Dielectric relaxation effect on flow behavior of electrorheological fluids

Zhiyuan Wang¹, Xinglong Gong¹, Fan Yang¹, Wanquan Jiang² and Shouhu Xuan¹

Abstract
The dielectric relaxation effect on the flow behavior of electrorheological fluids under dynamic shear was studied. The flow curves of electrorheological fluids in the dynamic state were simulated with shear rates from 0.1 to 1000 s⁻¹ under different relaxation times. When the magnitude of the relaxation time is smaller than 10⁻² s, the break shear rate changes little at different relaxation times. But the break shear rate changes obviously when the magnitude of the relaxation time is larger than 10⁻² s. To further understand the influence of the relaxation time, Sr/Ba-doped TiO₂ electrorheological fluids were prepared and their dielectric properties and flow curves under shear flow were tested. The relaxation time of the electrorheological fluid is influenced by the Sr/Ti mole ratio but not the Ba/Ti mole ratio, and the electrorheological effects of the fluids were highly influenced by varying the Sr/Ti mole ratios. The experimental results agreed well with the above computer simulation. Finally, a possible mechanism was proposed to explain the effect of dielectric relaxation on flow behavior of electrorheological fluids.

Keywords
Electrorheological fluids, break shear rate, relaxation time, flow curve

Introduction
Electrorheological fluids (ERFs), typically smart materials, are composed of microsized or nanosized dielectric particles dispersed in a liquid with a low dielectric constant (Halsey, 1992; Jiang et al., 2009, 2011; Wen et al., 2003). When an electric field is applied, the randomly dispersed particles are rearranged along the field direction and form complex column-like structures, which dramatically changes the apparent viscosity. The change is fast (milliseconds) and reversible, which makes the ERFs desirable for technological and industrial applications (Melrose, 1991; Tao and Sun, 1991; Weiss et al., 1993). During the past decades, various inorganic particles, liquid crystals, and polymers were used for preparation of ERFs (Choi and Jhon, 2009), and they were widely applied in damping devices (dampers of engine mounts); force transfers such as clutches, valves, and brakes; and other hydraulic systems or micro-robotics (Choi et al., 1990; Papadopoulos, 1998).

ER effect results from the formation of particles’ chain structure during the application of electric field. Several theoretical models, such as electric double-layer model (Klass and Martinek, 1967), water bridge model (Stangroom, 1983), and polarization model (Davis, 1992; Parthasarathy and Klingenberg, 1996) have been developed to explain the formation mechanism of chain structure. Among them, the polarization model was believed to be one of the most acceptable models, in which the ER effect was controlled by dielectric mismatch. The higher the dielectric mismatch, the stronger the ER effect is. Therefore, the dielectric properties of suspensions dominate the ER effect. Many research studies were concentrated on how the particles’ dielectric properties influence the ER effect. By comparing different kinds of ERFs, Ikazaki et al. (1998) pointed out that the relaxation frequency was in the range from 10² to 10⁵ Hz when the ERF had a large ER effect, and this effect increased with increasing difference between the dielectric constants below and above the relaxation frequency. Hao and colleagues (Hao, 1997; Hao et al.,

¹CAS Key Laboratory of Mechanical Behavior and Design of Materials, Department of Modern Mechanics, University of Science and Technology of China (USTC), Hefei, China
²Department of Chemistry, University of Science and Technology of China (USTC), Hefei, China

Corresponding author:
Xinglong Gong, CAS Key Laboratory of Mechanical Behavior and Design of Materials, Department of Modern Mechanics, University of Science and Technology of China (USTC), Hefei 230027, China.
Email: gongxl@ustc.edu.cn
1999; Hao and Xu, 1996) developed a dielectric loss model to study the dielectric relaxation influence on the ER effect and found that the ERF with a larger dielectric loss constant exhibited a larger ER effect. Cho et al. (2003) prepared the monodisperse polymer microspheres (PAPMMAs)-based ERFs and studied the dielectric relaxation time, polarizability, and Cole–Cole plot from the dielectric spectra. All the analysis indicated that there must be an inherent and natural connection between the dielectric relaxation of the ERF and its ER effect. However, the detailed mechanism of the dielectric relaxation effect on the ERFs is still unclear.

Moreover, the experiment can directly prove the connection between the particles’ characteristics and their ER properties. A large amount of research has been done to change the ER effects by modifying the ER particles. Wang et al. (2013) investigated the dielectric behaviors of TiO$_2$ ERFs with different TiO$_2$ polymorphs and found that rutile should have better ER activity than anatase by analyzing dielectric spectroscopy. Di et al. (2006) prepared a urea-doped mesoporous TiO$_2$ ERF showing a high ER behavior under an applied electric field. The dielectric spectra analysis showed that this suspension had a large difference in the dielectric constant below and above the relaxation frequency, and the maximum value of the dielectric loss was measured by ModuLab-MTS (Advanced Measurement Technology, Inc.).

**Model**

A model ER system studied in this article is supposed to consist of $N$ interacting spherical particles of dielectric constant $\varepsilon_p$ and diameter $\sigma$, suspended in a silicone oil fluid of dielectric constant $\varepsilon_f$ ($\varepsilon_f < \varepsilon_p$) and viscosity $\eta_f$. The model system is in a box with its volume $V = L_x \times L_y \times L_z$, confined between the two parallel electrodes at $z = 0$ and $L_z$. An external electric field is applied along the $z$-direction. A steady shear rate $\dot{\gamma}$ is also imposed along the $x$-direction (parallel with the plate). Here, the velocity field is varied linearly along the $z$-direction (the top electrode moves at a speed of $\dot{\gamma} L_z$). Because the particles are much larger than the liquid molecule, it is thought that slip happens between the particles and the electrodes but not between the liquid molecules and the electrodes. Before the application of the electric field, particles are randomly dispersed in the medium fluid.

The motion of the $i$th particle having mass $m$ at time $t$ and position $\mathbf{r}_i(t)$ is described by the following classical equation of motion (Guo et al., 1996)

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i - 3\pi \sigma \eta_f \left( \frac{d\mathbf{r}_i}{dt} \times \dot{\gamma}_z \mathbf{\hat{x}} \right) + \mathbf{R}_i$$

where $\mathbf{F}_i$ is the total force acting on the $i$th particle, the second term is the Stokes drag, and the last term is the Brownian random force. The Brownian force $\mathbf{R}_i$ is determined independently by a normal distribution with $\langle R_{i,\alpha}(0) \rangle = 0$ and $\langle R_{i,\alpha}(0) R_{i',\beta}(t) \rangle = 6\pi \eta_f T \sigma \eta_f \delta_{\alpha\beta} \delta(t)$, where $\langle ... \rangle$ denotes an ensemble average,

**Experiment**

The ERFs used in this experiment were made of Sr/Ba-doped TiO$_2$ particles in silicone oil with the volume fraction of 20%. Various moles of SrNO$_3$/BaCO$_3$ were added during preparation of TiO$_2$ particles to obtain needed Sr/Ba-doped TiO$_2$ particles. The viscosity and the dielectric constant of silicone oil are 0.1 Pa s and 2.6, respectively. The rheological behavior of the suspension was investigated by a rotational rheometer (Physica MCR 301; Anton Paar), ER HVS/ERD 180, and the CC10-E accessory. The dielectric data were measured by ModuLab-MTS (Advanced Measurement Technology, Inc.).
\[ \frac{dp}{dt} = \omega \times p - \frac{(p - p_0)}{\tau} \]  

(2)

where the dipole moment \( p = p_x \hat{x} + p_z \hat{z} \) at the steady state is expressed as

\[ p_x = \frac{\omega r_0 P}{1 + (\omega r_0)^2}, \quad p_z = -\frac{P_0}{1 + (\omega r_0)^2} \]  

(3)

where \( \tau \) is the relaxation time. In the rotational state, there is a tilt angle \( \phi \) between the dipole moment \( \mathbf{p} \) and \( \mathbf{u} \), the dipolar force acting on the \( i \)th particle at \( \mathbf{r}_i \) is given by

\[ \mathbf{F}_{ij}^{el,im} = F_0 \left( \frac{\sigma}{r_{ij}} \right)^4 \left\{ [1 - 3 \cos^2(\theta_{ij} - \phi)] \hat{r} - \sin[2(\theta_{ij} - \phi)] \hat{\theta} \right\} \]  

(4)

where \( p = |p| \), \( r_{ij} = r_i - r_j \), and \( r_{ij} = |r_{ij}| \); \( \theta_{ij} \) is the angle between \( r_{ij} \) and \( z \)-axis; \( \hat{r} = r_{ij}/r_{ij} \); and \( F_0 = 3p^2/(4\pi\varepsilon_0 \sigma^4) \).

To simulate the hard spheres and the hard sphere–hard wall interactions, an exponential short-range repulsive force between particles \( i \) and \( j \) is introduced as (Guo et al., 1996)

\[ F_{ij}^{rep} = 2F_0 \left( \frac{\sigma}{r_{ij}} \right)^4 \exp \left[ -100 \left( \frac{r_{ij}}{\sigma} - 1 \right) \right] \hat{r} \]  

(5)

and between particle \( i \) and the two electrodes

\[ F_{i \text{wall}} = 2F_0 \left( \frac{\sigma}{z} \right)^4 \exp \left[ -100 \left( \frac{z_i}{\sigma} - 0.5 \right) \right] \hat{z} \]

\[ -2F_0 \left( \frac{\sigma}{L_z - z_i} \right)^4 \exp \left[ -100 \left( \frac{L_z - z_i}{\sigma} - 0.5 \right) \right] \hat{z} \]  

(6)

For the boundary particles, the friction force between the boundary particles and the electrodes is expressed as (Gong et al., 2011)

\[ \begin{cases} 
F_{fric} = \mu N_i, & \text{when } N_i > 0 \\
F_{fric} = 0, & \text{when } N_i \leq 0 
\end{cases} \]  

(7)

\( N_i \) is the normal force acting on the \( i \)th boundary particle

\[ \begin{cases} 
N_i = \sum_{j \neq i} \left( F_{ij}^{el} + F_{ij}^{rep} \right) \cdot \hat{z}, & \text{for Cathode} \\
N_i = -\sum_{j \neq i} \left( F_{ij}^{el} + F_{ij}^{rep} \right) \cdot \hat{z}, & \text{for Anode} 
\end{cases} \]  

(8)

The dipolar force acting on the \( i \)th particle from the image particle at \( \mathbf{r}_i \) is given by

\[ \mathbf{F}_{ji}^{el,im} = F_0 \left( \frac{\sigma}{r_{ij}} \right)^4 \]  

\[ \left\{ [\cos 2\varphi - 3 \cos(\theta_{ij} - \varphi)] \cos(\theta_{ij} + \varphi) \right\} \hat{r} - \sin 2\theta_{ij} \hat{\theta} \]  

(9)

Now, the total force \( \mathbf{F}_i \) in equation (1) is given by

\[ \mathbf{F}_i = \sum_{j \neq i} \left( \mathbf{F}_{ij}^{el} + \mathbf{F}_{ij}^{rep} \right) + \sum_{j} \mathbf{F}_{ij}^{el,im} + \mathbf{F}_{i \text{wall}} + \mathbf{F}_{i \text{fric}}, \quad \text{for boundary particles} \]  

\[ \mathbf{F}_i = \sum_{j \neq i} \left( \mathbf{F}_{ij}^{el} + \mathbf{F}_{ij}^{rep} \right) + \sum_{j} \mathbf{F}_{ij}^{el,im} + \mathbf{F}_{i \text{wall}}, \quad \text{for the others} \]  

(10)

To study the parametric properties of many different ERFs, we define dimensionless quantities to scale equation (1): \( r_i = r_i/\sigma \), \( t = t/[3\pi\eta_i \sigma^2/(k_BT)] \), \( \mathbf{R}_i = \mathbf{R}_i/(k_BT/\sigma) \), and \( \mathbf{F}_i = \mathbf{F}_i/|p|^2/(\varepsilon_0 \sigma^4) \). So, equation (1) can be rewritten as

\[ \frac{Ad^2 r_i}{dt^2} = QF_i^{*} - \frac{dr_i^{*}}{dt} + 8P\varepsilon_0 \varepsilon^* \hat{x} + \mathbf{R}_i^{*} \]  

(11)

where \( A = m k_BT/(3\pi\eta_i \sigma^2)^2 \), \( Q = p^2/(\varepsilon_0 \sigma^3 k_BT) \), and \( P = 3\pi\eta_i \sigma^2^3/(8k_BT) \). For most real parameters of ERFs, the magnitude of \( A \) in equation (11) is very small \( (10^{-10}) \), so in the following simulations we neglect this inertial effect. Thus, it is simplified as

\[ \frac{dr_i^{*}}{dt} = QF_i^{*} + 8P\varepsilon_0 \varepsilon^* \hat{x} + \mathbf{R}_i^{*} \]  

(12)

Equation (12) is integrated with a time step \( \Delta t \leq 0.01/(F_{\text{max}}^*/Q) \) using Euler’s method; \( F_{\text{max}}^* \) is the dimensionless maximum interparticle force that acts on particles, thus the maximum displacement of particles cannot exceed 0.01\( \sigma \). Periodic boundary conditions are imposed in the \( x \)- and \( y \)-directions, reflecting boundary conditions in the \( z \)-direction.

In the dynamic state, rheological properties are determined by the effective viscosity \( \eta_{eff} = \langle \tau_{xx}/\dot{\gamma} \rangle \), where \( \tau_{xx} \) is the component of the stress tensor, which is an averaged value of the simulations. By using the Bingham model, \( \tau_{xx} \) is expressed as \( \tau_{xx} = \tau_E + \eta_{x} \dot{\gamma} \), where \( \eta_{x} \) is the viscosity of suspensions (without an electric field). But for these flow curves performed later, the Bingham fluid model is not able to fit them well. Therefore, Cho–Choi–Jhion (CCJ) model will be better (Cho et al., 2005). In order to definitely understand the relationship of the particle interactions, we focused on the electric field–induced shear stress \( \tau_{E} \), which was calculated by equation (13) (Sun et al., 2006).
Results and discussion

Our simulations have been done for the parameters: $T = 300 \text{ K}, e_p = 100, \epsilon_f = 2, \sigma = 1 \mu\text{m}, \eta_f = 0.1 \text{ Pa s}$, and $\mu = 0.4$ and carried out in a three-dimensional box ($L_x = 15\sigma, L_y = 5\sigma, L_z = 15\sigma$) with a system of $N = 240$ particles (20 stick to the top electrode and 20 stick to the bottom electrode).

Figure 1 shows the relation between the shear stress and the shear rate under different relaxation times and electric field strength through simulation. When the relaxation time is small, these flow curves show a trembling shear behavior, in which the shear stress increases and decreases with shear rate (Ko et al., 2008). Here, the shear stress decreases above a certain shear rate. This shear rate, which is defined as the break shear rate,
is proportional to the square of the electric field in quasi-static state, according to our previous research (Yang et al., 2011). Then, with the increase in the relaxation time, the break shear rate decreases gradually. This means that the ability of resisting breakage of the chains is weakened because of the increase in relaxation time. When the magnitude of the relaxation time exceeds $10^{-2}$ s, the break shear rate depends on the relaxation time, instead of the electric field. Therefore, the break shear rate of the chains depends on electric and relaxation time together when the magnitude of the relaxation time is less than $10^{-2}$ s, and the break shear rate is only decided by the relaxation time when it is greater than $10^{-2}$ s.

Figure 2 is the transformed data of Figure 1, which shows the relaxation time effect on the break shear rate at different electric fields. We find the change occurs between 0.002 and 0.2 s. When the dielectric relaxation time is smaller than 0.002 s, the curves overlap together; then, the curves are distributed dispersedly when the dielectric relaxation time is larger than 0.2 s. Thus, we deduce that the critical state of the dielectric relaxation time is the magnitude of $10^{-2}$ s. When the magnitude of the relaxation time is less than $10^{-2}$ s, the break shear rate changes little at different relaxation times. The break shear rate changes obviously when the magnitude of the relaxation time is greater than $10^{-2}$ s. With the increase in the relaxation time, the break shear rate decreases and the shear stress decreases at the same time, indicating that the structure strength of the chains is decreasing. Therefore, the ER effect is weakened because of the increase in the relaxation time. It was reported that the relaxation frequency is in the range from $10^2$ to $10^5$ Hz whenever the ERF has an obvious ER effect, and this effect increases with increased difference between the dielectric constants below and above the relaxation frequency (Ikazaki et al., 1998), which agreed well with our results. In comparison to large electric field, the relaxation time effect on the break shear rate at a small electric field is less obvious because the chains of ERFs are not completely formed at a small electric field. Therefore, Figure 2(a) only shows the changes in the incomplete chain structure of ERFs.

Figure 2. Relaxation time effect on shear stress–shear rate relationship at different electric fields: (a) $E = 0.5$ kV/mm, (b) $E = 1$ kV/mm, and (c) $E = 2$ kV/mm.
The decrease in the break shear rate means that the structure of the ERF is broken at a smaller shear rate. The nonlinear rheological behavior of the ERF after shear yield is caused by the special chain structure. As soon as the break shear rate is achieved, the chains are broken, then the shear stress reduces fast and the ERF becomes a Newtonian fluid from a non-Newtonian fluid. So, a larger relaxation time leads to a smaller break shear rate, and then the ERF works in a smaller efficient range.

Figure 3 shows the relation of the dielectric loss angle and the response frequency of Sr-doped TiO$_2$-based ER materials with different Sr/Ti mole ratios. The tan $\delta$ peak is related to the proper polarization response denoted by the relaxation time $\tau = 1/2\pi f_{\text{max}}$, where $f_{\text{max}}$ is the local frequency of the tan $\delta$ peak (Wu et al., 2012). Therefore, the response frequency is inversely proportional to the relaxation time. The response frequency decreases with the increase in the Sr/Ti mole ratio. When the mole ratio reaches 0.7, the response frequency is smaller than 100 Hz; so, the order of relaxation time is less than $10^{-2}$ s. Figure 4 presents the flow curves of 20 v/v% Sr-doped TiO$_2$ ERF with different Sr/Ti mole ratios. When the Sr/Ti mole ratio is 0 or 0.1 (Figure 4(a) and (b)), the ERF shows a trembling shear behavior, in which the break shear rate is

![Graph](image)

**Figure 3.** Curves of dielectric loss angle and response frequency of Sr-doped TiO$_2$ ER materials synthesized with different Sr/Ti mole ratios. ER: electrorheological.

![Graph](image)

**Figure 4.** Flow curves of Sr-doped TiO$_2$ ERF with different Sr/Ti mole ratios: (a) Sr/Ti = 0, (b) Sr/Ti = 0.1, (c) Sr/Ti = 0.3, and (d) Sr/Ti = 0.7.
proportional to the square of the electric field. When the Sr/Ti mole ratio is 0.7 (Figure 4(d)), the break shear rate is almost not influenced by the electric field. Figure 4(c) can be seen as a transitional state. The change in the curves of the ERF is decided by the relaxation time. The break shear rate depends on electric and relaxation time together when the magnitude of the relaxation time is less than $10^{-2}$ s, then the break shear rate is only decided by the relaxation time when the time is greater than $10^{-2}$ s. Clearly, this experimental research matches our simulation results very well.

Figures 5 and 6 are experiment results of Ba-doped TiO$_2$ ERF. In Figure 5, the response frequency is in the range from $10^2$ to $10^5$ Hz and almost not influenced by the Ba/Ti mole ratio. This means the Ba/Ti mole ratio cannot change the relaxation time of this ERF. In Figure 6, all the flow curves show a trembling shear behavior and present similar properties with the Ba/Ti mole ratios of 0, 0.3, or 0.5. Therefore, the ERFs with same relaxation time have similar property. This result further suggests that the dielectric relaxation affects the flow behavior of the ERF.

The mechanism of dielectric relaxation effect on the flow behavior of ERFs is further studied in this work (Figure 7). When the electric field exists alone, the chain structure is formed and the electric dipole moment is

Figure 5. Curves of dielectric loss angle and response frequency of Ba-doped TiO$_2$ ER materials synthesized with different Ba/Ti mole ratios.

Figure 6. Flow curves of Ba-doped TiO$_2$ ER fluid with different Ba/Ti mole ratios: (a) Ba/Ti = 0, (b) Ba/Ti = 0.1, and (c) Ba/Ti = 0.3. ER: electrorheological.
parallel to the electric field, as shown in Figure 7(a). In this situation, the attraction force between the particles is strongest and the structure of ERFs is the most stable. Then, an external electric field and a shear flow are applied to ERFs. When the relaxation time is too small to ignore the dielectric relaxation effect, the chains are structured with a tilt angle to the direction of the electric dipole moment because of the shear flow (Figure 7(b)). The difference in the direction between the chains and the electric dipole moment makes the chains weaker relative to Figure 7(a). Therefore, the ER effect is indistinctive when the relaxation frequency exceeds $10^5$ Hz in Ikazaki’s work. When the relaxation time is too large (Figure 7(c)), the particles have a significant dipole moment tilt angle under dynamic shear flow. This results in a tilt angle existing between the electric dipole moment and the chains, and the strength of the chains is not as strong as Figure 7(a). Larger relaxation time leads to a larger angle, which further weakens the structure of ERFs. An overlarge tilt angle will diminish the dipolar force between the rotational particles; even transmit the interparticle force from attractive to repulsive. Therefore, the chains cannot be maintained, the structure of ERFs is destroyed, and the stress decreases signally. Hence, the break shear rate decreases with the increase in the relaxation time when the relaxation time exceeds a certain value. As shown in Figure 7(d), a moderate relaxation time makes the electric dipole moment parallel to the electric field. Thus, the structure of ERFs is stable and the ERFs achieve a large stress under shear. Therefore, to obtain an obvious ER effect for the ERFs under steady shear flow, the materials should have a proper dielectric property.

### Conclusion

The dielectric relaxation effect on the mechanical property and flow behavior of ERFs is investigated by using both computer simulation and experiment investigation. The shear curves of ERFs in the dynamic state were simulated under different relaxation times. The experimental results of the flow curves match the simulation results very well and both indicate the dielectric relaxation effect on ERFs. When the magnitude of the relaxation time is less than $10^{-2}$ s, the break shear rate changes little at different relaxation times and the structural strength of ERFs is decided by electric and flow field. When the magnitude of the relaxation time is larger than $10^{-2}$ s, the break shear rate changes obviously and the structural strength is influenced by the relaxation time instead of electric field, leading to the decrease in ER effect. Therefore, the particles of ERFs should have proper dielectric relaxation time to obtain obvious ER effect under steady shear flow. The above work will be useful for understanding the mechanism of ERFs.
Declaration of conflicting interests
The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding
Financial supports from the National Natural Science Foundation of China (Grant No. 11125210) and the National Basic Research Program of China (973 Program, Grant No. 2007CB936800) are gratefully acknowledged.

References