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Preparation of superparamagnetic Fe_3O_4/PMMA nano composites and their magnetorheological characteristics

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Abstract

Fe_3O_4/PMMA composite particles were fabricated by a simple one-pot hydrothermal method. The magnetic measurement showed that the composite particles displayed a higher saturated magnetization and superparamagnetic property. The rheological properties of the magnetorheological fluids (MRFs) based on Fe_3O_4/PMMA particles were measured on a rotational rheometer with a magnetic field generator. It was found that the MRFs exhibited better MR effect and sendimentary stability than the similar materials.

Keywords: Fe_3O_4/PMMA composite; Hydrothermal; Magnetorheological fluids

1. Introduction

Magnetorheological fluids (MRFs), first reported by Rabinow in 1948 [1], exhibit a continuous, rapid and reversible change in the rheological characteristics when subjected to sufficiently strong magnetic fields. MRFs have important applications in devices for torque transfer, which include brakes, clutches, dampers and mounts for use in semi-active or adaptive vibration control and snubbing [2–4]. Up to now, carbonyl iron powder is the major magnetic material to prepare MRFs. These MRFs are provided with good mechanic properties such as high shear stress, but with poor stability and sedimentation. The incompatible density of particles and dispersive medium used in MRF are the major reasons to cause poor stability. Many ways were introduced to solve these problems, for example, using chemical modification or encapsulate of inorganic particles with surfactant or polymer, adding non-magnetic particles such as macromolecule protein or nano particles such as Fe–Ni alloy or magnetite in MRF. These methods can partially improve the properties of MRFs [5–7]. However, the problems still cannot be solved completely, and it is necessary to do further research.

In the present paper, Fe_3O_4/PMMA nano composite particles have been synthesized by a simple one-pot hydrothermal method. Fe_3O_4 nano particles are dispersed well in PMMA to form bigger magnetic composite particles. These polymer composite particles have special functional groups in the surface, which can improve the interaction between suspension particles and matrix. The composite materials exhibit superparamagnetic property and have higher MR effects in our measurement.

2. Experimental

2.1. Preparation of Fe_3O_4/PMMA

$FeSO_4 \cdot 7H_2O$ 0.56 g and sodium laurylsulfonate 0.12 g were dissolved in 25 ml bi-distilled water to form colloid solution, then ammonium peroxydisulfate (APS) 0.12 g was added and ultrasonicated for 10 min to make ferrous sufficient adsorb into APS, then methyl methacrylate (MMA) 5 ml was added dropwise and continued ultrasonication for another 15 min to obtain uniform solution.

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Finally, ammonium hydroxide 5 ml was added and stirred violently, and the black processor solution was obtained. The processor solution was sealed in a Teflon-lined stainless-steel autoclave (45 ml capacity) and maintained at 130 °C for 4 h in an oven. After cooling to room temperature naturally, the black products were obtained, washed several times with distilled water and methanol, respectively and then dried in vacuum at 50 °C for 12 h.

2.2. Preparation of MRFs

The composite magnetic particles were dispersed ultrasonically into silicone oil without any surfactant to prepare MRFs of 37, 56 and 74 wt%, respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Philips XPERT diffractometer with Cu Kα radiation ($\lambda = 0.151478$ nm) at a scanning rate of 0.02°/s in the range of $2\theta = 10$–70°. Infrared curves were measured on a Bruker FTIR (EQUINOX 55) spectrum instrument. The morphology of the particles was investigated by scanning electron microscopy (SEM, Sirion 200). Crystallite size was investigated on transmission electron microscopy (TEM, Hitachi H-800) with an accelerating voltage of 200 kV. The powder was dispersed in methanol by sonication, and a drop was dripped on a support copper grid. MR characteristics were examined using a rotational rheometer (Physica, MCR 301, Anton Paar, Austria) with the magneto-rheological device at 25 °C for all tests. A parallel-plate measuring system (PP20) with a diameter of 20 mm was used at a gap of 1 mm.

3. Results and discussion

Typical synthesis of Fe_3O_4/PMMA composite materials was carried out in a hydrothermal system. The crystalline structure was characterized by XRD. As shown in Fig. 1(a), the reflection peaks can be easily indexed as cubic system of Fe_3O_4, and the baseline is heaved because of the existence of PMMA, which is consistent with the results of FTIR shown in Fig. 1(b). It was shown that a strong absorption band at 580 cm^{-1} related to the vibrations of the Fe–O functional group in both curves. The band of –CO–OR and $–CH_2–$ appeared at 1730 and 1436 cm^{-1}, respectively, in composite's curve without appearing the MMA monomer's –C = C– absorption, which confirmed that the polymerized action was accomplished.

Representative TEM and SEM images of the sample are shown in Fig. 2. It can be seen that the sample is composed of a large number of congeries, and the small magnetite particles dispersed well in polymer matrix. In addition, the as-synthesized composite particles are polycrystalline, based on the ED characterization inset in Fig. 2(b).

In order to research the rheological characteristics of the composite particles, the experimental procedure was designed as follows. Firstly, the influence of shear rate and magnetic field on the shear stress of MRFs is shown in Fig. 3(a) and (b), respectively. It can be seen that the shear stress increased with the shear rate and magnetic field strength, and the higher of the mass fractions, the higher of the shear stress. The yield stress for each condition can be obtained by extrapolating the stress values at zero shear rate. This MRF of 74 wt% shows yield stress of approximately 10 kPa at 102 kA/m, which is a relatively high value compared with other similar MRFs [8,9]. In addition, Fig. 3(b) shows that the shear stress increasing clearly at a higher concentration because of the magnetization saturation related to the concentration of magnetic particles.

Secondly, Fig. 4 shows the oscillatory behavior of MRF as a function of angular frequency. Storage modulus of MRF increased slowly and became more magnetic field dependent as the concentration decreased. It is because that the solid-like property was increased and the fluidity was reduced when the concentration was too high although the composite particles increased the yield stress. In addition, this composite has the advantage of good dispersion stability, which may improve the well-known sedimentation problem of commercial MR materials to some extent. Fig. 5 shows the dispersion stability of MR suspensions with different magnetic particles. Each

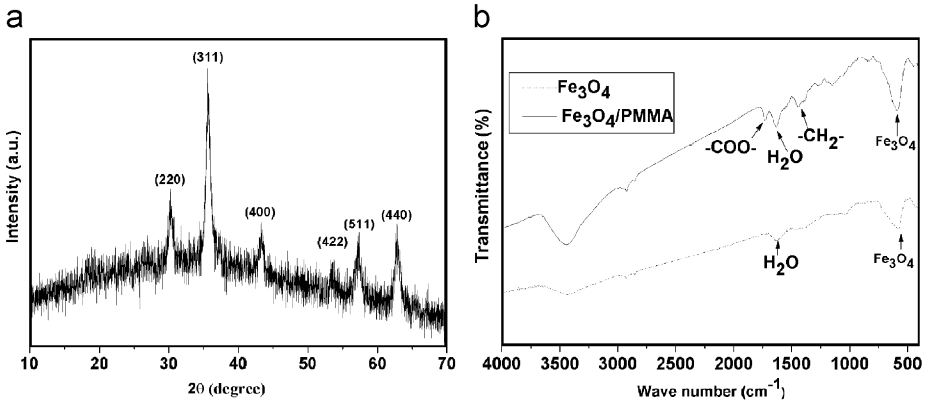

Fig. 1. (a) XRD patterns of Fe_3O_4/PMMA; (b) FTIR of Fe_3O_4 and Fe_3O_4/PMMA.

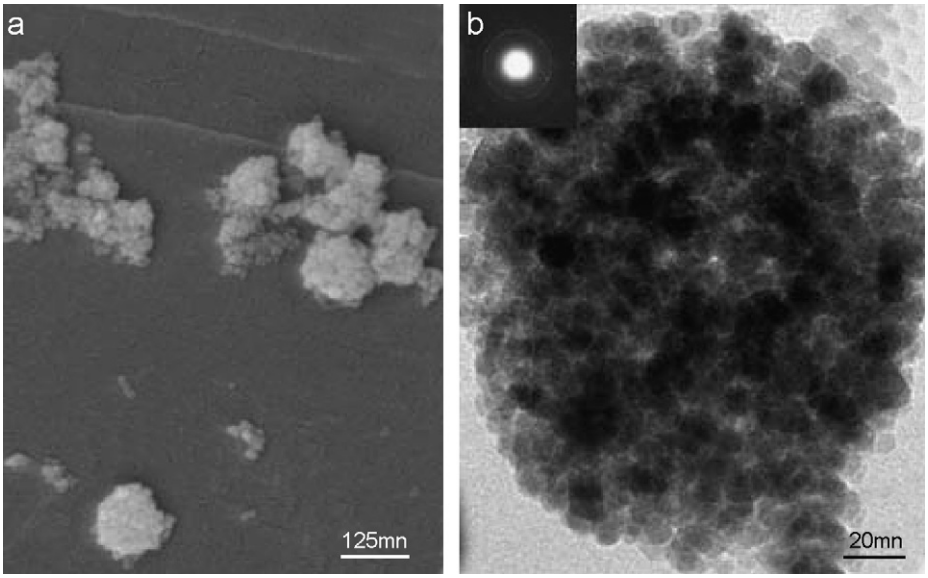

Fig. 2. (a) SEM and (b) TEM images of Fe_3O_4/PMM, the insert is the electronic diffraction of a composite particle.

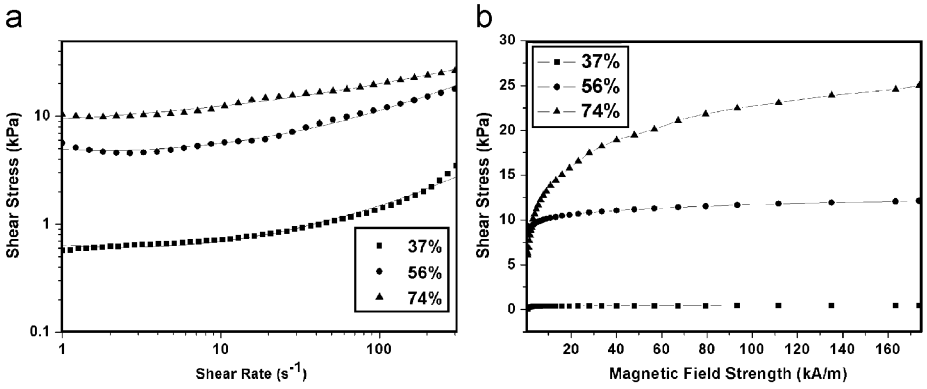

Fig. 3. Shear stress as a function of (a) shear rate and (b) magnetic field strength.

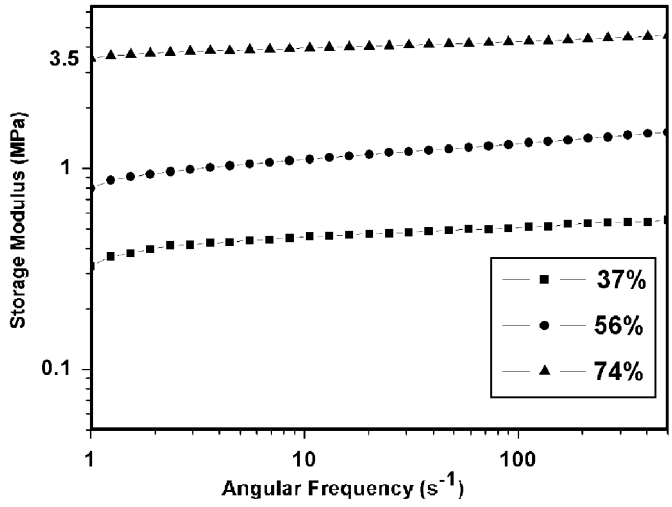

Fig. 4. Storage modulus as a function of angular frequency of different concentrations.

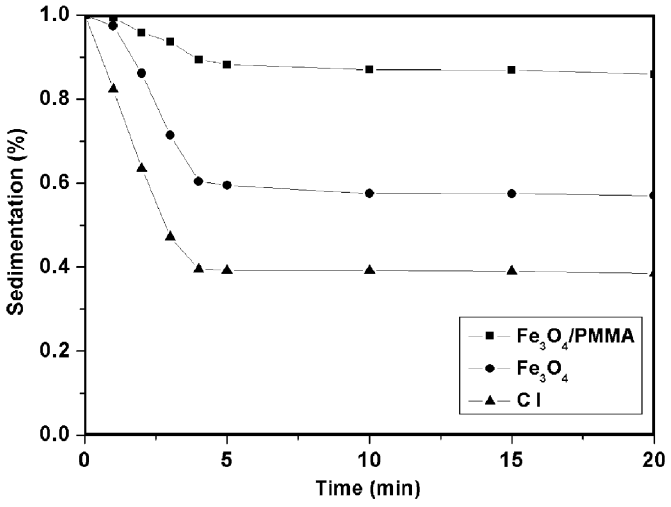

Fig. 5. Sedimentation ratio vs. time for MRFs of composite particles, magnetite and carbonyl iron.

suspension has the same mass fractions of 10% and is measured at the same rotation rate of 2500 rpm on a centrifugation equipment. The ratio of sedimentation is defined as

$$\text{Sedimentation } (\%) = \frac{\text{mass of the concentrated suspension}}{\text{mass of the entire suspension}} \times 100.$$

From Fig. 5 we can clearly see that the long-term stability of the composite particle suspensions was much better than that of the magnetite and carbonyl iron suspensions. This enhancement of dispersion stability is precisely due to the lower density of particles because of the actions of polymer components [10].

4. Conclusions

In conclusion, the Fe_3O_4/PMMA composite particles were synthesized by a simple one-pot hydrothermal method, and the magnetite dispersed well in the polymer matrix. MRFs based on the composite particles exhibited much higher yield stress and storage modulus compared with other similar materials. It is important that the stability of MRFs was enhanced because of the actions of PMMA, which also reduced the density of magnetic particles.

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