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SHORT COMMUNICATION

Synthesis and electrorheological properties of oxalate group-modified amorphous titanium oxide nanoparticles

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Abstract A kind of titanium oxide nanoparticles modified with varying amounts of oxalate group was prepared using a modified hydrolysis method. The microstructure, dielectric properties, and electrorheological (ER) performance were investigated. The results indicate that the oxalate group can effectively improve the dielectric properties and surface polarizability of the particles, and the ER performance of modified titanium oxide-based ER fluid is much higher than that of pure titanium oxide-based ER fluid. The shear stress of suitable oxalate group-modified amorphous titanium oxide-based ER fluid with a volume fraction of 30% reaches 47.5 kPa at $E=5$ kV/mm, and the current density is less than 18 μAcm^{-2}. The yield stress can be up to 114 kPa at $E=5$ kV/mm with a volume fraction of 40%.

Keywords Electrorheological fluid · Dielectric property · Titanium oxide · Oxalate group · Shear stress

Introduction

Electrorheological (ER) fluid is a suspension made of micrometer- or nanometer-sized dielectric particles dispersing in an insulating liquid. Under an applied electric field, the dispersed dielectric particles will be polarized and attracted to each other to form chain or column structures. These chains and columns enable ER fluid to suddenly increase its viscosity and even change from a liquid-like state to a solid-like state. The viscosity change or liquid–solid state transition of ER fluid is rapid and reversible as the change of applied electric field [1–4]. Because of its controllable viscosity and short response time, ER fluid has attracted much interest in various areas, such as clutches, damping devices, display, human muscle simulator, and so on [5–7]. Most of these applications need ER fluid possessing large shear stress, low electric current density, and high stability.

Much effort had been made to design and prepare high-performance ER materials since Winslow firstly discovered the ER effect over 50 years ago [1]. Various material systems including semiconductive polymer [8–10], core/shell composite particles [11, 12], and nanocomposite [13–15] have been synthesized and studied in the past years. In addition, the mechanism of the ER effect had been intensively discussed [16–20]. The particle polarization is believed to play an important role for the interaction forces that lead to the rheological change of ER fluid. The dielectric properties in connection with particle polarization have been accepted as the basic factors that dominate the ER effect. So titanium oxide was considered as a promising ER material for its high dielectric constant. However, the pure titanium oxide did not exhibit an appreciable ER effect, usually of only several kPa [13]. In recent years, several authors have reported that the yield stress of titanium oxide-based ER fluid can be effectively enhanced by coating polar molecules or groups on the particle surface [18, 21, 22]. However, up until now, little study has been devoted to the effect of polar groups doping into the particle inner-polymeric network. In this paper, a kind of titanium oxide nanoparticles modified with varying amounts of oxalate group was prepared by a modified hydrolysis method. The polar oxalate group was homodisperse in the—O–Ti–O—polymeric network by in situ condensation. Their physical properties and ER charac-

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teristics were investigated by Fourier transform-infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscope (SEM), LCR Tester and circular plate rheometer. The results show that the nanoparticles are amorphous and the polar oxalate group can effectively improve the dielectric properties and surface polarizability of the particles. The shear stress of suitable oxalate group-modified amorphous titanium oxide-based ER fluid with a volume fraction of 30% reaches 47.5 kPa at E=5 kV/mm. The yield stress can be up to 114 kPa at E=5 kV/mm with a volume fraction of 40%.

Experiments

Preparation of pure and oxalate group-modified titanium oxide particles

All the chemical reagents in this study were of analytical grade. Titanium butoxide ($Ti(C_4H_9O)_4$), oxalic acid, deionized water, and anhydrous ethanol were used as starting materials. Firstly, 34.1 ml titanium butoxide was dissolved in anhydrous ethanol and stirred for 3 h at 25 °C to get a uniform solution A. At the same time, 12.6 ml deionized water and 200 ml anhydrous ethanol were mixed with oxalic acid to form another homogeneous solution B. The added molar ratio (x) of $H_2C_2O_4/Ti$ is 0, 0.3, 0.6, 0.9, and 1.2 for different samples (S1–5), respectively. Secondly, freshly prepared solution (B) was dropped into solution (A) with vigorous stirring condition at the temperature of 25 °C to form pure or oxalate group-modified titanium oxide. Thirdly, the white precipitates so produced were filtered and washed several times with anhydrous ethanol, then dried in vacuum oven at 100 °C to get samples 1–5.

Preparation of ER fluids

The samples were milled for 10 h in a mortar and dried in vacuum oven at 110 °C for 5 h to remove physical adsorbed water. Subsequently, the dried samples were mixed uniformly with silicone oil. At room temperature the viscosity, density and dielectric constant of the silicone oil used in this ER fluid is 50 mPa·s, 0.973 g/cm^3 and 2.5, respectively.

Characterization and measurements of ER activity

The chemical structure was determined by a Perkin–Elmer system 2000 spectroscopy (FT-IR) spectrophotometer in which the IR spectra was recorded by diluting the milled powders in KBr. The concentrations of C, O, Ti elements in the final products were measured by C, O Elemental Analyzer (2400Π, Perkin–Elmer) and Plasma-Atomic Emission Spectrometry (Optima 2100, Perkin–Elmer). The X-ray diffraction patterns of the particles were recorded on a Rigaku D/Max-A diffractometer with CuKá radiation. The morphology and grain size of the samples were examined by a Hitachi S4800 field emission scanning election microscope. The dielectric properties of the ER fluids were measured with a LCR Tester (Hioki 3532, Japan). The electrorheology of the ER fluids at different DC electric field was determined by a circular plate rheometer (Haake RS6000, Germany). The diameter of the plate was 15 mm and the gap between two plates was 1.0 mm. The fluid was placed in the gap. A DC high-voltage generator (Spellman SL300, USA) and an ammeter (Agilent 34401A) were used to provide external electric field and monitor the current across the ER fluid, respectively. The shear stress of ER fluid was measured in the approach of controlled rate mode (γ=1 s^{-1}). And the yield stress was measured in the approach of controlled stress mode.

Results and discussion

Synthesis and characterization of materials

The synthesis route involves a two step reaction process: hydrolysis and condensation. The hydrolysis and condensation occur through Reactions (1) (2) (3):

$$\equiv \mathrm{Ti}-\mathrm{OR}+\mathrm{H_2O} \xrightarrow{\text{hydrolysis}} \equiv \mathrm{Ti}-\mathrm{OH}+\mathrm{ROH} \quad (1)$$

$$\equiv \mathrm{Ti}-\mathrm{OH}+\mathrm{HO}-\mathrm{Ti}\equiv \xrightarrow{\text{condensation}} \equiv \mathrm{Ti}-\mathrm{O}-\mathrm{Ti}\equiv +\mathrm{H_2O} \quad (2)$$

$$\equiv \mathrm{Ti}-\mathrm{OH}+\mathrm{HOOC}-\mathrm{COOH}+\mathrm{HO}-\mathrm{Ti}\equiv \xleftrightarrow{\text{condensation}} \equiv \mathrm{Ti}-\mathrm{OOC}-\mathrm{COO}-\mathrm{Ti}\equiv +2\mathrm{H_2O} \quad (3)$$

The hydrolysis Reaction (1) occurs upon the addition of water, when a hydroxyl ion attaches onto the metallic atom (Ti) resulting in the removal of the alkyl group (OR). This is followed by condensation, which involves the formation of (Ti–O–Ti, Reaction (2) and Ti–OOC–COO–Ti, Reaction (3)) bonds. In order to clarify the composition of the powders, the dried precipitates were subjected to IR and elementary analysis. Figure 1 shows the FT-IR spectra of the pure titanium oxide particles (S1) and the oxalate group-modified titanium oxide particles (S4). The broad band around 3,450 cm^{-1} of S1 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 absorption band of 500–800 cm^{-1} is attributed to

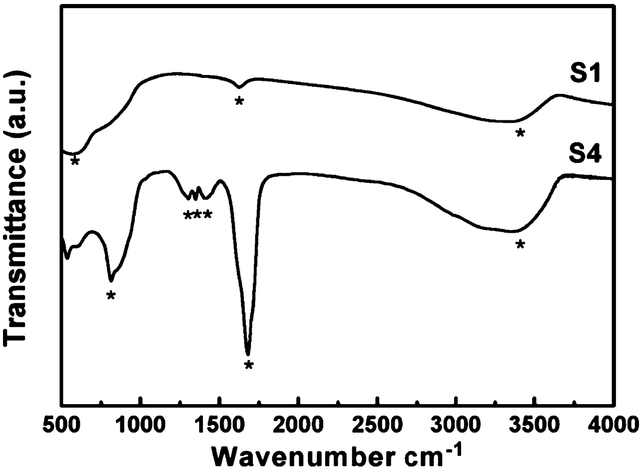

Fig. 1 The FT-IR spectra of the pure titanium oxide particles (S1) and the oxalate group-modified titanium oxide particles (S4)

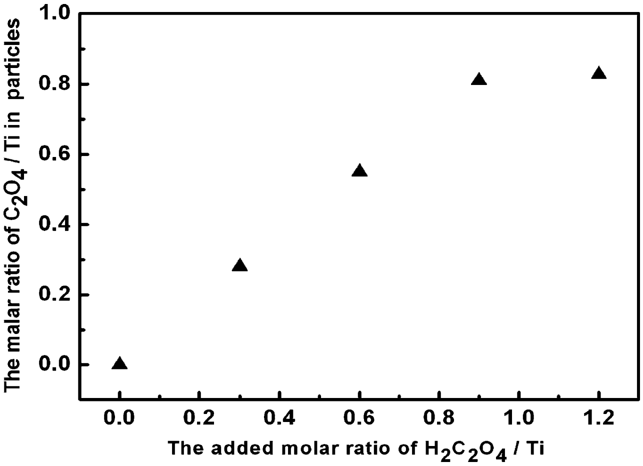

Fig. 2 The dependence of molar ratio of C_2O_4/Ti in the final product on the added molar ratio of $H_2C_2O_4$/Ti

the Ti–O vibrations. Compared with S1, the characteristic absorption bands of oxalate group are found in S4. The absorption peak at 1,680 cm^{-1} is assigned to C=O stretching mode, the bands at 1,410, 1,340, and 1,290 cm^{-1} are attributed to C–O vibration. The absorption peak at 810 cm^{-1} is assigned to the C–C band vibration [23]. The elementary analysis results are expressed in Table 1. The results show that the concentration of C, O elements in the final product increases and tends to saturate with the increasing content of oxalic acid. According to the concentration of C and Ti elements in the final product, we get the dependence of molar ratio of C_2O_4/Ti in the final product on the added molar ratio of $H_2C_2O_4$/Ti, which is expressed in Fig. 2. The XRD pattern and SEM photograph of S1 and S4 are shown in Fig. 3. The results indicate that the two kinds of particles are in an amorphous state. The diameters of pure titanium oxide (S1) and modified titanium oxide (S4) particles are distributed mainly in the range of 300–500 nm and 200–400 nm, respectively. The obvious distinction of the shape between the two kinds of particles is not observed.

Electrorheological and dielectric property

The shear stress and the corresponding current density (inset) of samples 1–5 ER fluids under different DC electric field are expressed in Fig. 4. The concentration of particles in ER fluid is 30 vol.%. In the case of pure titanium oxide-based ER fluid, the shear stress is rather low and the maximum shear stress is 4.0 kPa at E=5 kV/mm, while the oxalate group-modified titanium oxide-based ER fluids show a remarkably stronger ER effect. The maximum shear stress of S2, S3, S4, and S5 samples are 17.0, 30.0, 47.5 and 44.5 kPa, respectively, at E=5 kV/mm. This indicates that the oxalate group modifying can evidently enhance the ER performance of titanium oxide materials. According to widely accepted studies [24, 25], particle polarization is considered to be responsible for the interaction forces that lead to the rheological change of ER fluids. For the oxalate group-modified titanium oxide particles, the polar oxalate group is directly incorporated to the particle phase, which can effectively improve the dielectric properties. At the same

Table 1 The elementary analysis results of the pure and oxalate group-modified titanium oxide particles (S1–5)

Elements	S1	S2	S3	S4	S5
C (wt.%)	0.00	5.85	9.96	12.64	12.67
O (wt.%)	48.97	51.99	54.26	55.84	55.86
Ti (wt.%)	48.91	40.02	34.32	30.59	30.52

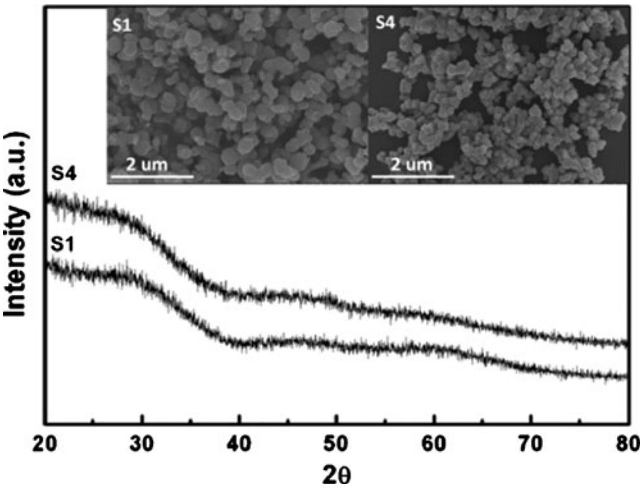

Fig. 3 X-ray diffraction pattern and SEM image of pure titanium oxide particles (S1) and the oxalate group-modified titanium oxide particles (S4)

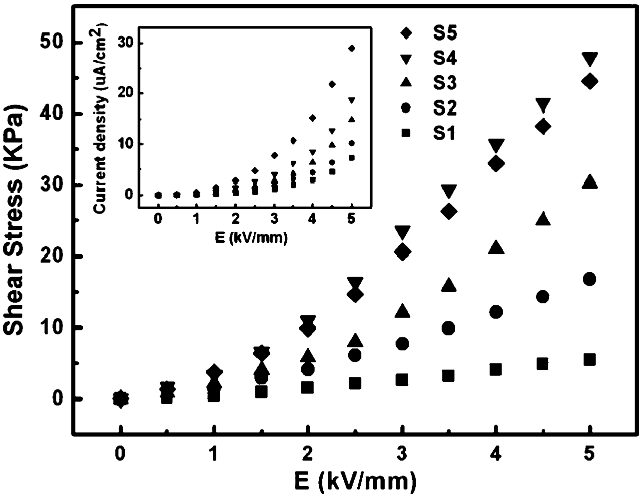

Fig. 4 The shear stress of the pure and oxalate group-modified titanium oxide (S1–5) ER fluids under different DC electric field. The current densities corresponding to those samples are shown in the *inset*

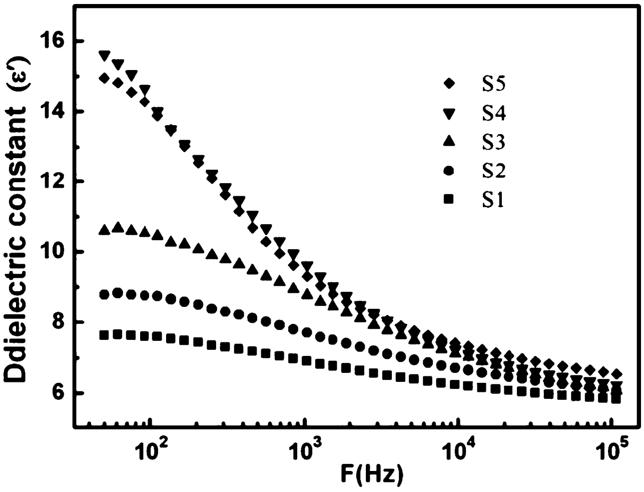

Fig. 5 The dielectric property of the pure and oxalate group-modified titanium oxide (S1–5) ER fluids in the frequency range 50–10^5 Hz

time, some oxalate groups can be adsorbed on the surface of particles, which would promote surface activity because they may produce synergetic effects or might react with each other, which leads to the corresponding enhancement of the interfacial polarization.

Figure 4 also shows that the shear stress is dependent of the oxalic acid content, the optimal molar ratio of $H_2C_2O_4$/Ti being about 0.9 (S4). When the concentration is above the critical point, some oxalate groups are more likely to be resolved in the fluid phase rather than adsorbed on the particle surface in the absence of an electric field. But in the presence of the electric field, the enriched oxalate groups in the fluid phase will gather into the interstices formed by neighboring particles in which a non-uniform high electric field is generated. However, the more polar groups lead to too much conductivity and relatively much leaking current density (see the inset in Fig. 4), which is relevant to the degradation of the ER properties at the high $H_2C_2O_4$/Ti concentration limit.

Figure 5 shows the dielectric spectra of the pure and oxalate group-modified titanium oxide (S1–5) ER fluids in the frequency range of 50–10^5 Hz. It is clearly found that the dielectric constant in low frequency is obviously enhanced by adding oxalate group and exhibits a dependence on oxalic acid content. The ER fluid of S4 with the added $H_2C_2O_4$/Ti molar ratio of 0.9 shows the highest dielectric constant at 1 kHz. At the same time, it can be found that the dielectric constant of the oxalate group-modified titanium oxide ER fluid shows a stronger frequency dependence, which indicates that slow polarization, especially interfacial polarization, is enhanced due to the addition of oxalate group. The dynamic shear stress of the pure and oxalate group-modified titanium oxide (S1–5) ER fluids as a function of shear rate is shown in Fig. 6. The concentration of particles in ER fluids is 30 vol.% and the applied electric field is 3 kV/mm. From Fig. 6, we can see that dynamic shear stress of the ER fluids is enhanced by adding oxalate group. The suspension of S4 has the best rheological properties in the range of shear rate; the dynamic shear stress is up to 23 kPa and maintains a stable level over the whole shear rate range of 1–100 s^{-1}. These results indicate that the ER fluids of sufficient oxalate group-modified titanium oxide particles have large polarizability and a rapid polarization response to produce stronger and faster electrostatic interaction that can maintain structures and rheological properties stable under shear flow.

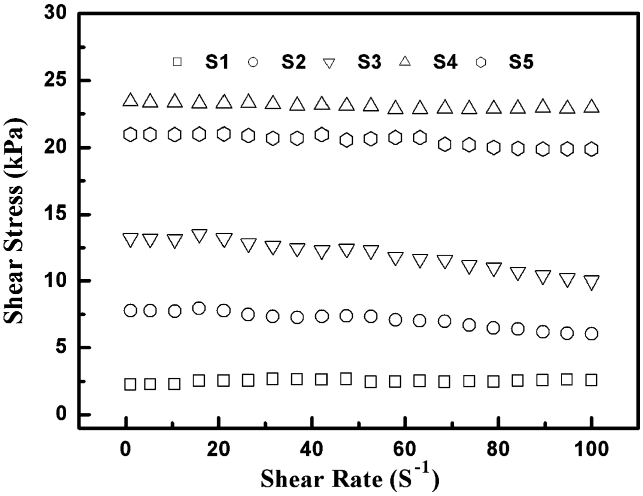

Fig. 6 The shear stress as a function of shear rate for the pure and oxalate group-modified titanium oxide (S1–5) ER fluids. The applied electric field is 3 kV/mm

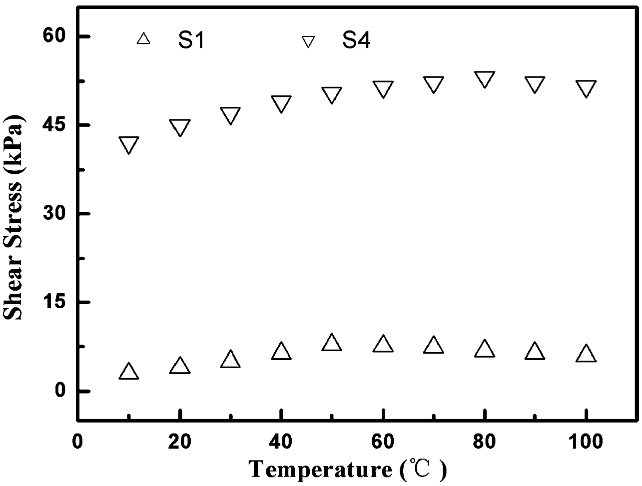

Fig. 7 Temperature dependence of shear stress of pure titanium oxide ER fluids(S1) and typical oxalate group-modified titanium oxide (S4). The applied electric field is 5 kV/mm

Temperature dependence of shear stress of pure titanium oxide ER fluids (S1) and typical oxalate group-modified titanium oxide (S4) is expressed in Fig. 7. The applied electric field is 5 kV/mm and the concentration of particles in ER fluid is 30 vol.%. Figure 7 shows that the shear stress of the typical oxalate group-modified titanium oxide (S4) ER fluid increases with temperature and reaches its maximum around 80 °C, whilst the shear stress of pure titanium oxide ER fluid declines after 50 °C. This can be explained by the difference in temperature dependence of dielectric constant between pure and modified titanium oxide ER fluids as shown in Fig. 8. The dielectric constant of modified titanium oxide ER fluid at 100 Hz increases with temperature and reaches its maximum around 80 °C, while the dielectric constant of pure titanium oxide ER fluid reaches saturation around 50 °C. These results indicate that modifying of oxalate group not only increases ER activity of titanium oxide, but also broadens its operational temperature range.

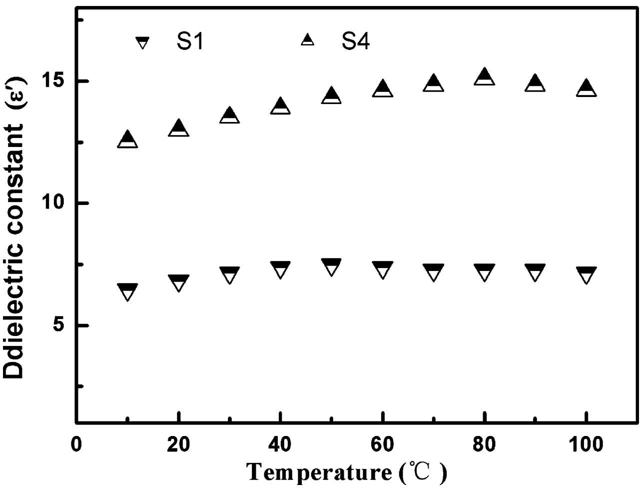

Fig. 8 Temperature dependence of dielectric constant (100 Hz) of pure titanium oxide ER fluids (S1) and typical oxalate group-modified titanium oxide (S4)

The effect of volume fraction of the S4 particles in ER fluids on the yield stress is given in Fig. 9. Figure 9 shows that the volume fraction has obvious effect on the yield stress. The ER fluids with a higher volume fraction have a higher yield stress under the same electric field. While the volume fraction is 40%, the yield stress reaches 114 kPa at *E*=5 kV/mm, which is 2.4 times of the yield stress of the ER fluid with volume fraction 30%. However, the zero field viscosity of the ER fluid with volume fraction 40% also obviously increases, reaches 38 Pa s at the shear rate of 10 s^{-1}, which is 3.2 times of the zero field viscosity of the ER fluid with volume fraction 30%.

Conclusions

A kind of oxalate group-modified titanium oxide nanoparticles was prepared using a modified hydrolysis method. The oxalate group was homodisperse in the polymeric network of particle by in situ condensation. The results show that the nanoparticles are amorphous and the polar oxalate group can effectively improve the dielectric properties and surface polarizability of the particles. The ER performance of oxalate group-modified titanium oxide-based ER fluid is much better than that of pure titanium oxide, the shear stress can reach 47.5 kPa at *E*=5 kV/mm with a volume fraction of 30%. The yield stress can be up to 114 kPa at *E*=5 kV/mm with a volume fraction of 40%.

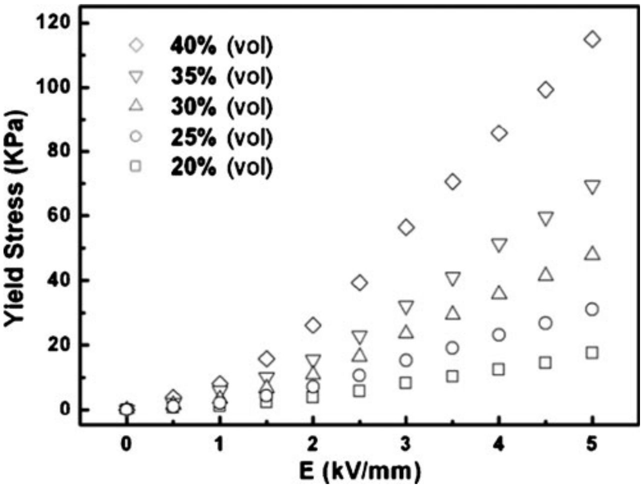

Fig. 9 The yield stress of the oxalate group-modified titanium oxide (S4) with different volume fractions under DC electric fields

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