case of $E = 0$ the polar molecules on the surfaces are arbitrarily distributed with an adsorbing geometry. So long as the applied field brings the particles approaching, together with E increasing, a high enough $E_{\rm loc}$ can be reached to cause the polar molecules to orientate along the field in the gap of two adjacent particles. However, since the fraction of the active molecules is very low and their volumes constitute only a very small part of the whole suspension, no proper technique is available at present to directly observe the rotation of the polar molecules in between the particles.

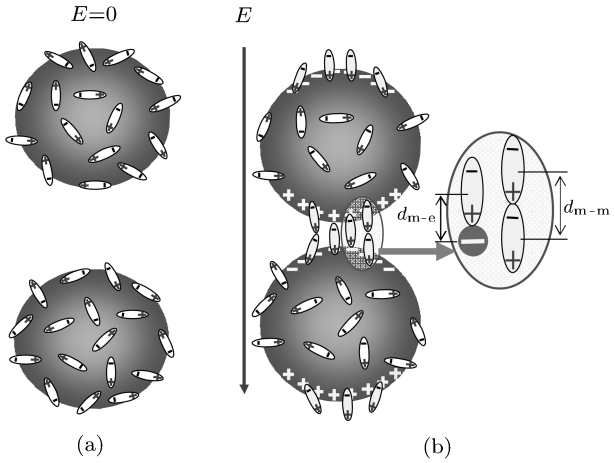


Fig.2. Schematic illustration of the polar molecules aligned in the gap of the particles under an electric field. (a) The polar molecules adsorbed on particle surface are arbitrarily oriented when $E = 0$. (b) The polar molecules in the gap of the particles are aligned along the field when E is high enough. In the enlarged image (right) two kinds of the interactions are shown: dipole–dipole interaction and dipole–charge interaction.

Once the polar molecules are orientated in between the particles, mainly two kinds of interactions may occur as shown in inset of Fig.2(b). The first one is the attraction between the polar molecules on the particle and the polarization charges on the nearby particle. The maximum attractive force of the polar molecule–charge is[21] $f_{\rm m-e} = e\mu/(2\pi\varepsilon_0\varepsilon_{\rm f}d_{\rm m-e}^3)$, where e is the charge, $d_{\rm m-e}$ is the distance from molecule centre to charge (approximately half the molecule size d, i.e. $d_{\rm m-e} \approx d/2$). Another one is the attraction between polar molecules on two nearby particles. The attractive force of a pair identical molecules in a head-to-tail line is[21] $f_{\rm m-m} = 3\mu^2/(2\pi\varepsilon_0\varepsilon_{\rm f}d_{\rm m-m}^4)$, where $d_{\rm m-m}$ is the centre-centre distance of two molecules $d_{\rm m-m} \approx d$. Usually $f_{\rm m-e}$ is much larger than $f_{\rm m-m}$ as $d_{\rm m-e} \approx d_{\rm m-m}/2$ and $f_{\rm m-e}/f_{\rm m-m} \approx 16ed_{\rm m-e}/(3\mu)$, For instance, if one polar molecule of $\mu = 2$ deb associates with a unit charge ($e = 1.6 \times 10^{-19}$ C) and $d_{\rm m-e} = 0.2$ nm, then $f_{\rm m-e} = 9.6 \times 10^{-10}$ N, whereas $f_{\rm m-m} = 3.8 \times 10^{-11}$ N when taking $d_{\rm m-m} = 0.4$ nm, namely $f_{\rm m-e}/f_{\rm m-m} \approx 25$. Therefore, the PM-ER effect must basically come from the attractive force $f_{\rm m-e}$ of polar molecule–charge. In the above calculations the point-dipole approximation is made and the influence of the induced polarization of the molecules is neglected, which enhances the interaction but its effect is much lower than that of inherent dipole moment.

The attractive force $F_{\rm m-e}$ of molecule–charge in a unit area perpendicular to the external field can be estimated. The area in between the particles separated by $\delta = d_{\rm m-e}$ is nearly $\pi rd/2$, where polar molecule-charge interactions occur effectively. In this region the number of active molecule–charge interactions is $N \propto \dfrac{\pi rd}{2}\rho_{\rm m}n(E)$, where $\rho_{\rm m}$ is the density of the polar molecules adsorbed on the particles, the probability $n(E)$ of the aligning polar molecules being nearly proportional to $\mu E_{\rm loc}$[22] in the case of $\mu E_{\rm loc} \sim U_{\rm ad}$ and then proportional to μE.[12] The number of the particle chains in a unit area is $3\phi/(2\pi r^2)$, where ϕ is the volume fraction of the particles in the suspension. Thus, the stress can be approximately expressed as

$$F_{\rm m-e} = \frac{3\phi}{2\pi r^2}Nf_{\rm m-e} = A\frac{3\phi\rho_{\rm m}e\mu^2E}{\pi r\varepsilon_0\varepsilon_{\rm f}d^2},$$

where the parameter A is related to the properties of the particle and oil, geometry of the particles in the oil, as well as the adsorption energy $U_{\rm ad}$ etc.

The expression of $F_{\rm m-e}$ indicates that the $F_{\rm m-e}$ increases linearly with E due to $n(E) \propto \mu E$ and consequently the yield stress of PM-ER fluid exhibits a nearly linear dependence on applied electric field as shown in Fig.1(a). $F_{\rm m-e} \propto r^{-1}$ means that the yield stress of the PM-ER fluid consisting of smaller particles is higher, as observed in the experiment.[23] This feature of PM-ER fluids is also different from that of the conventional ER fluid, in which the yield stress usually increases with particle size increasing.[11,12] The nano-particles not only are favourable for obtain-

ing high shear stress of PM-ER fluids, but also are advantageous for resisting the particle sedimentation in the fluids. The larger particles, however, are of benefit for getting higher local electric field. Using the particles with high dielectric constant can induce a higher local electric field in between the particles,[11,12] and as a result, the PM-ER response occurs at a lower applied field. For getting high local field in between particles, the particles are always necessary to be prepared in sphere-like shape. Choosing the polar molecules with larger dipole moment and smaller size is obligatory for gaining higher yield stress of PM-ER fluids because of the relation $F_{\mathrm{m-e}} \propto \mu^2 d^{-2}$. Also the polar molecules with larger μ can be aligned at a lower E. To enhance the yield stress of PM-ER fluids a higher ρ_{m} of the adsorbed molecules should be pursued since low ρ_{m} may cause the yield stress saturation at high E. It is obvious that in measuring the shear stress with an ordinary rheometer the boundaries between the metal electrodes and the fluids are not well adequate for the interaction of polar molecule–charge, where the attractive force must be reduced due to sliding. By using a redesigned method as shown in inset of Fig.1(a) the intrinsic yield stress of PM-ER fluids can be measured.[11] With the same reason in the measurement of the dynamic shear stress as shown in Fig.1(b) the surfaces of the electrodes were coated with special layers.

We can estimate the remarkable difference on the yield stress between PM-ER fluid and the ordinary ER fluid. As an example, we consider a system of $r = 30$ nm, $\delta = 0.2$ nm, $d_{\mathrm{m-e}} = 0.2$ nm, $N = 1$, $\mu = 2$ deb, and $\phi = 35\%$. Then $F_{\mathrm{m-e}} \approx 18$ N/cm^2 in the PM-ER fluid, corresponding to a stress of 180 kPa. Whereas, in ordinary ER fluid consisting of pure TiO_2 particles under a field of $E = 3 \times 10^6$ V/m, $f_{\mathrm{p-p}} \approx 3.2 \times 10^{-12}$ N[11,12] and then $F_{\mathrm{p-p}} \approx 0.06$ N/cm^2, i.e. the stress is 0.6 kPa. Even assuming there is only one polar molecule active in average on each particle in the calculation, $F_{\mathrm{m-e}}$ is 3×10^2 higher than $F_{\mathrm{p-p}}$. Therefore the yield stress τ_y of PM-ER fluids can also be 2–3 orders higher than that of conventional ER fluids. The more polar molecules are active on each particle, the higher yield stress of PM-ER fluids can be achieved.

Following the argument along this line, if a medium containing polar molecules can be prepared, instead of that adsorbed on the particles, PM-ER effect is also expected to occur. The polar molecules in the liquid will orientate along the field in between the particles and interact with the polarized charges on the neighbouring particles. In this situation the PM-ER effect is caused by the local freezing of the polar molecules and may be more effective.

The expression of $F_{\mathrm{m-e}}$ clearly indicates how to achieve the PM-ER fluids with higher yield stress by optimizing all the effective factors discussed above. It is then possible to obtain a PM-ER fluid with the yield stress τ_y up to MPa order if one adopts μ and ρ_{m} larger, and d and r small enough in material designing and manufacturing. For instance, assuming $\mu = 2$ deb, $r = 15$ nm, $d = 0.3$ nm, $N = 3$, $\phi = 35\%$ and the particles being sufficiently dispersed in the fluid, then the estimated τ_y can be about 1.7 MPa, where $\tau_y \approx F_{\mathrm{m-e}}/3$.

In conclusion, the yield stress of the PM-ER fluids we newly developed can reach hundreds of kPa. The polar molecules in between the particles play a crucial role in such PM-ER fluids. The PM-ER effect comes from the interaction of polar molecule–charge instead of that of the particles themselves as in conventional cases. When an external electric field polarizes the suspended particles, which align up to form chains, the local electric field in between the particles can be about 3 orders higher than the external field. The high local field causes the polar molecules in the gap to turn to the field direction and interact with the polarization charges of the neighbouring particles. The attractive force of the polar molecule–charge can be several orders higher than that of pure polarized particles as occurred in conventional ER fluids. The increment of the active polar molecules being proportional to the electric field implies a near-linear dependence of the yield stress on the applied field. Based on the principle of PM-ER effect we anticipate that the PM-ER fluids with the yield stress in MPa order can be attained by optimizing all the influencing factors in material manufacturing.

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