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Preparation and electrorheological properties of triethanolamine-modified TiO_2

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Abstract

The high molecular dielectric dipole moment of doping material is promising to improve the electrorhelegical (ER) effect. It is found that triethanolamine (the molecular dipole moment of triethanolamine is 3.48)-modified TiO_2 has good ER properties. Under 5 kV/mm external electric field, the yield stress is 32.6 kPa, which is about 50 times higher than that of pure TiO_2 and the leaking electric current density is lower than 16 μA/cm^2. The sedimentation rate is about 98% in 20 days.

Keywords: Electrorheological fluids; Molecular dipole moment

1. Introduction

Electrorheological (ER) fluid is a suspension made of micrometer- or nanometer-sized particles in an insulating liquid. If the external electric field is higher than a certain critical value, the liquid–solid transition happens in several milliseconds, and the transition is reversible as the electric field is turned off [1]. The industry applications of such smart materials are under the design by the engineers [2,3]. The most urgent mission is to enhance the shear stress of the ER materials.

It is found that the optimized ER materials are not micrometer- but nanometer-sized particles [4,5] or micrometer particles with nanometer-sized structures, such as pores or layers [6]. The ER fluids composed of nanometer-sized particles or particles with nanometer-sized structures show more advantages such as large yield stress, low current density, and low sedimentation. However, not all ER fluids that are composed of nanometer-sized particles would present large yield stresses. For example, nanometer-sized pure TiO_2 show very low ER effect with a yield tress of 0.6 kPa at 4 kV/mm [6]. The yield stress of inorganic ionic modified TiO_2 [7,8] is a few orders of magnitude higher than that of pure TiO_2. The characteristics above indicate that the properly modified materials with nanometer size or nanometer-sized structure are crucial to enhance the ER activity. In this paper, we prepare an ER fluid composed of an organic modified titanium dioxide (triethanolamine–TiO_2). The concentration of the ER fluid suspensions is denoted by the ratio of the mass of powders in grams to the volume of base oil in milliliters [9]. The rheological experiments show that the shear yield stress of the ER fluid with a concentration $\Phi = 0.68$ g/ml reaches 32.6 kPa at $E = 5$ kV/mm which can satisfy most industrial applications. The sedimentation ratio of the ER fluids is 98% in 20 days. The ER properties also present under AC electric field. Some detailed dielectric properties such as molecular dipole moment are used to analyze the ER property.

2. Experimental

2.1. Preparation of triethanolamine-modified TiO_2 particles

The triethanolamine–TiO_2 gel powders were prepared by a sol–gel method. Triethanolamine and titanium butoxide ($Ti(C_4H_9O)_4$) were used as starting materials; acetic acid (HAc, CH_3COOH), ethanol (C_2H_5OH) and deionized water were employed as solvents. First, a solution of

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triethanolamine and deionized water was mixed in ethanol. Secondly, $Ti(C_4H_9O)_4$ was dissolved in ethanol at a volume ratio of $Ti(C_4H_9O)_4$:ethanol = 1:2. In order to avoid precipitation, a small amount of acetic acid was added. Thirdly, triethanolamine solutions were added into $Ti(C_4H_9O)_4$ solution. The sol was kept in air at room temperature for within a minute yielding transparent gel. The triethanolamine-modified TiO_2 gel particles were obtained by drying the gel in an oven at 75 °C for 48 h.

2.2. Preparation of an ER fluid

The host insulating oil used in the ER fluid was silicone oil, and its dielectric constant is 2.5, density is 0.965 g/cm^3, and viscosity, 50 mPa s at 25 °C. The dried samples were mixed quickly with the silicone oil. The mixed suspension was milled for 2 h in a mortar, and then heated at 75 °C for 3 h.

2.3. Characterization

The microstructure and particle size of the gels were examined by scanning electron microscopy (SEM) and Submicron Particle Size Analyzer. The ER effect was characterized by the yield stress under DC/AC electric field. The experimental data were collected by a Mecmesin torque indicator with two parallel plates. The diameter of the plate is 20 mm and the gap between two plates is 1.0 mm. The quasi-static shear stress is measured at a relatively low shear rate of 0.06 s^{-1}.

3. Results and discussions

3.1. Materials characteristics

The SEM shows in Fig. 1(a) that the triethanolamine-modified TiO_2 powder morphology is very irregular, and the powder diameter is distributed mainly in the range from 1 to 100 μm. Fig. 1(b) shows that the diameters of powder particles are as small as 20 nm. Comparing the two graphs, one may find out that agglomeration is very serious in our sample. In our experiment, the yield stress is tested with the milled powders whose diameter distribution in Fig. 1(c) is narrow and the average size is about 350 nm tested by N4Plus Submicron Particle Size Analyzer of Beckman Coulter Company.

Fig. 2 gives the infrared spectra of triethanolamine-modified TiO_2 gel (a) and TiO_2 gel (b). The broad band around 3550 cm^{-1} is assigned to antisymmetric and symmetric stretching vibration of −OH group. The band around 1600 cm^{-1} is assigned to the H–O–H bending vibration. The band ranging from 1430 to 1470 cm^{-1} stands for C–H_3 and C–H_2 distortion in both samples (a) and (b). In sample (a), a narrow band around 1070 cm^{-1} is attributed to the C–OH stretching vibration. The IR absorption band at 487 cm^{-1} originates from the Ti–O stretching vibrations. To conclude, it shows that triethanolamine-modified TiO_2 has more polar groups such as −OH than TiO_2. In addition, existed C–OH in triethanolamine-modified TiO_2 proves that the TiO_2 is really modified by triethanolamine.

3.2. Rheological properties of ER suspension

The yield stresses of giant ER fluids in some references [9] are measured using square-wave voltage pulses. One reason of using square-wave voltage pulses is to observe response time easily; and the other one is to avoid large leaking current. Considering industrial applications of ER fluids, in our experiment, DC voltage is adopted. Fig. 3 shows the yield stress and current density of the triethanolamine-modified TiO_2. The data of yield stress are collected every 10 ms. The reported nanometer-sized ER materials [9] with high yield stress show a slow response time that is longer than 1 s. The response time of triethanolamine-modified TiO_2 is less than 10 ms. Under a low electric field, the yield stress has square relation with the external electric field. However, under the electric field

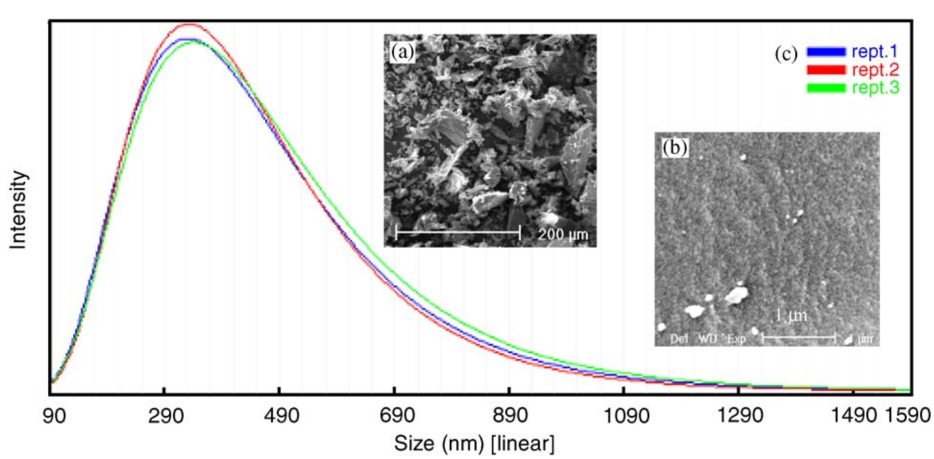

Fig. 1. SEM of the triethanolamine-modified TiO_2 gel particles and the diameter distribution of the triethanolamine-modified TiO_2 particles.

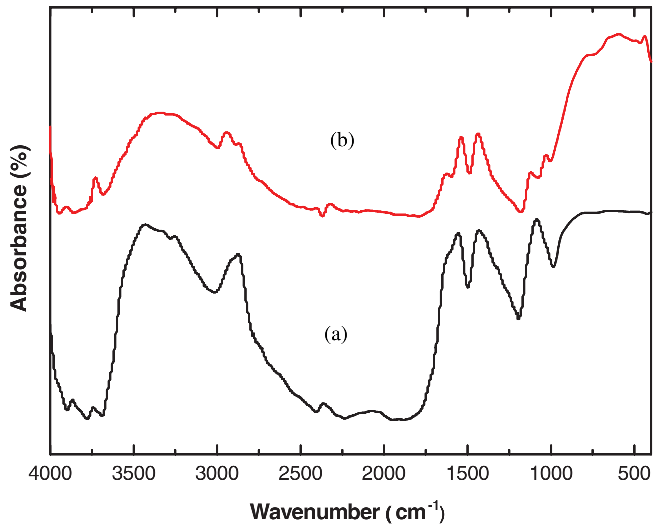

Fig. 2. The FT-IR spectra of triethanolamine-modified TiO_2 (curve a) and TiO_2 (curve b).

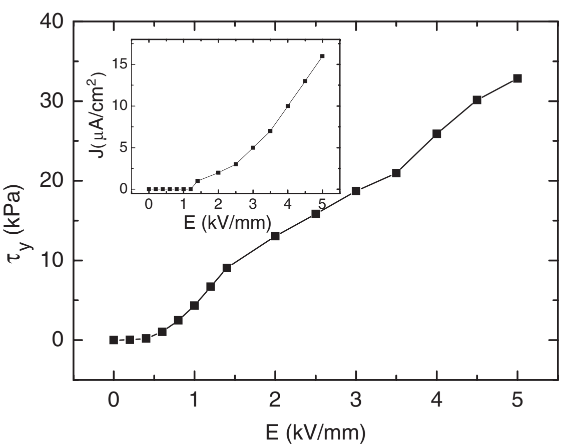

Fig. 3. The yield stress and current of triethanolamine-modified TiO_2 under DC electric field.

higher than 1 kV/mm, the relation is linear. The current density is quite low and even less than 16 μA/cm^2 under 5 kV/mm.

3.3. Dielectric properties of ER suspensions

An AC electric field was used to study the dielectric properties of the ER materials. The yield stress of the triethanolamine-modified TiO_2 ER fluid decreases noticeably with increasing frequency (Fig. 4). It can be explained from the dielectric and conductive properties of the ER particles. To detect the dielectric properties, the triethanolamine–TiO_2 powder was pressed into a thin disk 2 mm thick and 14 mm in diameter. The relative dielectric constant (ε_p) and conductivity (σ_p) are measured with a Hewlett Packard 4284A Precision LCR Meter. The dielectric constant of the particles decreases (Fig. 5) dramatically with frequency and approaches constant values at high frequency under fixed field strength. The conductivity (σ_p) of the powder disk is in the order of 10^{-6} S and is almost frequency independent. ε_f and σ_f are the dielectric constant and conductivity of silicone oil, respectively, and vary slightly with frequency. Γ_ε and Γ_σ are defined as $\varepsilon_p/\varepsilon_f$ and σ_p/σ_f, respectively. Γ_ε is in the order of 10–10^2. Large dielectric constant ratio is favorable for ER effects. Γ_σ is in the order of 10^5. The frequency dependence of shear stress is accord with Wu and Conrad's analysis [10,11]. If $\Gamma_\sigma \gg \Gamma_\varepsilon$, the conductivity mismatch dominates the ER strength at low frequency and the ER fluid has a high shear yield stress at a low frequency electric field.

There are two attitudes in judging whether a material is ER active or not. For one point, Wen et al. [5] point out that the organic material coated particles have high values in both molecular dipole moment and dielectric constant. For another, the interfacial polarization mechanism [12–15] proposes that good ER fluids should have a dielectric relaxation peak in dielectric loss in the frequency range of 10^2–10^5 Hz. Generally, the mechanism treats particle polarization by using complex dielectric constant, $\varepsilon = \varepsilon' - i\varepsilon''$, where the real part ε' is related to polarizability

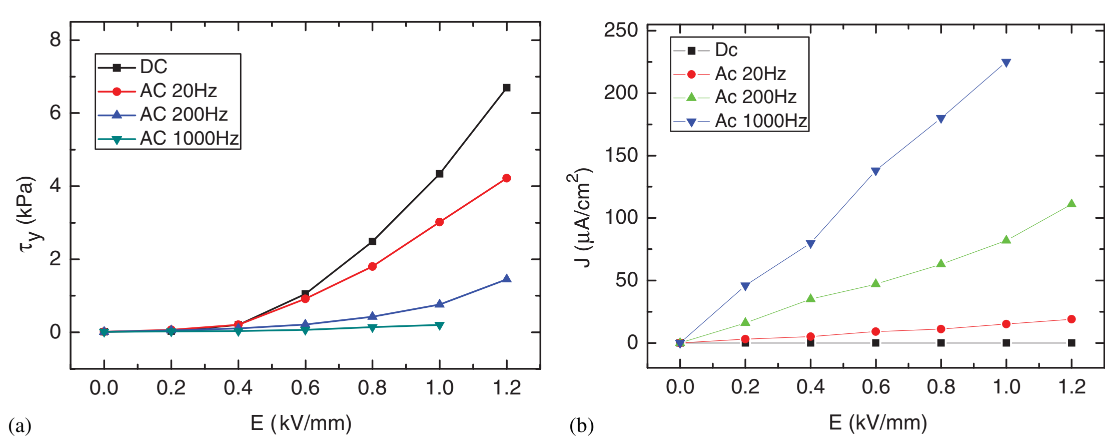

Fig. 4. Yield stress (a) and current density (b) of triethanolamine-modified TiO_2 under DC electric field.

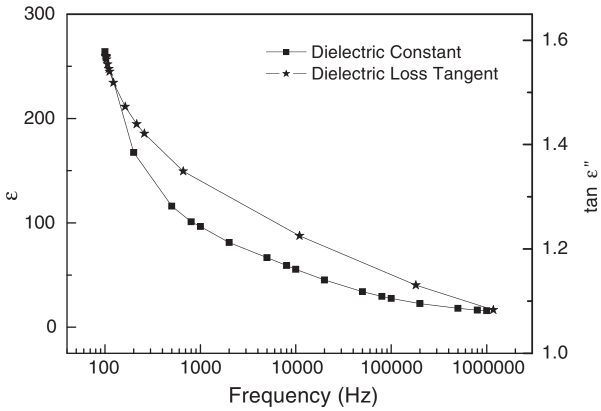

Fig. 5. The dielectric properties of triethanolamine-modified TiO_2.

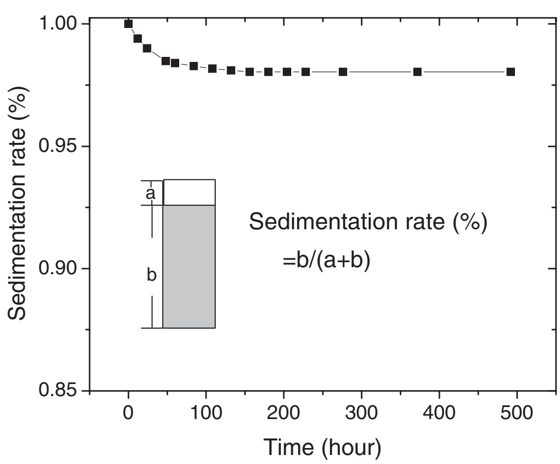

Fig. 6. Sedimentation rate of triethanolamine-modified TiO_2 ER fluid versus the static time.

and the imaginary part ε'' is related to the dielectric loss, and can be expressed as $\sigma/2\pi f$, where σ is the conductivity and f is frequency of the external electric field. This theory is supported by recent experiments on mesoporous cerium-doped TiO_2 [6], and amorphous $Ba_xSr_{1-x}TiO_3$ [16]. However, there is no dielectric relaxation peak in triethanolamine-modified TiO_2 shown in Fig. 5. The experimental result shows that the dielectric constant of the ER fluid is about 16 in low frequency. The molecular dipole moment of triethanolamine is 3.48 calculated with the method of general gradient approximation (GGA). This result can be understood by Wen's theory, which explains the organic modified material. The organically coated material is soft which can make closer particle contact and larger contact area. The close distance and high molecular dipole moment induce local electric fields as high as 10^8 V/m, which cause high yield stress. To confirm the role of the triethanalamine, the powders are washed with ethanol many times (triethanalamine can be dissolved in ethanol). As a result, the shear stress is nearly zero for the bare TiO_2.

3.4. Sedimentation stability of ER fluid

Fig. 6 shows the sedimentation rate of triethanolamine-modified TiO_2 ER fluid versus the static time. According to Fig. 6, the triethanolamine-modified TiO_2 suspensions possess an excellent antisedimentation stability. The sedimentation ratio is only about 98% within 20 days.

4. Conclusions

In this study, we choose TiO_2 and achieve its ER enhancement under AC and DC electric field by doping triethanolamine, which is synthesized with the sol–gel technique. Under a DC electric field, the ER fluids shows large yield stress of 32.6 kPa at 5 kV/mm, and low leaking current density of 16 A/cm^2. High dielectric constant and high molecular dipole moment are the major condition for the high values of yield stress of the material. However, under an AC electric field, the yield stress decreases noticeably and the current increases dramatically with frequency. This can be understood as the competition between the conductivity effect and dielectric effect. The sedimentation ratio of the ER fluids with concentration of 0.68 g/ml is 98% in 20 days.

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