

Effect of modified Fe₃O₄ nanoparticles on the preparation of PMMA/Fe₃O₄ microspheres via suspension polymerization

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Abstract. In the presence of modified Ferro ferric oxide, PMMA/Fe₃O₄ microspheres have been successfully synthesized via a facile suspension polymerization. The effect of modified Fe₃O₄ on the preparation of Fe₃O₄/PMMA microspheres was investigated by X-ray diffraction (XRD), the morphology of magnetic microspheres was studied by Scanning electron microscope (SEM). Thermal performance of magnetic polymer microspheres was studied by Thermo gravimetric (TG). From the above, with the increase of modified iron oxide, the magnetic polymer microspheres have enhanced magnetic properties and heat resistance.

1. Introduction

In recent years, magnetic polymer particles have been extensively studied due to their wide applications in the fields of biotechnology, for example, drug delivery, magnetic resonance imaging, selective separation of biomolecules, hyperthermia therapy, and so on [1-4]. Magnetic polymer composite particles could be prepared by encapsulated magnetic nanoparticles (Fe₃O₄ and c-Fe₂O₃) into polymer via emulsion polymerization, soapless emulsion polymerization, inverse emulsion polymerization, miniemulsion polymerization, and suspension polymerization [5]. Suspension polymerization has been considered as one of the most advantageous methods to prepare magnetic polymer composite particle with moderate diameter and high saturation magnetization [6, 7]. However, the magnetic polymer composite particles with irregular morphology and wide size distribution were often obtained. In order to prepare magnetite/polymer composite particles with regular morphology. We found that the use of sodium chloride as dispersant, water as solvent, methyl methacrylate (MMA) as monomer, divinyl benzene (DVB) as cross-linking agent, benzoyl peroxide (BPO) as initiator, PMMA/Fe₃O₄ composite particles have been successfully synthesized via a facile suspension polymerization.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, Tianjin bei lian fine chemicals development company); Nano ferroferric oxide (20 nm spherical, Shanghai Aladdin biological technology co., LTD.); Oleic acid (luo yang



chemical reagent factory); Toluene (tian jin fu yu fine chemical co., LTD.); Gelatin (Guangdong foshan chemical industry research institute); Benzoyl peroxide (BPO, national medicine group chemical reagent co., LTD.); Divinyl benzene (DVB, national medicine group chemical reagent co., LTD.)

2.2. Modification Fe_3O_4 nanoparticles

4.0g Fe_3O_4 nanoparticles and 4.0g Oleic acid were redispersed in anhydrous ethanol (100 mL) by ultrasound. Then transferred into 250 ml three-neck flask. The suspension was stirred for 2 h in 80°C water-bath. The modified Fe_3O_4 nanoparticles were separated with a magnet, washed three times with anhydrous ethanol to remove excess Oleic acid.

2.3. Preparation of PMMA/ Fe_3O_4 composite particles

A typical preparation procedure of PMMA/ Fe_3O_4 composite particles was detailed as follows: 0.4g gelatin and 0.2g sodium chloride was dispersed in the solution of 100ml distilled water, stir to dissolve them in 60 °C constant temperature water bath. Then a certain amount of modified Fe_3O_4 nanoparticles, with 15.0g Methyl methacrylate, 1.5g divinyl benzene (DVB), 0.15g benzoyl peroxide (BPO) was added into the three-neck flask, the suspension was stirred for 20min in 60°C water-bath, And then raise the temperature to 80 degrees; After 12 h, the PMMA/ Fe_3O_4 composite particles were obtained.

3. Characterization

Fourier transform infrared (FTIR) spectra were recorded on an Avatar 360 (Nicolet) instrument by dispersing the sample in a KBr pellet. Scanning electron microscopy (SEM) was carried out on a Quanta 200FEG. X-ray powder diffraction patterns were obtained on a scanning electron microscope (Japan, Shimadzu). The diffraction data were recorded in the 2θ range of 10-80° with a scan rate of 2°/min. Thermo gravimetric analysis (TGA) was performed with a TG-209-F3 (PerkinElmer) under the nitrogen atmosphere at a heating rate of 20 K/min from 30 to 550 °C.

4. Results and discussion

4.1. Modified Fe_3O_4 nanoparticles

The IR analysis could provide some insights into the Fe_3O_4 nanoparticles. As shown in Fig.1. The strong vibrations at 572 cm^{-1} observed was assigned to Fe-O stretch of the Fe_3O_4 nanoparticles (Fig.1.a). Modified Fe_3O_4 also showed the strong peaks at 2920 ($\nu_{as}CH_2$) cm^{-1} , 2852 ($\nu_{s}CH_2$) cm^{-1} , and 1466 ($\nu_{s}CH_2$) cm^{-1} were attributed to the presence of oleic acid on the particle surfaces. The existence of CH_2 indicated that Fe_3O_4 nanoparticles were modified with oleic acid [8, 9].

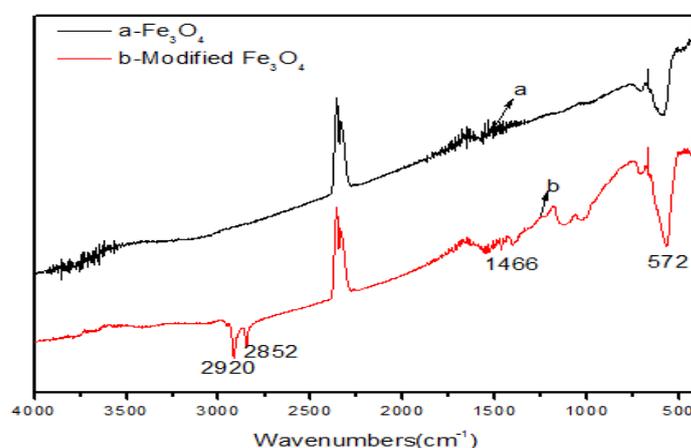


Figure 1. FT-IR spectra of: a. Fe_3O_4 nanoparticles, b. modified Fe_3O_4 nanoparticles

4.2. SEM morphology

The SEM images of pure PMMA and PMMA/2.0wt% Fe_3O_4 composite particles were shown in Fig. 2a and 2b respectively. It was observed that the resultant PMMA microspheres have smooth surface and uniform in dimension with a mean size of 0.7 μm . While the PMMA/ Fe_3O_4 magnetic microspheres with irregular morphology, rough face, and weak uniformity due to the addition of Fe_3O_4 .

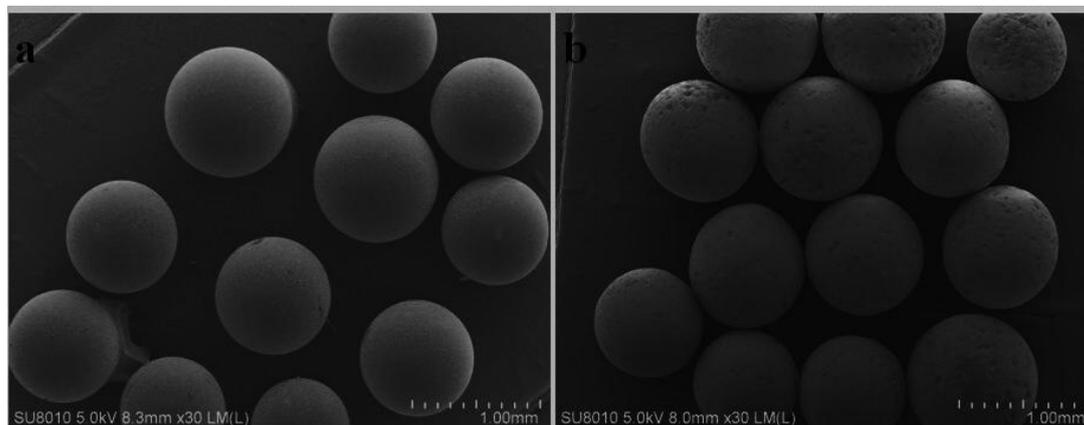


Figure 2. SEM images of PMMA microspheres (a) and PMMA/ 2.0% Fe_3O_4 microspheres

4.3. XRD patterns

X-ray diffraction (XRD) measurement was an effective approach to investigate the existence of intercalation in composites. XRD patterns of (a) Fe_3O_4 nanoparticles, (b) PMMA microsphere (c) magnetic PMMA/ 1.0% Fe_3O_4 composite (d) magnetic PMMA/ 2.0% Fe_3O_4 composite were shown in Fig.3. Based on Fig. 3a, characteristic diffraction peak at 2θ of 30.2° , 35.5° , 43.2° , 53.3° , 57.2° and 62.6° , which were assigned to [220], [311], [400], [422], [511], and [440] lattice planes of Fe_3O_4 . A broad peak at around $2\theta=16^\circ$ was associated with PMMA (Fig. 3b). In addition; it was clearly observed that XRD patterns in both Fig. 5(c) and (d) were consistent with that of Fe_3O_4 nanoparticles. So the spinel structures of magnetite in the samples were retained. However, the intensity of diffraction peaks for the Fe_3O_4 /PMMA composite became lower as the Fe_3O_4 content decreased. On the basis of the above analysis, it was confirmed that Fe_3O_4 was existed in the PMMA microspheres [10].

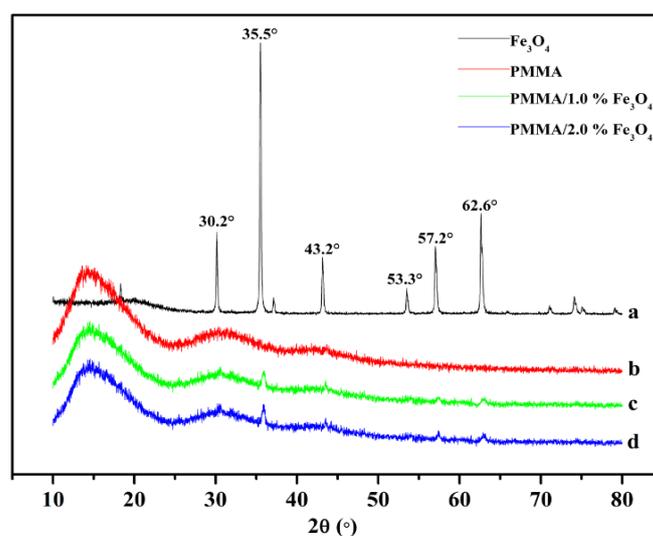


Figure 3. XRD patterns of: (a) Fe_3O_4 nanoparticles (b) PMMA microspheres (c) PMMA/ 1.0% Fe_3O_4 microspheres (d) PMMA/ 2.0% Fe_3O_4 microspheres

4.4. TGA

TGA results of the achieved composite microspheres were depicted in Fig. 4. Pure PMMA (Fig. 4a) showed no residual weight due to the complete decomposition of PMMA. The thermal stability of the PMMA/ Fe_3O_4 composite particles was significantly better than pure PMMA. The temperature at which the weight drastically decreased and the plateau region appeared increased with increasing Fe_3O_4 content. Moreover, around 425 °C, at which temperature residual PMMA was completely degraded, the PMMA/ Fe_3O_4 composite particles showed higher residual weights. In view of these results, the high Fe_3O_4 content could enhance the thermal stability of composite particles dramatically. This phenomenon should be attributed to the unique morphology of PMMA/ Fe_3O_4 composite [11].

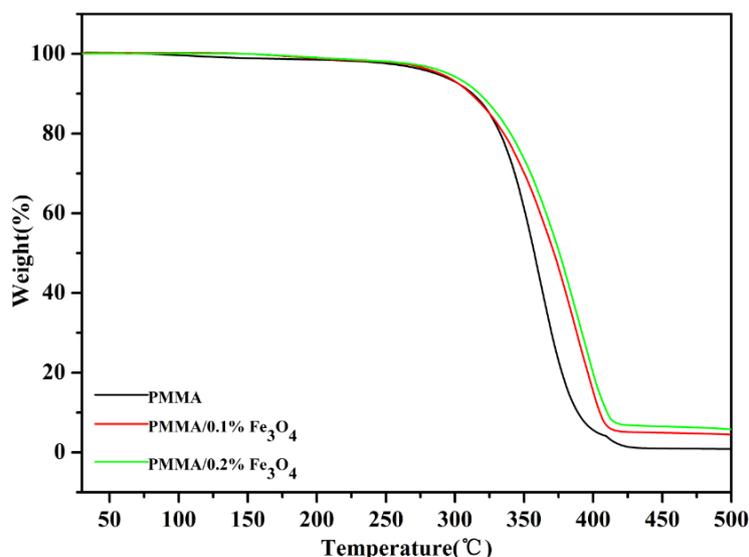


Figure 4. TGA curves of: (a) pure PMMA (b) PMMA/ 1.0% Fe_3O_4 microspheres (c) PMMA/ 2.0% Fe_3O_4 microspheres

4.5. PMMA/ Fe_3O_4 composite's apparent Magnetic properties

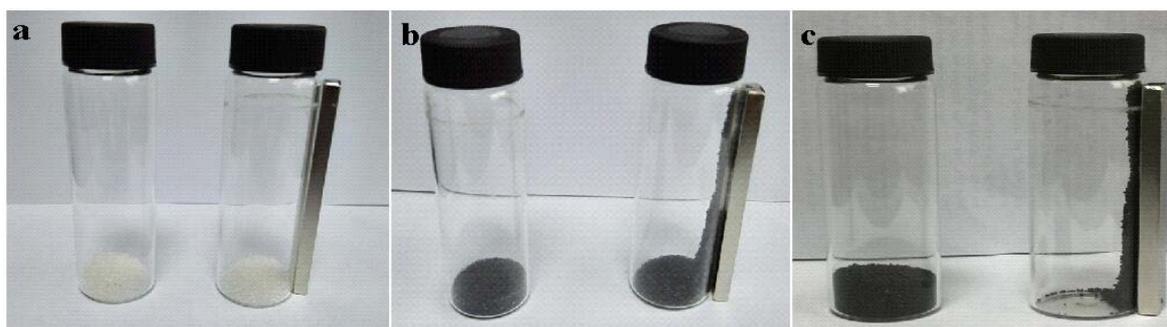


Figure 5. Magnetic adsorption test of (a) pure PMMA (b) PMMA/ 1.0% Fe_3O_4 microspheres (c) PMMA/ 2.0% Fe_3O_4 microspheres

The apparent magnetic properties of PMMA/ Fe_3O_4 composite particles were characterized by magnet. As shown in Fig. 5, both of PMMA/ 1.0% Fe_3O_4 composite and PMMA/ 2.0% Fe_3O_4 composite were superparamagnetic, while pure PMMA have no magnetic. With the addition of modified Fe_3O_4 , PMMA magnetic polymer microsphere magnetism is gradually enhanced.

5. Conclusion

In conclusion, we have developed a facile suspension polymerization method for the controlled synthesis of PMMA/Fe₃O₄ magnetic composite particles. In our synthesis system, Oleic acid was used to modify Fe₃O₄ nanoparticles, using gelatin and sodium chloride as dispersants, distilled water as solvent. The SEM show that the modified Fe₃O₄ is covered with polymer, and the color of magnetic polymer microspheres increases with the addition of the modified Fe₃O₄. The PMMA/Fe₃O₄ polymer microsphere is magnetic and increases with the addition of the added amount. XRD result showed the modified Fe₃O₄ is coated with polymer, and the addition of adding quantity, the more the coating, the more obvious the diffraction peak. TG and DSC tests showed that the thermal stability of PMMA/Fe₃O₄ magnetic polymer microspheres increased with the addition of trioxide.

Acknowledgments

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