Preparation of magnetic Fe$_3$O$_4$/PAM composite microspheres by inverse emulsion polymerization

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The stable micro-aqueous groups (MAGs) were prepared by using sodium dodecyl sulfate (SDS) and sorbitan fatty acid ester (Span80) as emulsifiers. Fe$_3$O$_4$/PAM composite microspheres (CMPs) were obtained by inverse emulsion polymerization in MAGs. The experimental results showed that the size of the spherical Fe$_3$O$_4$/PAM CMPs was about 135-420nm and the saturation magnetization value of them was about 23.3emu/g. In the Fe$_3$O$_4$/PAM CMPs, the mass fraction of PAM was about 76.5%. The viscosity of the emulsion containing Fe$_3$O$_4$/PAM CMPs increased with the increase of current and decreased with the increase of shear rate.

1. Introduction

Over the years, the application and development of composite nanomaterials have gradually received continuous attention. Among them, magnetic composite microspheres (MCMPs) are particularly prominent [1-3]. MCMPs are composed of magnetic nanoparticles (MNPs) and a support material, where MNPs can provide a strong magnetic response and the support material can effectively prevent the agglomeration of particles. MCMPs have been widely studied in various biological applications such as drug delivery, micromachinery, magnetic resonance imaging and other fields due to the advantages of MNPs contained in MCMPS, such as superparamagnetization, high biocompatibility and high permeability [4-7].

There are many methods to prepare MCMPs, such as suspension polymerization and dispersion polymerization [8,9]. Recently, the preparation of MCMPs by inverse emulsion polymerization has been paid more and more attention [10-12]. This method can not only quickly and effectively prepare MCMPs, but also the process is relatively simple and the cost is relatively low.

Generally speaking, the preparation of MCMPs by inverse emulsion polymerization is primarily based on the formation of stable micro-aqueous groups (MAGs) at the interface between oil and water through the amphiphilic structure of surfactant molecules. It is precisely in MWGs that MCMPs are synthesized [13-15]. However, how to construct stable MAGs is rarely mentioned in the previous literature. In fact, only after the formation of sufficiently stable MAGs, it is possible to achieve polymerization reactions in them.

In this paper, the inverse emulsion containing stable MAGs was prepared by adjusting the dosage of sodium dodecyl sulfate (SDS) and sorbitan fatty acid ester (Span80). On this basis, Fe$_3$O$_4$ / PAM composite microspheres (CMPs) with good dispersity and magnetism were synthesized by inverse emulsion polymerization. The properties of Fe$_3$O$_4$/PAM CMPs were characterized and the effects of Fe$_3$O$_4$/PAM CMPs on the emulsion viscosity were studied.

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2. Experimental

2.1. Reagents

Acrylamide (AM) was purchased from Tianjin Da-mao chemical reagent Factory. Iron chloride tetrahydrate (FeCl$_2$·4H$_2$O), iron chloride hexahydrate (FeCl$_3$·6H$_2$O), SDS and potassium peroxodisulfate (KPS) were obtained from Sinopharm group chemical reagent Co. LTD. The manufacturer of Span80, toluene and ammonia was Shenyang Quan-rui Reagent Factory. All of the above chemical reagents were analytically pure, and were not re-purified before using.

2.2. Preparation of Fe$_3$O$_4$ particles and Fe$_3$O$_4$ / PAM CMPs

0.05M 10 mL FeCl$_2$ and 0.05M 20 mL FeCl$_3$ were added to the three-necked flask. After the reaction temperature was raised to 60℃, ammonia was added to the flask. Soon the solution turned black and Fe$_3$O$_4$ particles was prepared [16]. The reaction continued for 2 hours. The black Fe$_3$O$_4$ particles were collected and cleaned with distilled water 3 times for subsequent use.

An aqueous solution was prepared by adding 2.0g AM, 0.12g SDS and 0.43g Fe$_3$O$_4$ particles into 10mL water and dispersing them by ultrasonic wave for 15 minutes. At 2000 RPM, the aqueous solution was slowly added to a three-necked flask containing 2.88g Span80 and 30 mL toluene. After 1.5 hours, a black inverse emulsion was obtained which contained stable MAGs. Then nitrogen was injected into the emulsion for 0.5 hours to remove oxygen from it. When the temperature rose to 60℃, 0.03g KPS was added to the emulsion to initiate polymerization. After 4 hours of polymerization, Fe$_3$O$_4$/PAM CMPs was prepared in the inverse emulsion. The mass ratio of Fe$_3$O$_4$ to PAM was about 21.5%.

Because the obtained Fe$_3$O$_4$/PAM CMPs had a large interface energy and were easy to agglomerate, which may have a negative effect on their magnetic properties and dispersity, we selected anionic surfactant SDS as one of the emulsifiers. The objective was to make the surface of Fe$_3$O$_4$/PAM CMPs negatively charged by adsorbing SDS. This may reduce the agglomeration of Fe$_3$O$_4$/PAM CMPs under the action of the same charge repulsion. The synthesis diagram of Fe$_3$O$_4$/PAM CMPs was shown in Fig. 1. Fig. 1 (a) showed a negatively charged MAG by adsorbing SDS. Fe$_3$O$_4$ particles and AM were included in the MAG. After adding initiator KPS to the emulsion, the AM was polymerized in situ to PAM. At the same time, the MAG was transformed into negatively charged Fe$_3$O$_4$/PAM CMP, as shown in Fig. 1 (b).
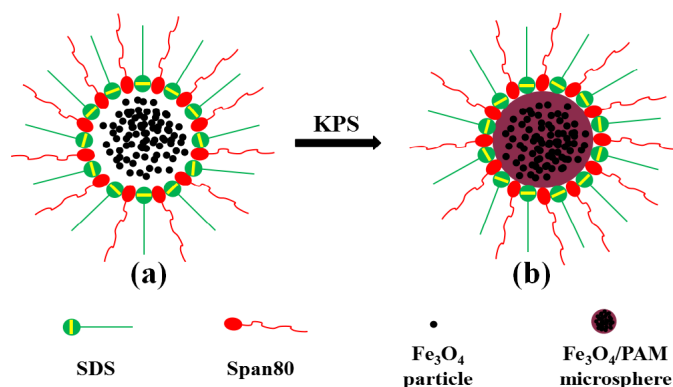

Fig. 1. The synthesis diagram of Fe$_3$O$_4$/PAM CMP.

2.3. Analytical methods

The inverse emulsion containing MAGs was added to a test tube and its stability was tested at room temperature for 95 hours. The emulsion stability parameter (Vt) was obtained by dividing the remaining emulsion volume in the test tube at a certain time by the initial emulsion volume in the test tube.

The Fe$_3$O$_4$/PAM CMPs were dispersed uniformly in ethanol by ultrasonic wave and then the morphology of them was observed by transmission electron microscopy (TEM, Hitachi H-600-

II, Japan).

The XRD data of the Fe_3O_4/PAM CMPs were tested by a diffractometer (Bruker D8 Discover 20kV, Cu Kα radiation).

The TGA data of the Fe_3O_4/PAM CMPs were tested by a thermogravimetric analyzer (DTG-60H, Shimadzu, Japan) at a heating rate of 10℃min^{-1}.

FT-IR spectra of the Fe_3O_4/PAM CMPs were tested using Fourier Transition infrared spectroscopy (Spectrum400, PerkinElmer, USA).

The magnetic data of sample were tested by a vibrating sample magnetometer (VSM, Lake Shore 7410, USA).

Viscosity data for emulsions containing Fe_3O_4/PAM CMPs were measured by a rheometer (MCR 301 physical-anton Paar, Austria).

After the Fe_3O_4/PAM CMPs were dispersed uniformly in ethanol by ultrasonic waves, the particle size distribution and average particle size of them were measured by a laser particle analysis system (ZetaPlus, Brookhaven Instruments Corporation, USA).

3. Results and discussion

It has been known from the previous discussion that stable MAGs were the key to the synthesis of Fe_3O_4/PAM CMPs by inverse emulsion polymerization. Since the MAGs existed in the inverse emulsion, it was necessary to prepare a stable inverse emulsion in order to obtain stable MAGs. According to relevant literature [17,18], usually when the hydrophilic lipophilic balance value (HLB) was 5.6-5.8, the stability of the inverse emulsion was very good. In view of this, 0.12g SDS and 2.88g Span80 were used as emulsifiers to prepare the inverse emulsion with HLB value of 5.73. Fig. 2 showed the stability curve of the inverse emulsion containing MAGs tested for 95 hours. In Fig. 2, the emulsion Vt value was always greater than 86% within 80 hours, which indicated that the emulsion had good stability. This may be due to the addition of an anionic surfactant SDS in the inverse emulsion, which made the MAGs surface with negative charge. Under the action of the same charge repulsion, the coalescence of MAGs was reduced and the emulsion stability was improved.
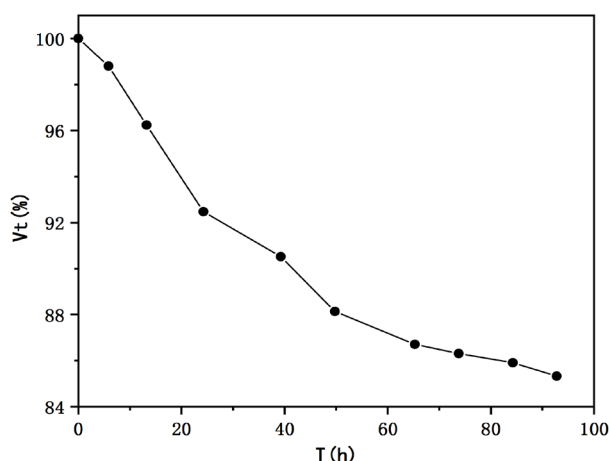

Fig. 2. The stability curve of the inverse emulsion containing MAGs.

Fig. 3 showed the XRD curve of the Fe_3O_4/PAM CMPs sample. The diffraction peaks in Fig. 3 were (220), (311), (400), (422), (511), and (440), which were consistent with Fe_3O_4 (JCPDS card 19-0629). It can be concluded that the sample contained Fe_3O_4.
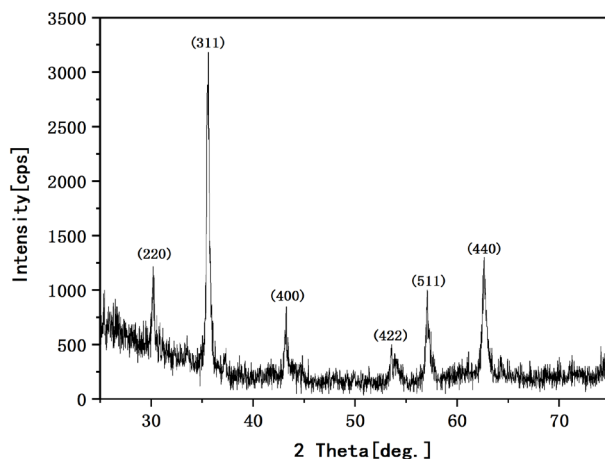
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Fig. 3. XRD curve of Fe₃O₄/PAM CMPs.

Fig. 4 showed the FT-IR curve of the Fe_3O_4/PAM CMPs sample. It can be seen from the FT-IR curve that the characteristic peak appearing at 3193cm^{-1} was attributed to the tensile vibration peak of N-H. The characteristic peaks at 2928 and 2851cm^{-1} corresponded to the characteristic peaks of -CH$_2$ and -CH$_3$ respectively. The characteristic peaks in 1667, 1425 and 1119cm^{-1} were C=O tensile vibration characteristic peaks, C-N tensile vibration characteristic peaks and O-C-O tensile vibration characteristic peaks respectively. The characteristic peak at 598cm^{-1} was attributed to the characteristic peaks of the Fe-O bond. The characteristic peaks in the FT-IR curve confirmed that the sample contained PAM and Fe_3O_4.
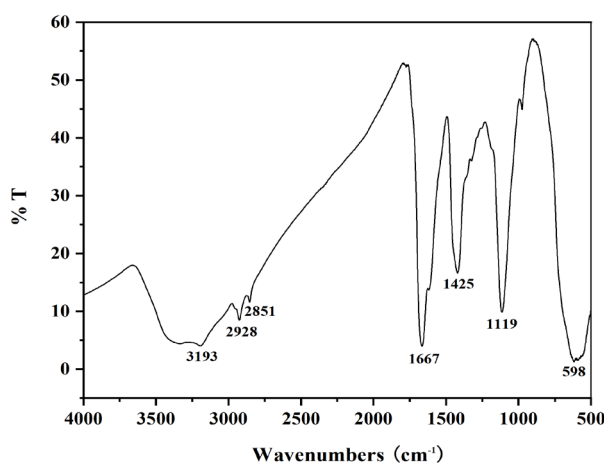

Fig. 4. FT-IR curve of Fe₃O₄/PAM CMPs.

Fig. 5 showed the thermogravimetric analysis curve of Fe_3O_4/PAM CMPs samples. It can be seen from the Fig. 5 that the sample had a rapid weight loss rate at 75-530°C and had a slight weight loss at 530-800°C. The heat loss was the result of thermal decomposition of PAM. The total weight loss of the sample was about 76.5%.
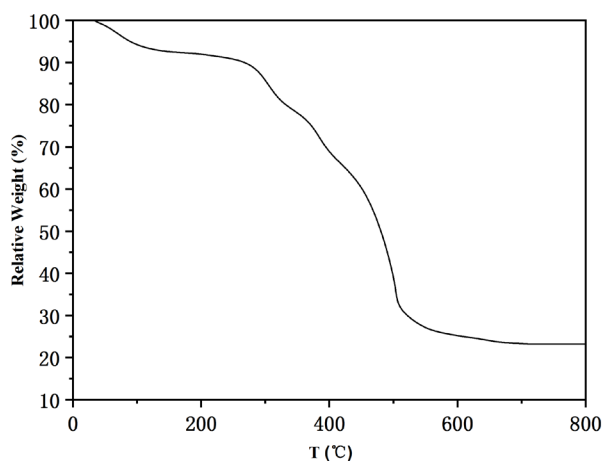
Fig. 5. TGA curve of Fe$_3$O$_4$/PAM CMPs.

The magnetization curves of Fe$_3$O$_4$ particles and Fe$_3$O$_4$/PAM CMPs were shown in Fig. 6. As can be seen from the Fig. 6, the saturation magnetization of Fe$_3$O$_4$ particles and Fe$_3$O$_4$/PAM CMPs was 57.9 and 23.3emu/g respectively. The saturation magnetization of Fe$_3$O$_4$/PAM CMPs was about 40.2% of that of Fe$_3$O$_4$ particles. It can be seen that the Fe$_3$O$_4$/PAM CMPs had a good saturation magnetic strength.
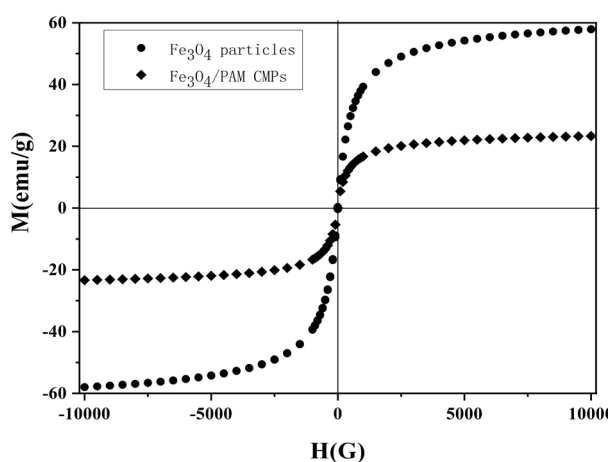

Fig. 6. Magnetization curves of Fe$_3$O$_4$ particles and Fe$_3$O$_4$/PAM CMPs.

Fig. 7 showed TEM photo (a) and particle size distribution histogram (b) of Fe$_3$O$_4$/PAM CMPs. As can be seen from Fig. 7 (a), the Fe$_3$O$_4$/PAM CMPs were close to the spherical shape with a size of about 135-420nm. It can be seen from Fig. 7 (b) that the mean diameter of Fe$_3$O$_4$/PAM CMPs was about 332nm.
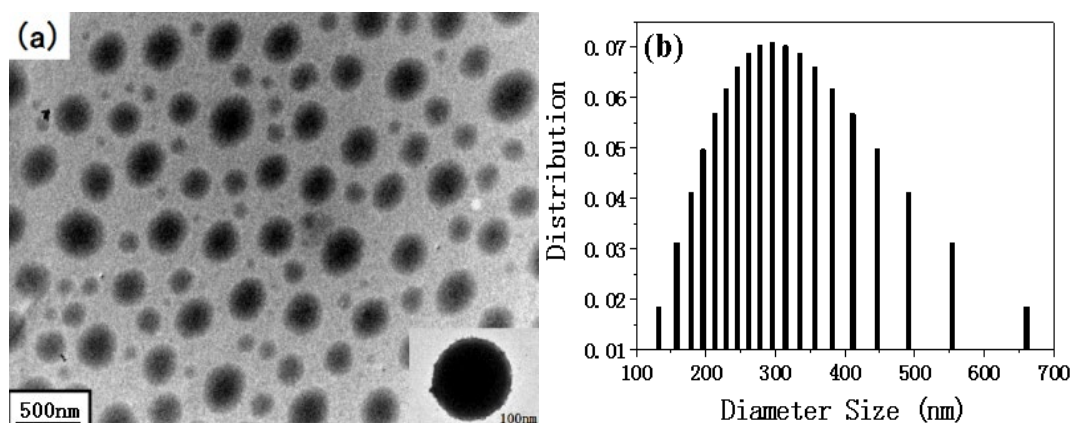
Fig. 7. TEM photo (a) and particle size distribution histogram (b) of Fe$_3$O$_4$/PAM CMPs.

Fig. 8 showed the pictures of the emulsion containing Fe$_3$O$_4$/PAM CMPs being attracted by a magnet (a) and the TEM photo of Fe$_3$O$_4$/PAM CMPs under an applied magnetic field (b). In Fig. 8 (a), due to the magnet attraction, a part of the emulsion was tightly adsorbed on the side wall of the test tube and the other part of the emulsion was even adsorbed on the top of the test tube without dripping down. Fig. 8 (b) showed that the Fe$_3$O$_4$/PAM CMPs in the TEM photo were no longer in a disordered arrangement but in a linear arrangement under the action of an applied magnetic field. This linear arrangement of Fe$_3$O$_4$/PAM CMPs was likely to be microscopic evidence that the emulsion was attracted by the magnet.
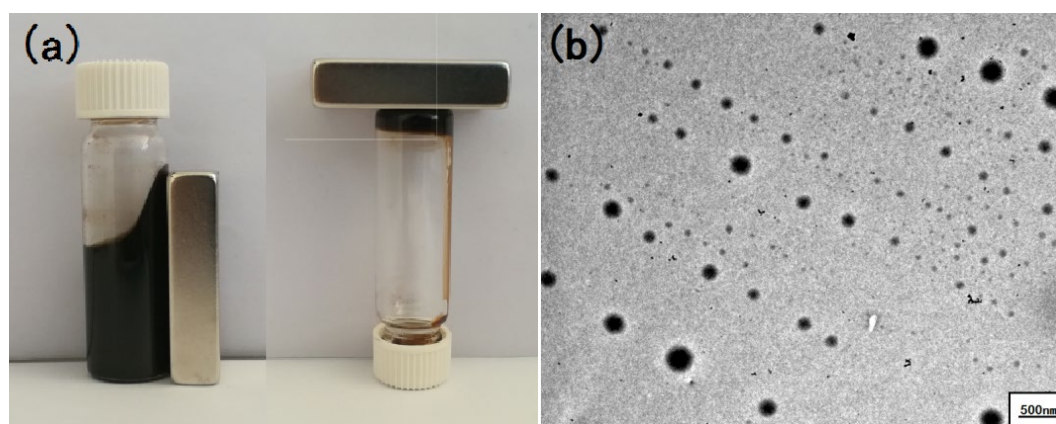

Fig. 8. The pictures of the emulsion containing Fe$_3$O$_4$/PAM CMPs being attracted by a magnet (a) and the TEM photo of Fe$_3$O$_4$/PAM CMPs under an applied magnetic field (b).

Fig. 9 showed the correlation curves of viscosity with current (a) and shear rate (b) for the emulsion containing Fe$_3$O$_4$/PAM CMPs. In Figure 9 (a), at a shear rate of 100 s^{-1}, the emulsion viscosity gradually increased as the current increased from 0A to 3A. As can be seen from Fig. 9 (b), the emulsion viscosity decreased first rapidly and then slowly with the increase of shear rate. The emulsion viscosity at the current of 3A was always greater than that at the current of 0A. This may be because the Fe$_3$O$_4$/PAM CMPs in the emulsion formed a linear arrangement under the magnetic field generated by the current, which led to the increase of the emulsion viscosity.
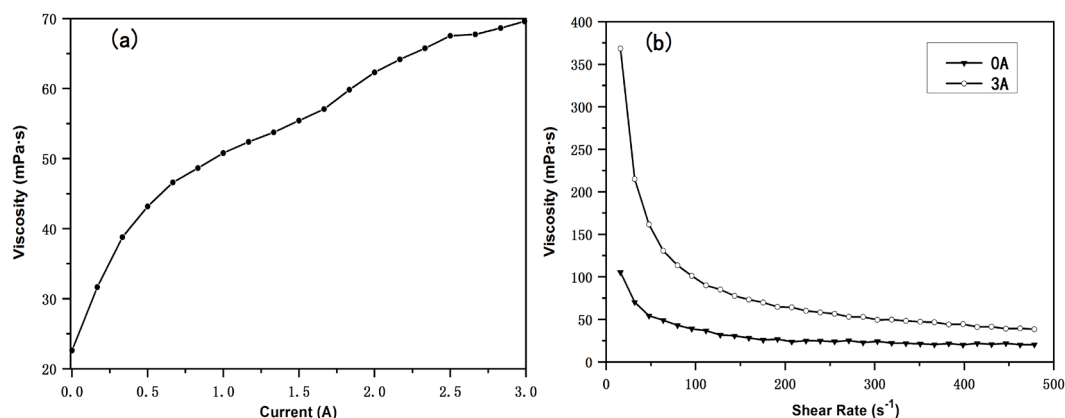
Fig. 9. The correlation curves of viscosity with current (a) and shear rate (b) for the emulsion containing Fe$_3$O$_4$/PAM CMPs.

4. Conclusions

The stable MAGs were prepared by using anionic surfactant SDS and non-ionic surfactant Span80 as emulsifiers. Fe$_3$O$_4$/PAM CMPs were obtained by inverse emulsion polymerization in MAGs. The XRD data showed that Fe$_3$O$_4$/PAM CMPs contained Fe$_3$O$_4$. According to the characteristic peaks in FT-IR, there were PAM and Fe$_3$O$_4$ in Fe$_3$O$_4$/PAM CMPs. TGA data showed that the mass fraction of PAM in Fe$_3$O$_4$/PAM CMPs was about 76.5%. The size of the spherical Fe$_3$O$_4$/PAM CMPs was about 135-420nm and the saturation magnetization value of them was about 23.3emu/g. The Fe$_3$O$_4$/PAM CMPs showed a linear arrangement under the action of an applied magnetic field. The viscosity of the emulsion containing Fe$_3$O$_4$/PAM CMPs increased with the increase of current and decreased with the increase of shear rate.

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