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Synthesis and rheological investigation of a magnetic fluid using olivary silica-coated iron particles as a precursor

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ABSTRACT

A new type of magnetic fluid was prepared by dispersing monodispersed iron–silica ($Fe–SiO_2$) composite particles in polyethylene glycol (PEG) 400. The composite particles $Fe–SiO_2$ were synthesized by hydrogen reduction from α-Fe_2O_3–SiO_2 spheres. Their microstructures were observed by a high-resolution transmission electron microscope (HRTEM) and the magnetism was characterized with a superconducting quantum interference device (SQUID) magnetometer. Both steady-state and dynamic rheological properties of the magnetic fluid under different magnetic fields were studied by using a rheometer. Experimental results show that this magnetic fluid has a relatively high magnetoviscous effect at low shear rates. The yield stress of this material shows an increasing trend with a magnetic flux density. Also, viscoealstic properties of such materials are different from conventional ones.

1. Introduction

Magnetic fluid is a kind of colloidal suspension with magnetic nanoparticles in a carrier liquid. The material exhibits the combination of both normal liquid behavior and magnetic controllable properties. This intelligent material has attracted much attention due to its potential applications in aviation, apparatus, industrial and biological fields, etc. Compared with other colloidal systems, the magnetic fluid is thermodynamically and hydrodynamically instable, which consequently prevents its applications. In order to stabilize magnetic particles in carrier liquids, many researches have focused on fabrication of ultrafine magnetic particles, which are expected to have good stabilization in carrier liquids, and high saturation magnetization as well. Magnetic Fe_3O_4 powders, which are non-toxic and easily synthesized, have been intensively investigated and used widely in traditional magnetic fluids. But their lower saturation magnetization and poor inoxidizability have limited some applications of magnetic fluid in technological fields. On the other hand, employing ferrite particles in magnetic fluid often leads to sedimentation and aggregation problems in use.

To overcome these shortcomings, recent efforts have been directed towards incorporating magnetic particles into core–shell structures and introducing them into the preparation of magnetic fluids. Core–shell composite particles are a class of high functional materials and they often exhibit improved physical and chemical properties [1]. The "shell" component, such as amorphous silica, can inhibit particles aggregation effectively and immunize the encapsulated species against environmental degradation effects while retaining their intrinsic properties [2]. Moreover, the nonspherical "core" component of the particles and their ordered assembly structures would endow the material with magnetic anisotropy character.

Up till now, some findings have been reported about the preparation and characterization of magnetic fluid containing core–shell magnetic particles [3–6]; however, synthesis of magnetic fluid using non-spherical core–shell magnetic particles, especially the investigation on its mechanical properties, has received much less attention. It has been reported that the size [7] and shape [8,9] of magnetic particles have a decisive influence on the rheological properties of magnetic fluid. In this paper, a novel kind of polyethylene glycol (PEG) 400-based magnetic fluid using olivary composite particles iron–silica ($Fe–SiO_2$) was successfully synthesized. The rheological properties of the magnetic fluid were characterized using a rheometer.

2. Experimental

2.1. Synthesis of $Fe–SiO_2$ olivary core–shell nanoparticles

Typical $Fe–SiO_2$ monodisperse particles were fabricated by hydrogen reduction from α-Fe_2O_3–SiO_2, which were synthesized

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by the “hard template” method based on hematite olivary particles. The preparation of α-Fe_2O_3–SiO_2 was detailed in our previous work [10]. The thickness of silicon shells was controlled by varying the concentration of TEOS precursor.

In the reduction process, the pre-synthesized α-Fe_2O_3–SiO_2 particles were placed in a quartz tube, and then heated to 600 °C in a H_2 atmosphere. After 6 h of reduction, the quartz tube was naturally cooled to room temperature in a H_2 flow. And then, the olivary Fe–SiO_2 particles were synthesized.

2.2. Preparation of Fe– SiO_2 magnetic fluid

To prepare Fe–SiO_2 magnetic fluid, PEG 400 and Fe–SiO_2 were mixed together, and the weight fraction of suspensions was about 10%. Due to the presence of negative charges on the surfaces of the silica-coated particles in neutral aqueous solution, the magnetic composite particles dispersed homogeneously in PEG 400 without the assistance of other surfactants. The mixture was milled and stirred for a moment. Finally, the Fe–SiO_2 magnetic fluid was obtained.

2.3. Characterization methods and magnetorheological measurement

The size and shape of the Fe–SiO_2 nanoparticles synthesized were observed from TEM image using high-resolution transmission electron microscope (HRTEM, JEOL-2010). The magnetization was characterized by a superconducting quantum interference device (SQUID, MPMSXL5) magnetometer in 300 K. To get a deep insight in the rheological properties of Fe–SiO_2 magnetic fluid and compare them with those of traditional ones, rheological measurements were undertaken, including the tests of the basic features of a magnetic fluid—the change of viscosity and dynamic yield stress with magnetic field strength, and the linear viscoelastic behavior. The investigation was done by an Anton Paar Physical MCR301 rheometer with a magnetorheological device. All the tests were conducted at room temperature of 25 °C.

3. Results and discussion

3.1. Characterization of Fe– SiO_2 olivary core– shell nanoparticles

Fig. 1 is the TEM image of Fe–SiO_2 particles. It is obvious to distinguish between the comparatively bright SiO_2 shells and dark Fe cores. The cores have distorted to small pieces inside the silica capsules after the hydrogen reduction. The thickness of olivary shells is about 10 nm. The hollow structures would endow the composite particles with low density, and this would be of advantage to confront sedimentation effects in a magnetic fluid.

The magnetic properties were measured in 300 K using a SQUID magnetometer. In Fig. 2, the saturation magnetization of Fe–SiO_2 composite particles is evaluated to be 48.56 emu/g at about 12,000 Oe, and the values of the coercive force and residual magnetization are 311.55 Oe and 4.45 emu/g, respectively.

3.2. Rheological characterization of Fe– SiO_2 magnetic fluid

Experimental studies [11] showed that the rheological properties of magnetic fluid are correlative to their microstructures. The magnetic particles would aggregate to form chain-like structures, which are parallel to the external magnetic field. Fig. 3 shows the magnetoviscosity effect of the magnetic fluid. The viscosity increased with the enhancement of magnetic flux density at low shear rates $\dot{\gamma}$. However, this phenomenon is not obvious any more

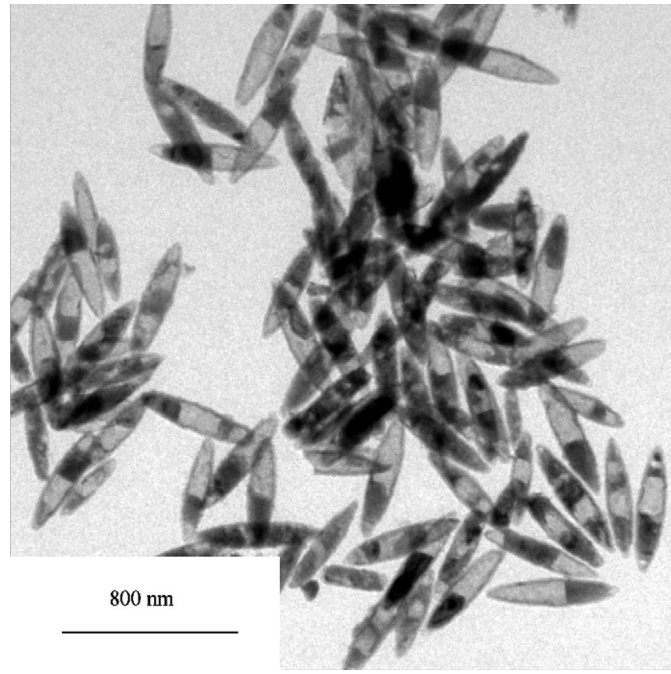

Fig. 1. TEM image of Fe–SiO_2 core–shell composite particles.

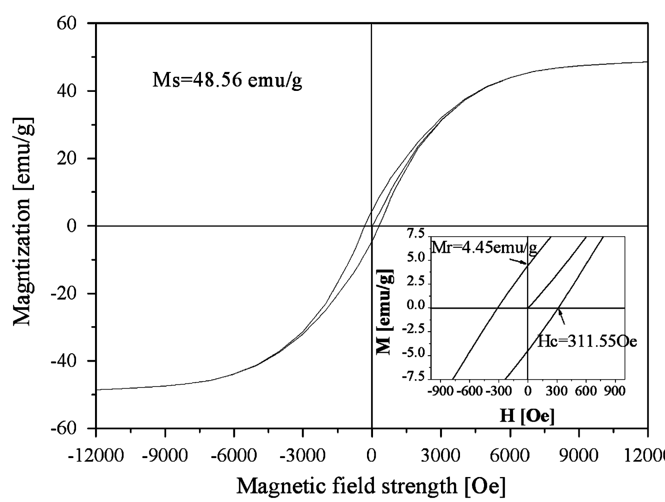

Fig. 2. Magnetic hysteresis loops of Fe–SiO_2 spheres.

when the shear rate $\dot{\gamma}$ was relatively high ($\dot{\gamma}>25\,s^{-1}$). It could be explained by the mechanism of the initial structures in the magnetic fluid [12]: the chain-like aggregates formed by the field would be diverted by the mechanical torque induced by the shear flow in the fluid; at the same time, the external magnetic field would give rise to a magnetic torque to counteract this action; when the shear rate was large enough such that the aggregate structures had been broken, the viscosity would not change any more with the increasing magnetic field.

Fig. 4 is the flow curve of the magnetic fluid under different magnetic fields. Without a magnetic field, i.e., $B=0$, the shear stress τ increases linearly with shear rates $\dot{\gamma}$, and the value (about 0.13 Pa) does not vanish when$\dot{\gamma}=0$, which implies that the magnetic fluid could not be simply described by the Newtonian model; for a magnetic field, i.e., $B>0$, the flow curve is no longer straight and it could be described by the “Herschel–Bulkley” model [13].

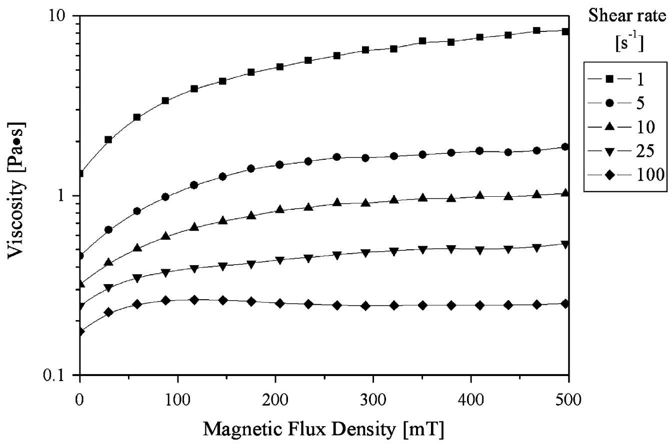

Fig. 3. The viscosity of the Fe–SiO_2 magnetic fluid as a function of magnetic flux density for different shear rates.

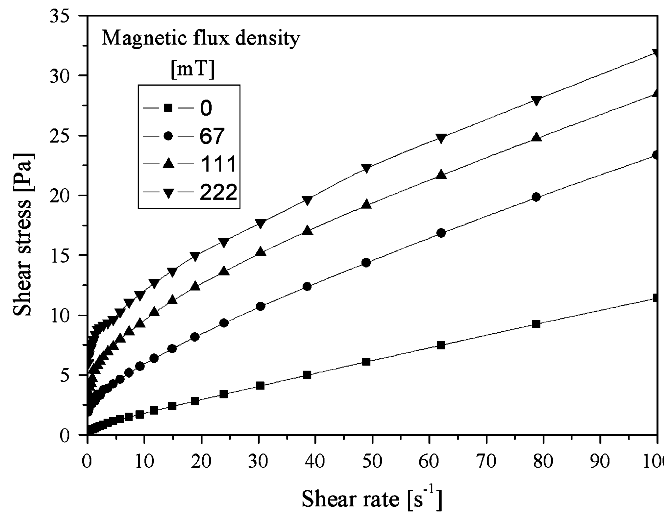

Fig. 4. The shear stress of Fe–SiO_2 magnetic fluid as a function of shear rates under different magnetic field.

The dynamic yield stress τ_y can be obtained by extrapolating the shear rate to zero from the flow curve. Fig. 5 is the variation of the dynamic yield stress τ_y with the external magnetic field. The plot reveals that τ_y increases as the magnitude of $B^{1.12}$, but not the same square of B as the behavior of other conventional magnetic fluids.

In order to compare the mechanical properties of Fe–SiO_2 magnetic fluid with the other conventional ones, an oscillating load [14] was subjected to the Fe–SiO_2 magnetic fluid and its response, in terms of the storage modulus, was studied in detail. Storage modulus represents the ability of a viscoelastic material to store elastic energy during deformation. The behavior of the standard magnetic fluid can be described by the Maxwell model when the magnetic field strength $H>0$, while become the Newtonian type for vanishing field [12]. This theory predicts that the storage modulus G' increases quadratically with increasing angular frequency ω for small values, and reaches a plateau for larger values. During the test, the strain amplitude was 0.001% in order to ensure that the deformation process of chain-like structures was on linear viscoelastic state. In Fig. 6, it is clearly seen that G' increases with ω in the testing range when $B>0$; however, the value of G' is a nonzero constant when $B=0$, which indicates that its viscoelastic behavior could not be described by the model of Newtonian fluid at this moment, because of the existence of faint interaction forces among the magnetic particles [12]. The distinction between the Fe–SiO_2 magnetic fluid and the conventional one could be ascribed to the big size and one-dimensional configuration of the Fe–SiO_2 magnetic particles which had much stronger interaction in the matrices. Moreover, the value of storage modulus G' and the slope of the lines both ascend with the increase of magnetic flux density, which demonstrated that the new structures strengthened by the external magnetic field would enhance the elastic component of complex modulus of the magnetic fluid.

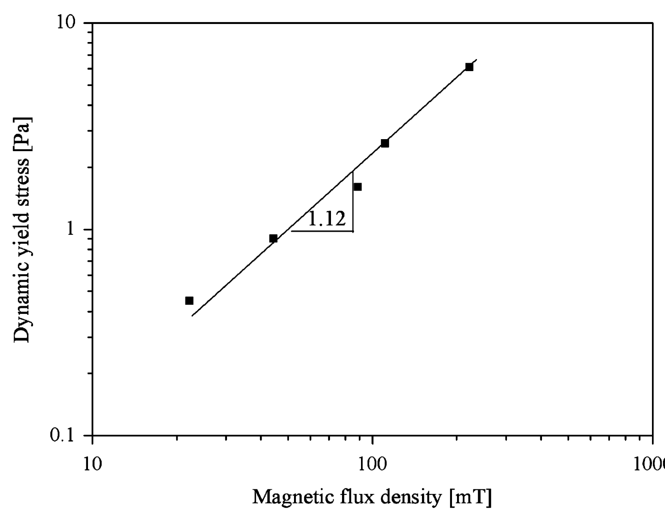

Fig. 5. The dynamic yield stress of Fe–SiO_2 magnetic fluid as a function of magnetic flux density.

4. Conclusion

In this study, the novel Fe–SiO_2 magnetic fluid was synthesized using Fe–SiO_2 nanoparticles as the magnetic phase and PEG 400 as the matrix. The particles are olivary silica capsules encapsulated iron pieces and have relatively high magnetization. Experimental results show that, the Fe–SiO_2 magnetic fluid exhibits relatively strong magnetoviscosity effect when the shear rate is less than $25\,s^{-1}$; besides, the yield stress of magnetic fluid increases as $B^{1.12}$ and its special linear viscoelastic properties which could not be simply described by the Maxwell model, both

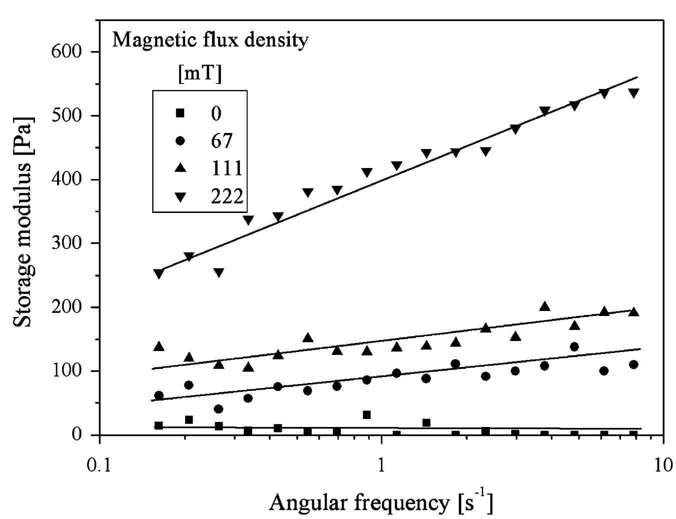

Fig. 6. The storage modulus of Fe–SiO_2 magnetic fluid as a function of the angular frequency of the oscillating load for different magnetic flux densities.

indicate the distinctive rheological characteristics of Fe–SiO_2 magnetic fluid. These may be due to the peculiar functional Fe–SiO_2 magnetic particles.

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