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Synthesis and magnetorheological effect of Fe3O4-TiO2 nanocomposite

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Abstract. Aimed to obtain a material with improved rheological property, the Fe_3O_4-TiO_2 nanocomposites were prepared by a modified sol-gel processing. The structure and morphology of the Fe_3O_4-TiO_2 nanocomposites were examined by transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis and Fourier transform infrared spectroscopy (FT-IR) analysis, etc. The magnetic property and the magnetorheological properties of the coated particles were also examined in detail. The experimental results demonstrated that such materials exhibited favorable magnetorheological (MR) effect, and the MR performance of them were dependent on the relative content of TiO_2 in the composite.

1. Introduction

The rheological properties of some fluids can be reversibly modified in the presence of an external field, such as electrorheological (ER) fluids and magnetorheological (MR) fluids. The ER fluids and MR fluids, known as smart liquids for their apparent viscosity capable of experiencing a rapid, reversible change upon application of an external electric field or magnetic field [1-3], have potentially important application in numerous electromechanical devices, such as valves, dampers, and clutches in the automotive and robotics industries, etc. Recently, Wen and other researches [4-6] reported a theoretical research on the electro-magneto-rheological (EMR) effect, the combination of an ER effect and a MR effect, which provides us with a new strategy to control the rheological properties of fluid materials. Although the results for the theoretical research were inspiring, the experimental research on EMR fluids was less reported until now.

In general, the desired particles used in MR or EMR suspensions should have both tiny or no coercive force and large saturated magnetization strength (M_s), such as carbonyl iron, ferrite (including Fe_3O_4) and their composites etc. [7-9] Due to large saturated magnetization strength, Fe_3O_4 nanoparticles have been widely used to form ferrofluids and MR fluids. However, unmodified Fe_3O_4 nanoparticles usually incline to aggregate into the clusters, have poor ability of anti-oxidation and poor thermal stability. To overcome this problem, the coating processing with insulating oxide on the magnetic nanoparticles was usually employed. In this paper, we report a novel composite, a simple chemical synthesis to coat Fe_3O_4 nanoparticles with TiO_2 layer. The TiO_2 dielectric coating was fulfilled by a modified sol-gel process and the thickness of coating layer was governed by solution concentrations and processing durations. The TiO_2 coating on magnetic nanoparticles was beneficial to minimize aggregation of Fe_3O_4 nanoparticles and therefore, improve the chemical stability and thermal stability, keeping Fe_3O_4 nanoparticles from oxidation. What is more, it also enhance the dielectric response of the nanoparticles. As a result, Fe_3O_4-TiO_2 composites can possess both dielectric and magnetic properties simultaneously with improved stability, which make it an ideal candidate for using in EMR fluid. The Fe_3O_4-TiO_2 nanocoposites were often used as magnetic photocatalyst, but their MR or EMR properties were less reported until now. In the paper, we report the MR effect of Fe_3O_4-TiO_2 nanocomposites based MR fluids. The EMR performance of the materials will be reported later.

2. Experimental

2.1 Preparation of Fe_3O_4-TiO_2 nanocomposites

The nanosized Fe_3O_4 particles were prepared by a chemical coprecipitation method [10]. The Fe_3O_4 nanoparticles were coated with TiO_2 by a modified sol-gel method. In a typical coating procedure, a suitable amount of magnetite particles dispersed in ethanol was ultrasonic for 1h, then, $Ti(OR)_4$, polyethylene glycol, diethylamine and water were slowly added into the mixture. The reaction was allowed at room temperature for 3h under continuous stirring. And then the reaction was continued at 85°C in a rotary evaporation meter to make the solvent fully evaporating. Finally, the resultant powder was heat treated at 100 °C for 8h to remove any trace of water. Here, diethanolamine was used as an additive to prevent the precipitation of titanium butoxide from the alcoholic in the presence of excess water. PEG was added to increase the content of surface hydroxyl in the composite.

2.2 Characterization and measurement

The morphologies of the samples were investigated by transmission electron microscopy (TEM, JEM JEOL-2010). The crystal phase of the prepared products were analyzed by X-ray powder diffraction (XRD, Model Japan Rigaku D/max-γA K_{II} , Cu-target, λ = 0.1541nm). The TEM photographs and XRD patterns reveal that the Fe_3O_4 nanoparticles with diameter about 10nm were completely covered by the amorphous TiO_2 layers. The densities of the particles were measured with a pycnometer by dispersing particles in silicone oil. The densities of the coated particles change from 2.36 to 2.83g/cm^3 with different TiO_2 content, which are far less than the density of Fe_3O_4 4.25g/cm^3. Low particle density is beneficial to the stability of MR fluids.

The chemical structure was determined by a Nicolet Dx-10 Fourier transform infrared spectroscopy (FT-IR) spectrophotometer. The hystersis cycles of magnetite nanoparticles and Fe_3O_4-TiO_2 composites were recorded at room temperature by using a vibrating-sample magnetometer (VSM, EG&G Princeton Applied Research Vibrating Sample Magnetometer, Model 155). An Anton Paar Physica MCR301 rheometer in parallel-plate configuration was used to measure rheological properties of the composite. All the experiments were conducted at the room temperature.

3. Results and Discussion

3.1 Structure and magnetic properties

Figure1 shows the FT-IR spectra of (a) the mixture of Fe_3O_4 and TiO_2 (b) and Fe_3O_4-TiO_2 nanocomposites respectively. The spectrum (a) shows that the broad band around 3413cm^{-1} is the asymmetric and symmetric stretching vibrations of O-H group, whereas the band around 1636cm^{-1} is the H-O-H bending of the coordinated water, the band at 1451 cm^{-1} and 1384 cm^{-1} is the bending vibrations of C-H group, the band at 1087 cm^{-1} and 950cm^{-1} is the charateristic vibrations of Ti-O-C group, and the band at 500-700 cm^{-1} is attributed to the Ti-O-Ti or Fe-O stretching vibrations. In comparing the two spectra in Figure1, it is noted that although the two spectra are similar as a whole, there are some observable differences as marked on spectrum(b), the band at 3413cm^{-1} in spectrum(a) shift to 3385 cm^{-1} in spectrum (b) , and getting into broader, whereas the band at 1636 cm^{-1} in spectrum (a) shift to 1627 cm^{-1} in spectrum (b) and a new peak appeared at around 890 cm^{-1}. So, we infer there must exist some interactions between the Fe-OH and Ti-O-Ti band, the interaction make them uneasy to separate.

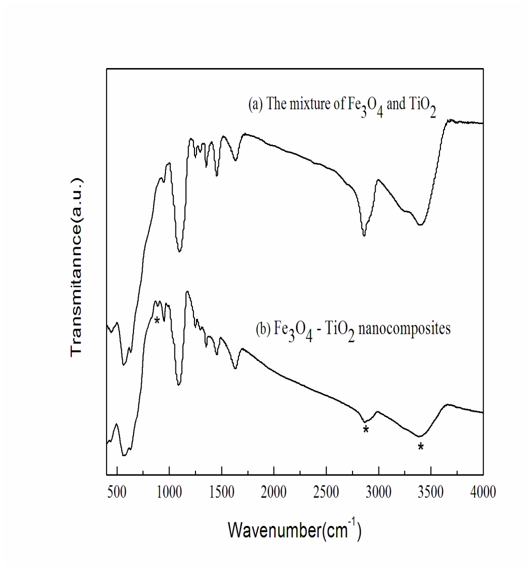

Figure 1. FT-IR spectra for (a) the mixture of Fe_3O_4 and TiO_2 (b) Fe_3O_4-TiO_2 nanocomposites

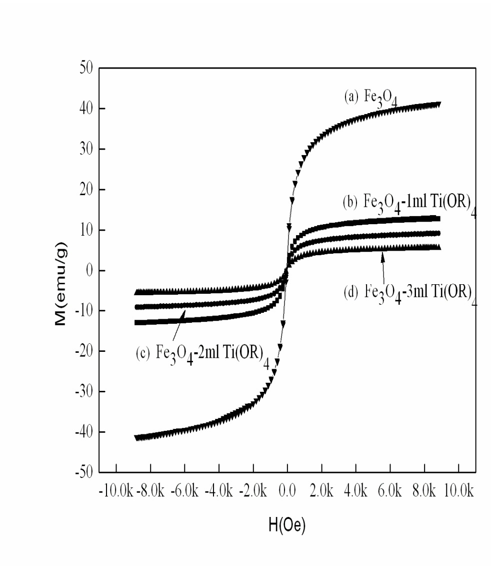

Figure 2. Hysteresis loops of Fe_3O_4 nanoparticles and Fe_3O_4-TiO_2 nanocomposites at room temperature

The hysteresis loops of Fe_3O_4 nanoparticles and Fe_3O_4-TiO_2 nanocomposites are shown in Figure 2. For Fe_3O_4 nanoparticles, saturated magnetization (M_s), remmant magnetization (M_r) and coercive force(H_c) are estimated to be M_s= 41.6emu/g, M_r=0, and H_c=0. No hysteresis loop is observed, indicating a super paramagnetic behavior. For composite structures with 1ml $Ti(OR)_4$ precursor, its saturated magnetization was 12.9emu/g. With the increasing of the TiO_2 content in the composite, the saturation magnetization of the particle decreases. Moreover, these saturation magnetization values are inevitably much lower than that of pure Fe_3O_4 particles, which is consistent with the mass proportion of the magnetite nanoparticles in the coated particles. In addition, Fe_3O_4-TiO_2 nanocomposites also show super paramagnetic character. These particles having no coercivity seem to give a distinct switching response of the MR effect if the field is switched on and off, respectively, which is beneficial to its applications in MR fluids.

3.2 MR effect

MR fluids of pure Fe_3O_4 and Fe_3O_4-TiO_2 nanocomposites at a concentration of 30 wt% in silicone oil were prepared. Rheological behavior of MR suspensions was investigated under steady shear flow and static magnetic field. Figure 3 shows the response of shear stress with shear rate for the Fe_3O_4-TiO_2 nanocomposites based suspension with and without magnetic field. The induced magnetic moment of the particle caused by an applied magnetic field is parallel to the field direction. The MR suspension exhibited significant rheological properties in the range of shear rate from **.1 1/s to .100 1/s**. The flow behavior of suspensions made of Fe_3O_4-TiO_2 nanocomposites only shows a slight departure from Newtonian fluid without the magnetic field. With the application of magnetic field, the MR fluids exhibit the Bingham plastic behavior and the shear stress increases with the increasing of the magnetic field strength.

Figure 4 shows the effects of the TiO_2 contents on MR properties of the Fe_3O_4-TiO_2 nanocomposites based MR fluids. It can be seen that the MR fluid of the composites with 1ml $Ti(OR)_4$ precursor showed the largest shear yield stresses over the other composites based MR fluid due to the higher iron oxide content. However, the composites based MR fluids show significant improved shear stress compared with that of pure magnetite nanoparticles. The possible reason maybe the outer

TiO_2 layer inhibiting the direct contact of Fe_3O_4 particles, which facilitate the particle orientation and the rearrangement upon a magnetic field and make it easy to recover the normal state of dispersion after the removal of the field. In addition, sufficient active groups on the surface of particles promote the surface activity, which further promote the MR performance. However, with the increasing of TiO_2 content in coated particles, the magnetic property decreases, which reduced the MR performance accordingly. So, in this report, the MR fluid of the composites with 1ml $Ti(OR)_4$ precursor showed the optimum shear yield stresses over the other Fe_3O_4-TiO_2 nanocomposites based MR fluid.

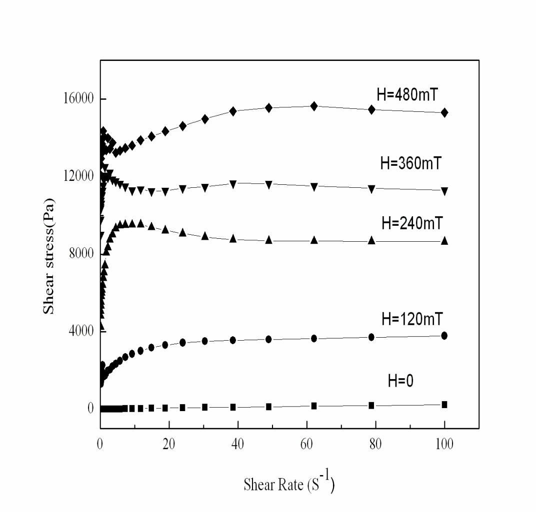

Figure 3. Influence of shear rate on shear stress for Fe_3O_4-TiO_2 nanocomposites based MR fluids under various magnetic fields

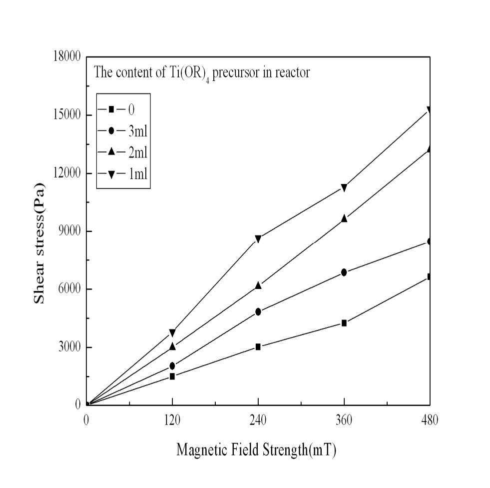

Figure 4. Effects of the TiO_2 contents on MR properties of the Fe_3O_4-TiO_2 nanocomposites based MR fluids.

4. Conclusions

A novel composite, Fe_3O_4-TiO_2 (TiO_2-coated Fe_3O_4) nanocomposites were prepared by modified sol-gel method. The FT-IR spectra infer the existence of interaction between Fe_3O_4 and TiO_2. The Fe_3O_4-TiO_2 nanocomposites show a superparamagnetic, without coercivity or remanence at room temperature, the magnetic property of the particles can be adjusted by the relative content of Fe_3O_4 and TiO_2. The MR fluids containing such materials in silicone oil show significant improved shear stress compared with that of pure magnetite nanoparticles, the shear stress of composite based MR fluids decreases with the increasing of the relative content of TiO_2.

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