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The synthesis and electrorheological effect of a strontium titanyl oxalate suspension

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Abstract
Strontium titanyl oxalate (STO) particles were synthesized with the co-precipitation method. Suspensions made by dispersing the STO particles in silicone oil exhibit an excellent electrorheological (ER) effect with high yield stress, high shear stress at higher shear rate, and low current density. By analyzing the Fourier transform infrared spectra of STO particles heated at different temperatures and measuring the yield stresses of the corresponding ER fluids, it is confirmed that the polar molecules absorbed on the particles play a crucial role in the giant ER effect. The phenomena observed in STO ER fluids can be explained by using the model of a polar molecule dominated electrorheological (PM-ER) effect.

1. Introduction

Electrorheological (ER) fluids consisting of micron- or nano-size dielectric particles dispersed in insulated liquid possess the character of a rapid liquid–solid transition under application of an electric field. The novel property of such smart material has attracted much attention because of its wide potential applications in technology. The mechanism of traditional ER fluids is based on the dielectric interaction of particles [1–3]. According to the prediction of first-principle calculations with dielectric theory, the upper limit of the yield stress for such traditional ER fluids is less than 10 kPa [4], while the yield stress of available ER fluids can only reach a few kPa. This great shortcoming of low yield stress for the traditional ER fluids has blocked their applications for half a century.

In recent years, ER fluids with a yield stress of more than 100 kPa have been fabricated [5–10], which is much higher than that of conventional ER fluids. For such newly developed ER fluids there must be a new principle that is different from the traditional dielectric one to govern their behaviors. A model was proposed based on polar molecules aligning along the field direction in between the particles and the interaction of the polar molecule charge to explain the mechanism of the giant ER fluids, which was defined as the polar molecule dominated ER (PM-ER) effect [9]. With this model the observed phenomena in those newly developed ER fluids can be well explained.

Up to now mainly three types of ER fluid with high yield stress have been reported: they consist of Ba–Ti–O, TiO_2, and Ca–Ti–O particles coated with polar molecules [5–10]. From the principle of the PM-ER effect, the particles should possess high enough dielectric constant to create high enough local electric field in between the particles. $SrTiO_3$ is one of the most popular dielectric materials with a sufficiently high dielectric constant. Although there was a study on Sr–Ti–O particle based ER fluid [11], the yield stress was only 27 kPa under an applied electric field of 3 kV mm^{-1}.

In the present paper the study on the Sr–Ti–O ER fluid has been extended in terms of both the preparation of the sample and the measurement of the properties. The yield stress of the ER fluid consisting of STO particles suspended in silicon oil can reach 85 kPa with the current density less than 1 μA cm^{-2} in a DC electric field of 5 kV mm^{-1}. The measured shear stress versus shear rate shows a good ER response at high shear rate. These properties of the Sr–Ti–O ER fluid can meet the requirements for applications. We will also demonstrate that the high ER effect of the STO suspensions is attributed to the polar molecules or polar groups adsorbed on the particles and can be well explained with the PM-ER model.

2. Experimental details

The STO particles were fabricated by a co-precipitation method with the following procedures. Oxalic acid was

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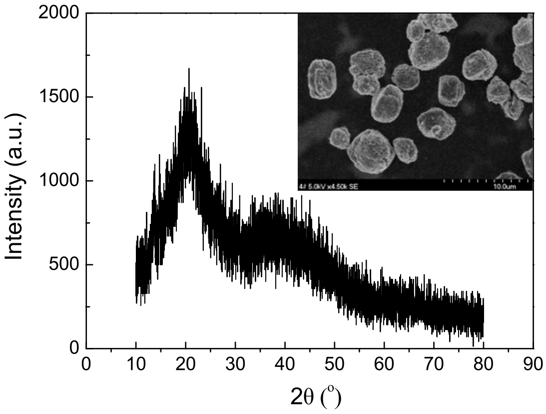

Figure 1. X-ray diffraction pattern and SEM image of strontium titanyl oxalate (STO) particles (inset).

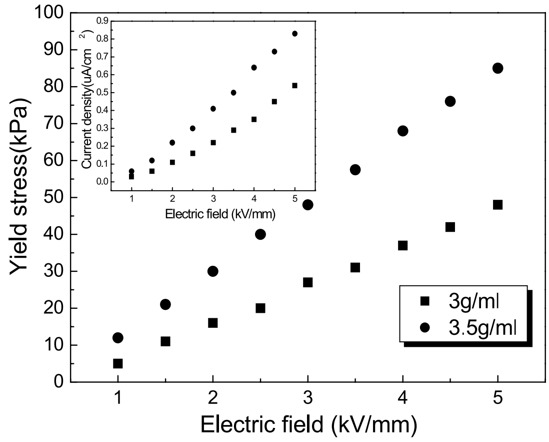

Figure 2. Measured yield stress plotted as a function of electric field, for STO ER fluids with different particle concentration. The current densities corresponding to those samples are shown in the inset.

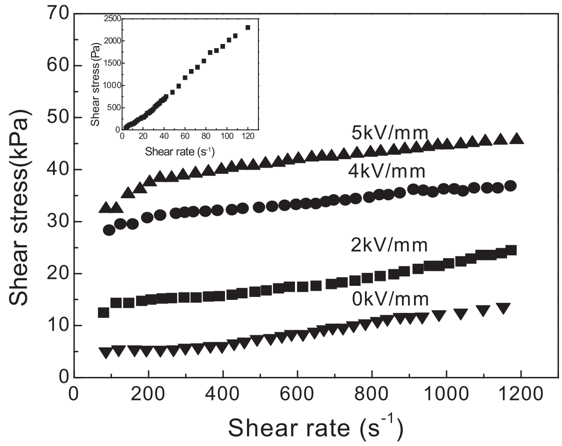

Figure 3. Variation of the shear stress versus shear rate, measured in different DC electric fields.

dissolved in distilled water at 55–65 °C, while tetra-*n*-butyl titanate and strontium chloride were dissolved in ethanol solution. Then the two solutions were mixed and vigorously stirred at 60 °C to form a white precipitate. After ageing, centrifugation, washing, and drying the precipitate in air, strontium titanyl oxalate particles were obtained. The SEM image and x-ray diffraction pattern shown in figure 1 indicate that the particles are in an amorphous state, with a diameter of 2–6 μm.

The ER fluids were prepared by dispersing the STO powder into silicone oil and grinding with a high-speed grinding mixer to ensure uniformity of the suspension. Before dispersion, the oil and the powder were heated at 120 °C for 3–5 h, to remove any trace of water. The concentration of the STO ER fluids is given in units of g ml^{-1} which represents the mass of the powder divided by the volume of silicone oil, because of the uncertainty of the particle density.

The yield stress of ER fluids versus electric field is measured by a homemade rheometer with two parallel plates as electrodes, which satisfies with the measurement of high yield stress. The shear stress versus the shear rate at different electric fields is detected with a sealed cylindric rheometer. The measured magnitudes of the shear stress with this method are apparent and little higher than the real ones because of the friction of the seal ring assembly [9]. The electrodes in the measurements are modified to avoid the slide between electrodes and ER fluid under application of an electric field. A detailed description of the electrode modification is given elsewhere [12].

3. Results and discussion

The yield stress τ_y and current density versus field strength E of the STO ER fluid are given in figure 2. The results show that the prepared STO ER fluids possess high yield stress and low current density. For the STO ER fluid with a concentration of 3.5 g ml^{-1} the yield stress is about 85 kPa and the current density is less than 1 μA cm^{-2} at a field of 5 kV mm^{-1}. The shear stress versus shear rate of the STO ER fluid with a concentration of 3 g ml^{-1} is shown in figure 3. The relatively high shear stress at zero electric field is mainly due to the friction in the sealing cylinder. For a comparison the dependence of the shear stress on the shear rate at 0 kV mm^{-1} measured with a conventional viscometer in double cylinder mode is shown as an inset in figure 3.

It can be seen in figure 2 that the yield stresses of STO ER fluids are much higher than the upper limit of conventional ER fluids predicted with dielectric theory, and they exhibit a linear dependence on applied electric field unlike the relation $\tau_y \propto E^m$ ($m = 2$ or $3/2$) in the conventional fluids [4, 13–15]. The high yield stress and its near-linear dependence on the electric field indicate that the behaviors of our STO ER fluids cannot be explained by the traditional dielectric theory. However, with the model of the polar molecule dominated ER (PM-ER) effect [9] the phenomena we observed in STO ER fluids can be well explained. The PM-ER effect is based on the interaction of the polar molecule polarization charge between the particles, where the local electric field is much higher than that of the external field [13, 14], and results in the polar molecules aligning in the direction of the electric field. It is the probability of the polar molecules aligning in the electric field being proportional to the field [9, 16] that causes the linear dependence of the shear stress on the electric field.

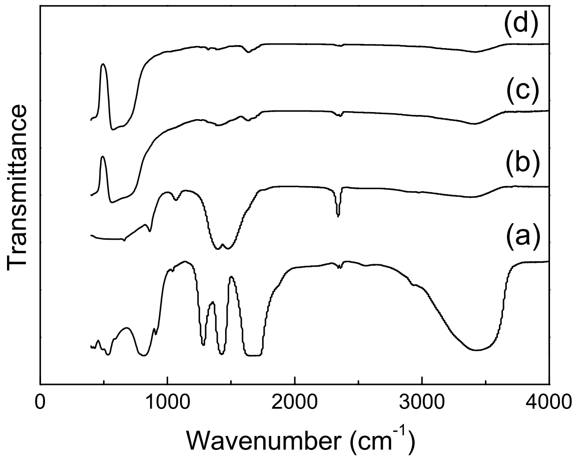

Figure 4. FT-IR spectra of STO powders heated at different temperatures: (a) 120 °C, (b) 400 °C, (c) 600 °C, and (d) 800 °C.

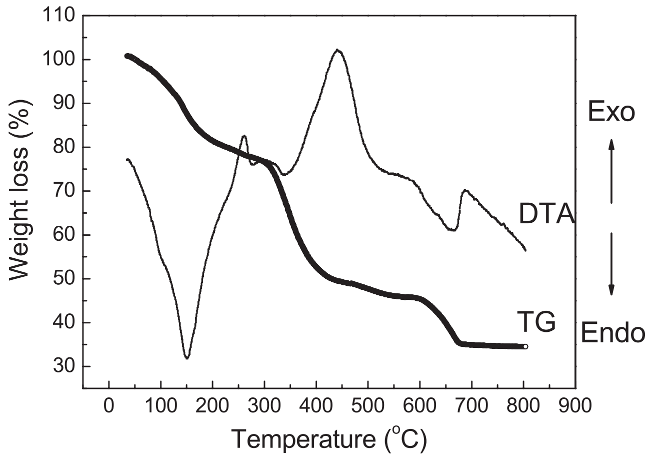

Figure 5. DTA–TG curves of as-dried STO powder.

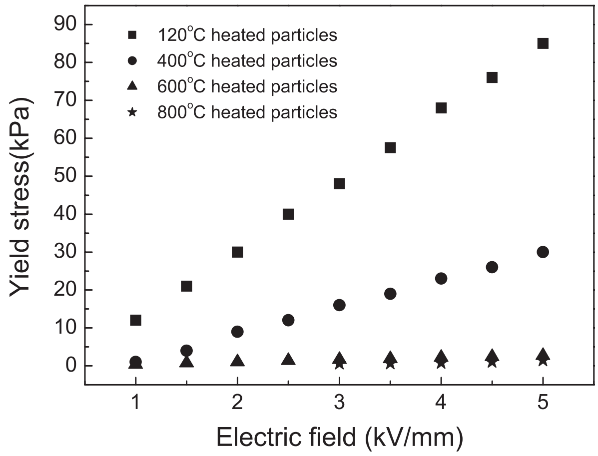

Figure 6. The yield stress of the powders heated at different temperatures versus electric field.

The composition of STO particles depends most strongly on the pH value and on the ratio of Ti^{4+} and $C_2O_4^{2-}$. The STO particles fabricated by controlling the reaction condition consist of $SrTiO(C_2O_4)_2{\cdot}nH_2O$. Oxalate groups and hydrated molecules play a key role in the improvement of the ER effect on the particle surface.

In order to judge whether the polar molecules play a crucial role in STO ER fluids an experiment has been performed. If there are polar molecules or polar groups adsorbed on STO particles, they must evaporate away at higher temperatures. Unheated and heated STO particles can be representative for samples with and with fewer polar groups, respectively. By analyzing the Fourier transform infrared (FT-IR) spectra of those different STO particles and measuring the yield stresses of the corresponding ER fluids, the effect of the polar molecules can be ascertained. First, STO particles with high ER response were analyzed with FT-IR spectroscopy; the particles were dried at 120 °C for 2 h to eliminate any humidity effect. As shown in figure 4(a), the broad band around 3400 cm^{-1} corresponds to asymmetric and symmetric stretching vibrations of the OH group, and the absorption bands at 1650, 1425, and 1280 cm^{-1} may be assigned to the different modes of vibration of oxalate groups. However, for the STO particles heated at 400, 600, and 800 °C for 2 h, the FT-IR spectra of them, as shown in figures 4(b)–(d), respectively, are different. It can be seen that the absorption bands of the polar groups have mostly disappeared, although the sizes and the shapes of all the heated particles are not much changed. The FT-IR spectra indicate that the absorbed polar molecules on the particles are reduced and even all evaporated for the heat treated particles. The differential thermal analysis/thermogravimetric (DTA/TG) curves of the prepared particles carried out in the temperature range 35–800 °C, as shown in figure 5, indicate the process of the compositional change in three steps: (i) removal of hydrated molecules in the range 35–200 °C, (ii) decomposition of oxalate in the range 200–600 °C, and (iii) formation of $SrTiO_3$ in the range 600–700 °C. The DTA/TG results show that polar groups such as hydroxyl groups and oxalate groups gradually evaporated on increasing the temperature. Correspondingly, the measured yield stresses under various applied electric fields of the ER fluids made of all those STO particles are shown in the figure 6. It is obvious that the yield stress of the ER fluids is very sensitive to the heating temperature of the particles. By increasing the heating temperature of the particles the ER effect is drastically weakened. For instance, under a field of 5 kV mm^{-1}, the yield stress of ER fluid consisting of STO particles dried at 120 °C is 85 kPa, while the yield stresses of that containing particles heated at 400 °C and higher temperatures are 30 kPa and nearly zero, respectively. The FT-IR spectra and the ER effect of the powders demonstrate that the polar molecules adsorbed on the particles play a decisive role in determining the characteristics of the STO ER fluids.

4. Conclusion

In this study, the ER fluid composed of strontium titanate oxalate powder dispersed in silicone oil is fabricated. The yield stress of the STO ER fluid is as high as 85 kPa with low current density at a field of 5 kV mm^{-1}. Also, the STO ER fluid exhibits excellent behavior of shear stress at high shear rate. It is clear that the polar molecules and/or polar groups adsorbed on the particles are decisive to the high ER effect. The phenomena observed in STO ER fluids can be well understood with the model of the PM-ER effect. STO ER fluid should be a good potential candidates for applications.

Acknowledgments

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