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Electrorheological fluids containing Ce-doped titania

X. P. ZHAO*, J. B. YIN, L. Q. XIANG, Q. ZHAO
Institute of Electrorheological Technology, Department of Applied Physics,
Northwestern Polytechnical University, Xi'an 710072, People's Republic of China
E-mail: xpzhao@nwpu.edu.cn

A new type of water-free electrorheological (ER) material of anatase titania doped with Ce has been synthesized by a sol-gel technique. The thermal character and crystal structure of doped titania are characterized with FT-IR, DSC-TG and XRD. The ER behaviors of the suspension made of such particles dispersed in silicone oil at a volume fraction of 18% are investigated in a DC electric field. The results show that the doped titania ER suspension has a much increased shear stress compared with the pure titania one. The shear stresses of 1.7 kPa at 3 kV/mm and 2.6 kPa at 4 kV/mm can be induced in a 8.5 mol% cerium-doped titania ER suspension, which is 5 times higher than that of the pure titania one. Moreover, the induced shear stress has a significant dependence on the Ce/Ti molar ratio and the maximum shear stress can be obtained when Ce/Ti molar ratio is about 0.1. In addition, significant differences in the temperature dependence of shear stress between the pure and doped titania ER suspensions are found. The working temperature range is extended by Ce doping. The obvious improvement in the ER effect resulting from Ce doping can be explained in terms of the dielectric and conduction properties of the ER suspensions.

1. Introduction

Using electric fields to control the viscosity or shear stress of electrorheological (ER) fluids has many potential applications areas such as clutchs, dampers, robotics, publishing, and even optical devices [1, 2]. This kind of control is quick and reversible, but the poor ER properties of current ER fluids including low shear stress, temperature instability and tendency to sedimentation limit their applications [3]. The original ER fluids, which were dispersions of active powders in non-conducting oil, were water-containing ER fluids, in which the "water bridge" and electrical double layer were believed to be critical to their ER effect [4, 5]. Some researchers considered that the mechanism of the ER effect in water-containing ER fluids was almost exclusively water-promoted ionic polarization [6]. Temperature instability was one of the biggest obstacles to the development of these ER materials. To overcome the shortcomings of water-containing ER fluids, water-free ER fluids using polymer semiconductors that have a strong ER effect when dry were developed [7]. The strong polarization caused by the π-conjugate bonding and suitable conductivity that could be controlled by the degree of doping were used to explain the strong ER effect of this kind of materials. Although these ER materials opened a new horizon in understanding ER mechanisms and preparing ER materials, low shear stress, poor heat-resistance and toxicity limited their uses in practical applications. Recently, based on the theories of dielectric constant mismatch [8] and conductivity mismatch [9], micro-structured composite particles [10, 11] have been designed and prepared for use in ER materials.

Special attention has been paid to titania as a potential candidate component for a high performance ER fluid due to its high dielectric constant [9, 12, 13]. However, some investigations have shown that there was no ER activity when pure dried titania was used as the dispersal phase of the ER fluid. It has been reported that its ER activity was promoted by absorption of moisture [9, 12], but the shear stress is still low and the working temperature range is very narrow. In this work, a new type of ER material made of Ce-doped titania is considered. The aim of doping with a large radius rare earth ion is to introduce large lattice distortion and more charge carriers into titania so as to modify the dielectric and conduction properties, and improve the ER effect.

2. Experimental

Particles of pure and Ce doped titania were prepared by means of a sol-gel technique [14], using tetrabutyl titanate, rare earth chloride or nitrate, water-free alcohol, HCl or HNO_3, all of chemical purity. First, Ce chloride or nitrate and distilled water were dissolved in 20 mL water-free alcohol to form a transparent

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[*] Author to whom all correspondence should be addressed.

solution which then was slowly added dropwise into a diluted tetrabutyl titanate solution with 20 mL water-free alcohol at room temperature. The H_2O/Ti molar ratio was 1.5 and the Ti concentration was 0.8–1.0 M. The Ce/Ti molar ratio varied in the range 0 to 20.0 mol%. The resulting clear yellow solution, for which the pH was controlled in the range 3 to 4 by adding HCl or HNO_3, was aged at room temperature for 12–48 hours to form a transparent wet gel. The wet gel was dehydrated in vacuum for 8 hours at 80°C to form a dry gel. The dry gel was ground and subjected to the following stepwise calcination programs in air: 2 h at 200°C, 2 h at 400°C, and 2 h at 550°C. Then, the crystalline pure TiO_2 and doped TiO_2 particles were produced.

DSC-TG (SH-500, NET2SCH-Gerateban Gabh Thermal Analysis, Germany), was used to study the thermal decomposition of the xerogels and the thermal character of particles with a heating rate of 10°C/min in dry air. The change in chemical structure of the xerogel during the calcination process was determined by FT-IR (EQUIOX55, Germany) using pressed thin discs of KBr and the sample. X-ray powder diffraction (D/MAX-IIIC, Japan) using Cu K_α radiation was used to study the crystal structure of the calcined samples.

The pure and doped titania particles were initially dehydrated at 150°C for 8 h in vacuum to remove any trace of water, then quickly suspended in dimethysilicone oil ($\varepsilon_f = 2.60$–2.80, $\rho_f = 0.996$–1.003 g/mL, and $\eta = 500$ mPa · s at 25°C) at a 18% volume fraction to produce ER suspensions. No additives were used in these suspensions. Electrorheological experiments were performed using a coaxial cylinder rotational viscometer (NXS-11A, China) with a Couette geometry, a DC high-voltage generator (WYZ-010, China) and oil bath for temperature control in the range 0 to 150°C. The gap between the rotating inner bob and stationary outer cup was 2.00 ± 0.01 mm. Suspensions were placed in the gap and sheared at a shear rate which varied from 1.441 to 66.89 s^{-1}. The suspensions were sheared for about 30 min to ensure sufficient dispersion and then the electric field was applied. A micro-ammeter was used to monitor the current across the ER suspensions. The dielectric constant and conductivity of ER suspensions were measured with an automatic LCR meter (WAYNE KERR-4225, Germany).

3. Results and discussion

3.1. Thermal character and crystal structure of doped titania ER materials

Fig. 1 shows FT-IR absorption spectra for a typical doped titania dry gel and calcination products at different temperatures. It should be noted that the characteristic OH-stretching absorption band in the range 3700 cm^{-1}–3300 cm^{-1}, the C-H-bending absorption band at 1255 cm^{-1} and the free H_2O-bending adsorption band at about 1645 cm^{-1} have been noted in spectra at temperatures lower than 200°C. Only the M-O-bending absorption band at about 420 cm^{-1} has been noted in spectra at temperatures higher than 400°C. Hence, there is not any impurity from organic groups after calcination.

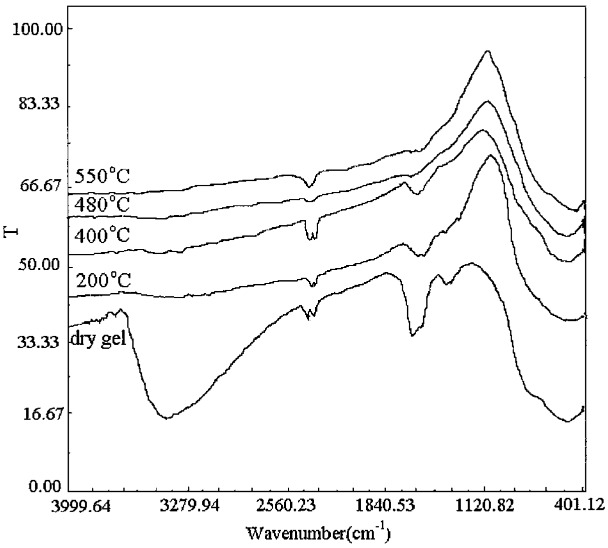

Figure 1 The FT-IR spectra of Ce-doped titania xerogel powders at different temperatures.

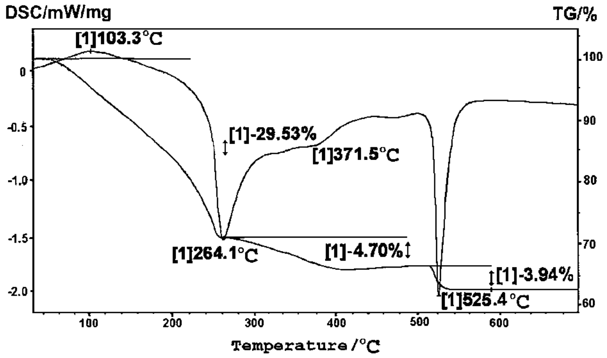

Figure 2 The DSC-TG curve of Ce-doped titania xerogel. Sample: 24.368 mg; Material: TiO_2 doped by Ce; Range: 20°/10.0 (K/min)/ 700°C; Remark: air.

The DSC-TG curve of this doped titania xerogel is shown in Fig. 2. It should be noted that there are four peaks including a weak endothermic peak at 103.3°C and three strong exothermic peaks at 264.1°C, 371.5°C and 525.4°C. The weak endothermic peak at 103.3°C and initial mass loss before 150°C are due to loss of residual water and solvent from the xerogel. The exothermic peaks at 264.1°C and 371.5°C and the main mass loss in the temperature range 200–450°C are attributed to the decomposition of a residual alkyl group. The exothermic peak at 525.4°C corresponds to the crystallization of titania [15]. Thus, after the heat treatment at temperatures higher than 550°C, the crystalline pure and doped titanias have been obtained. This is in good agreement with XRD results.

Fig. 3 shows typical XRD patterns for the final products of pure and 8.0 mol% Ce-doped titania. The patterns are in accordance with the standard pattern of anatase titania [16]. The XRD patterns show no evidence of any second phase of rare earth oxide when the Ce/Ti is below 10.0 mol%.

3.2. ER properties of doped titania ER suspensions at DC electric field

Fig. 4 shows that the shear stress of the ER suspension as a function of electric field strength at 25°C and a shear

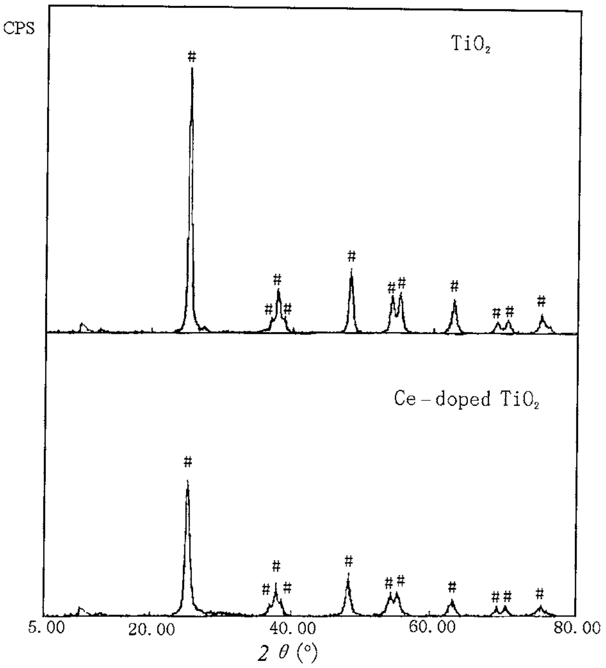

Figure 3 The XRD patterns of pure and Ce-doped titania (Ce/Ti = 8.0 mol%) after 550°C.

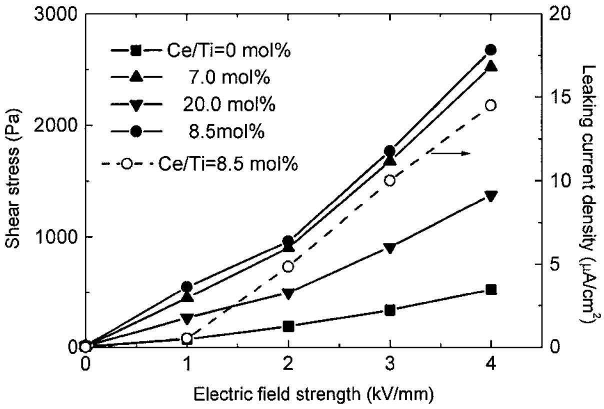

Figure 4 The shear stress and current density as a function of DC electric field for pure and doped titania ER suspensions ($T = 25°C$, $\dot{\gamma} = 1.441\ s^{-1}$).

rate of 1.441 s^{-1}. It is found that the shear stresses developed in doped titania ER suspensions are much higher than those in a pure titania ER suspension in a DC electric field. The induced shear stress is about 1.7 kPa at 3 kV/mm and 2.6 kPa at 4 kV/mm, which is nearly 5 times higher than that of a pure titania ER suspension synthesized in the same way. The induced shear stress of 1.7 kPa at 3 kV/mm is about 60 times higher than the shear stress of 11.4 Pa at zero field. The current density of the doped titania ER suspension is smaller than 10 $\mu A/cm^2$.

Figs 5 and 6 show the shear stress and apparent viscosity of a typical 8.5 mol% Ce-doped titania ER suspension as a function of shear rate at different electric field strengths and a temperature of 25°C. In this range of shear rate, an obvious ER effect can be seen. In the absence of electric field, the suspension behaves as a Newtonian fluid. In the presence of an electric field, the suspension behaves as a Bingham fluid, which shows a significant yield stress. The shear stress and apparent viscosity of the suspension increase quickly with increasing electric field strength.

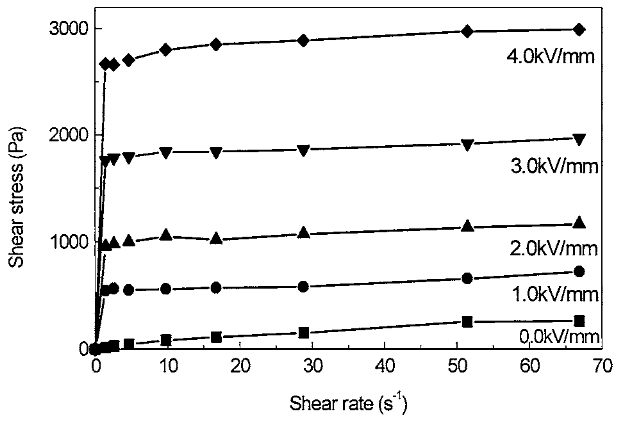

Figure 5 The shear stress as a function of shear rate for doped titania ER suspension (Ce/Ti = 8.5 mol%, $T = 25°C$).

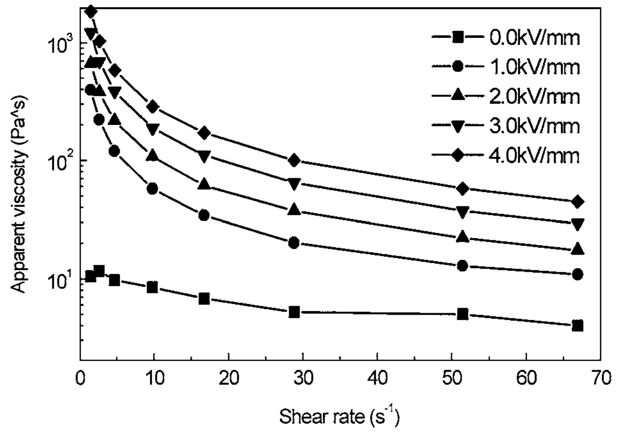

Figure 6 The apparent viscosity as a function of shear rate for doped titania ER suspension (Ce/Ti = 8.5 mol%, $T = 25°C$).

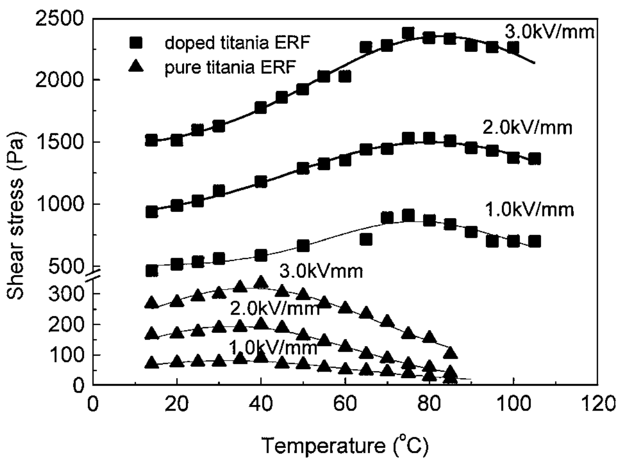

Figure 7 The temperature dependence of shear stress of pure and doped titania ER suspensions ($\dot{\gamma} = 1.441\ s^{-1}$).

Interestingly, it is found that doping titania with a rare earth increased the working temperature range of the ER suspension. Fig. 7 shows that the dependence of shear stress on temperature for a pure and a typical 8.5 mol% Ce-doped titania ER suspension. A strong ER effect can be induced in the range 10–100°C for the doped titania ER suspension. The induced shear stress increases with temperature and reaches a maximum value at around 80°C in doped titania ER suspension. However, shear stress induced in the pure titania ER suspension decreases sharply

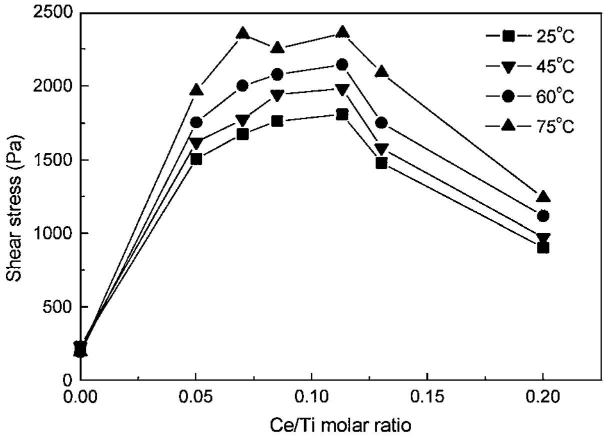

Figure 8 The dependence of shear stress of ER suspensions on RE/Ti molar ratio ($\dot{\gamma} = 1.441\ \mathrm{s}^{-1}$, $E = 3$ kV/mm).

when the temperature exceeds 40°C. A more detailed investigation and discussion of the temperature effect in doped titania ER suspensions has been reported previously [17].

The induced shear stress shows a significant dependence on the doping concentration of the rare earth. Fig. 8 shows the dependence of shear stress on the Ce/Ti molar ratio at 3 kV/mm electric field and different temperatures. The shear stress increases with Ce/Ti molar ratio and reaches its maximum when the Ce/Ti molar ratio is about 0.1, then the shear stress decreases as the doping concentration increases.

3.3. Dielectric and conduction properties of the doped titania ER suspensions

The ER effect originates from the dielectric polarization of particles dispersed in the oil [2, 18]. The parameters such as dielectric constant, dielectric loss and conductivity have been accepted as basic factors controlling the ER effect. It has been reported that the occurrence of strong ER activity correlates with a local maximum in the loss factor in the frequency range 0.1 to 100 kHz and a strong decrease in the dielectric constant, and that the loss tangent at 1 kHz should be about 0.1 and the dielectric constant of the ER fluids should be large [18–22].

Fig. 9 shows the dependence of dielectric constant (ε') of ER suspensions on the Ce/Ti molar ratio at a frequency of 100 Hz and different temperatures. The ε' of the titania ER suspension is increased significantly by doping with Ce. The ε' increases with Ce/Ti molar ratio and reaches a maximum value at about 0.1 Ce/Ti, then decreases. At the same time, the dielectric loss increases strongly with Ce doping and a maximum in the loss tangent ($\tan\delta$) can be observed in doped titania ER suspensions in the frequency range investigated. The $\tan\delta$ is about 0.15 at 1 kHz and 25°C in a doped titania ER suspension, while the $\tan\delta$ is lower than 0.02 in for a pure titania suspension. Using the relation $\sigma = \omega\varepsilon_0\varepsilon' \tan\delta$, (where ω is the angular frequency of the *bias* field and ε_0 is the dielectric constant of a vacuum), the relationship between the conductivity of ER suspensions and the Ce/Ti molar ratio can be obtained (see Fig. 10). A three-orders-of-magnitude increase in the conductivity is found in a doped titania ER suspension compared with a pure one. The conductivity increases with Ce/Ti molar ratio and also reaches a maximum at about 0.1 Ce/Ti. It is found that the dielectric constant, loss tangent and conductivity of doped titania ER suspensions increase with temperature. However, the dielectric constant, loss tangent and conductivity of the pure titania ER suspension decreases slightly with temperature. It can be inferred that the polarization strength of doped titania increases with temperature, while it decreases with temperature in pure titania. These results can explain the improvement in shear stress in doped titania ER suspensions and its dependence on Ce/Ti molar ratio. The weak ER activity of pure titania may be caused by its low dielectric loss or conductivity and a slight decrease in dielectric constant. The results also confirm that it is possible to increase the polarization strength of titania particles by modifying dielectric and conduction properties using Ce doping.

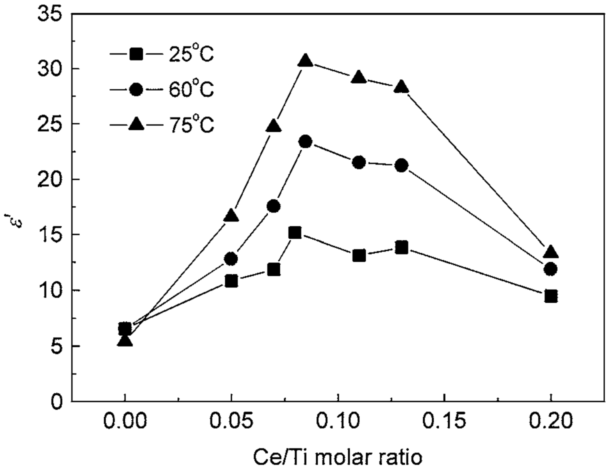

Figure 9 The dependence of the dielectric constant of ER suspensions on the Ce/Ti molar ratio at 25, 60 and 75°C ($f = 100$ Hz).

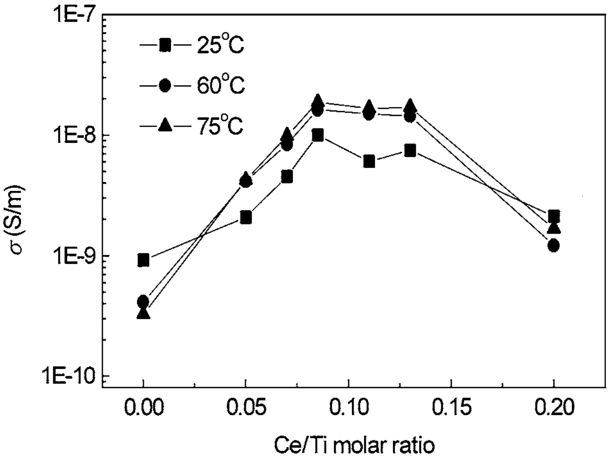

Figure 10 The dependence of the conductivity of ER suspensions on the Ce/Ti molar ratio at 25, 60 and 75°C ($f = 100$ Hz).

4. Conclusions

A new type of ER material containing anatase Ce-doped titania has been synthesized using a sol-gel technique. The ER properties of the suspension made from such particles in silicone oil at a loading of 18 vol% have been investigated in a DC electric field. The following are the conclusions derived from this work.

1. Doping titania with Ce improves its ER activity in a DC electric field. The induced shear stress of a doped titania ER suspension is 5 times higher than that of a pure titania one. Further, the induced shear stress can be controlled by the Ce/Ti molar ratio.

2. The working temperature range of a titania ER suspension can be extended by Ce doping. A strong ER effect can be induced in the range 10–100°C in a doped titania ER suspension. The induced shear stress increases with temperature and reaches a maximum value at around 80°C. However, the induced shear stress of a pure titania ER suspension decreases sharply at temperatures above 40°C.

3. The dielectric constant, dielectric loss and conductivity of a titania ER suspension have been increased by Ce doping and show a sharp dependence the Ce/Ti molar ratio. This explains the improvement in shear stress in the doped titania ER suspensions and its dependence on Ce/Ti molar ratio.

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