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TIO_2 BASED ELECTRORHEOLOGICAL FLUID WITH HIGH YIELD STRESS

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We have fabricated several TiO_2 based ER fluids with doping and without designed doping, which exhibit the high yield stress up to more than 100kPa. The titanium oxide nanoparticles were synthesized by using wet chemical method. The ER effect of those materials is dominated by the special additives, such as amide or its ramification, as well as the remained molecules or ions in the sample preparation. It is found that the yield stress is also strongly dependent on the viscosity of the oil. The prepared ER fluids possess other attractive characters, for instance the current density is low and against sedimentation.

1 Introduction

An electrorheological fluid (ERF) can be transformed into a solid-like state when an electric field is applied and was expected to be widely applied in the technology. In 1985 Block[1] created a water-free ERF as a new type one which was different from the hydrous ERF developed before. Afterwards, though many efforts were made for getting high shear stress ERF, mostly the shear stress of ERF was less than 5kPa. Several years ago, Zhang et al [2,3] synthesized a ERF consisting of surface modified complex strontium titanate (STO) particles, of which the yield stress reached as high as 27 kPa (the volume fraction was 36% and at 3kV/mm). That was the highest strength value of ERF at that time. Inspired by the fact that a trace of water can greatly enhance ER effect, the additives with high dipole moment and high boiling points (higher than 100°C) were mixed with STO to enhance the yield stress. Later Wen et al [4,5] created a giant electrorheological (GER) fluid with the urea coated Ba-Ti-O (BTO) nanoparticles dispersed in silicone oil. The yield stress can reach up to 130 kPa and even higher. A great confidence was gained from these results to obtain high shear stress ERF.

TiO_2 is a popular material with high dielectric constant and easily to be manufactured. Many investigations were done on the ER fluids consisted of TiO_2 materials. The shear stress of pure TiO_2 ER fluids is rather low. By using double coating TiO_2 /Ni on the particles, Y. Tam et al [6] created an ER fluid of which the yield stress had about two orders of magnitude enhancement than pure TiO_2 ER fluids. An ER fluid consisted of TiO_2 coating graphite-particles synthesized by Xu et al [7] also had an order of magnitude increase on the shear stress compared with pure TiO_2 ER fluids. However, by using such technique the enhancement on the shear stress was limited to be several kPa. There were also some efforts for improving the response of TiO_2 ER fluids by using particles with doping elements. The ER fluids containing Ce and Cr doped TiO_2 particles [8,9] exhibited a 10kPa yield stress (at 3kV/mm), which was the highest value achieved in the family of TiO_2 ER fluids.

Recently we have fabricated several TiO_2 based ER fluids with doping and without designed doping which exhibit high ER performance: high yield stress up to more than 100kPa, low current density and anti-sedimentation. The titanium oxide nanoparticles were synthesized by using wet chemical method. ER effect of those materials is dominated by the dipole molecules, such as additive amide or its ramification, as well as the remained molecules in the sample preparation. In this paper we are going to show the results mainly for three TiO_2 based ER fluids.

2 Experimental

The titanium oxide nano-particles were prepared by using sol-gel method. Orthotitanate, ethylene glycol, absolute ethyl alcohol, de-ionized water, etc. were made into an initial solution. The pH value of the solution was in the range 2 to 3 controlled with HCl or HNO_3. After 4 days aging at room temperature, the transparent wet gel was dehydrated in vacuum for 10h at 70°C to form white precursor. The precursor was washed, centrifuged, filtrated, and then dried in vacuum to obtain TiO_2 particles. Special additives with dipole molecules (such as amide or its ramification etc.) were doped into the TiO_2 particles. The TiO_2 particles and silicone oil were heated at 120°C for 3h, respectively, to remove any trace water, and then were sufficiently mixed to a designed concentration. In general, the concentration of particles in ER fluids is defined as volume fraction $\phi = \dfrac{V_p}{V_p + V_f}$, where V_p, V_f are the volumes of particle and oil, respectively. When the particle density is not easily to be measured, we also use weight percentage defined as $W_t = \dfrac{W_p}{W_p + W_f}$, where W_p, W_f are the weights of particle and oil, respectively.

The shear stress of ER fluid was measured by a circular plate type viscometer which was self-constructed. Two parallel plates of 10mm in diameter were separated with 1mm gap. The lower plate was driven by a step motor and the upper plate was connected to a torque sensor (AFT1, Mecmesin Ltd, UK). The ER fluid was filled in between two plates which were connected to a high voltage electric source. By measuring the torque the rheological properties of ER fluids were recorded. The measured yield stress was compared with that measured with Haake Rheometers and the results were quite similar.

3 Results and Discussions

Quite a few species of TiO_2 particles were prepared with different procedures [10].

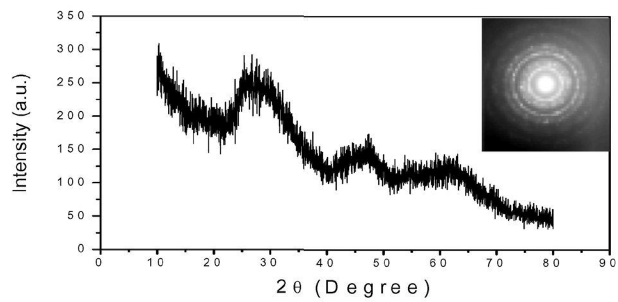

Figure 1. X-ray diffraction pattern of doped TiO_2 and the electron diffraction pattern (inset)

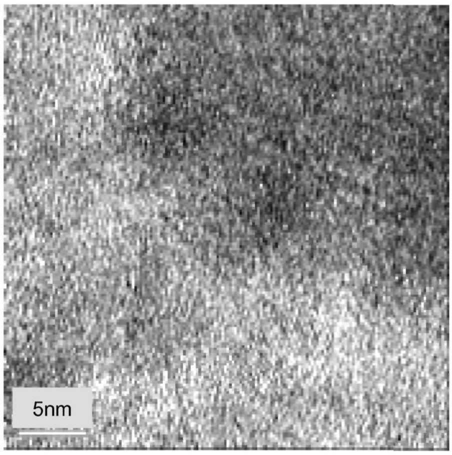

Figure 2 Photo of high resolution TEM for TiO_2 particle. The size of crystalline TiO_2 grain is about 10nm.

The sizes of the synthesized TiO_2 particles were in the range of 50-70nm measured by a scanning electron microscope. Although the X-ray diffraction of the particles shows amorphous-like pattern (Fig.1), the electron diffraction image (inset of Fig.1) and the high resolution TEM photo (Fig.2) have proved that the TiO_2 particles are in microcrystalline state. From Fig.2 the size of the crystal grain in the particles can be estimated to be about 10nm.

The ER fluids consisted of some of those TiO_2 particles possess very good ER response. Here we just give three examples to describe the characters. Fig.3 shows the yield stress as the function of DC field strength for the TiO_2 ER fluids (for **specimen 1** with doping)

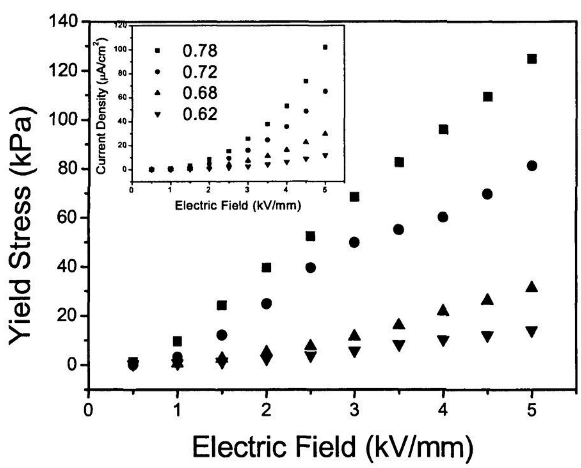

Figure 3 Yield stress as function of field strength at different concentrations (for specimen 1 with doping). The current densities vs. electric field are shown in the inset.

with various weight percentages of particles. The corresponding current densities are plotted in the inset of Fig.3. It can be seen that the sample exhibits strong yield stress up to 140kPa, however, the yield stress displays near-linear dependence on the electric field unlike the usual quadratic behavior in the dielectric particle ERF.

We find that yield stress of TiO_2 particles based ER fluids is also sensitive to the viscosity of the silicone oil as shown in Fig.4 (for **specimen 2** with doping). When the viscosity of based oil is 10mm^2/s, the yield stress of the ER fluid is more than 200kPa at 4.5kV/mm. However, the yield stress of ER fluid is only 20kPa when the TiO_2 particles suspend in 100mm^2/s silicone oil. We have also observed some other situations such as the yield stresses do not change with the oil viscosity or it increases with the viscosity decreasing for different particles prepared with different conditions. If the nanoparticles are wetted well with the oil, thus the ER fluids look like a gel and exhibit strong ER effect. Otherwise, the ER fluids become clay-like and display poor ER effect. This vagarious dependence of yield stress on the oil viscosity can not be understood based on the dielectric theory, because the permittivity is almost same ($\approx$ 2.5) for different silicone oils. This phenomenon might be due to the wetting character between oil and nanoparticles or the electro-wetting effect. Further work is needed for explaining these special characteristics.

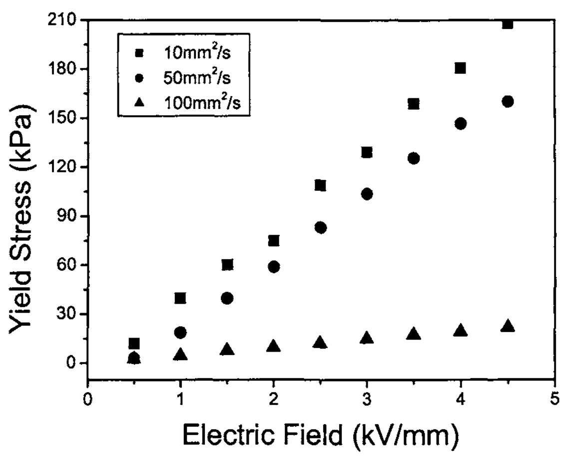

Figure 4 The yield stress vs. the field strength of TiO_2 particles dispersed (ϕ=40%) in the silicone oils with different viscosities. (for **specimen 2** with doping)

Even if there were not designedly doping molecules in the particles we could still get the high performance ER fluids as shown in Fig. 5 (for **specimen 2** without designed doping). The chemical analysis indicated that there was a trace of groups such as O-H, C-H etc. remained in the particles during the processing of samples.

The processing conditions can greatly affect the yield stress as well as the current density of ER fluids. The current densities of our TiO_2 ER fluids change from μA/cm^2 to mA/cm^2 from sample to sample prepared with various processing conditions. Moreover, the yield stress of ER fluids is not strongly related to the current density, i.e. both high and low current density samples can exhibit high yield stress. In selected processing condition, we can fabricate TiO_2 particles based ER fluids with the yield stress of more than 100kPa

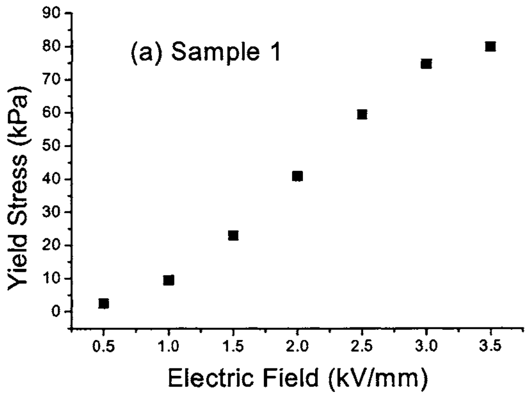

Figure 5 The yield stress vs. the field strength for the ER fluid containing TiO_2 particles (for **specimen 2** without designed doping).

and current densities as low as $10\mu A/cm^2$. The TiO_2 nano-particle ER fluids also possess an advantage against particles settling. There was not obvious sedimentation happened in the suspensions in a few months period.

To explain the origin of high yield stress and its linear dependence on the field strength in the urea coating $BaTiO(C_2O_4)_2$ ER suspension a model was proposed based on the surface saturation polarization of the coating layer [4]. However, in our TiO_2 based ER fluids there are some additional characters which can not be explained by the proposed model. Firstly, some undoped TiO_2 ER fluids with only very little impurity remained in the particles and without the coating layer on the particles still exhibit large ER effect. Secondly, our TiO_2 particles are in crystalline state unlike the amorphous state in reported $BaTiO(C_2O_4)_2$ particles. The amorphous state of the particles was necessary for creating the surface saturation polarization layer in the proposed model. Thirdly, a quadratic dependence of shear stress on the field strength can be observed some times in our TiO_2 ER fluids. All these facts indicate that a further work is needed to explain the behavior of such new type ER fluids. A brief description on the mechanism for those ER fluids is presented in another paper [11] and a strict calculation is still going on.

4 Conclusion

We have developed a series of TiO_2 nano-particle based ER fluids showing strong ER effect with doping or without designed doping in the particles. The yield stress can reach up to 100kPa, or 200kPa in a DC field. The ER fluids also possess other advantages such as low current density, anti-sedimentation and low cost. These advantages of our TiO_2 ER fluids are very attractive for the applications, although the mechanism of the ER effect should be studied further.

5 Acknowledgement

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