Modern Physics Letters B
Vol. 26, No. 13 (2012) 1250079 (7 pages)

DOI: 10.1142/S0217984912500790

LANTHANUM TITANATE NANOPARTICLES ER FLUIDS WITH HIGH PERFORMANCE

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Received 26 September 2011
Revised 29 February 2012

A new type of electrorheological (ER) fluid consisting of lanthanum titanate (LTO) nanoparticles is developed. The ER fluids were prepared by suspending LTO powder in silicone oil and the particles were fabricated by wet chemical method. This ER fluid shows excellent ER properties: The static yield stress reaches over 150 kPa under 5 kV/mm with linear dependence on the applied DC electric field, and the current density is below 10 μA/cm^2. In order to investigate the affect factor on the ER behavior, the LTO powder were heated under different temperatures. The ER performances of two particles treated under different temperatures were compared and the composition changes for those particles were analyzed with TG-FTIR technique. It was found that the static yield stress of the suspensions fell from over 150 kPa to about 40 kPa and the current densities decreased prominently as the rise of the heating temperature. TG-FTIR analysis indicated that polar groups remained in the particles such as alkyl group, hydroxyl group and carbonyl group etc., contribute to the ER effect significantly. The experimental results are helpful to understand the mechanism of the high ER effect and to synthesize better ER materials.

Keywords: Electrorheological fluid; nanopowders; yield stress.

1. Introduction

Electrorheological fluid is a kind of novel intelligent materials consisting of micron or nanometer scale solid particles with high dielectric property and insulated oil. Under an external electric field, the apparent viscosity of ER fluids will rise rapidly and reversibly,[1–4] and transforms from liquid-like to solid-like state due to chain structure of polarized particles. The ER fluids will come back to the low viscosity state when the electric field is removed. Because of the continuous controllable and reversible ER properties, the ER fluids have attracted a lot of attentions.[5–7]

To satisfy the requirement of the application for an ER fluid, the shear stress should be high enough and the leaking current density should be low under an electric field. A mass of ER materials including organic and inorganic particles[6–11] were created in past decades, especially after the giant ER effect was discovered.[12] A large number of polar molecule dominated ER materials were developed.[13–16] The yield stress of which has far broken the limit of the traditional ER fluids, and some of which reached over 200 kPa.[7,12,13,15] So the polar molecules or polar group contained in the particles could highly enhance the ER performance.

In this paper, we report a new type of ER fluids with suspending La–Ti–O (LTO) based powder in silicone oil, which possesses the properties of high shear stress and low current density. The analysis and the rheological behavior measurement of the samples indicate that polar groups remained in the particles, mainly hydroxyl groups, contribute to the giant ER effect.

2. Experiment

Nanometer scale LTO powders were prepared by a simple co-precipitation procedure.[17] 25 g Lanthanum chloride (Sinopharm Chemical Reagent Beijing Co., Ltd, AR) was dissolved in 200 ml deionized water, and 25 g oxalic acid (Sinopharm Chemical Reagent Beijing Co., Ltd, AR) and 20 ml tetrabutyl titanate (Sinopharm Chemical Reagent Beijing Co., Ltd, CP) were suspended in 600 ml absolute alcohol (Sinopharm Chemical Reagent Beijing Co., Ltd, AR), respectively. Then, the water solution was added to the alcohol solution drop by drop with strong stirring at 40°C. White precipitation appeared immediately in the mixed solution when the lanthanum chloride solution was dropped in. The suspension was aged in a water bath for 4 h at 40°C, and then the precipitation was filtrated, washed and dried in a drying oven at 50°C for 2 days and at 80°C or 120°C for 2 h. The morphology and size of the particles were detected by a field emission scanning electron microscope. The suspension was prepared by dispersing dried powders in silicone oil (10cSt, Beijing Huaer Co. Ltd., dried at 120°C for 2 h) in a mortar grinded for 2 h. The volume fractions of LTO particles in ER fluids were calculated from measured density 2.45 g/cm^2 of the powders by using a pycnometer (AccuPyc II 1340 Pycnometer, Micromeritics). The static yield stress was measured by using a rotational rheometer fabricated by our group. The rheometer was in a mode of parallel plates with 20 mm diameter and 1 mm gap and the yield stress was measured at a shear rate of 0.2 s^{-1}. The shear stress versus shear rate at zero electric field was measured using Anton Paar Physica MCR 501 rheometer with concentric-cylinders mode. In the measuring cell, the outer cylinder was fixed and the cylindrical rotor immersed into it. The diameter and the length of cylindrical rotor were 16.660 mm and 24.956 mm, respectively and the diameter of outer cylinder is 18.074 mm in our experiment. The relation of shear stress and shear rate in the case for applied electric field was measured with a home made rheometer using concentric-cylinders mode. The diameter and the length of interior cylinder were both 20 mm and the gap between the cylinders was 1 mm. In order to avoid the slide at electrodes the surfaces of the electrodes in both parallel plates mode and concentric-cylinders mode were all coated with diamond grains[17] for measuring the yield stress or shear stress versus shear rate at applied electric field.

To study the influence of the drying temperature, TG-FTIR co-analysis was conducted.[18] The sample was put in thermo gravimetric analyzer (NETZSCH STA 409C), and the gases vaporized during the TG analysis process were transformed into a FTIR spectrometer (Thermo Nicolet Nexus 670 FTIR Spectrometer) through a heated pipe for getting FTIR spectra of the decomposition products synchronously. Coupling the TG curve and IR spectra we can identify the components of decomposition products at a specified temperature.

3. Results and Discussion

The SEM photograph of LTO particles dried at 120°C is shown in Fig. 1. It can be seen that the grain size is about 100 nm with polydisperse and irregular shape. The atomic ratios of C, O, Ti and La in the sample are 38.56%, 48.81%, 4.84% and 7.80%, respectively, detected with EDAX technique.

All the electrorheological data was collected at room temperature. Figure 2(a) shows the static yield stress of the LTO/silicone oil ER fluids with solid volume fraction of 60%, of which the particles were dried at 80°C and 120°C, respectively. The relation of the shear stress and shear rate for the sample dried at 80°C at zero fields is shown in the inset of Fig. 2(a), in which the shear stress versus shear rate at 1000 V/mm is also shown for a comparison. The yield stress of both sample rises

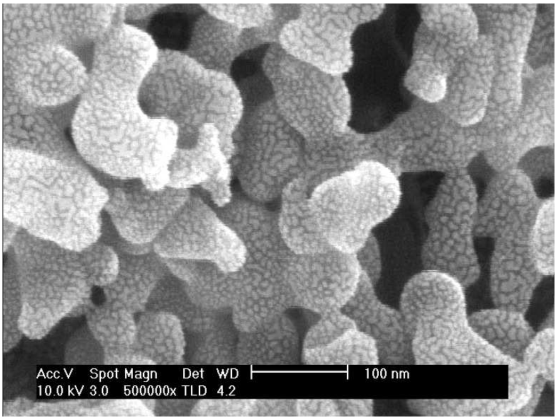

Fig. 1. SEM photographs of La–Ti–O (LTO) nanoparticles dried at 120°C. The light island shape spots on the surface of LTO particles are Aurum particles sprayed to enhance the conductivity of LTO particle for SEM measurement.

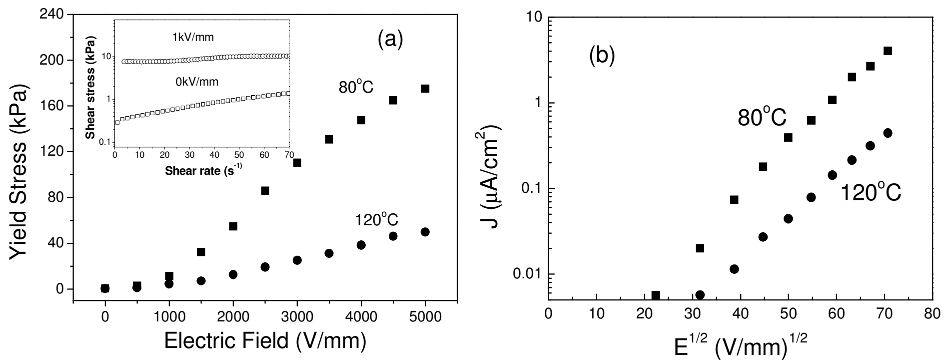

Fig. 2. (a) The relation of yield stress versus electric field (b) the behavior of current densities versus sqrt(E) of ER fluid for the La–Ti–O (LTO) powder dried at 80°C and 120°C with the volume fraction about 60%. The inset of Fig. 2(a) shows the shear stress versus shear rate at zero field and 1 kV/mm for the sample dried at 80°C.

lineally with the increase of the applied DC electric field. The yield stress can reach about 170 kPa at 5000 V/mm for the sample consisted of powders dried at 80°C and that is much lower, about 40 kPa at 5000 V/mm, for the sample dried at 120°C. The electric current densities of these two samples shown in Fig. 2(b) decrease with drying temperature increasing, 6 $\mu A/cm^2$ and 0.4 $\mu A/cm^2$ for the samples dried at 80°C and 120°C under applied electric field 5000 V/mm, respectively. There is nearly one order difference on the current density J for the ER fluids consisted of the particles treated at different temperatures.

The shear stress varying with shear rate is difficult to be measured at higher shear rate with a conventional rheometer, because the samples in between electrodes will be squeezed out and thrown off if they are tough to a certain degree, above 10 kPa for instance. Although, efforts have been made to measure the behavior of PM-ER fluids at high shear rate with a sealed or confined rheometer,[14,15] of which the results must contain additional factors. Instead, we measured the dependences of shear stress on shear rate for the LTO sample dried at 120°C with volume fraction of 45% at different electric field as shown in Fig. 3.

The high yield stress and the current density following an exponential dependence with the square root of the field indicate that LTO based ER fluid does not belong the conventional dielectric ER fluid,[19] but the polar molecule dominated ER (PM-ER) fluid.[12,15] The apparent difference of the ER performance arising from the treating temperature of the particles implies that the LTO powder's components and structure may appear a remarkable change with the temperature.

The TG-FTIR results are shown in Figs. 4 and 5. TG curves illustrated in Fig. 4 show that when the temperature climbs over 100°C, the TG curve of 80°C dried powder declines rapider than that of 120°C dried one. Obviously, in between 100°C to 150°C, a decomposition procedure occurs for the powder dried at 80°C. This is also demonstrated by the simultaneous FTIR analysis in same temperature

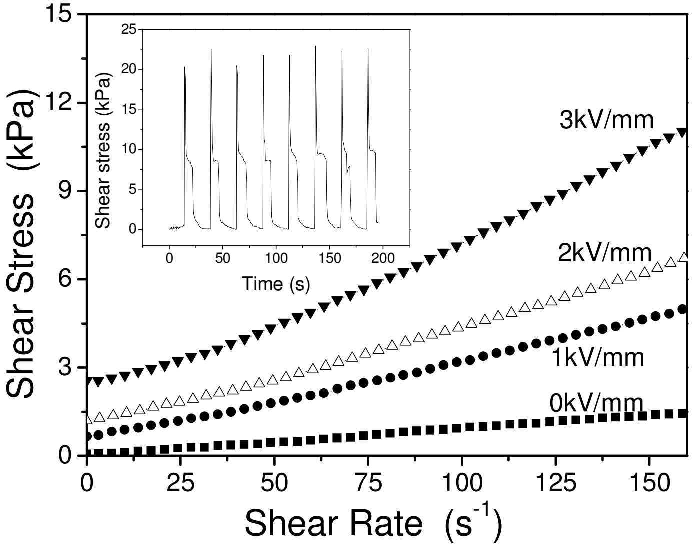

Fig. 3. The shear stress versus shear rate of the sample dried at 120°C with volume fraction of 45% at different electric field. Inset is the shear stress in an on/off mode of 3 kV/mm field at shear rate 3.6 s^{-1}.

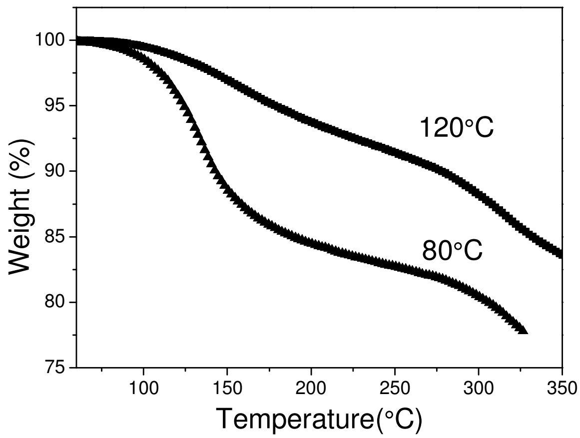

Fig. 4. TG curves of LTO particles dried at 80°C and 120°C.

region showing a fast increase of the decomposition products. The FTIR spectra of decomposition products vaporized from the TG measurement at 120°C for the particles dried at 80°C is illustrated in Fig. 5(a). Compared with the standard FTIR spectra of CO_2 and water [shown in Figs. 5(b) and 5(c)], it can be concluded that all the decomposition products between 100°C to 150°C are water and CO_2. Combining the TG and FTIR results, we evaluated that some components of polar

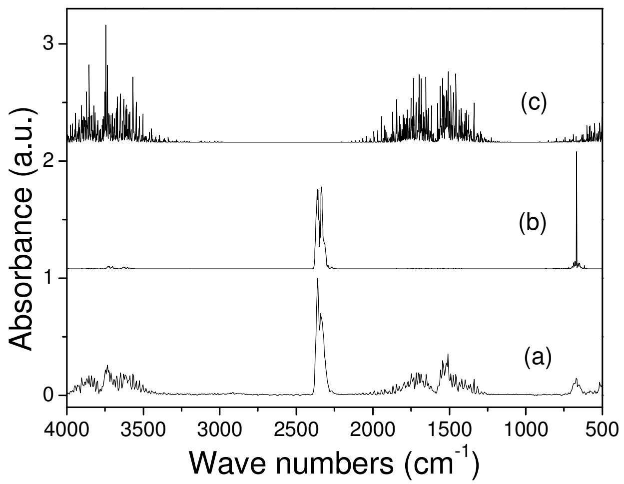

Fig. 5. FTIR spectra: (a) Gases vaporized at 120°C of 80°C dried LTO powder; (b) CO_2; (c) water.

group such as alkyl group, hydroxyl group and carbonyl group are decomposed to form water and CO_2 during the heating process. Both the ER behavior and the TG-FTIR analysis prove that the high performance of the LTO based ER fluid comes from the polar groups in the particles. The lower yield stress for the ER fluid consisted of the particles dried at 120°C is due to that some polar groups, mainly hydroxyl, are lost during the drying procedure at higher temperature. With the decrease of polar groups in the particles, the ER effect falls down quickly, but the current density decline.

4. Conclusion

La–Ti–O (LTO) based ER fluids with high performance have been developed through a simple convenient and cheap wet chemical method, and the ER properties may reach the demand of potential applications. By analyzing the samples heated at different temperatures and studying their ER behavior, it is indicated that polar groups remained in the particles such as hydroxyl group etc., contribute to the ER effect significantly.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Grant Nos. 10674156 and 11174332), the National Basic Research Program of China (Grant No. 2009CB930800), the Knowledge Innovation Project of Chinese Academy of Sciences (Grant No. KJCX2-YW-M07), and the Instrument Developing Project of the Chinese Academy of Sciences (Grant No. YZ200758).

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