

Wettability of urea-doped TiO₂ nanoparticles and their high electrorheological effects

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Abstract Aimed at the increasement of ER effects, a novel composite, urea doped-TiO₂ particles (TU) were prepared by using a modified sol–gel method. The structure and morphology of the TU particles were observed and analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectrometry (FT-IR) and X-ray photoelectron spectrum (XPS). The dielectric properties of the TU particles and the ER effects based on the TU particles were investigated. The influence of wettability on the ER performance between the particles and silicone oil was examined.

Keywords Wettability · Electrorheological effect · Sol–gel · Dielectric properties

1 Introduction

ER fluids are known as smart liquids for their apparent viscosity capable of experiencing a rapid, reversible change upon application of an electric field. The ability to control the apparent viscosity electrically makes ER fluids potentially important in numerous electromechanical devices, such as valves, dampers, and clutches in the automotive and robotics industries, etc [1–3]. Particle polarization is

now widely thought to be responsible for the interaction forces that lead to the rheological change of ER fluid. The parameters in connection with particle polarization, such as high dielectric constant and suitable dielectric loss and conductivity, have been accepted as the basic factors that dominate the ER effects [4–6].

As far as the particles polarization are concerned, the wetting property of particle's surface is also very important to the high performance ER effect [7–9]. In recent years, a number of groups have reported the photo induced wettability conversion of TiO₂ surface. For example, the TiO₂ particles show hydrophobicity and super-hydrophilicity at different conditions, and the wettability can be switched reversibly by alternation of ultraviolet light illumination of the surface or by changing the chemical adsorbed polarized radical, such as –OH, –COOH, –CN, –CONH₂, –COOR, etc on the surface of TiO₂ particles [10–15]. In addition, TiO₂ is also a promising ER materials for its high dielectric constant around 85 or 173 (depending on its crystallization state). However, the dried TiO₂ based suspensions have quite low ER responses, usually of only several kPa. When these particles absorb a small amount of water, their ER response can be substantially improved. The presence of water can dramatically enhance the interaction of the particles, but the shortcomings of water (with its high current density, high temperature evaporation and low frozen point) make it unsuitable for many applications. To overcome the problems brought by water, new materials with favorable wettability and high dielectric performance were expected.

In this letter, we report a new type of anhydrous ER fluid consisting of TU particles suspended in silicone oil. Urea, which has a high dipole moment of 4.56 Debye, a high decomposing temperature of 133 °C and with the polarized radical –CONH₂ in its molecular structure [16, 17], doped

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in TiO₂ gel, was expected to increase the dielectric performance and wettability of TiO₂ particles and to avoid the large leaking current density through an ER fluid, and consequently was expected to result in enhanced ER performance ultimately.

2 Experimental

2.1 Preparation of TU samples

All the chemical reagents in this study were analytical grade. A typical preparation processing is as follows: Firstly, titanium butoxide (Ti(OC₄H₉)₄) as an inorganic precursor was first dissolved in water-free alcohol. DEA (diethylamine) and PEG(polyethylene glycol) were added to form a clear solution. Here, DEA was used as an additive to prevent the precipitation of oxides from the alcoholic titanium butoxide in the presence of excess water. PEG, a kind of water soluble organic polymer, contains hydroxyl group at each end of the ethyleneglycol chain, benefits to the wetting performance of TiO₂ nanoparticles. Secondly, water-free alcohol and H₂O were mixed with urea to form another homogeneous solution. In the preparation, the volume ratio of H₂O and C₂H₅OH is kept at 1:9, and the added urea is 1, 3, 5, 7 wt% for different samples. The second solution was then added into the first solution, which resulted in a transparent sol after 1 h of stirring, the particles were formed when the sols were allowed to age for 24 h at the room temperature. Thereafter, the solid material was filtered off, washed with deionized water several times and dried at 100 °C by degassing for 12 h to remove any trace of water.

2.2 Characterization and measurement

The chemical structure was determined by a Perkin-Elmer system 2000 spectroscopy (FT-IR) spectrophotometer in which the IR spectra were recorded by diluting the milled powders in KBr. The X-ray photoelectron (XPS) measurements were performed using an ESCLAB MKII spectrophotometer manufactured by VG Scientific Corporation. All binding energies were calibrated by the binding energies of C1 s, which provides an accuracy of ±0.1 eV. The crystalline structure was measured using a Rigaku D/Max-A X-ray diffractometer (XRD) with a CuK α source in the 2-theta mode over the range of 20° < 2 θ < 80°, and the XRD analysis results inferred the amorphous properties of TU particles. The particle densities were determined by pycnometry using silicone oil as the dispersing medium, and the density of the particles was measured to be 1.711–1.818 g/cm³. The dielectric performance of the particles was measured using an Agilent 4294A precision impedance analyzer.

2.3 The measurement of contact angle and ER effect

The wettability of the TU particles with silicone oil was evaluated by the contact angle measurement, which was performed at ambient conditions using a commercial contact angle meter. A typical measurement process was as follows: the TU precursor sol were first prepared and coated on a glass substrates by dipping processing, the dip coating was repeated five times and then dried at 100 °C for half an hour. By using a microsyringe, a droplet of fluid (silicone oil) typically 5 μ L was drop on the film surface. By using a CCD camera and an image analysis system, the imbibitions process was recorded and quantified. The values of Contact angle in text are the averaged value of three replicates.

The ER suspension was prepared by grinding and dispersing a weighed amount of particles in a weighed amount of silicone oil. The ER suspensions with 30 vol% of particles were prepared by magnetic stirring for 8 h. The rheological behavior of the suspensions was investigated by a circular-plate type viscometer (TA ARES) with a gap width of 1 mm, under d.c. applied voltage up to 4 kV/mm. We used a PM5134 functional generator to generate linear and step signals for driving the dc high-voltage source. The electric field was applied to the ER colloid sandwiched between two parallel plates. An ammeter was used to monitor the current across the ER fluid. The static yield stress was obtained from the controlled shear stress mode measurements at a constant shear rate 1 s⁻¹. Experimental data were collected with the help of the software package Rheowin. All the experiments reported in this paper were performed at room temperature of about 20 °C. These measurements were performed in triplicate so as to get an average value of the response of the material.

3 Results and discussion

3.1 Structure of TU particles

Figure 1 shows the FT-IR spectra of the pure TiO₂ particles and the 3 wt% TU particles. The spectrum for pure TiO₂ shows that the broad band around 3,450 cm⁻¹ is both asymmetric and symmetric stretching vibrations of O–H group, whereas the band around 1,615 cm⁻¹ is the H–O–H bending of the coordinated water, the IR absorption band at 657 cm⁻¹ is attributed to the Ti–O–Ti stretching vibrations. Comparing the two spectra in Fig. 1, it is noted that although the two spectra are similar as a whole, there are some observable differences as marked on spectrum (b). In spectrum (b), the absorption band at 3,259 cm⁻¹ is attributed to the H–O stretching vibrations of the absorbent water of the urea molecules, the new appeared bands at

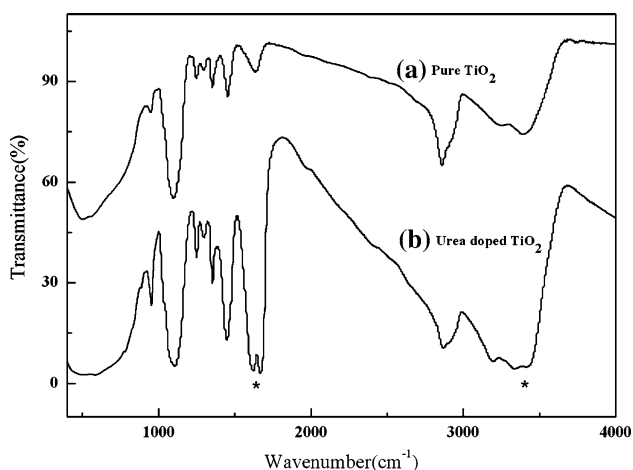


Fig. 1 The FT-IR spectra of pure TiO₂ particles and TU particles

3,400 cm⁻¹ and 1,630 are attributed to the N–H stretching vibrations and the band at 1,710 cm⁻¹ is attributed to unsaturated C=O vibration absorption [18, 19]. Spectrum (b) confirms the existence of urea molecule in TiO₂ particles and infers that TU particles possess more unsaturated groups than that of the pure TiO₂ particles. Sufficient active groups on the surfaces of particles would promote surface activity because they may produce synergetic effects or might react with each other.

X-ray photoelectron spectroscopy(XPS) is often used to characterize the surface of the samples. Figure 2 shows the wide scan XPS spectra of TU and pure TiO₂ particles, respectively. From XPS spectra, it can be seen that the

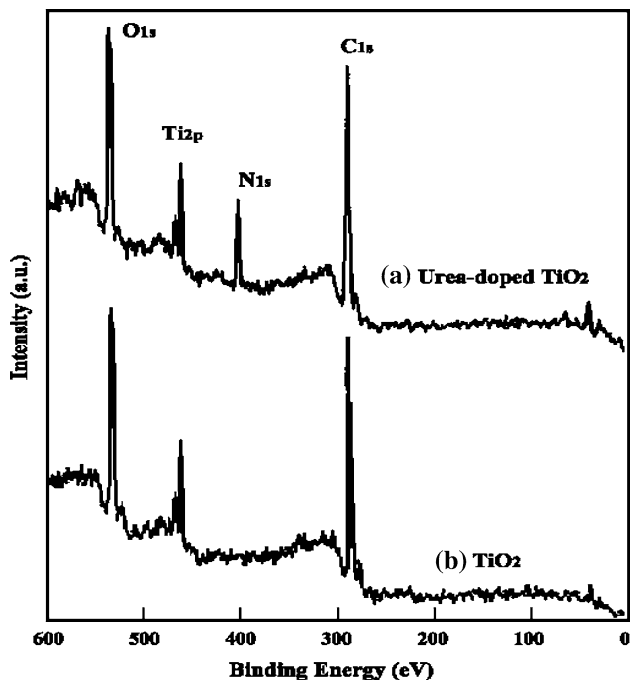


Fig. 2 The XPS Spectra for pure TiO₂ particles and TU nanoparticles

surface of the TU particles is composed of Ti, O and N except for C, where C includes not only C compounds adsorbed by the samples from air, but also oily dirt from the apparatus. The photoelectron peak for Ti 2p appears clearly at the binding energy of 458 eV, C 1s at 284 eV and O 1s at 529 eV. The XPS peak of N 1s around 400.1 eV assigned as γ -N₂ molecular chemisorbed to titanium from the literature [20, 21]. From the FT-IR and XPS analyses results, we speculate that TU particles are made of Ti–O–Ti polymeric networks and the urea molecules are contained in this network.

3.2 Electrorheological properties

Figure 3 shows the dependence of the shear stress of the TU particle-based ER suspensions with different doping degree on the external electric field. The viscosity of silicone oil used here was 100 mPas. In the case of pure amorphous TiO₂ particle based ER fluids, the shear stress is rather low and the maximum shear stress is 2.5 kPa at E = 4.0 kV/mm, while the urea-doped particle based ER fluids show a remarkably stronger ER effect. The maximum shear stress of 1, 3, 5 and 7 wt% TU particles are 5.62, 17.20, 11.04 and 6.87 kPa at E = 4 kV/mm, respectively. In those ER fluids, the dependence of yield stress on the electric field shows a near-linear behavior instead of the quadratic behavior in ordinary ER fluids, which is agree with the surface saturation polarization mechanism proposed by Wen and Sheng [4, 22]. In their opinion, the static yield stress is proportional to the energy density $-\mathbf{P} \cdot \mathbf{E}$, where \mathbf{P} is the polarization density. A linear dependence of \mathbf{P} on \mathbf{E} , that is, $\mathbf{P} = \chi\mathbf{E}$, implies a quadratic field dependence of the yield stress. The observed near-linear field dependence suggests the ER mechanism to involve a constant P₀, that is, a saturation polarization.

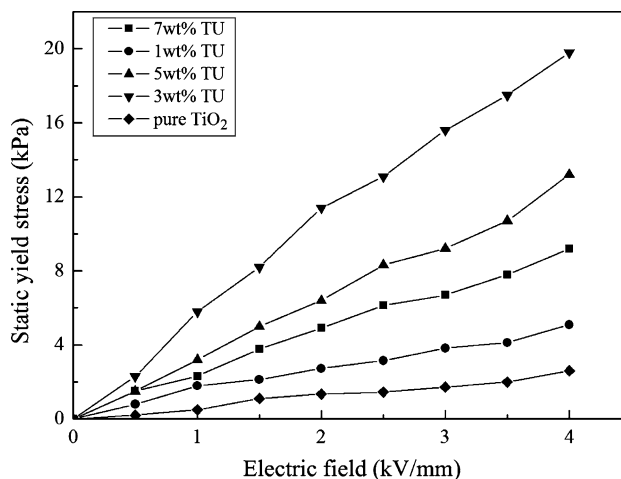


Fig. 3 The relationship between static yield stress and electric field for ER fluids of pure TiO₂ particles and TU particles

Table 1 The dielectric constant, conductivity (at 1 kHz) and the current density (at $E = 4$ kV/mm, $\gamma = 1$ s⁻¹) for TU particles with varying urea content

	Pure TiO ₂	1 wt% TU	3 wt% TU	5 wt% TU	7 wt% TU
Dielectric constant	17.8	31.2	62.5	44.5	35.3
Conductivity (S/m ⁻¹)	2.0×10^{-9}	3.3×10^{-8}	5.6×10^{-7}	1.2×10^{-6}	8.9×10^{-6}
Leaking current density (μ A/cm ²)	4.35	9.92	16.58	20.33	27.52

In addition, it can be seen that the ER effects of the TU particle based ER fluids is much better than that of the pure TiO₂ particle and the optimal doping concentration of urea is about 3 wt%. According to the theory of Espin and the others [23–29], because of urea is directly incorporated to the particle phase, the application of the electric field provokes the formation of multiple liquid bridges among close particles. These bridges increase the attraction among particles provoking an increase in the ER effect. However, if the amount of additive is high enough, a single macroscopic bridge is formed between particles giving rise to an attraction force significantly lower than that corresponding to multiple bridges and resulting in the weakened of the ER performance.

In addition, when the urea concentration is above the critical point, the urea molecules are more likely to be resolved in the fluid phase rather than adsorbed on the TiO₂ particle surface in the absence of an electric field. On one hand, the enriched urea molecules in the fluid phase will gather into the interstices formed by neighboring particles in which a non-uniform high electric field is generated. On the other hand, the more polar groups lead to too much conductivity and relatively much leaking current density (see Table 1), which is relevant to the degradation of the ER properties at the high urea concentration limit.

In addition, we also found that the static yield stress of TU particles based ER fluids were sensitive to the viscosity of the silicone oil as shown in Fig. 4. For the 3 wt% TU particle based ER fluids, when the viscosity of silicone oil are 25 and 100 mPas, the yield stress of the ER fluids are 22.4 and 19.6 kPa at $E = 4$ kV/mm, respectively; when the viscosity of silicone oil is 500 mPas, the yield stress of the ER fluids is 7.6 kPa at $E = 4$ kV/mm, which is far less than the former. From the morphology, it's found that the ER fluids with the silicone oil viscosity of 25 and 100 mPas had more homogeneous morphology than that of 500 mPas. This phenomenon might be due to the wetting character between oil and nanoparticles. The wettability of the particles with respect to the liquid is the key to the dispersion of the particles in the liquid, the dispersity of particles suspended in a liquid has a direct effect on the ER effects [30–33]. The contact angles (CA, θ) is usually referred to as the wettability of the surface, the contact angles for silicone oil with different viscosity are measured by the large sessile droplet method (see Table 2).

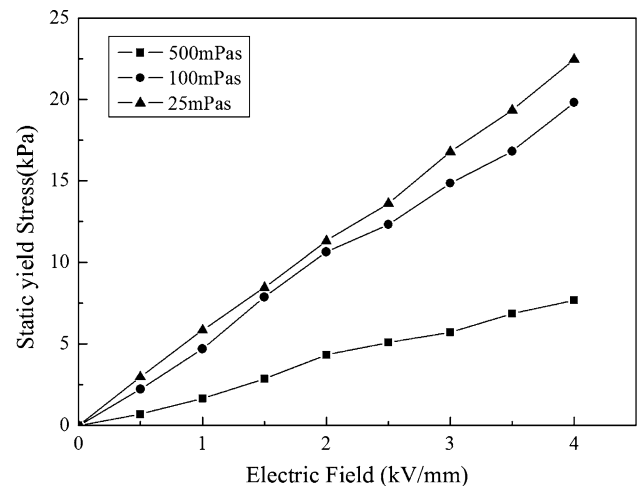
**Fig. 4** The relationship between static yield stress and viscosity of silicone oil for 3 wt% TU particles-based ER fluids

Table 2 shows the contact angle for different samples with silicone oil under different viscosity. For pure TiO₂ particles, the contact angle with silicone oil increases from 122° to 155° when the viscosity of silicone oil changes from 25 to 500 mPas. For 3 wt% TU particles, the contact angle with silicone oil increases from 21.2° to 69.5° when the viscosity of silicone oil changes from 25 to 500 mPas. Obviously, the pure TiO₂ particle is hydrophilic to the silicone oil (the existence of –OH may be the origin). When doped with urea, the TiO₂ nanoparticles changes from hydrophilic to oleophilic (wettability), which means that there are more oil in the particle gap, and more electron double layer polarization taken place and resulting in stronger ER effect [7, 34]. The smaller the contact angle, the more wettability and the higher ER performance. So the ER performances of the 3 wt% TU particles with 25 and 100 mPas silicone oil are better than that of with 500 mPas silicone oil.

4 Conclusions

ER fluids based on TU particles and silicone oil were investigated at the room temperature under an applied dc electric field. The TU particles have the amorphous structure and irregular morphology. The ER performance of

Table 2 Contact angles for different samples with silicone oil under different viscosity

Viscosity of silicone oil (mPas)	Contact angle for 3 wt% TU particles	Contact angle for pure TiO ₂ particles
25	21.2° (wetting or oleophilic, 0° < θ < 90°)	122° (non-wetting 90° < θ < 180°)
100	25.2° (wetting or oleophilic, 0° < θ < 90°)	132° (non-wetting 90° < θ < 180°)
500	69.5° (wetting or oleophilic, 0° < θ < 90°)	155° (non-wetting 90° < θ < 180°)

TU-based ER fluid is much better than that of pure TiO₂ based ER fluids, the shear stress of 3 wt% urea doped TiO₂ can reach 22.4 kPa at $E = 4$ kV/mm with a volume fraction of 30%. The ER effect also shows the dependence on the viscosity of the silicone oil. The optimum doping degree is 3 wt%. A model for explaining the mechanism is proposed and described briefly based on the saturated polarization theory and wetting theory.

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