Preparation and Electrorheological Characteristics of Rare-Earth-Doped TiO_2 Suspensions

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Received October 12, 2001. Revised Manuscript Received February 11, 2002

According to the dielectric design, a new kind of rare-earth (RE)-doped TiO_2 particle was synthesized by means of sol−gel technique for use in electrorheological (ER) fluids. A distinct enhancement in the yield stress under dc electric field was found by using such particles, when compared with that of pure TiO_2. The yield stress of typical cerium-doped TiO_2 suspension was about 5.0 kPa at 3 kV/mm and 7.0 kPa at 4 kV/mm, which were 10 times higher than that of a pure TiO_2 suspension. The yield stress showed a marked dependence on RE-doping degree. Substitution of 10 mol % cerium or 8 mol % lanthanum for Ti could obtain the highest yield stress. These were well explained by the dielectric measurements that showed an increase in the dielectric loss and the dielectric constant at low frequency and their regular change with rare earth content. The lattice distortion and defects in the TiO_2 crystal caused by substitution for Ti with large-radius RE ions may be responsible for the obvious improvement noted above.

Introduction

Electrorheological (ER) fluid consists of a suspension of micrometer-size dielectric particles in insulating liquid of low dielectric constant. Under the influence of an electric field, ER fluid can suddenly change its viscosity and even changes from a fluidlike state to a solidlike state that has a yield stress.[1,2] This property makes ER fluid hold potential for many applications such as dampers, clutches, robotics, and so on.[3] A new patent,[4] in which a piezoelectric source was used to make the ER damper work, may open a novel way to combine the ER system with other intelligent systems.

Up to now, two different formations including extrinsic (water-containing) and intrinsic (water-free) ER materials have been developed. The extrinsic ER materials, such as silica gel,[5] poly(lithium latamethacry),[6] cellulose,[7] mesoporus molecular sieve,[8] almost all require the presence of water or other polar liquids adsorbed onto the surface of particles to produce ER effect. The function of the adsorbed water or other polar liquids is supposed to create mobile charge carriers on the surface of the particles. The migration of these charge carriers causes an interfacial polarization to induce ER effect under electric field. However, adsorbed water also increases the current density of ER fluids and limits working temperature stability because of the diminution of adsorbed water at high temperature. To overcome the shortcomings of the extrinsic ER system, water-free ER fluids have been investigated with anhydrous particles including zeolite,[9,10] PZT,[11] modified $BaTiO_3$,[12,13] Ni(Al)/poly(methyl methacrylate) composite,[14] glass/Ni/TiO_2 composite,[15] and various semiconducting polymers such as polyaniline,[16,17] copolyaniline,[18] polyurethane,[19] poly(*p*-phenylene),[20] poly(acene quinoune),[21] polymer-clay nanocomposites,[22−24] CMS/TiO_2 organic−inorganic hybrid composite,[25] and β-cy-

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10.1021/cm011522w CCC: $22.00
Published on Web 04/05/2002

clodextrin self-assembly complex.[26] These water-free ER materials, which possess a wide working-temperature range and a relatively low current density, have intrinsic charge carriers in either the bulk particles or their surfaces that can move locally to induce bulk or interfacial polarization under an applied electric field.[17,20,27,28] However, the present ER materials do not still have an optimal yield stress for use in practical applications.

Special attention has been paid to TiO_2 as a potential candidate for high-performance ER system because of its high dielectric constant.[29−32] However, the fairly weak shear stress of this ER fluid is in contrast with its distinct chain structure when in dry state.[29,30] It has been reported that the ER activity is promoted by adsorption of moisture,[29] but the extrinsic effect of water does not endure a further understanding of weak ER activity and a more optimal ER performance. Physically, ER effect originates from the dielectric polarization of particles dispersed in medium oil.[33,34] The parameters in connection with particle polarization such as dielectric constant, dielectric loss, or conductivity have been accepted as basic factors dominating ER effect. Recent studies, furthermore, have proposed that the high dielectric constant related to a polarizability and the suitable dielectric loss or conductivity related to a polarization response were important to obtain high ER activity.[27,35−40] It's well-known that the chemical natures including molecular and crystal structure of materials are critically important to the dielectric and polarization properties. Thus, it is possible to modify the dielectric and polarization properties to increase ER activity by designing the molecular and crystal structure of ER materials. Doping, as one means of modifying the properties of a wide variety of materials, has not received comparable attention in the improvement of ER activity, although it has been investigated in catalyst and optical properties of TiO_2 particles.[41] In this work, we present a new ER system composed of doped TiO_2 with rare earth and focus on the effect of rare earth doping on ER behaviors of TiO_2. The choice of substitution for Ti with large-radius rare-earth ions is aimed at modifying dielectric and polarization properties of TiO_2, so as to improve its ER activity. The rheological properties are studied as a function of electric field strength, doping degree, and shear rate. On the basis of the investigation about the dielectric properties of ER fluids, we present a preliminary discussion of the effect of rare-earth doping on ER behaviors of TiO_2.

Experimental Section

Materials Synthesis and Structure Characterization. The particles of pure and doped TiO_2 with different rare-earth content were synthesized by means of the sol−gel technique.[42] Tetrabutyl titanate, rare-earth nitrate [or RE chloride, RE is lanthanum (La), cerium (Ce), etc., light rare-earth elements) and distilled water were solved into anhydrous alcohol. The H_2O/Ti molar ratio was 1.5 and Ti concentration was 0.8∼1.0 M. The resulting clear yellow solution, whose pH value was controlled in a range of 3∼4 with HNO_3, was aged at room temperature for 12∼48 h to form a transparent gel. The transparent gels were then dried at 78 °C for 8 h to form a solid gel. The solid gel was ground and sieved and subjected to the following stepwise calcination programs in air in a furnace: 2 h at 200 °C, 2 h at 400 °C, and 2 h at 550 °C. (Notice that high-boiling-point oil was mixed with sieved gel particles before calcination to avoid particle coagulation during calcination.[42]) Then, the crystalline pure TiO_2 and doped TiO_2 particles were produced.

To determine the thermal character and change of chemical structure of xerogel during calcination process and the crystal structure of produced particles, differential scanning calorimetry-TG (DSC-TG) (SH-500, NET2SCH−Gerateban Gabh Thermal Analysis, Germany), Fourier transform infrared spectroscopy (FT-IR) (EQUIOX55, Germany), and X-ray diffraction (D/MAX-γ A, Japan) techniques were adopted.

The produced particles were 5∼10 μm in size and microsphere in shape, estimated by an high-definition optical microscopy (ALPHAPHOT-2, Nikon, Japan). The series of particles had a similar low porous character by the adsorption of N_2. The density of the series of pure and doped TiO_2 powder was determined to be in the range of 3.68∼3.80 g/cm^3 by using a pycnometer. The particles were initially dehydrated for 8 h in a vacuum at 150 °C to remove any trace of water, then mixed quickly with dimethy-silicone oil ($\epsilon_f = 2.60\sim2.80$, $\sigma_f \approx 10^{-12}$ S/m, $\rho_f = 0.997\sim1.003$ g/cm^3, and η=500 mPa·s at 25 °C) to produce ER suspensions. No additives were added into these suspensions.

Rheological Measurements. Rheological experiments were performed by using a coaxial cylinder rotational viscometer (NXS-11, China) with a Couette geometry (T3 and T4), a dc high-voltage generator (WYZ-010, China) and oil bath for temperature control in the range from 0 to 150 °C. The gaps of T3 and T4 were both 2.0 ± 0.01 mm, and their maximum measurable stresses were 2.760 and 11.420 kPa, respectively. The suspensions were placed in the gap between the stationary cup and the rotating bob. In general, before reading stresses, we had the suspensions initially sheared for 30 min for sufficient dispersion and then applied the electric field.

Dielectric Measurements. Because of the difficulty of directly measuring the dielectric properties of particles, we used suspensions to make dielectric investigation. Having considered the influence of the particle arrangement induced by an external electric field on the dielectric property,[43,44] we kept the ER fluids in a randomly dispersed system whose structure would not be disturbed by the bias field of 2 V/mm to make a reasonable comparison for a series of materials with different doping degrees. The capacitance C and dielectric loss tangent (tan δ) of suspensions were measured by an automatic

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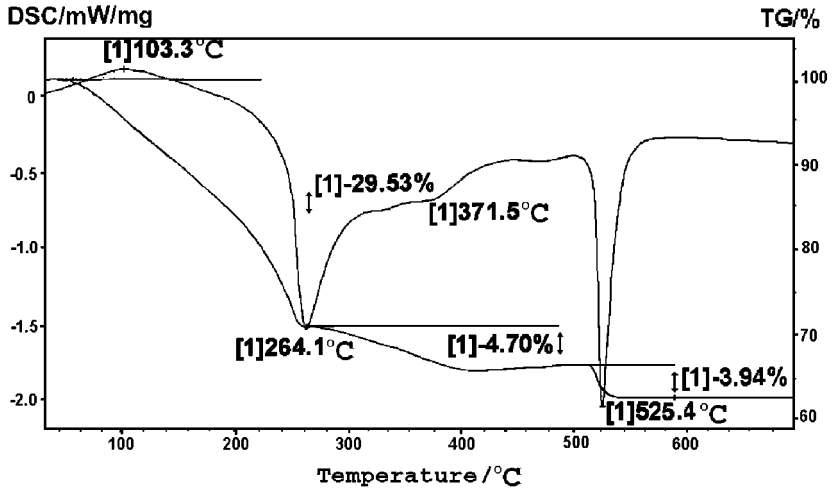

Figure 1. The DSC-TG curve of doped TiO_2 xerogel powders.

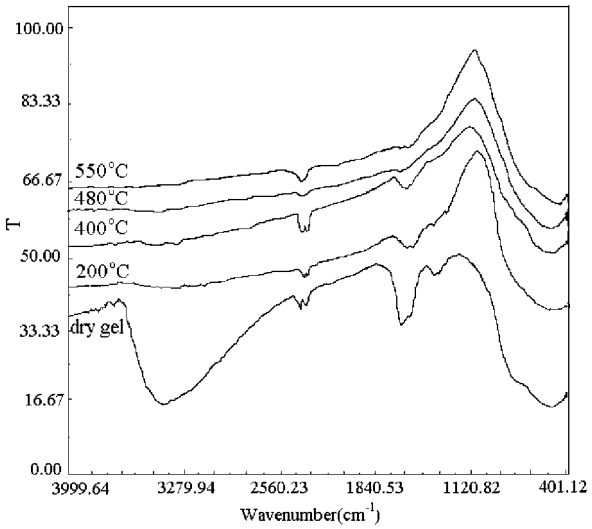

Figure 2. The IR spectra of doped TiO_2 xerogel.

LCR meter (WK-4225, Germany) with a temperature control instrument in the range from 0 to 120 °C at the frequency of 10^2, 10^3, and 10^4 Hz, respectively. The dielectric constant was derived from the measured C according to the conventional relation, $\epsilon = Cd/(\epsilon_0 S)$, where ϵ_0 is the dielectric constant of vacuum, i.e. 8.85×10^{-12} F·m^{-1}, and d is the thickness of the gap between electrodes and S is the contact area of the electrodes.

Results and Discussion

Thermal Character and Crystal Structure. We examined the changes in charring TiO_2 xerogel by heating at temperatures ranging from room temperature to 700 °C in air at a rate of 10 °C/min. The DSC-TG patterns of the typical doped TiO_2 xerogel are shown in Figure 1. The endothermic effect at 103.3 °C and the sample weight loss represent the loss of residual water and solvent. The exothermic peaks at 264.1 °C and 371 °C are attributed to the combustion of residual alkyl groups. The exothermic peak at 525.4 °C is considered to be the formation of anatase. Thus, after the heat treatment at temperatures higher than 550 °C, the crystalline pure and doped TiO_2 have been obtained. This is in good agreement with X-ray diffraction (XRD) patterns results. Figure 2 is the IR spectra of doped TiO_2 xerogel at different temperatures. The −OH-stretching adsorption band at 3340 cm^{-1} and the C−H-bending adsorption 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. These adsorption bands disappeared with increasing temperature and only the Ti−O-bending adsorption band at about 425 cm^{-1} has been noted in spectra at temperatures higher than 400 °C.

The calcined pure and doped TiO_2 particles exhibit the anatase phase,[45] and none of the peaks of rare earth oxide are found when Ce/Ti is smaller than 10 mol % or when La/Ti is smaller than 8 mol %. (Figure 3 gives the typical XRD patterns of Ce-doped TiO_2.) The value of lattice spacing (d) increases significantly with the doping degrees. (Figure 4 gives the d value of Ce-doped TiO_2.) These indicate that the large-radius rare-earth ions (much larger than that of Ti^{4+}) substitute for Ti and cause lattice distortion. However, the values of lattice spacing are tend to saturate when Ce/Ti is beyond 10 mol % or when La/Ti is beyond 8 mol %, and some weak peaks of rare-earth oxide appear and become stronger with increasing doping degrees. These indicate that more rare earth ions fail to substitute for Ti when the doping degree is beyond critical value.

Electrorheological Properties. Figure 5 shows typical ER behavior of yield stress as a function of electric field strength for pure and doped TiO_2/silicone oil suspensions. It can be found that the yield stresses of 27 vol % pure TiO_2/silicone oil suspension are 480 Pa at 3 kV/mm and 520 Pa at 4 kV/mm, respectively. Doping with rare earth obviously enhances ER effect of TiO_2. The yield stresses are about 5.0 kPa for 8.5 mol % cerium-doped TiO_2 suspension at 3 kV/mm and 7.0 kPa at 4 kV/mm, which are 10 times larger than those of pure TiO_2 ER fluid. It's well-known that a yield stress is required to break the solidlike state that forms because of the fibril structure of particles in ER suspensions, and then make it flow. The fibril structure originates from the attractive force between the polarized particles under electric field. Therefore, the enhancement of yield stress infers the increase of attractive force between the particles.

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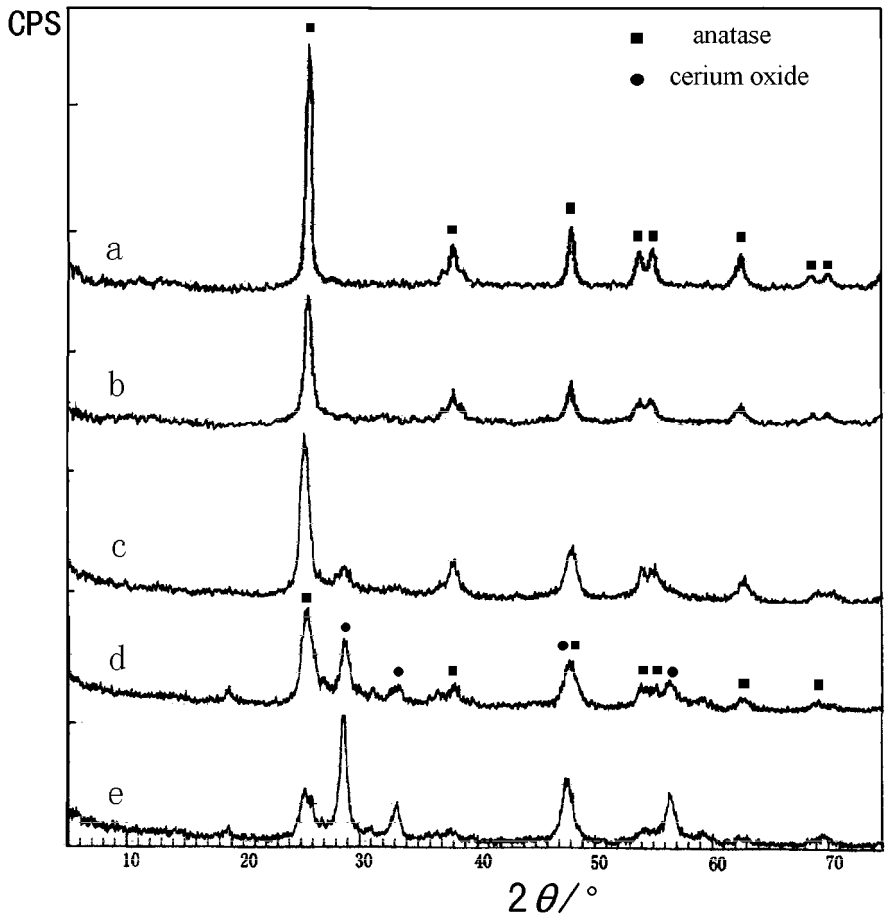

Figure 3. The XRD patterns of powder a (Ce/Ti = 0 mol %), b (7 mol %), c (10 mol %), d (20 mol %), and e (35 mol %).

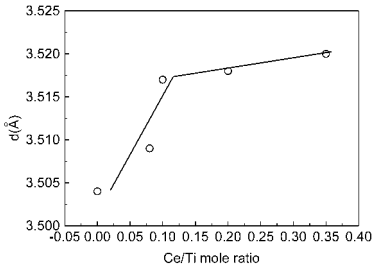

Figure 4. Dependence of the value of lattice spacing d(101) on rare-earth content.

We find that the yield stress shows an obvious dependence on doping degrees of rare earth. Figure 6 is the dependence of yield stress of suspension on the RE/Ti mole ratio under 3 kV/mm electric field and particle concentration of 18 vol %. The yield stress is initially enhanced with the doping degree, and the highest yield stress can be obtained with 10 mol % Ce or 8 mol % La substitution for Ti, then the yield stress declines as the doping degree increases.

We also investigated ER properties of the pure rare earth oxide/silicone oil suspensions and the simple mixture of TiO_2 and rare earth oxide/ silicone oil suspensions. The very low yield stresses of 380 Pa in the pure rare-earth oxide/silicone oil suspensions and 450 Pa in the simple mixture of TiO_2 and rare-earth oxide/silicone oil suspensions at 3 kV/mm have been found. This indicates that suitable rare-earth substitution for Ti in doped TiO_2 is the key to the modification of ER activity of TiO_2. We give a preliminary discussion

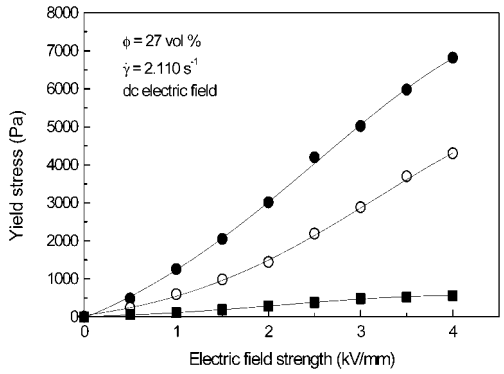

Figure 5. Yield stress of pure TiO_2 (solid square), typical 6.0 mol % La-doped TiO_2 (open circle), and 8.5 mol % Ce-doped TiO_2 (solid circle) suspensions as a function of electrical field strength at 25 °C (the density of particles $\rho_p = 3.78$ g/cm^3 for pure TiO_2 and about $\rho_p = 3.81$ g/cm^3 for doped ones).

about the effect of doping on ER behaviors of TiO_2 according to the dielectric investigation in following section.

Figure 7a and b show the flow curves of shear stress τ and apparent shear viscosity η vs shear rate $\dot{\gamma}$ for typical Ce-doped TiO_2 suspension at 27 vol %, respectively. Here, the apparent shear viscosity η is defined as $\eta = \tau/\dot{\gamma}$. The shear stress and apparent shear viscosity were measured in the range from 2.110 to 75.69 s^{-1}. The basic ER behavior was characterized in curves. In the absence of electric field, the suspension is like a conventional suspension that shows a Newtonian fluid behavior. Only a slight departure from Newtonian fluid

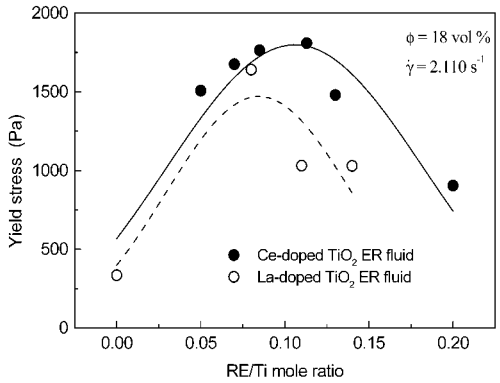

Figure 6. Dependence of yield stress of suspensions on the content of rare earth at 25 °C and 3 kV/mm dc electric field.

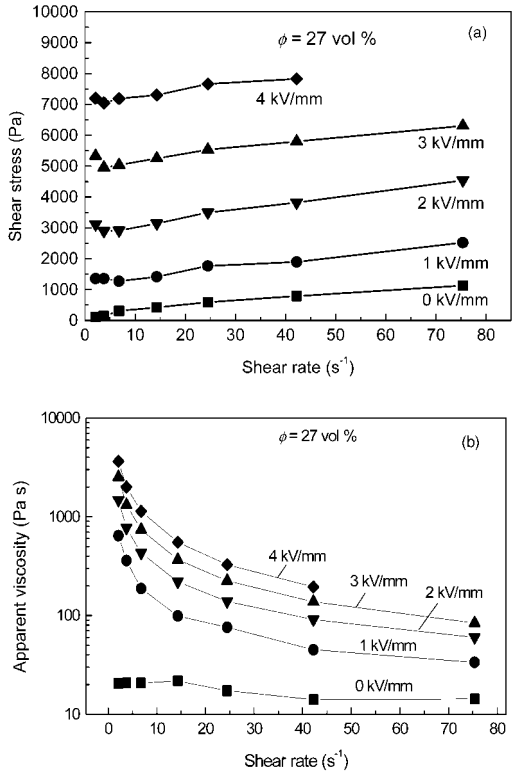

Figure 7. Shear stress (a) and shear apparent viscosity (b) of Ce-doped TiO_2/silcone oil suspension as a function of shear rate under different values of dc electric field (Ce/Ti = 8.5 mol %, T = 25 °C).

behavior appears. In the presence of electric field, the shear stress and apparent shear viscosity increase quickly with electric field strength, and the suspension is like a Bingham fluid that presents a significant yield stress.

A striking difference in temperature effect on shear stresses between pure and RE-doped TiO_2 ER suspensions is also observed. The operational temperature range of ER suspensions can be amplified through doping with rare earth. The maximum shear stress of typical doped TiO_2 ER fluid appears around 80 °C, and the shear stress is still higher after 100 °C than at room temperature. But the shear stress of pure TiO_2 suspension declines quickly when the temperature exceeds 40 °C. More detailed results about the temperature effect of doped TiO_2 ER fluid has been reported in ref 46.

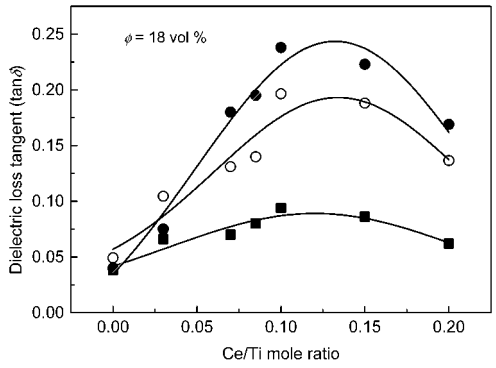

Figure 8. Dielectric loss tangent of suspensions as a function of cerium content at different frequency and 25 °C (solid circle for 10^2 Hz; open circle for 10^3 Hz, and solid square for 10^4 Hz).

Dielectric Properties. By measuring the dielectric constant and loss tangent of series of ER suspensions, we find that doping caused a significant change in the dielectric properties of TiO_2. Some typical results are shown in the following.

Figure 8 shows dielectric loss tangent (tan δ) as a function of doping degree for cerium-doped TiO_2 suspensions at 25 °C. Note that the dielectric loss tangent of suspension is obviously increased by doping with cerium ion and reaches the maximum when Ce/Ti is about 10 mol %. The dielectric constants of doped TiO_2 suspensions are much larger than that of pure TiO_2 suspension at 10^2 Hz and 10^3 Hz, and decrease with frequency. While dielectric constant of pure TiO_2 suspension is almost independent of frequency. Excitedly, ϵ at low frequency and $\Delta\epsilon = \epsilon_{10^2\mathrm{Hz}} - \epsilon_{10^4\mathrm{Hz}}$ are also found to show an obvious dependence on doping degrees. The maximum of ϵ or $\Delta\epsilon$ can be found when Ce/Ti is about 10 mol %.[47]

The striking difference in temperature dependence of dielectric properties between pure and doped TiO_2 suspensions is found. Figure 9a and b show the temperature dependence of dielectric properties for pure and typical 8.5 mol % cerium-doped TiO_2 suspensions at 10^3 Hz and 10^4 Hz, respectively. The dielectric constant of doped TiO_2 suspension increases with temperature and tends to saturate after 80 °C. The dielectric loss tangent seems to peak at about 70 °C, indicating the remarkable dielectric relaxation across the measured temperature range. The dielectric constant and loss tangent at 10^3 Hz also increase with temperature, but no peak in loss tangent can be observed in temperature range investigated. However, the dielectric constant and loss tangent of pure TiO_2 suspension are almost independent of temperature. Because the dielectric constant ($\epsilon \sim 2.70$) and loss tangent (tan $\delta \sim 0.002$) of silicone oil remain relatively independent of frequency and temperature in 0∼120 °C, it is believed that the dielectric properties of ER fluids are mainly influenced by the dielectric properties of dispersal particles in silicone oil according to the relation of mixture model used in ER fluids.[38,44] Therefore, the results of dielectric measurements present that doping with rare earth causes changes in dielectric and polarization properties of TiO_2. Furthermore, our previous study[46] about the temperature effect of rheological and electric properties of doped TiO_2 suspension

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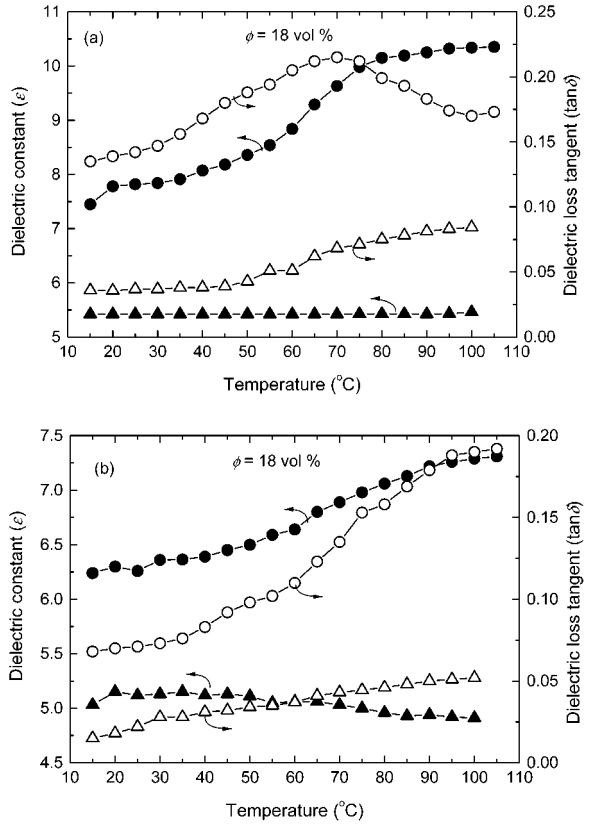

Figure 9. Temperature dependence of dielectric properties of the pure TiO_2 suspension (triangles) and the typical Ce-doped TiO_2 suspension (circles) at 10^3 Hz (a) and 10^4 Hz (b) (Ce/Ti = 8.5 mol %).

show that dc and ac conductivity increase with temperature for the doped TiO_2, but remain invariable with temperature for the pure TiO_2 suspension. This indicates that the potential the bound charge carriers, which can be activated to enhance polarization under the thermal influence, is greater in the doped TiO_2 than in the pure TiO_2.

On the basis of the results above, it's clear that there is a striking difference in dielectric properties of TiO_2 with and without doping. According to the widely accepted studies of Block and other researchers,[27,33−39,48,49] not only the large polarization ability relating to the high dielectric constant but also the suitable polarization response related to the suitable dielectric loss (tan δ > 0.1 at 10^3 Hz[38]) or conductivity ($\sigma \sim 10^{-7}$ S/m[48]) mainly dominates high ER effect. The dielectric measurement results of pure TiO_2, which remain independent of frequency and temperature, imply that its ER effect may arise from ionic or atomic polarization mainly. It's difficult for these types of polarization to induce large dielectric loss for high ER activity under dc or low-frequency electric field. However, doping with rare-earth ions remarkably enhances the dielectric loss or conductivity of TiO_2. The improvement of dielectric loss in the range of frequencies investigated and the occurrence of dielectric relaxation at high temperature at 10^3 Hz in doped TiO_2 suspension somehow reflect a large proportion of slow polarization such as defect dipolar orientation or relaxation polarization, even interface polarization. It is found in the XRD patterns that substitution for Ti^{4+} by rare-earth ions having large ionic radius (much larger than that of Ti^{4+}) cause expanding lattice distortion or defects in TiO_2. These potential factors influencing polarization or charge carriers state may be responsible for the modification of dielectric and conduction properties of TiO_2 for high ER activity.[50,51] Unfortunately, the appearance of another phase (in Figure 3) shows that the further substitution of rare-earth ions for Ti^{4+} fails when Ce/Ti mole ratio exceeds the saturation value, 10 mol %, and La/Ti mole ratio, 8 mol %. It results in preventing the further modification of dielectric and polarization for inducing a higher ER effect.

Conclusion

A new class of water-free electrorheological fluids based on doped TiO_2 with rare earth in silicone oil was prepared by means of sol−gel technique. It was found that doping with rare earth could enhance the ER activity of TiO_2 and broaden the working temperature range. The typical yield stress of Ce-doped TiO_2 suspension reached 5.0 kPa under 3 kV/mm and 7.0 kPa under 4 kV/mm dc electric field, which is 10 times higher than that of the pure TiO_2 suspension. More interesting is the important influence of doping degrees of rare earth on ER effect. Substitution for Ti with 10 mol % Ce or 8 mol % La obtained the highest yield stress. We attributed the enhancement of ER activity of doped TiO_2 to the modification of dielectric and polarization properties, particularly the increase of dielectric loss and conductivity, by doping with rare earth. The work of understanding further mechanisms of this new kind of ER material is in progress.

Acknowledgment. The authors are grateful to the National Natural Science Foundation of China (no. 59832090) and the National Natural Science Foundation of China for distinguished Young Scholars (no. 50025207) for supporting the research.

CM011522W

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