

Preparation and Properties Magnetite/Polyimide Composites

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To make the polyimide (PI) composite material having both heat resistance and magnetic permeability, Fe₃O₄/PI magnetic polyimide composite powder was synthesized by one-step solvothermal method. 4,4'-diaminodiphenyl ether (ODA) as monomers, ether anhydride polyamic acid (PAA) was designed and prepared by Fe³⁺ and polyimide precursor-polyamic acid triethylamine salt (PAAS) was reacted in a reactor, and the PI/Fe₃O₄ composite powders were synthesized under the condition of high temperature and high pressure. The obtained PI/Fe₃O₄ composite powders were analyzed by infrared spectroscopy, microscopic morphology and thermal properties. The morphology and structure of the samples were both characterized by scanning electron microscopy (SEM) and infrared spectroscopy (IR). The thermal properties of the composite microspheres were studied via thermogravimetric analysis (TGA) and the magnetic properties were determined by a vibrating sample magnetometer (VSM). The saturation magnetization decreases gradually, increasing the polyimide content, with a saturation magnetization of PI/Fe₃O₄ determined to be 20.29 emu/g.

Keywords: polyimide, magnetism, composite powder, one-step solvothermal method.

1. INTRODUCTION*

Polymer-based magnetic composites have received extensive attention in the industrial field in recent years. Due to their concentration of excellent properties of both inorganic and polymers, the design and preparation of different types of composite nanostructures have become the focus of research and development [1–3]. Magnetite (Fe₃O₄) is one of best-known magnetic materials and has been extensively studied in terms of properties involving high saturation magnetization, biocompatibility and low toxicity [4, 5]. Due to its superior performance characteristics, the material has been widely used in applications such as catalysis [6, 7], wave absorption [8, 9], environmental remediation, biotechnology/biomedicine [10, 11] and magnetic resonance imaging [12, 13]. However, bare magnetite microspheres proved to be highly reactive, and prone to oxidation and agglomeration in air. This usually results in a loss of magnetism and dispersibility.

Polyimide has excellent mechanical properties, thermal properties, electrical insulation properties, etc. As a high-performance polymer material, it has been widely used in aerospace, electronic packaging, rail transit and other fields. The composites prepared by combining Fe₃O₄ have both magnetic permeability and material properties. Specific applications such as matrix resins for composite materials, high-strength films and coatings, etc. Due to the potential applications of high-performance polyimide, various functional nanomaterials based on PI materials have also been developed and fabricated. Such as low-dielectric materials, high-temperature nanovessels, and nano-reaction vessels with heat resistance [14–16].

However, due to the rigid structure of polyimide, the composite powder is limited. It may also be that the low solid content in the experimental stage, the huge solvent consumption, and the difficulty in controlling the morphology have affected the successful preparation of the composite material. To solve this problem, in this study, PI@Fe₃O₄ magnetic polyimide composite powder was prepared by one-step solvothermal method, using the composite microsphere salt of poly(amic acid) triethylamine (PAAS) and ferric chloride hexahydrate (FeCl₃·6H₂O) as the precursor of the reaction. The preparation of Fe₃O₄ does not need to be completed separately, which avoids the complicated production process caused by first preparing Fe₃O₄ and then compounding PI. In addition, no additional precipitant other than triethylamine is required to be added to the reaction system, which greatly simplifies the experimental process.

Polyimide (PI) is a kind of polymer material containing an imide ring in a molecular main chain, which is generally obtained by stepwise polymerization of a dibasic anhydride and a diamine. Since the aromatic ring on the main chain of the molecule is a rigid and very stable structure, the polyimide has outstanding heat resistance, mechanical properties and electrical properties [17–19]. In this report, we describe the development of a facile one-step solvothermal method for the preparation of PI@Fe₃O₄ composite microspheres using poly(amic acid) triethylamine salts (PAAS) and ferric chloride hexahydrate (FeCl₃·6H₂O) as starting materials [20–22]. Subsequently, the thermal and magnetic properties of the prepared samples were tested.

2. EXPERIMENTAL

Diphenyl ether tetraacid dianhydride (Sinopharm Chemical Reagent Co., Ltd.); 4,4'-diaminodiphenyl ether

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Polystyrene nanoparticles (Jenus New Materials Co., Ltd.); (Sinopharm Chemical Reagent Co., Ltd.); N,N-dimethylacetamide (AR Tianjin Komi Chemical Reagent Co., Ltd.); Ethylene glycol(AR Tianjin Komi Chemical Reagent Co., Ltd.); Triethylamine (AR Tianjin Komi Chemical Reagent Co., Ltd.); $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (analytical grade and purchased from Zhongguo Group Chemical Reagent Co., Ltd.); Absolute ethanol (Tianjin Yongda Chemical Reagent Co., Ltd.); the water used in the experiment is distilled water.

The structures of nanoparticles and nanocomposites were investigated by Lambda 7600 -FT-IR. A JEOL JSM-6700F scanning electron microscope (SEM) with primary electron energy of 3 keV was employed to examine the surface morphologies of products. X-ray diffraction (XRD) data were collected on an X'Pert PRO X-ray diffractometer. TG data was collected on a TG209F3 thermogravimetric tester by NETZSCH, Germany.

0.1 mol ODA was placed in a 500 mL three-neck flask, added 250 mL of DMAc with a mechanical stirrer. After ODA was completely dissolved in DMAc, 0.1 mol of ODPA was added in batches. After the ODPA was dissolved, the reaction was continued. After stirring for 6 h, 0.2 mol of triethylamine was gradually added dropwise with a dropper, so that the carboxylic acid in the generated polyamic acid was completely reacted with triethylamine. After the triethylamine was added dropwise, the mechanical stirring was continued for 2 h, and the stirring was stopped after the reaction was complete, and the finally obtained triethylamine salt solution of polyamic acid was allowed to stand for later use. Then $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in ethylene glycol to prepare a 0.5 mol/L Fe^{3+} solution. A certain amount of polyamic acid triethylamine salt solution was mixed, Then Fe^{3+} solution, ethylene glycol and DMAc, were stirred evenly and transferred to the reaction kettle, the products were placed in the reaction kettle in a blast drying oven. After the reaction, the products were separated with a magnet, washed three times with distilled water and anhydrous ethanol, and dried in an oven at 60 °C for 6 h to obtain the final products.

3. RESULTS AND DISCUSSION

In previous studies, scholars have found that polyamic acid was prone to flocculation in the presence of ethylene glycol, and cannot exist stably in a solvent containing ethylene glycol. A necessary condition for the sphere, it acts as a reaction medium and a reducing agent in the reaction, so this study excludes the use of polyamic acid as the precursor of polyimide; polyamic acid ester can exist in alcohols such as ethylene glycol [7]. In the solvent, however, to precipitate Fe^{3+} , the additional precipitating agent needs to be added to the reaction. After adding an alkaline precipitating agent, it will cause the rapid precipitation of polyamic acid ester, and it cannot exist stably; in the test of polyamic acid triethylamine salt It is found that it can exist stably in a solvent containing ethylene glycol, and when synthesizing $\text{PI}/\text{Fe}_3\text{O}_4$ composite microspheres, polyamic acid triethylamine salt is used as the precursor of polyimide without adding a

precipitant to make Fe^{3+} Precipitation yields a magnetic substance. Therefore, in this study, different from other researchers in the past, polyamic acid triethylamine salt was used as the precursor of polyimide to synthesize $\text{PI}/\text{Fe}_3\text{O}_4$ composite microspheres.

The whole procedure to prepare $\text{Fe}_3\text{O}_4/\text{PI}$ magnetic polyimide composites is illustrated in Fig. 1.

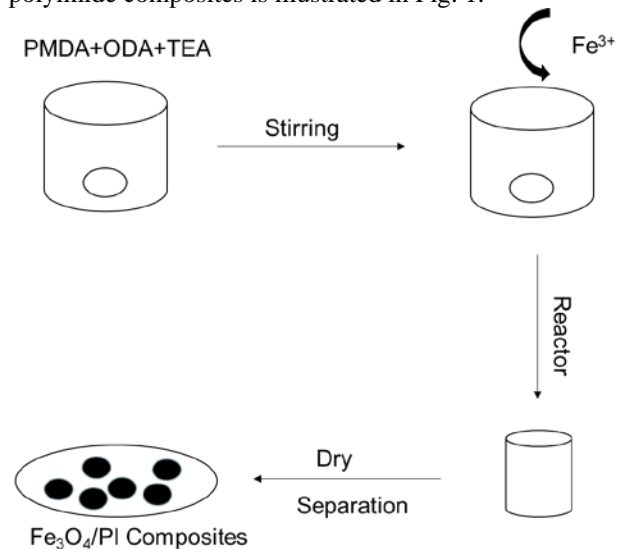


Fig. 1. Synthesis route to $\text{Fe}_3\text{O}_4/\text{PI}$ magnetic composites

A possible mechanism for the synthesis of $\text{PI}@/\text{Fe}_3\text{O}_4$ composites is illustrated in Fig. 1. At first, a polyimide precursor (PAAS) was synthesized. PAAS was dissolved in a mixed solvent consisting of DMAc and EG and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in ethylene glycol was added dropwise.

In the teflon-lined autoclave and with rising temperature, triethylamine gets removed from the PAAS main chain and dissipates in solution. Then combine it with Fe^{3+} solution mixing, high in the reactor $\text{PI}/\text{Fe}_3\text{O}_4$ composites were synthesized under the condition of high temperature and high pressure.

The entire process for preparing the $\text{Fe}_3\text{O}_4/\text{PI}$ magnetic polyimide composites is shown in Fig. 1. First, the PAAS were dispersed in ethylene glycol, amount of Fe^{3+} solution was added into the above solution with mechanical stirring. After stirring evenly, it was transferred to the reaction kettle, and the reaction kettle was heated to 200 °C in a blast drying oven to make the reaction. Then the $\text{Fe}_3\text{O}_4/\text{PI}$ magnetic polyimide composites were obtained.

Fig. 2 shows the IR spectra of pure Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{PI}$ composites. Curve a in Fig. 2 is the infrared spectrum of pure Fe_3O_4 . In the spectrum of pure Fe_3O_4 , an intense absorption band at 586 cm^{-1} can be observed, which is the stretching vibration peak of Fe–O. This signal can be assigned to a characteristic band of the Fe–O group, characteristic for the presence of Fe_3O_4 . Curve b is the infrared spectrum of $\text{PI}/\text{Fe}_3\text{O}_4$ composite powder. On curve b, the band at 1776 cm^{-1} is the stretching vibration peak of carbonyl in polyimide, and the band at 1367 cm^{-1} is the stretching vibration of polyimide C–N bond. The peak at 1262 cm^{-1} is the stretching vibration peak of $=\text{C}-\text{O}-\text{C}=\text{}$, and these absorption peaks can be regarded as the characteristic absorption peaks of polyimide.

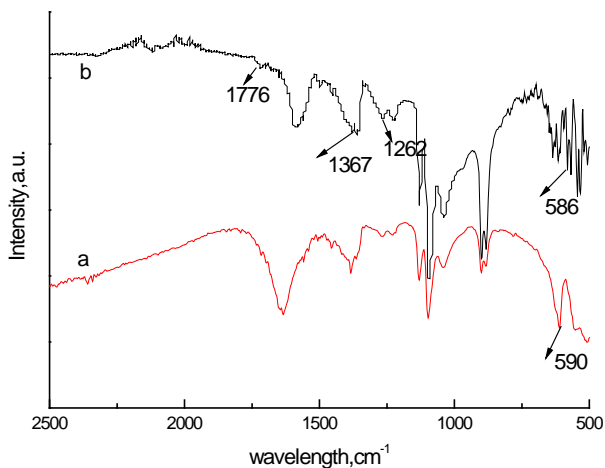


Fig. 2. Infrared spectra of composites: a – Fe₃O₄; b – Fe₃O₄/PI

At the same time, the stretching vibration peak of Fe–O also appeared at 590 cm⁻¹, and the characteristic absorption peak of polyimide and Fe₃O₄ coexisted on curve b. It can be seen that PI has successfully interacted with Fe₃O₄. Combined, it shows that the preparation of Fe₃O₄/PI composites is completed.

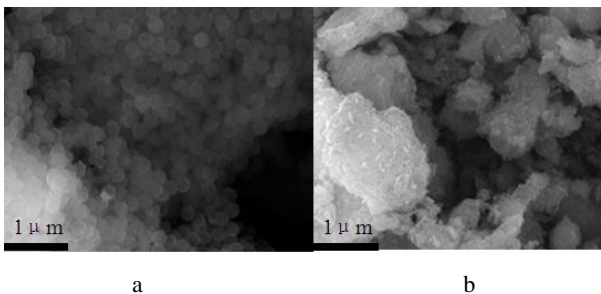


Fig. 3. SEM images of composites: a – Fe₃O₄; b – Fe₃O₄/PI

Fig. 3 a is a scanning electron microscope picture of pure Fe₃O₄ particles. It can be seen from the picture that the particles are spherical and the particle size is about 200 nm. Fig. 3 b is the SEM photo of PI/Fe₃O₄ composites. Comparing the pictures of pure Fe₃O₄ particles and composite microspheres, it can be seen that there are polymer fibers on the surface, but the PI/Fe₃O₄ composites are no longer spherical. This is since PI is wrapped on Fe₃O₄, but the composite microspheres are stuck together due to the excessive concentration of triethylamine salt of polyamic acid, so the synthesized PI/Fe₃O₄ composites do not present a spherical structure.

The EDS analysis in Fig. 4 a shows that oxygen accounts for 35.5 % and iron 64.5 %. Fig. 4 b shows that carbon accounts for 68.3 %, nitrogen 1.2 %, oxygen 23.8 % and iron 6.7 %. Fe₃O₄ composite microspheres have a wide range of applications. Due to the variety of polymers and the fact that the polymer itself has functional groups, the PI/Fe₃O₄ composite microspheres can have functional groups without further modification. Fe₃O₄ composite microspheres have received extensive attention. However, most polymers have low thermal decomposition temperature, which limits their application in some fields. Therefore,

the high temperature resistant polyimide material can break this temperature limit well [23, 24].

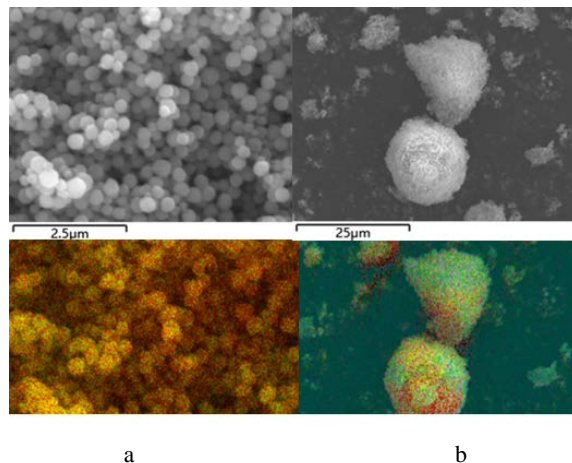


Fig. 4. EDS images of composites: a – Fe₃O₄; b – Fe₃O₄/PI

Thermogravimetric analysis (TGA) measurements were carried out with Fe₃O₄ microspheres and PI/Fe₃O₄ composites in the air. The corresponding TGA curves are shown in Fig. 5. Due to the oxidization of magnetite in air, the curve a of the pure Fe₃O₄ curve shown in Fig. 5, the weight loss is partly due to the loss of oxygen of metal oxides at high temperature, and it may also be due to some residual solvent and some hydroxyl groups on the surface of Fe₃O₄ during the preparation of Fe₃O₄. Mass loss due to solvent volatilization and radical removal.

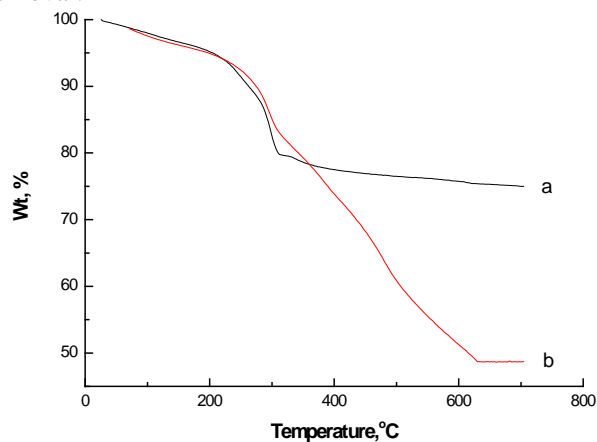


Fig. 5. Thermogravimetric curves of composites: a – Fe₃O₄; b – Fe₃O₄/PI

The DSC test was performed on the Fe₃O₄/PI composites to investigate whether the PI in the Fe₃O₄/PI composites has been completely imidized. The corresponding DSC curve is shown in Fig. 6. From the DSC curve of the Fe₃O₄/PI composites, it can be seen that the Fe₃O₄/PI composites have no reaction peak between room temperature and 500 °C, so it can be recognized that the polyimide in the Fe₃O₄/PI composites is in the reaction kettle has been completely imidized. Magnetism is an important physical parameter of all ferrite magnetic materials. For Fe₃O₄ particles, people were most concerned about their magnetic response intensity (saturation magnetization, *M_s*).

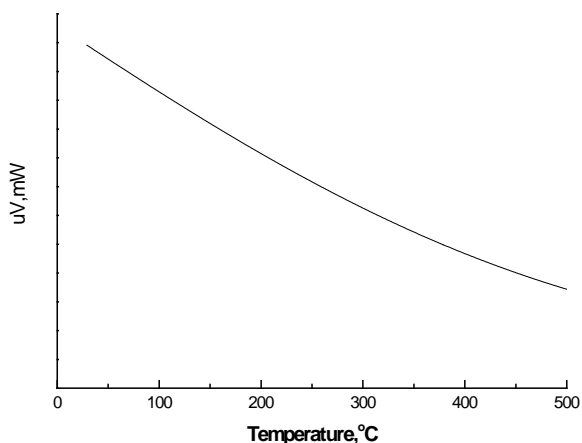


Fig. 6. DSC curve of Fe₃O₄/PI composites

The saturation magnetization meant that the magnetic moment of the magnetic domain tends to the same direction as the external magnetic field under the action of the external magnetic field, and thus forms a magnetization vector. When the external magnetic field gradually increased, its magnetization also increased until it reached the maximum value, the higher the saturation magnetization, the better the performance as a permanent magnet material. The magnetization behavior was investigated by applying a magnetic field to pure Fe₃O₄ as well as PI/Fe₃O₄ composite microspheres with a vibrating sample magnetometer (VSM) [25].

The reason for this phenomenon was that the PI coating on the surface of Fe₃O₄ made Fe₃O₄ in the composite microspheres. The proportion of PI decreased, the proportion of PI increased, and PI did not respond to the magnetic field; and during the resynthesis of PI/Fe₃O₄ composite microspheres, Fe³⁺ was first complexed to the main chain of PAAS, which hindered the formation of Fe₃O₄ crystals. It may make the Fe₃O₄ crystallization not perfect. The Fe₃O₄ content and saturation magnetic field strength of the PI/Fe₃O₄ composite microspheres were presented in Fig. 7.

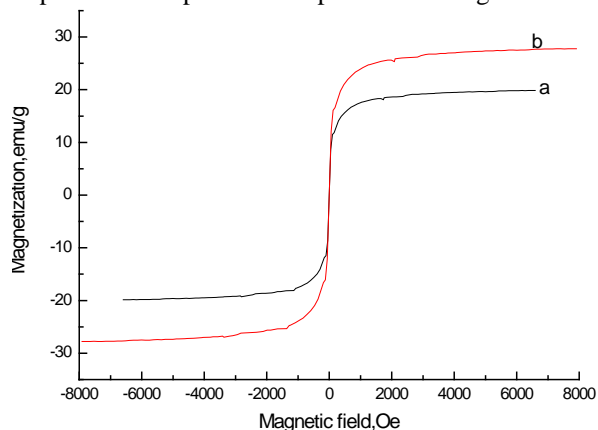


Fig. 7. VSM curves of PI@Fe₃O₄ composites: a – pure; b – Fe₃O₄

It can be seen from Fig. 7 that the saturation magnetization of PI/Fe₃O₄ composite microspheres with higher Fe₃O₄ content was also higher, indicating that the saturation magnetic field strength of PI/Fe₃O₄ composite

microspheres is positively correlated with the Fe₃O₄ content [26]. This phenomenon can be attributed to the nonmagnetic polyimide coated on the Fe₃O₄ surface as well as the incomplete crystallization caused by the polyimide permeated throughout the crystals. The saturation magnetization decreases gradually, increasing the polyimide content, with a saturation magnetization of PI/Fe₃O₄ determined to be 20.29 emu/g.

To observe the magnetic response of the Fe₃O₄/PI composites more intuitively, the samples were dispersed in ethanol, and the photos before and after applying the magnetic field were taken as shown in Fig. 8. It can be seen from Fig. 8 a that the composites are uniformly dispersed in the ethanol solution before applying the magnetic field, and it can be seen from the Fig. 8 b that the sample aggregates to the side close to the magnet after applying the magnetic field, which can intuitively show that the synthesized Fe₃O₄/PI composites have a certain magnetic response.

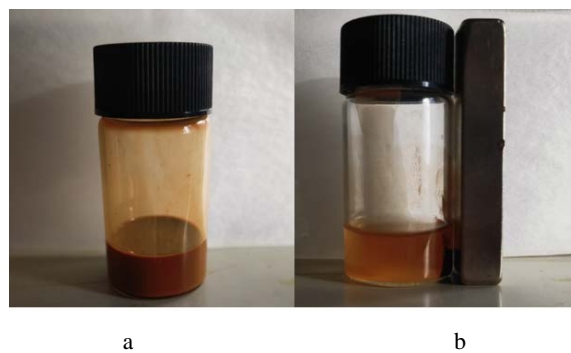


Fig. 8. Photographs of the Fe₃O₄/PI composites ethanol dispersion before and after applying a magnetic field: a – without an applied magnetic field; b – with an applied magnetic field

4. CONCLUSIONS

Compared with other methods, the preparation process of polymer Fe₃O₄ composite microspheres does not require pre-preparation of Fe₃O₄ particles, but a one-step solvothermal method to prepare Fe₃O₄/PI composite powder. One-step synthesis of Fe₃O₄/PI composite powder. Not only the method is simple and the conditions are mild, but also the experimental loss of first generating Fe₃O₄ and then coating its surface is avoided. The results show that the surface of Fe₃O₄ can be successfully combined with PI, and PI penetrates into the whole crystal through the self-assembly process. The Fe₃O₄/PI composites exhibit certain magnetic properties and excellent thermal properties and have the potential to be used as high-performance absorbing materials and other applications. The morphology and structure of the samples were both characterized by scanning electron microscopy (SEM) and infrared spectroscopy (IR). The thermal properties of the composite microspheres were studied via thermogravimetric analysis (TGA) and the magnetic properties were determined by a vibrating sample magnetometer (VSM). The saturation magnetization decreases gradually, increasing the

polyimide content, with a saturation magnetization of PI/Fe₃O₄ determined to be 20.29 emu/g.

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