十六烷基三甲基溴化铵改性凹凸棒石黏土及其电流变性能

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摘 要: 采用不同浓度的十六烷基三甲基溴化铵 (CTAB) 对凹凸棒石黏土 (ATC) 进行改性, 对比了施加电场前后其电流变性能的变化规律, 结果表明: 改性凹凸棒石黏土在电场 $E$ 作用下表现出 Bingham 流体特性, 并且屈服应力 $\tau_y$ 与 $E^{0.4}$ 成正比; 65 ℃是电流变性能突变的临界温度; 通过介电性能的测试, 发现 CTAB 对电流变响应的贡献较大。60 d 后, 改性凹凸棒石黏土的悬浮率仍可达到 91%。

关键词: 凹凸棒石黏土; 十六烷基三甲基溴化铵; 改性; 电流变效应; 介电性能


Modification of Attapulgite Clay with Cetyl Trimethyl Ammonium Bromide and Its Electrorheological Properties

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Abstract: The electrorheological effect of cetyl trimethyl ammonium bromide (CTAB) modified attapulgite clay (ATC) in the absence and presence of electric field $E$ was investigated. The results show that the ATC modified with CTAB appears the Bingham fluid behavior, and the yield stress $\tau_y$ is proportional to $E^{0.4}$. The critical temperature on the ER response is 65 ℃. The ER response mechanism is supposed based on the results of dielectric constant, and the CTAB is mainly contributed to the ER response. The clay suspension with the concentration of 91% after the modification with CTAB is still stable after 60 d.

Keywords: attapulgite clay; cetyl trimethyl ammonium bromide; modification; electrorheological effect; dielectric property

1 Introduction

Electrorheological (ER) fluid, one of smart materials that typically consists of electrical polarization particles dispersed in an insulating solvent, has attracted recent attentions. The unique characteristics include relatively high mechanical properties with enhanced stiffness, rheological responses controllable in a few milliseconds, low energy consumption, and thermal/electrical features. The ER effect is generated according to that the dispersed particles are polarized and aligned into fibrillar structures or columns along the direction of electric field apparently increasing viscosity when an external electric field is applied[1]. The performance of the ER fluid resembles the Bingham plastic behavior along the electric field direction, transforming to the Newtonian fluid in the absence of the field. Based on the characteristics of ER effect, the ER fluid has a promising potential for industrial applications including robotic arms, clutches, dampers and actuators[2–10]. The applications require the ER fluids to possess a high ER response, suspension stability, chemical inertness, proper conductivity and fast response time. In addition, it also should be non-abrasive, non-corrosive and environmental friendly[11–13]. Some studies tried to clarify the mechanisms of ER response and thereby to overcome the problems that hinder its industrial applications. There are the main mechanisms formed basing on electrostatic polarization[14–15], electric double layers[16–17], formation of water bridge between particles[18], interfacial polarization[19–22] and inter-
electrode circulation of particles\textsuperscript{[23–24]}. A complete understanding of the underlying mechanism could favor the development of high-performance ER fluids that can be used in industrial applications.

The ER suspensions contain additives such as activators or surfactants. The former are used to enhance the ER response and the latter are added to improve the colloid stability of the dispersed particles and to increase the ER activity. The most commonly used activator is water although there are also some other polar substances such as alcohol, ethylene glycol, dimethyl amine or formamide that can activate the ER suspensions\textsuperscript{[23,25–26]}. The disadvantages of water activated ER effect are a restricted temperature of operation and increased conductivity even if water-activated materials exhibit a high yield stress. Surfactant is applied as an activator based on its main functions of promoting colloid stability and controlling the rheological properties\textsuperscript{[23,27–29]}. Even if water and surfactant have some limits and their effect on the ER activity is not fully understood yet, they provide additional and improved advantages including the flexibility of design when it is impossible to obtain the high ER effect by simply justifying the composition of dispersive and continuous phases.

The dispersed particles of ER fluid include inorganic materials, polymer and organic-inorganic materials. Chemical durability at a high temperature, smoothness of operation and mechanical simplicity of the inorganic electrorheological material has attracted much attention. Filisco et al\textsuperscript{[30]} designed the first on-aqueous inorganic electrorheological materials based on aluminosilicate. Böse et al\textsuperscript{[31]} discussed the ER effect of zeolite. Zhang\textsuperscript{[32]} and Hyun\textsuperscript{[33]} illustrated the shear stress at an applied electric field based on palygorskite ER fluid and demonstrated the polarizability and relaxation time. Attapulgite (AT, also known as palygorskite) is a type of aluminum-magnesium silicate natural fibrillar clay present in nature with an ideal formula of Mg\textsubscript{5}Si\textsubscript{8}O\textsubscript{20}(OH)\textsubscript{2}(OH\textsubscript{2})\textsubscript{4}·4H\textsubscript{2}O. A unique crystal structure, presenting in nature with an ideal formula of Attapulgite (AT, also known as palygorskite) is a type of demonstrated the polarizability and relaxation time.

The ER suspensions were centrifuged and washed by distilled water until free CTAB was removed ultimately according to the detection of Br\textsuperscript{−} in CTAB by AgNO\textsubscript{3}. The resultant samples, namely, ATC-CTAB (0.1), ATC-CTAB (0.2), ATC-CTAB (0.3), ATC-CTAB (0.4), ATC-CTAB (0.5), were obtained after dried in vacuum at 70 °C for 12 h, respectively.

The amount of ATC-CTAB was dispersed in dried silicon oil under ultrasonification at room temperature for 20 min in order to obtain a stable suspension, which can be applied to measure the ER properties.

2.3 Characterizations

In Fig. 1, the rheological response of ER fluid was measured by a model NXS-11B a rotary viscometer (Chengdu Instrument Factory, China, the gap is 2 mm between the outer cup and the inner), which is connected with a model HYG2671A high-voltage DC power source ( Wuhan Hua Neng Electrical Co., China). The shear rate, $\dot{\gamma}$, changes from 3 to 209 s\textsuperscript{−1} and the max voltage is 10 kV. In order to illustrate the effect of temperature on EF response, thermo set is also built up outside the outer cup of viscometer by a liquid paraffin as a bath medium. The dielectric properties were characterized via a model E4980A LCR meter (Agilent Technology Co., USA). The chemical structures of ATC-CTAB were characterized by FTIR on a model Tensor-37 instrument (Bruker Co., USA) in the range from 4 000 cm\textsuperscript{−1} to 400 cm\textsuperscript{−1}. The phase structures of ATC and ATC-CTAB were recorded on a model D/max220 diffractometer (20 kV, 20 mA, Rigaku Co., Japan) using Cu $\text{K}_{\alpha}$ radiation for recording data in the range of 20°=0°–90°. The morphologies were observed by a model H-600 transmission electron microscope (75 kV, Hitachi Co., Japan).

![Fig. 1 Schematic diagram of designed electrorheometer](image)

<table>
<thead>
<tr>
<th>H.V DC</th>
<th>Stainless steel inner cup</th>
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<tbody>
<tr>
<td>Container</td>
<td>ER fluid</td>
</tr>
<tr>
<td>Thermostat</td>
<td>Stainless steel outer cup</td>
</tr>
<tr>
<td>Liquid paraffin</td>
<td></td>
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</table>

2.2 Preparation of ATC-CTAB and ER fluid

2.0 g of ATC was mixed with various concentrations of CTAB (i.e., 0.1, 0.2, 0.3, 0.4 and 0.5 mol/L) in 200 mL distilled water under stirring at 80 °C for 90 min, respectively. The suspensions were then centrifuged and washed by distilled water until free CTAB was removed ultimately according to the detection of Br\textsuperscript{−} in CTAB by AgNO\textsubscript{3}. 2.0 g of ATC was mixed with various concentrations of CTAB (i.e., 0.1, 0.2, 0.3, 0.4 and 0.5 mol/L) in 200 mL distilled water under stirring at 80 °C for 90 min, respectively. The suspensions were then centrifuged and washed by distilled water until free CTAB was removed ultimately according to the detection of Br\textsuperscript{−} in CTAB by AgNO\textsubscript{3}.

2.1 Materials

Attapulgite clay (Hao Di Co., China) was used directly without further purification. Cetyl trimethyl ammonium bromide (364 g/mol, AR grade, Fu Chen Agent Ltd. Co., China), AgNO\textsubscript{3} (AR grade, San You Agent Ltd. Co., China), dimethyl silicon oil ($\sigma$= 10\textsuperscript{−12} N/m, $\varepsilon_r$=2.60–2.80, $\rho$=0.97 g/mL, $\eta$=1 Pa·s, AR grade, Yong Sheng Agent Ltd. Co., China) were used as a modifier, a detection agent and a basic fluid in ER fluid, respectively. The distilled water was used in the experiments.
3 Results and discussion

3.1 Influence of CTAB on ER response

Figure 2(a) and 2(b) show the shear flow curves (i.e., shear stress vs shear rate) measured by the controlled shear rate mode for suspensions containing pure ATC and modified ATC with CTAB under electric field intensity $E=0$ kV/mm and $E=1.5$ kV/mm, respectively. In the absence of electric field, the shear stress increases with the shear rate as a typical Newtonian fluid behavior for the ATC and the modified ATC. The difference of shear stress between the ATC and the modified ATC is rather small. This illustrates that CTAB can not affect the viscosity of suspension in the absence of electric field. In contrast, when an electric field ($E=1.5$ kV/mm) is applied, the ER fluids of ATC-CTAB exhibit an increase in the shear stress. Before the shear rate of 116 s$^{-1}$, the shear stress shows a decrease to the minimum value, i.e., so-called critical shear rate, and after the appearance of the yield stress the shear stress increases again$^{[42–43]}$. It is well known that the flow behavior is a result of the change of the ER structures, which is dominated by the competition between the electrostatic interaction among suspension particles induced by an external electric field and the hydrodynamic interaction induced by an external shear stress. The electrostatic interaction is responsible for the ER structures and hinders the flow, while the latter tends to destroy the ER structures and promote the flow. At a low shear rate, the electrostatic interaction is considered to be dominant, compared to the hydrodynamic interaction. The aligned ER structures begin to break with the increase of shear rate, while the broken structures tend to then reform into the chains in an applied electric field. After the critical shear rate, the hydrodynamic interaction begins to dominate the flow behavior and the ER fluids appear a pseudo-Newtonian behavior. For the ATC-CTAB(0.2), it shows that the shear stress is a little higher in the whole shear rate range. In the absence and presence of electric field, the shear stress of the ATC ER fluid changes little since the ATC is polarized difficultly in an electric field and thus generates poor polarized charges. This can be proved by the following dielectric measurement. It is indicated that the CTAB should contribute to the ER response positively, which is similar to the previous results$^{[44–46]}$.

![Flow curves of shear stress versus shear rate under $E=0$ and $E=1.5$ kV/mm for ATC and ATC-CTAB](image1)

![Flow curves of shear stress versus electric field (shearing rate $D_s=88$ s$^{-1}$)](image2)
Figure 4 shows the effect of volume fraction of ATC-CTAB(0.2) ER fluid on the ER behavior in the presence of electric field at 20 °C. Clearly, the shear stress increases with increasing the volume fraction of sample ATC-CTAB(0.2). The ER properties of ATC-CTAB ER fluids totally depend on the amount of CTAB adsorbed on ATC. ATC only acts as a carrier, which is regarded as a backbone to burden CTAB. ATC itself has little contribution to the ER effect directly (see Fig. 3), and only amorphous or ionic crystal nanofibers can be used as a high-performance ER fluid[47]. The cationic surfactant CTAB is thus polarized obviously with increasing the volume of ATC-CTAB(0.2) in an electric field. The chain-like CTAB aligned with the direction of electric field enhances the shear stress. The following ER mechanism model can be used to interpret this phenomenon.

Figure 5 shows the shear stress of ATC-CTAB(0.2) as a function of shear rate in various electric field strengths (E=0−2 kV/mm) at 20 °C. It is seen that the ER fluids show the conventional Newtonian fluid behavior at 0 kV/mm and performs as the Bingham plastic fluid in the presence of the electric field. This is a typical ER phenomenon[32], that is since the viscosity is not a constant any more but is an increased value with enhanced electric field. The leaking current density is also an important indicator, which can demonstrate the ER fluid life and the detection in this protocol. The leaking current density is 19 μA/cm² at 3.5 kV/mm. According to Hao et al[48], if the leaking current density is lower than 20 μA/cm², the ER fluid can be applied. Correspondingly, the effect of the electric field on the macroscopic mechanic properties is based on the induced modification of the structure of ATC-CTAB(0.2). A way to determine the nature of the interactions in charge of such a modification is plotting the yield stress as a function of the field strength, as shown in Fig. 6. Here, the yield stress is obtained by extrapolating the shear stress to a zero shear rate[49]. The Bingham model can be used as a suitable rheological model for the steady shear behavior of the EF fluids as follows[49]:

\[
\tau = \tau_y + \eta \gamma \quad \tau \geq \tau_y \\
\gamma = 0 \quad \tau < \tau_y
\]

where \(\tau_y\) is yield stress as a function of electric field strength \(E\), \(\gamma\) is the shear rate, and \(\eta\) is the shear viscosity. Table 1 shows the results. The yield stress increases with increasing the electric field due to the common ER effect. From Fig. 6, the yield stress increases proportionally to \(E^\alpha\) in the whole field strength range. The magnitude of exponent \(\alpha\) is obtained by a linear fit of the relation of \(\lg(\tau_y) \propto \alpha \lg E\). The \(\alpha\) value is 0.4, which is differ from that \(\tau_y\) is proportional to the electric field \(E^2\) predicted by the classic polarization model[50]. In the polarization model, the electrostatic interaction between dielectric spheres is treated in a point-dipole limit and each sphere is treated as a dipole only. Therefore, this model with point-dipole approximation is ideal. However, in the factual ER fluid, the \(\alpha\) often differs from 2 due to a few factors[50–51]. From the TEM images, nanofibrous ATC-CTAB is entirely anisotropic. This may be the main factor for the departure from 2. The electric field strength induces the electrostatic interactions among ATC-CTAB particles and also between the particles and electrodes.

![Fig. 4 Flow curves of shear stress of ATC-CTAB(0.2) ER fluid versus shear rate at various volume fractions (20 °C)](image)

![Fig. 5 Flow curves of shear stress vs shear rate for ATC-CTAB(0.2) ER fluid at various electric fields](image)

<table>
<thead>
<tr>
<th>Electric field (kV/mm)</th>
<th>(\tau_y) (Pa)</th>
<th>(\eta) (Pa·s)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>3.409</td>
<td>1.113</td>
</tr>
<tr>
<td>1.0</td>
<td>4.545</td>
<td>1.110</td>
</tr>
<tr>
<td>1.5</td>
<td>4.545</td>
<td>0.829</td>
</tr>
<tr>
<td>2.0</td>
<td>6.818</td>
<td>0.834</td>
</tr>
</tbody>
</table>

Table 1 Fitting parameters of Bingham model equations
Fig. 6 Yield stress as a function of electric field for ATC-CTAB (0.2) ER fluid

The different flow behavior with temperature reveals the change of electrostatic interaction, the Brownian movement and fluid viscosity. The electrostatic interaction becomes stronger when heating the ER fluid, which shows the increase of polarizability and polarization response. In addition, decreased medium viscosity due to temperature increase possibly makes particles form the chains readily and thus also leads to an improved ER effect\(^{[52]}\). The Brownian movement appears obviously with elevated temperature, which destroys the chains-like trend and weakens the ER effect. Also, the viscosity of silicone oil becomes lower further. Thus, the two reverse facets lead to the real ER behavior (see Fig. 7). The temperature of 65 °C is the critical value. The results are different from those obtained by Yin \(^{[53]}\) since the electric conductivities are different. The temperature dependence of pure ATC shows little change, illustrating that ATC cannot be polarized efficiently due to its low dielectric constant and thus CTAB has a great contribution to the ER effect.

Fig. 7 Shear stress of ATC and ATC-CTAB(0.2) ER fluid versus temperature (\(D_0 = 3s^{-1}, 1.5 kV/mm\))

3.2 Dielectric property of ATC and ATC-CTAB (0.2)

Figure 8 shows the dielectric properties of ATC and ATC-CTAB(0.2) solid powder measured by using a LCR meter in the frequency range of 1–1 kHz. The polarized degree of samples can be described as \(\varepsilon_r\), which is calculated by

\[
\varepsilon_r = \frac{C \cdot d}{\varepsilon_0 \cdot S}
\]

where \(\varepsilon_0\) means dielectric constant in vacuum, that is 8.854×10\(^{-12}\) F/m, \(C\) refers to capacitance and \(S, d\) is area and thickness of sample, respectively. It is interesting to find that ATC-CTAB(0.2) has the similar dielectric constant value as ATC, but the latter seems a little greater. It is predicted that the form what we examine the dielectric property is powder, which is entirely different from a fluid \(^{[54]}\), thus CTAB only acts as a shield coated on ATC surface and reduce the capacity of dipoles derived from ATC responding to the frequency field. The dielectric constant obtained is 8.0 under the same testing condition (see Fig. 8). The value is seldom reported. A high ER effect is correlated to several factors, i.e., high dielectric constant and appropriate loss factor, and mediate electric conductivity (\(\sigma = 10^{-14} - 10^{-7} S/cm\)). A high dielectric constant may not attain a high ER effect\(^{[55]}\). In Fig. 8(b), the regular of loss factor is corresponding to what we studied before\(^{[56–57]}\). In this work, the difference of dielectric constant between ATC-CTAB (0.2) and silicone oil is narrow, and thus their dielectric mismatch is not the main reason bringing a high ER response as Hoffman et al reported\(^{[58]}\). The ER effect is supposed to be generated by CTAB. The CEC of attapulgite is in the range of 30–40 mmol/100 g\(^{[59]}\). In this work, 40 mmol of CTAB and 2 g of ATC were provided, thus forming a few layers on ATC surface, which still has a 82.5% surplus of CTAB adsorbed loosely on the surface. The weak adsorption force between the loose CTAB and ATC exists. ATC-CTAB is dispersed randomly in silicone oil in the absence of electric field. Fig. 9 shows the images for the ER response of ATC and ATC-CTAB (0.2) in an electric field.

In Figs. 9 (a) and 9(c), ATC and ATC-CTAB (0.2) particles are dispersed randomly without electric field. After the electric field is applied, ATC-CTAB (0.2) particles show the ER effect and a chain-like formation appears, causing the gellification of the fluid and the increased yield stress. However, ATC particles show little change in an electric field. These results can indicate that the ER effect is enhanced after the organification of ATC by CTAB, and a high concentration of CTAB and a high volume of ATC-CTAB can increase the shear stress.

3.3 Suspension stability of ATC and ATC-CTAB (0.2)

Figure 10 shows the suspension stabilities of ATC and ATC-CTAB(0.2) ER fluid at different sedimentation durations. The ratio of ATC-CTAB(0.2) ER fluid still can be a high value of 91% after two months (see Fig. 10), while that of ATC ER fluid can be only 85%. CTAB is a cationic surfactant, which can adsorb onto the negatively charged sites on the ATC surface. Hydrophobic hexadecyl groups existed in CTAB improve the compatibility between
ATC and silicone oil and reduce the aggregation among ATC particles efficiently. In general, suspensions that are stabilized against sedimentation show a higher yield stress at a given field strength. This can be proved according to the ER results above. The suspension stability of ATC-CTAB is satisfied with the commercial electrorheological materials requirement.

3.4 Structure of ATC and ATC-CTAB (0.2)

Figure 11 shows the FT-IR spectra of ATC and ATC-CTAB (0.2). Clearly, the sharp peaks at 3620 cm\(^{-1}\) and 1030 cm\(^{-1}\) are due to the typical silicate clay absorption, which can be attributed to \(\nu\)\(\text{OH}\) stretching mode and Si-O stretching vibration of Si-OH, respectively. After the modification by CTAB, there are two intense peaks appeared at 2919 cm\(^{-1}\) and 2851 cm\(^{-1}\), which is assigned to \(\nu\)\(\text{as C-H}\) and \(\nu\)\(s\) C-H, respectively. These two typical absorptions derive from hexadecyl group existed in CTAB. It is indicated that ATC is modified by CTAB due to the physical adsorption.

Figure 12 shows the XRD patterns of ATC and ATC-CTAB (0.2). The diffraction peaks are arisen from ATC, white mica, dolomite, feldspar and quartz. Clearly, there is no new crystal formation and the layer distance of is not changed after the modification by CTAB. CTAB modified ATC is only due to the physical adsorption.
3.5 TEM analysis

Figure 13 shows the TEM photographs of ATC and ATC-CTAB, respectively. Clearly, the crystal beams with the average diameter of 35 nm and various lengths appear. There are also sheet-like matter appeared in AT and they are mainly from illite and mixed clays accompanying with AT. After the modification by CTAB, AT shows loose, and the rod-like crystal beams are dissociated due to the reduced surface energy by hydrophobic hexadecyl groups introduced. It is indicated that ATC-CTAB could have better suspension stability than ATC.

Fig. 12 XRD patterns of ATC and ATC-CTAB(0.2)

(a) ATC (b) ATC-CTAB

Fig. 13 TEM photographs of ATC and ATC-CTAB

4 Conclusions

The ATC modified with CTAB was prepared, and the ER properties of ATC and ATC-CTAB were investigated. The results showed that the ATC-CTAB based fluids showed the Bingham fluid behavior and the suspension particles increased the ER response after the modification. ATC-CTAB(0.2) based ER fluid showed a relatively higher shear stress especially after 2.0 kV/mm and optical breakdown voltage of 3.5 kV/mm. The shear stress increased with increasing the particles volume in a solidified electric field of 1.5 kV/mm. The yield stress also increased with increasing the electric field at the exponent of $E^{0.4}$. The temperature had an effect on the shear stress of ATC-CTAB(0.2) based ER fluid, leading to the ER effect obviously at $T=65^\circ$C. The suspension stability could be satisfied with the commercial electrorheological materials requirement (The sedimentation duration for the suspension was 60 d at the concentration of 91%). ATC-CTAB(0.2) only had a physical interaction between ATC and CTAB. The TEM images showed that ATC had dissociated crystal beams with the diameter of 35 nm.

References:


