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SHORT COMMUNICATION

Synthesis and characterization of polystyrene-grafted magnetite nanoparticles

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Abstract Magnetite (Fe_3O_4) nanoparticles were synthesized by chemical precipitation. To reduce the aggregation of Fe_3O_4 nanoparticles, an effective surface modification method was proposed by grafting polystyrene onto the Fe_3O_4 particles. The results of Fourier transform infrared spectra and elemental analysis showed that the polymer chains have been successfully grafted from the surface of the Fe_3O_4 nanoparticles and that the percentage of grafting can reach 73%. Transmission electron microscope showed that grafted polymer chains on nanoparticles could prevent the aggregation of Fe_3O_4 nanoparticles markedly in toluene and improve their compatibility with organic phase. Another finding was the grafting reaction did not alter the crystalline structure of the Fe_3O_4 nanoparticles according to the X-ray diffraction patterns, and the saturation magnetization of PS-Fe_3O_4 nanoparticles was found to be lower than bulk magnetite.

Keywords Fe_3O_4 · PS · Nanoparticles · Grafting polymerization · Dispersion

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Introduction

In recent years, there is an increasing trend of utilizing nanosized powders in various aspects, such as toughening of plastics [1], thermal and tribological performance enhancement of polymers [2, 3]. In all these applications, establishment of modification technique for the nanoparticles' surface is strongly desired to improve dispersibility of the powders in polymer matrices and to tailor the interface interaction. The surface grafting of inorganic particles with polymers has been widely investigated to improve surface properties of inorganic particles. There are different approaches to graft a polymer coating onto the particulate core particle [4–9]. One method employs vinyl-containing agents where this vinyl group co-polymerizes with other dissolved monomers in the reaction medium [4, 8, 9].

Black pigment Fe_3O_4 is a compound oxide with spinel structure which has been used in the coating industry, coloration and light-resistance, and construction industry due to its excellent alkali resistance. Chemical co-precipitation has been widely used to produce magnetite nanoparticles due to its ease and large volume capability [10–13]. However, iron black particles are naturally hydrophilic due to plentiful hydroxyls on the particle surface. Additionally, Fe_3O_4 nanoparticles, like other nanoparticles, possess high surface energy, which may result in the agglomeration of particles when Fe_3O_4 nanoparticles are dispersed in organic solvent and matrices. Therefore, the surface coating or modification of iron black particles is very important in many applications. Fe_3O_4 nanoparticles have been coated by polystyrene using dispersion and reversible addition–fragmentation chain transfer (RAFT) polymerization, respectively [14, 15].

In the present investigation, polystyrene-grafted (PS)-grafted Fe_3O_4 nanoparticles were accomplished by a threestep process: (1) the Fe_3O_4 nanoparticles were synthesized by chemical precipitation; (2) the Fe_3O_4 nanoparticles were modified by KH570 (γ-methacyloxypropyl trimethoxy silane, KH570-Fe_3O_4); and (3) the polystyrene chains were grafted onto the surface of the functional Fe_3O_4 nanoparticles (PS-Fe_3O_4). The product was characterized by FT-IR, EA, TEM, viscosity test, XRD, and VSM.

Experimental

Materials

Analytical grade ferric chloride hexa-hydrate ($FeCl_3{\cdot}6H_2O$), ferrous chloride tetra-hydrate ($FeCl_2{\cdot}4H_2O$), ammonium hydroxide (NH_4OH, 25% of ammonia), and azobisisobutyronitrile (AIBN) were purchased from Tianjin Chemical Reagent Co., Tianjin, China and used directly. Silane-coupling agent (KH570) was chemical grade. Styrene (St) was purified by distillation under nitrogen at reduced pressure.

Synthesis of Fe_3O_4 nanoparticles

A volume of 70 ml of deionized water was placed in a round-bottomed flask; subsequently, the water was deoxygenated by bubbling N_2 gas for 30 min. Later, 10 ml of ferrous chloride, 0.1 M, and 20 ml of ferric chloride, 0.1 M, were added. After the solution was heated to 80 °C, 5 ml of NH_4OH (25% *w*/*w*) are added rapidly to it under vigorous stirring; immediately, a black precipitate appeared. The resulting suspension was maintained at 80 °C for 1 h while being stirred and then cooled to room temperature. The precipitated particles are washed five times with water and alcohol.

Preparation of Fe_3O_4 nanoparticles modified by KH570 (KH570-Fe_3O_4)

The introduction of C=C groups onto the surface of Fe_3O_4 nanoparticles was achieved through the reaction between KH570 and the hydroxyl groups on the nanoparticle surface. Typically, 2.0 g Fe_3O_4 nanoparticles and 2.0 ml KH570 in 50 ml toluene were kept at 110 °C for 24 h under stirring and N_2 protection. Then, the Fe_3O_4 nanoparticles were collected by centrifugation and rinsed three times with acetone [16]. Afterwards, the treated nanoparticles were dried under vacuum for 12 h.

Preparation of PS-grafted Fe_3O_4 nanoparticles (PS-Fe_3O_4)

The grafting polymerization was performed by the reaction of KH570-Fe_3O_4 with St monomer. A typical procedure was as follows: 1.0 g KH570-Fe_3O_4, 50 ml toluene, 4 ml St, and 80 mg AIBN were put in a flask under stirring and N_2 protection at 80 °C for 5 h. Then, the suspension was centrifuged and washed with acetone for three times. Afterwards, the obtained powder was dried under vacuum for 12 h. The PS-grafted Fe_3O_4 nanoparticles (PS-Fe_3O_4) were separated from the non-grafted PS in the dried powder by extraction with toluene using Soxhlet apparatus until no PS was eluted in the refluxing solvent [4].

Instruments

Fourier transform infrared spectroscopy (FT-IR) analysis was performed on a Nicolet AVATAR 360 spectrophotometer employing a KBr pellet method. Elemental analysis (EA) of carbon, hydrogen, and nitrogen was performed with an Elementar Vario EL instrument. The dispersion property of PS-Fe_3O_4 in organic solvent was performed on H-600 transmission electron microscope (TEM). The PS-Fe_3O_4 nanocomposite was dispersed in toluene in an ultrasonic bath for 15 min, and then deposited on a copper grid covered with a perforated carbon film. The viscosity measurement was carried out to study the modification effect using a NDJ-1 spin viscosity meter at 25 °C [17]. The X-ray diffraction (XRD) scans were recorded at room temperature on an X-ray diffractometer (XRD, SHLMADZU-6000) with CuKα radiation and Ni filler ($\lambda=1.5405$ Å) at a scan rate of 0.0167°/s. Magnetic properties were examined at room temperature using a vibrating sample magnetometer (VSM, Lakeshore 7304).

Results and discussion

Introduction of vinyl groups onto the surface of the Fe_3O_4 particles

It is well known that, in general, inorganic particles have hydroxyl groups on their surface, which can react with alkoxy silanes. Therefore, silane coupling agent is suitable for the introduction of functional groups onto the surface of inorganic particles. Figure 1a and b are the FT-IR spectra of blank Fe_3O_4 particles and modified Fe_3O_4 particles, respectively. It can be seen that FT-IR spectrum of the modified Fe_3O_4 appeared absorption bands at 2,931 cm^{-1} and at 1,726 cm^{-1}, resulting from the C–H stretching vibration and C=O stretching mode in KH570. However, the FT-IR spectrum of the blank Fe_3O_4 particles does not show absorption bands at 2,931 cm^{-1} and at 1,726 cm^{-1}. Moreover, a peak at 980 cm^{-1}, ascribed to Fe–O–Si, is observed in the silanized Fe_3O_4 spectrum. It indicated that KH570 was immobile on the Fe_3O_4 nanoparticles and the

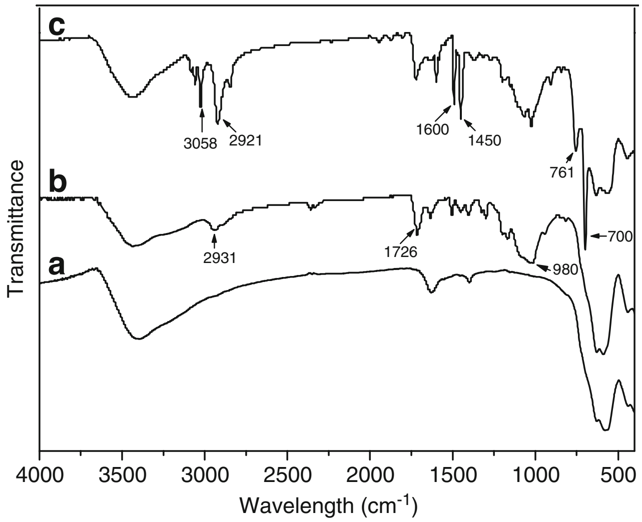


Fig. 1 FT-IR spectra of *a* blank Fe_3O_4, *b* KH570-Fe_3O_4 and *c* PS-Fe_3O_4

content of C=C on the KH570-Fe_3O_4 was 0.876 mmol/g calculated from the carbon element analysis (Table 1) [7].

Polymerization of St from the surface of the modified Fe_3O_4 particles

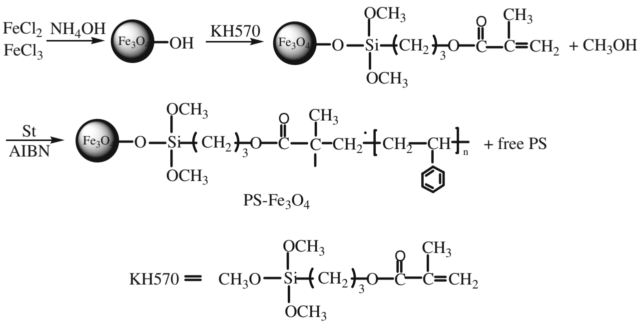
In the FT-IR spectrum of PS-Fe_3O_4 nanoparticles (Fig. 1c), the KH570-Fe_3O_4 nanoparticles grafted by polystyrene was characterized by the C–H aromatic stretching vibration at 3,058 cm^{-1}, the C–H stretching vibration at 2,921 cm^{-1}, and the phenyl ring stretching vibration at 700, 761, 1,450, and 1,600 cm^{-1} where the typical absorption bands for polystyrene were clearly seen. So it was illustrated that the chains of PS were covalently anchored on the surface of Fe_3O_4 nanoparticles, and the percentage of grafting could reach 71% [7]. The preparing procedure of PS-Fe_3O_4 nanoparticles could be shown as Scheme 1.

The dispersion ability of PS-Fe_3O_4 in organic solvent

Figure 2 showed the morphologies of the nanoparticles after the grafting treatment. Due to the serious aggregation resulting from the high-specific surface area, the untreated Fe_3O_4 nanoparticles aggregate severely (TEM photograph of Fe_3O_4 nanoparticles in toluene was not given.). When the nanoparticles were grafted by PS, they could be well dispersed in the solvent and showed much better dispersibility. It demonstrated that after the surface of Fe_3O_4 nanoparticles was grafted by PS, the aggregation of Fe_3O_4 nanoparticles was greatly reduced, which would benefit the subsequent composites manufacturing.

Table 1 Elemental analysis results

Element (%)	KH570-Fe_3O_4	PS-Fe_3O_4
C	7.362	31.14
H	0.915	3.017



Scheme 1 The preparation procedure of PS-Fe_3O_4 nanoparticles

As shown in Fig. 3, the nano-suspension of bare Fe_3O_4 particles was 930 mPa·s at a solid concentration of 12.3%, and the viscosity increased rapidly; whereas when the viscosity of the nano-suspension of PS-Fe_3O_4 particles was 99 mPa·s at the same concentration, the viscosity increased slowly. It was because the hydrophilic surface of unmodified Fe_3O_4 was badly wetted by apolar liquid olefin and interparticle interaction was strong enough to result in huge viscosity; the hydrophobic surface of PS-Fe_3O_4 could be better wetted by liquid olefin, which weakened particle interaction and was favorable for particle dispersion in liquid olefin [18]. The results showed that the surface modification by grafting PS onto Fe_3O_4 nanoparticles enhanced the dispersion of Fe_3O_4 nanoparticles, increased the hydrophobic property of nanoparticle surface, and reduced the aggregation of the Fe_3O_4 nanoparticles in organic phase.

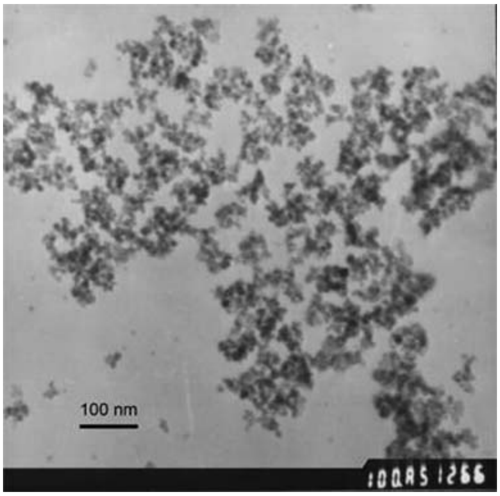


Fig. 2 TEM photograph of PS-Fe_3O_4 nanoparticles in toluene

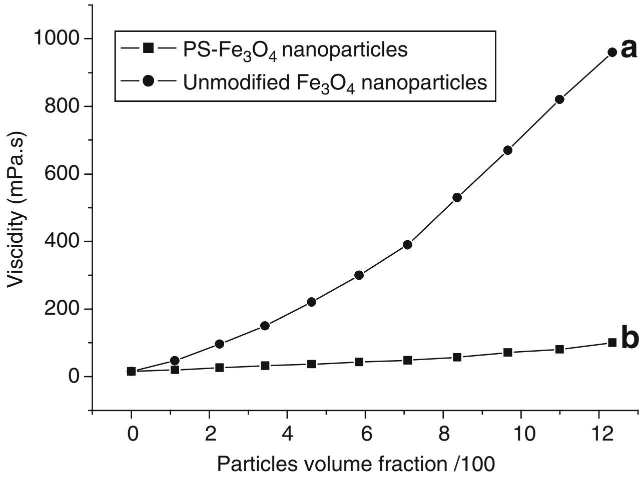


Fig. 3 Suspension viscosity of Fe_3O_4 in liquid olefin at various volume fractions: *a* Fe_3O_4, *b* PS-Fe_3O_4

Crystal phase analysis

Figure 4 showed the X-ray diffraction patterns for Fe_3O_4 and PS-Fe_3O_4. For Fe_3O_4, all the peak positions are basically consistent with the standard data for Fe_3O_4 structure (JCPDS card file No. 3-863), and no other unexpected peaks are present. The result demonstrated that the sample was pure phase nanometer Fe_3O_4. The sample powder has an average particle diameter of 10 nm, which was estimated from Scherrer's formula using peak width at half height of the X-ray diffraction, while the PS-Fe_3O_4 particle size was about 13 nm observed by TEM (Fig. 2), which was a little thicker than Fe_3O_4 because of the presence of PS on PS-Fe_3O_4 particles. From the X-ray diffraction pattern for PS-Fe_3O_4, it was found that the characteristic peaks of PS-Fe_3O_4 nanoparticles were almost the same as those of bare Fe_3O_4 particles, suggesting that the grafting polymerization did not alter the crystalline structure of Fe_3O_4 nanoparticles.

Magnetic properties

Figure 5 showed the plots of the magnetization M versus the applied magnetic field H (between ±12,000 Oe) for the PS-Fe_3O_4 nanoparticles at 300 K. It is worthy to note that the measured magnetization of hybrid particles (Ms= 40.4 emu/g) was considerably lower than the values measured from bulk magnetite (Ms=84 emu/g) and the pure Fe_3O_4 nanoparticles (Ms=65 emu/g). This interesting phenomenon was also observed in other polymer composites with nanosized superparamagnetic particles [19–22]. By now, there is no definite explanation of this discrepancy. It is generally attributed to the small size of superparamagnetic particles and the interactions between the polymer and iron oxide nanoparticles [12, 23]. The observed zero residual magnetism and zero coercive force suggested that the as-synthesis magnetic particles were superparamagnetic, which could be used for the magnetic fluid and the biological medicine field [24, 25].

Conclusions

Grafting polymerization of PS onto the surface of Fe_3O_4 nanoparticles could be successfully achieved by free radical polymerization after Fe_3O_4 nanoparticles were treated with the coupling agent, KH570, which introduced the reactive double bonds onto Fe_3O_4 nanoparticles. The dispersibility of Fe_3O_4 nanoparticles in organic solvents could be remarkably improved by the grafting PS, which facilitated

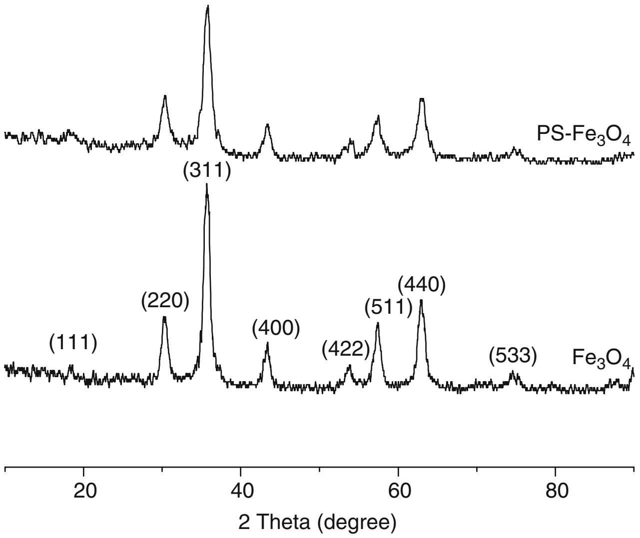


Fig. 4 XRD patterns of Fe_3O_4 and PS-Fe_3O_4

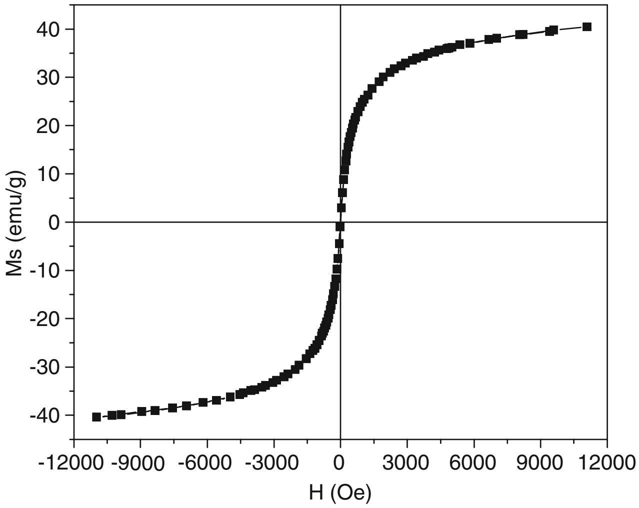


Fig. 5 Magnetization curves for the PS-Fe_3O_4 nanoparticles

its application in many fields. The grafting polymerization did not alter the crystalline structure of Fe_3O_4 nanoparticles, but lowered the saturation magnetization.

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