Colloids and Surfaces A: Physicochem. Eng. Aspects 329 (2008) 153–160

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Electrorheological properties of titanate nanotube suspensions

Jianbo Yin, Xiaopeng Zhao*

Institute of Electrorheological Technology, Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710072, PR China

ARTICLE INFO

Article history:
Received 4 January 2008
Received in revised form 25 June 2008
Accepted 6 July 2008
Available online 15 July 2008

Keywords:
Titanate
Nanotube
Electrorheology
Dielectric properties

ABSTRACT

Titanate nanotubes were synthesized by hydrothermal reaction of titania nanoparticles in alkali solution and the electrorheological (ER) properties of titanate nanotubes/silicone oil suspension were investigated. Compared to the titania nanoparticle suspension, the nanotube suspension showed better ER effect. The effects of material structure and external temperature on ER properties were especially investigated. It was found that the alkali-ions, intercalated in the interlayer of nanotube, were important to the ER activity of titanate nanotube. Removal of alkali-ions by acid-treatment did not destroy the nanotube morphology but weakened ER effect. According to dielectric analysis, the change of dielectric properties after removing alkali-ions may be the reason of the decrease of ER properties of nanotube. In addition, the ER effect of titanate nanotube suspension increased with temperature, which was in accordance with the improving particle polarization by dielectric measurement. Temperature effect became poor after removal of alkali-ions.

1. Introduction

Electrorheological (ER) fluid is a smart material, which is made of small dielectric particles in an insulating liquid. Under the electric field, ER fluid can suddenly increase its viscosity and even change from liquid-like state to solid-like state accompanied with a large yield stress about several kPa [1–4]. As a result, ER fluid would possess widely potential applications in smart control of conventional and intelligent devices [5–8]. However, the practical applications of ER fluid are hampered due to its insufficient yield stress, poor temperature effect, and suspended instability. In order to accelerate applications, researchers made many efforts to develop methods and materials to improve the performance of ER fluid. Monkman had reported an interesting way where a polar fabric layer was added to electrodes' surface to enhance the available torque of ER clutch, because fabric polarizations reduce the near-wall effects of ER particles [9–11]. More researches focused on the developments of a variety of ER materials including organic [12–17], inorganic [18–25], composites [26–28] or nanocomposites [29–33]. These ER materials show to some extent the improved ER performances, but the practical applications of them are still limited by either low yield stress or suspended instability. The problem of the suspended instability has been expected to be overcome using nanosize particles as ER dispersal phase [34]. However, the theoretical investigations showed that the ER effect of nanosuspension was weak compared to microparticle suspension due to Brownian motion and small polarizability of nanoparticle [6]. Therefore, nano-ER fluids have not received essential attention until 2003, at which a novel urea-coated nanoparticles fluid that exhibited giant ER (GER) effect was reported [35]. The static yield stress of the GER fluid exceeded 130 kPa at 5 kV/mm, which was one order as high as that of conventional ER fluid. Since then, some other GER fluids based on polar molecular-modified nanoparticles were also developed [36–40].

Besides nanoparticles, one-dimension nanomaterials, such as nanowire and nanotubes, have also been used as the dispersal phase or additives of ER fluids or magnetorheological (MR) suspensions recently [41–46]. Thanks to the characteristics of nanosize and anisotropic morphology, these one-dimension nanomaterials were found to improve the dispersion stability of ER fluids or MR suspensions and even enhance ER or MR effect [42,45,46]. In our previous work [42], we reported a new ER fluid using titanate nanotubes as dispersal phase. This nanotube suspension, which was easily synthesized by a hydrothermal procedure, showed advantages including dispersion stability and effective ER response. In the present work, to further understand ER properties of the nanotubes suspension, the effects of materials structure and external temperature on ER properties were especially investigated and discussed based on dielectric analysis. The results showed that the stronger ER effect of titanate nanotube suspension compared to titania nanoparticle suspension was in accordance with the superior dielectric property of nanotube suspension. The alkali-ions, intercalated in the interlayer of nanotube, were found to be important to the ER activity. Removal of alkali-ions by acid-treatment

---

* Corresponding author. Tel.: +86 29 8849 5950; fax: +86 29 8849 1000.
E-mail address: xpzhao@nwpu.edu.cn (X. Zhao).

0927-7757/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2008.07.006

resulted in the decrease of ER effect, which may be due to the weakened dielectric or polarization properties. Furthermore, the ER efficiency of nanotube ER fluid increased with increasing external working temperature, while temperature effect of nanotube ER fluid becomes poor after removal of alkali-ions by acid-treatment. This was discussed according to the temperature dependence of dielectric properties.

2. Experiment

2.1. Synthesis of titanate nanotubes

The titanate nanotube was synthesized by a known hydrothermal method [47,48]. The process is shown as follows. First, anatase-type titania nanopowders (5 g, the particle size about 30 nm, purchased from Haitai Nano. Ltd. Co., China) were dispersed in an aqueous solution of NaOH (10 M, 500 ml) under stirring. Second, the resulting suspension was transferred into Teflon-lined autoclaves and heated at 130 °C for 72 h. Third, the precipitate was filtered and divided into two parts. The first part was suspended with deionized water, then filtered and washed with deionized water repeatedly till pH of the filtrate was near 7 (called this product as Na-titanate nanotube); the left precipitate was suspended with HCl 0.1 M solution and deionized water to make a pH 2, filtered again, and the process repeated (called this product as H-titanate nanotube). Thus, these different water or acid-washing procedures aimed at producing distinct residual sodium ions in the interlayer in order to help us to understand the internal structure and compositions of nanotubes. Finally, in order to prepare water-free ER nanomaterials and further understand the structure of nanotubes, the as-made samples were annealed in a furnace under air atmosphere for 2 h at the temperatures of 250 and 400 °C, respectively.

2.2. Preparation of titanate nanotube ER fluids

The above calcined samples was cooled to 180 °C in furnace and mixed quickly with dimethyl-silicone oil ($\eta = 25$ mPa s at 25 °C, Shin-Etsu Silicone Co., Japan). Then, the additional silicone oil was further added into the above suspension in order to obtain resultant ER fluid with a particle volume fraction of 5%. Here, the volume fraction is defined by the ratio of particle volume to total volume of ER suspension. The apparent density of nanotube had been determined to be 1.85–2.0 g/cm^3, which is lower than that of the raw material of anatase titania nanoparticle (3.85 g/cm^3). Finally, the suspension was dispersed by ultrasonic for 5 h to form stable nanotube suspension. No additives were added into the fluid in order to clearly understand the relationship between structure and rheology.

2.3. Characterization

2.3.1. Structure characterization

The phase structure was determined by the powder X-ray diffraction (XRD) patterns at a Philips X'Pert Pro X-ray diffractometer with Cu Kα irradiation (40 kV/35 mA) and step size of 0.033° in the 2θ range of 5–70°. The thermogravimetric (TGA–DTA) curve (Universal V2.6D TA instrument) with a heating rate of 10 °C/min in the temperature range of 40–900 °C was used to analyze the thermal properties. The particle morphology and structure were observed by scanning electron microscopy (SEM, JSM-6700) and field emission transmission electron microscopy (TEM, JEM-2100F, acceleration voltage of 200 kV). The chemical composition and content were analyzed by the energy-dispersive X-ray spectroscopy (EDS, JSM-6700). The particle's apparent density was determined using a pycnometer method in water.

2.3.2. Electrorheological measurements

The ER properties were measured by a THERMAL HAAKE RS600 stress-controlled electro-rheolometer with a parallel plate system PP 60ER, a WYZ-010 dc high-voltage generator (the maximum voltage of dc high-voltage generator was 10.0 kV and the current limitation was 2.0 mA), PC-controlled circular oil bath system (Silicone oil, −25.0 to 125.0 °C) for temperature control, and a microdetector for detecting current through ER fluid. The gap of parallel plates was 0.5 mm. The rheological curve was measured by controlled shear rate (CR) mode. Before reading stresses, we had initially applied the electric field on suspensions for 10.0 s and then sheared. The basic rheological measurements were all tested at 23.0 °C. The temperature dependence of electrorheology was measured by CR mode at some selected temperature points. The ER efficiency is calculated with $(\tau_E - \tau_0)/\tau_0$ at shear rate of 10 s^{-1}, where τ_E is the shear stress with electric field and τ_0 is the shear stress without electric field, respectively.

2.3.3. Dielectric analysis

The dielectric spectra of ER fluid were measured by an impedance analyzer (HP4284A) within the frequency range from 20 Hz to 1 MHz using a measuring fixture (HP16452A) for liquids. The 1 V of bias potential was applied to the fluid during measurement. It was small so that no chain was induced within the ER fluid, thus we could obtain the true behavior of the interfacial polarization between dispersal phase and medium and well compare the dielectric behaviors. The HP16452A fixture was immerged into controlled oil bath system (Silicone oil, −25.0 to 125.0 °C) for measuring the temperature dependence of dielectric properties.

3. Results and discussion

3.1. Material characteristic

Fig. 1 shows field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of samples. It is found that the morphology of sample obtained by hydrothermal treatment is different from the used titania nanoparticle and it is uniform nanotube with outer diameter of 10 nm and length about 100–200 nm after ultrasonic (see Fig. 1b). High-resolution TEM in Fig. 1d shows that the nanotube consists of the roll multilayered structure with hollow inner diameter of 3 nm. The selected area electron diffraction (SAED) of the nanotube is significantly different from that of the titania nanoparticle. The brighter spots in one direction, due to the perpendicularity to the nanotube axis, reveal the layered structure [49]. After acid-treatment, the nanotube-like morphology shows less change (see Fig. 1e). The energy-dispersive X-ray spectroscopy (EDS) analysis shows the Na-titanate nanotube contains Na, Ti, and O elements. But no sodium element can be detected in the H-titanate nanotube, indicating that the sodium ions has been removed from the interlayer of nanotube by the acid-treatment.

Fig. 2 shows the X-ray diffraction (XRD) patterns of samples. It is found that the Na-titanate nanotube shows the peaks at 2θ angles of 9.2°, 24.0°, 28.0° and 48.0°, which are different from the diffraction peaks of anatase of used raw material of titania nanoparticle. These peaks, in particular the strong broad peak at $2\theta \sim 9.2°$ attributed to the interlayer distance, correspond to the layered trititanate structure [49–51]. After acid-treatment, the intensity of 9.2° peak decreases and the intensity ratio of 28.0° peak relative to 24.0° peak also decreases (see curve c). This is attributed to the fact