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Electrorheological effect coordinated by kaolinite–carboxymethyl starch hybrid materials

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Kaolinite–carboxymethyl starch nanocomposite particles were synthesized using a displacement method and the electrorheological properties coordinated by the particles in silicone oil were investigated; it was found that the hybrid electrorheological fluid displays a significant coordinated electrorheological effect under a dc electric field.

Electrorheological (ER) fluid is a smart material. ER fluids typically consist of electrically polarizable particles dispersed in low dielectric constant oils. Application of an electric field can induce polarization of the suspended particles. As a result, a chainlike structure can be formed along the electric field direction in a few milliseconds, and the apparent viscosity can be enhanced greatly.[1,2] Because of their controllable viscosity and short response time, ER fluids are regarded as potential smart materials for active devices, such as brakes, clutches, shock absorbers, and actuators. But some of the shortcomings of these materials, such as low shear stress, poor temperature stability, easy sedimentation, and high cost, have greatly restricted their industrial development.[3–6] Hence, research into ER fluids that are cheap and show useful properties and high performance is the key to electrorheological technology.

In recent years, polymeric modified layered silicate nanocomposites (PLSN) have become the subject of considerable interest for the design of high performance engineering materials with enhanced stiffness, strength, two-dimensional stability, and thermal and self-extinguishing characteristics.[7] Recently, many silicate–polymer composites have been reported, but they all use silicates, mainly montmorillonite. Kaolinite is an aluminosilicate with the ideal composition $Al_2Si_2O_5(OH)_4$. Moreover, kaolinite is a 1 : 1 dioctahedral clay mineral whose structure is composed of interstratified $AlO_2(OH)_4$ octahedral sheets and SiO_4 tetrahedral sheets. Consequently, the interlayer space is unsymmetrical, which is not found in other layered materials.[8] Examples of kaolinite intercalation with small polar molecules, such as dimethyl sulfoxide (DMSO) and potassium acetate, are frequently reported in the literature.[9] The intercalation of other compounds (especially polymers) using the above-mentioned compounds as intercalated precursors is known as the "displacement method". In order to research the ER properties of kaolinite hybrids, we employed the intercalation method to prepare the ER fluids of kaolinite–polar liquid intercalation composites. When a shear rate of 5 s^{-1} is applied to the ER fluids (30 wt%) at 25 °C, the shear stress can be 600 Pa in electric fields of 3 kV mm^{-1}.[10] In order to enhance the properties of the ER fluids, a new type of organic–inorganic hybrid colloid, made of carboxymethyl starch (CMS) and titanium oxide, was synthesized by an *in situ* sol–gel technique. The static yield stress of CMS–TiO_2 ER fluid is much higher than starch, TiO_2, and their simple blends.[11] Based on these results, we chose kaolinite and CMS to prepare a special hybrid, expecting a coordinated effect, which would improve the ER effect notably.

Using a combination of physical and chemical designs,[12,13] the choice of kaolinite intercalated with CMS was aimed at modifying the dielectric and polarization properties of kaolinite so as to improve its ER activity. Kaolinite–CMS hybrids were prepared by means of the displacement method. DMSO was used as a precursor. Because potassium acetate can intercalate directly into the kaolinite (d_{001} interlayer spacing can be increased from 0.715 to 1.440 nm), the potassium salt of carboxymethyl starch, possessing a similar group structure to potassium acetate, was used to carry out the displacement. When the the kaolinite–CMS hybrid had been prepared, its rheological properties were studied as a function of shear rate and component.

The kaolinite sample employed in this work was from Shanghai, China. It was received as a finely divided white powder of high purity, and the phase composition of the kaolinite were examined by XRD. The median particle size of the kaolinite was 2 µm. The kaolinite ($Al_{0.225}Si_{0.255}O_{0.516}$-$Fe_{0.0025}Ti_{0.0015}$) used to prepare the hybrid composites was used without further purification. Starch was purchased from Tan jin Chemical Third Co. Dimethyl sulfoxide (Beijing Yatai Co.), potassium hydroxide (Xi′an Chemical Factory), and chloroacetic acid (Cheng Du Associated Chemical Institute) were used as received.

Kaolinite (10 g) was mixed with 20 × 10^{-6} m^3 of DMSO and stirred at 80 °C. After 24 h, the resulting material (kaolinite–DMSO) was filtered and dried in an oven at 50 °C for 3 h to eliminate the excess DMSO. Then, 10 g starch and 40 ml ethanol were placed in a 100 ml vessel and stirred with a magnetic stirrer for 1 h. Potassium hydroxide (1.5 g) was added at 30 °C and reacted for 0.5 h to activate the starch. After that, 1.5 g potassium hydroxide and 5 g hydrated chloroacetic acid were added to the vessel at 50 °C and the mixture stirred for 3 h. The product was filtered off and washed three times with ethanol, then dried under vacuum at 50 °C for 1 h. The resulting carboxymethyl starch (CMS) was crushed in a mortar. Finally, 8 g of kaolinite–DMSO and 150 ml of distilled water were mixed in a 500 ml vessel and stirred at 30 °C for 2 h, then the appropriate amount of CMS was dissolved in 100 ml distilled water and dripped into the vessel at 60 °C. After the addition was complete, the temperature of vessel was increased to 80 °C and the mixture stirred for 8 h. The product was filtered off and washed three times with ethanol, then dried under vacuum at 60 °C for 3 h and at 80 °C for 0.5 h. The obtained kaolinite–CMS hybrid was then crushed in a mortar. The silicone oil was first dried at 100 °C for 2 h, and then hybrid ER fluids were prepared by dispersing the hybrid particles (at 31 vol%) in the poly(dimethylsiloxane) oil (ε_f = 2.60–2.80,

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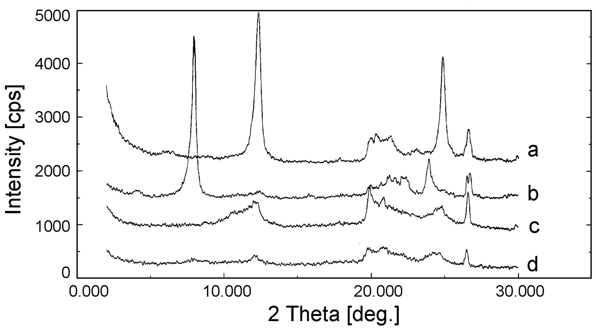

Fig. 1 XRD patterns of the raw kaolinite (a), kaolinite–DMSO (b), kaolinite–CMS (30 wt% CMS) (c), and kaolinite–CMS (50 wt% CMS) (d).

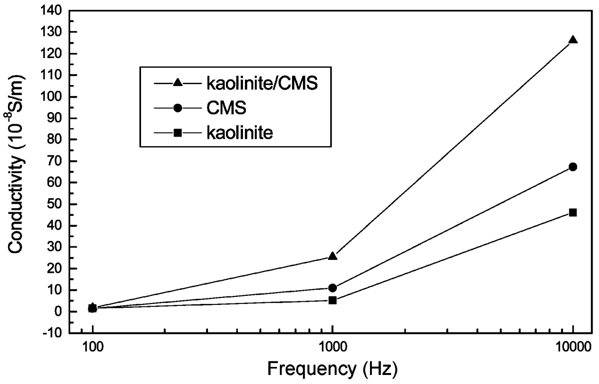

Fig. 2 Plots of conductivity *vs.* frequency for the ER fluids.

$\sigma = 10^{-12}$–10^{-13} S m^{-1}, $\rho = 0.9$–1.0 g cm^{-3}, $\eta = 500$ mPa s, 25 °C).[14]

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku diffractometer (D/III-γA, Japan) using Cu-K$_\alpha$ radiation with a dwell time of 1° min^{-1}. All measurements were taken using a generator voltage of 40 kV and a current of 20 mA. The dielectric properties of the ER fluid were measured with an automatic LCR meter (WK-LCR 4225, China) at different frequencies (100,1 k and 10 kHz). A rotary viscometer (NXS-11 A, China; the gap between the outer cup and the inner bob is 2 mm) and a high voltage dc power source (GYW-%, China; 0–10 kV) were used to research the rheological properties of the ER fluids (shear rate range 1.605–105 s^{-1}).

The X-ray diffraction spectra of kaolinite (a), kaolinite–DMSO precursor (b), kaolinite–CMS (CMS content 30 wt%) and kaolinite–CMS (CMS content 50 wt%) (d) are illustrated in Fig. 1. Very intense, sharp, and narrow peaks characteristic of raw kaolinite are observed at $2\theta = 12.6°$, which corresponds to the basal spacing of kaolinite (0.715 nm). As expected, the X-ray diffraction patterns of the intercalated kaolinites are dramatically different to that of the precursor. The peak at $2\theta = 12.6°$ in the original kaolinite, assigned as the first basal peak, d_{001}, is greatly shifted in the pattern of the DMSO intercalate to a small reflection angle due to the expansion produced by the presence of intercalated DMSO (1.120 nm, an increase of about 0.405 nm over the raw kaolinite).[15,16] From Fig. 1(c), it can be seen that when the content of CMS in the kaolinite–CMS hybrids is low (*e.g.* 30 wt%), the characteristic diffraction peak (d_{001}) decreases sharply in intensity and becomes a wide split peak. The diffraction pattern in Fig. 1(c) shows that most kaolinite layers were exfoliated, while some layers retained their basal spacing. But with increased CMS content (50 wt%), the characteristic d_{001} peak vanished, showing that all the kaolinite layers had basically been exfoliated. The homogeneous phase material on the nanometer scale was formed due to the single layer of kaolinite dispersed into the CMS, so the layer of kaolinite was mixed uniformly with the CMS on the nanometer scale.

The dielectric properties of the ER fluids were measured using an automatic LCR meter at frequencies of 0.1, 1, and 10 kHz. For each of the different ER fluids, the dielectric constant (ε), conductivity (σ), and dielectric loss ($tg\delta$) were measured. As is shown in Fig. 2, the conductivity of kaolinite–CMS ER fluid is 2.73 times that of kaolinite ER fluid and 1.87 times that of CMS ER fluid ($\omega = 10$ kHz, 25 °C). Furthermore, the dieletric constant of kaolinite–CMS ER fluid is 2.07 times that of pure kaolinite ER fluid, and 1.78 times that of CMS ER fluid ($\omega = 100$ Hz, 25 °C). Moreover, the dielectric loss of kaolinite–CMS ER fluid is 2.67 times that of kaolinite ER fluid ($\omega = 100$ Hz, 25 °C).

It is well known that a high dielectric constant and dielectric loss, and good conductivity is the physical basis to obtain the optimum electrorheological effect.[13] The dielectric constant is connected to the polar strength, but dielectric loss and conductivity are associated with the stability of the polar response and effect between particles.[17,18] Davis[19] proposed that in dc and low frequency electric fields, the conductivity plays an important role in the ER effect. According to the conductivity mismatch model, the static force between the particle is in direct proportion to the conductivity mismatch coefficient (eqn. 1)

$$\beta = \frac{\sigma_p - \sigma_f}{\sigma_p + 2\sigma_f} = \frac{\Gamma - 1}{\Gamma + 2} \qquad (1),$$

where $\Gamma = \sigma_p/\sigma_f$ (σ_p and σ_f are the bulk conductivity of the particles and the oil, respectively). Therefore, a large Γ value is required to enhance the mechanical strength of the ER fluid. But if the Γ value and the conductivity of the particles are so large that the particles become conductors, the fluid will no longer show the ER effect. Block *et al.*[20] reported that ER fluids with a conductivity of around 10^{-7} S m^{-1} usually showed the largest ER effect, because in this case, the strength of the interfacial polarization can reach a maximum. In our work, the dielectric constant and dielectric loss of the kaolinite–CMS ER fluids both increased notably and the conductivity remained at 10^{-8}–10^{-7} S m^{-1}. These properties are customary for the electrorheological effect.

The shear stress of kaolinite–CMS (component proportion 1 : 1) ER fluids (31 vol%) *versus* the change in shear rate was measured using a rotary viscometer under an applied electric field (*ca.* 0–3 kV mm^{-1}), and the results are plotted in Fig. 3. It can be seen that the ER fluids initially behave as Bingham fluids and show significant electrorheological effects; once the electric field is removed, they function as Newtonian fluids.[21–23] The shear stress of the ER fluids increases with increasing shear rate. Under the conditions 31 vol%, 25 °C, $E = 3$ kV mm^{-1}

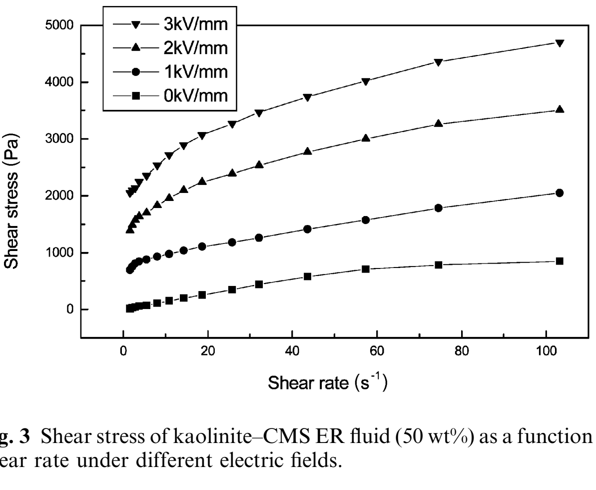

Fig. 3 Shear stress of kaolinite–CMS ER fluid (50 wt%) as a function of shear rate under different electric fields.

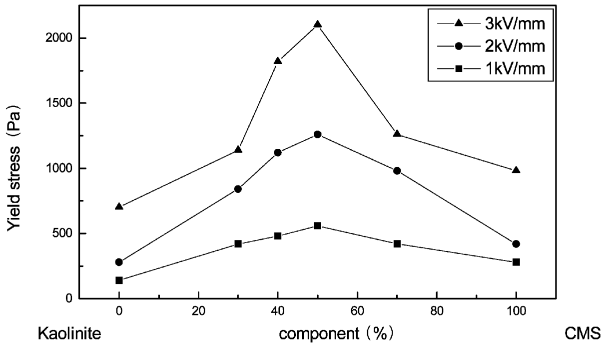

Fig. 4 Yield stress of kaolinite–CMS ER fluids as a function of composition under different electric fields.

(dc), $\gamma = 105\ \mathrm{s}^{-1}$, the shear stress ($\tau$) of the composite ER fluid is 4690 Pa, but when the electric field is removed, τ is only 725 Pa. The former is 6.25 times latter, which shows that kaolinite–CMS fluids demonstrate a significant ER effect.

The yield stress of kaolinite–CMS ER fluid as a function of composition under different electric fields is shown in Fig. 4. It can be seen that at the same volume fraction, the mechanical properties of pure kaolinite and CMS ER fluids poor. But the yield stress of the hybrid ER fluids increased enormously, because of the stronger coordinated effect, and the ER effect also increased significantly. The yield stress of the hybrid ER fluids increases with increasing CMS content at first, then reaches a maximum at a critical content; after this point, further increases in CMS content cause the yield stress to drop. From the XRD patterns, it can be seen that with low CMS content, the kaolinite layer is partly exfoliated, but some portion of the kaolinite is not. So the coordinated effect of the material is not obvious and the mechanical properties of the hybrid ER fluids is poor. When the mass ratio of the components is around 1 : 1 (or 50 wt%), as shown in the XRD patterns, the layer of kaolinite is basically exfoliated and the single layer dispersed into the CMS. A uniform phase material at the nanometer scale is formed and the coordinated effect becomes stronger, so the ER effect is optimized. However, with further increases in CMS content, the CMS begins to aggregate and form the CMS phase, with the result that the coordinated effect decreases and lead to the ER effect being reduced.

In summary, a new type of ER material, containing a kaolinite–CMS hybrid, has been synthesized using a secondary displacement intercalation technique. The structure analysis shows that the layers of kaolinite were exfoliated by the intercalation of CMS and the layers dispersed into the CMS. The dielectric properties of kaolinite–CMS hybrid ER fluids are greatly increased over those of the fluids containing the pure single components. The conductivity of kaolinite–CMS ER fluid is 2.73 times that of pure kaolinite ER fluid and 1.87 times that of CMS ER fluid ($\omega = 10$ kHz, 25 °C). The ER activity of the hybrid ER fluids is improved under dc electric fields. Under the conditions 31 vol%, 25 °C, $E = 3\ \mathrm{kV\ mm}^{-1}$ (dc), $\gamma = 105\ \mathrm{s}^{-1}$, the shear stress of the composite ER fluids is 4690 Pa. When the component ratio is close to 1 : 1, the coordinated effect is stronger and the ER effect is optimimized. All of these results exemplify a new method for the preparation of ER fluid materials with good cost performance.

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