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Electrorheological behavior of titanate nanotubes suspensions under oscillatory shear

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Abstract. In this study, titanate nanotubes (TNTs) were synthesized by hydrothermal treatment of TiO_2 powder (P25) in a NaOH solution. The as-synthesized TNTs exhibit high surface area and large aspect ratio. Rheological properties of TNTs suspensions were then investigated under oscillatory shear. The TNTs fluid shows viscoelastic behavior and the dynamic moduli (G',G'') increase significantly by about 4 orders of magnitude as the electric field strength is up to 2.0 kV/mm. The complex modulus of TNTs fluids is sensitive to temperature while that of P25 fluid become insensitive at higher temperature. Dynamic viscoelastic behavior suggests that structure of P25 to TNTs transition merits the enhancement of ER activity of TNTs fluid.

1. Introduction

The past few years have witnessed significant progress in the design and fabrication of versatile nanomaterials with novel structures due to their unique properties. Among such materials, one-dimensional (1D) nanostructures (nanotubes, nanowires and nanofibers) have attracted extraordinary attention recently, mainly because of their novel physical properties as well as potential applications in nanoscale electronic and optoelectronic devices. However, very recently interesting electrorheological (ER) behavior induced by 1D nanomaterials based fluids [1-3] has also become the research focus inspired by the discovery of the giant electrorheological (GER) effect [4].

1D nanotubes have received particular interest in ER systems owing to their high aspect ratios and good suspended stability, which probably favor the enhanced ER activity. In this respect, Zhao et al. recently reported a new ER fluid based on titanate nanotubes (TNTs) in steady flow, which shows better dispersion stability and a notable ER activity [5,6]. In this work, in order to further investigate the changes of the microstructures of 1D nanotubes based ER fluids, the ER behavior of TNT fluids is measured under oscillatory shear. Investigation of ER properties of TNTs by the dynamic oscillation tests will be helpful in understanding the nature of the interactions among particles forming the internal structures which is vital for the optimization of 1D ER materials.

2. Experimental

2.1. Synthesis of TNTs

TNTs were prepared according to the previous report [7] with a minor modification. In a typical synthesis, 1 g of TiO_2 powder (P25, Degussa AG, Germany) was mixed with 60 ml of 10 M NaOH solution, which was followed by hydrothermal treatment of the mixture at 130 °C in a 100 ml Teflon-lined autoclave for 24 h. The white precipitate was separated by filtration and washed with ethanol and distilled water until pH~7 was reached. The samples were then dried in an oven at 60 °C for 12 h.

2.2. Preparation of ER fluids

The apparent density of TNTs was measured to be around 1.95 g/cm^3. Before the preparation of the suspensions, the dried TNTs were calcined in an oven at 250 °C for 2 h to get dehydrated TNTs. Then the TNTs and dried P25 particles were dispersed by ultrasonic in silicone oil (Fluid 200, Dow Corning, UK; viscosity η_c = 108 mPa s, density ρ_c = 0.965 g/cm^3) to form stable suspension with a particle volume fraction of 5 % (v/v) for each material separately.

2.3. Electrorheological measurements

Measurements of rheological properties of the prepared fluids were carried out using a coaxial cylinder viscometer (Bohlin GEMINI, Malvern Instruments, UK). The suspensions were placed in the Couette cell with the rotating inner cylinder of 14 mm diameter and the outer cylinder separated by a 0.7 mm gap. They were connected to a DC power supply producing a field strength E = 0–2 kV/mm. Further, dynamic viscoelastic tests were performed by dynamic strain sweeps and frequency sweeps. The strain sweep was carried out with applied strains of 0.0001 to 1.0 at a frequency of 62.8 rad/s under an electric field to determine the linear viscoelastic region. The rheological parameters were then obtained from the frequency sweep tests (0.1 to 100 rad/s) at a fixed strain amplitude in the linear viscoelastic region. All experiments were performed at 25 ºC.

3. Results and discussion

3.1. Characterization of materials

The morphologies of P25 nanoparticles and TNTs were characterized by TEM. Most particles are nearly globular and the average particle size of P25 is around 20 nm. While after hydrothermal treatment, the P25 particles almost convert into TNTs with diameters in the range of 8-10 nm and lengths of up to several hundreds of nanometers. The results are in good agreement with previous report [8]. Meanwhile, TNTs exhibit obviously larger length-diameter ratios than that of P25 particles.

The structure effects of P25 particles to TNTs transition were further investigated by the N_2 adsorption/desorption isotherm. As P25 is converted into TNTs, there is a remarkable increase for S_{BET} from 49.7 to 381.9 m^2/g and for pore volume from 0.05 to 1.02 cm^3/g. This significant increase in surface area and pore volume mainly results from the formation of tubular nanostructures.

3.2. Rheological properties of ER suspensions

To study the dynamic characteristics of microstructures formed in ER suspension, oscillatory shear tests were performed. Figure 1 depicts storage modulus, G', and loss modulus, G'', versus strain for TNTs fluid under various electric field strengths. Without an electric field, the suspension shows liquid-like behavior, i.e. viscosity is dominant over elasticity and G'' is larger than G'. When an electric field is applied to the TNTs suspension, both G' and G'' increase rapidly with the electric field strength over the whole strain range, but G' becomes significantly higher than G'' in the linear viscoelastic region. Especially in the case of E = 2.0 kV/mm, G' is higher than that at zero electric filed by four orders of magnitude. This dramatic change in rheological properties arises from the formation of chain-or column-like structures in TNTs suspension. Under an external electric field the polarized TNTs particles attract each other due to dipole-dipole interactions to form particle chains

along the field direction. These chain-like structures make the suspension in the electric field to behave as solid at small strains. With increasing E the particular microstructures become stiffer to sustain the larger strain, and the elasticity dominates viscosity (i.e. $G' > G''$) in the linear viscoelastic region. However, as the strain is increased, the chains experience continuous deformation and finally destruction occurs above some critical value, and the TNTs suspension starts to flow demonstrating viscous behavior (i.e. $G'' > G'$) [9,10]. Note that with increasing E linear viscoelastic region is shorter and the critical strain becomes lower, indicating the particle chain-like structures are also fragile at relatively small strain.

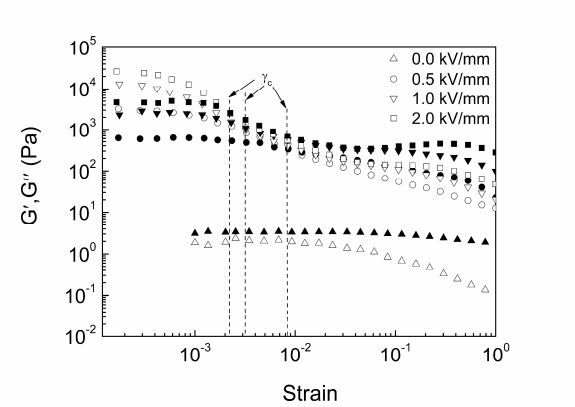

Figure 1. Strain dependence of G' and G'' for 5 vol.% TNTs ER fluid under different electric field strengths: open symbols for G', solid symbols for G''.

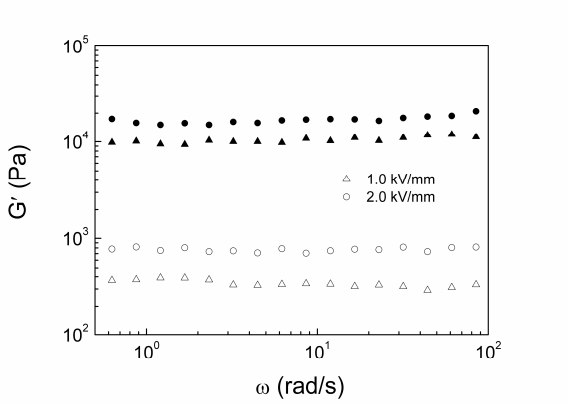

Figure 2. G' as a function of frequency at E = 1.0 and 2.0 kV/mm for both suspensions: open symbols for P25, solid symbols for TNTs.

The structural effect of P25 to TNTs transition on viscoelastic properties of both fluids are also reflected in figure 2. It is evident that G' for TNTs fluid is much higher than that for P25 fluid. As mentioned above, TNTs possess larger aspect ratios and higher surface area than P25, which may bring about large interfacial polarization of TNTs in suspension. Larger interfacial polarization in turn merits the optimal ER effect. Therefore, the stronger polarizability of TNTs particles in ER fluid induced by the electric field results in the stiffer chain structures showing a large G' than that of P25 fluid in the linear viscoelastic region. Similar behavior of TNTs in steady shear was also observed in [6].

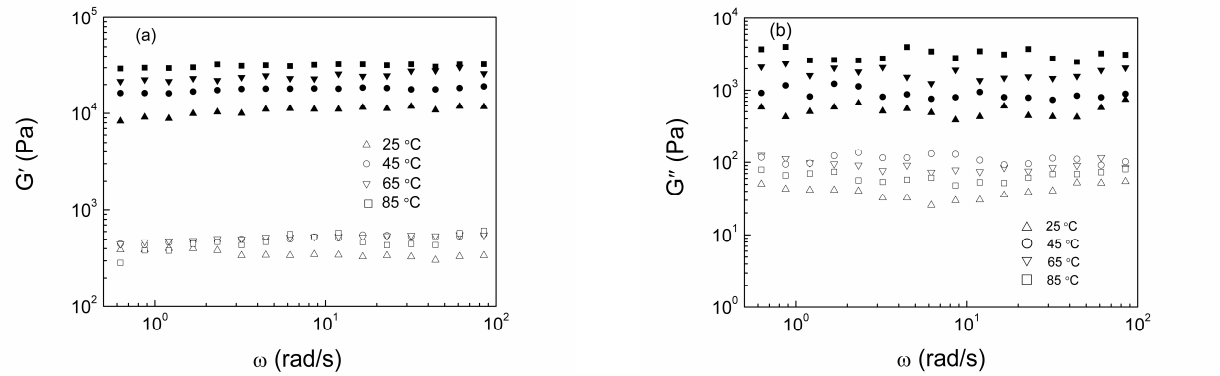

Figure 3. Dependence of storage modulus G' (a) and loss modulus G'' (b) for both suspensions on frequency at various temperatures (E = 1.0 kV/mm): open symbols for P25, solid symbols for TNTs.

Viscoelastic properties are also influenced by the temperature. G' and G'' dependence on frequency for both suspensions at various temperatures, T, is shown in figure 3. As can be seen, G' for TNTs fluid is

larger than that for P25 fluid at the same E and T, and it is nearly independent of frequency. With increasing T, G' for TNTs fluid increases whereas that for P25 fluid does not follow this trend; and there is no distinct difference in G' between 45 and 85 °C. Meanwhile, G'' for both fluids shown in figure 3b also shows similar change with T. Usually, the temperature effect on the rheological properties of ER suspension includes the heat-induced change of polarization behavior and the thermal convection of fluid [11,12]. Recent study [6] indicates that the temperature positively affects the dielectric or polarization properties of Na-titanate nanotubes based suspension. Thus, the heat-induced polarization is dominant and the chain structures become more rigid with increasing T, manifested in an increase of G'. As for P25 fluid, with increase T the thermal convection of fluid dominates gradually to weaken the structures formed by polarized P25 particles, so G'' start to decrease at higher temperature (e.g. 85 °C).

Conclusions

Hydrothermal treatment of P25 in a NaOH solution results in the formation of TNTs with large surface area. This TNTs based fluid exhibits typical viscoelastic behavior under applied electric field. In comparison with P25, TNTs fluid shows larger G' in the linear viscoelastic region, which originates from the large aspect rations and high surface area of TNTs. Furthermore, the temperature plays a different impact on the dynamic modulus of both suspensions due to their variously inherent chemical structure. Investigation of ER properties of TNTs fluid will further favor the optimization of 1D ER materials.

Acknowledgements

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