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Synthesis of conducting and magnetic nanocomposite of cross-linked aniline sulfide resin

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Abstract. Magnetic and conducting aniline sulfide resin cross-linked (ASC-Fe3O4) nanocomposite has been prepared in the presence of aniline sulfide resin (ASR), aniline, Fe_3O_4 coated by polyethylene glycol (PEG) and initiator. The magnetic properties of the resulting composites showed ferromagnetic behavior, such as high-saturated magnetization (Ms= 41 emu/g), and coercive force (Hc=1.5 Oe). The saturated magnetization was increased by increasing of Fe_3O_4 content and decreased by increasing aniline ratio. The transmission electron micrograph (TEM) and X-ray diffraction proved that nanometer-sized about 20-30 nm Fe_3O_4 in the composite. The average size of ASC-Fe_3O_4 nanocomposite with core-shell structure was about 50-60 nm, and polydisperse. This approach may also be extended to the synthesis and modification of other polymers. Electrical conductivity of aniline sulfide resin cross-linked (ASC) nanocomposite has been studied by four-point probe method and produced 3.3×10^{-4} S/cm conductivity for it. The conductivity of the composites at room temperature depended on the Fe_3O_4, aniline ratio and doping degree. The thermogravimetry analysis (TGA) results showed that this resin is thermal resistance near of 500 °C. So, It can be used for resistance thermal coating for military applications. Fe_3O_4-PASC nanocomposite has been flexible structure with electrical and magnetic properties.

Keywords: aniline-sulfide resin; magnetic; conducting polymer; nanocomposite

1. Introduction

Conducting polymers continue to be the focus of active research in diverse fields, including electronics, energy storage, catalysis, chemical sensing (Thomas *et al*. 2013 and Hosseini 2013).

Polyaniline is unique among conducting polymers in its wide range of electrical, electrochemical, and optical properties, as well as good stability (Hosseini *et al*. 2005). Polyaniline is typically synthesized by oxidizing aniline monomer either electrochemically or chemically (Hosseini *et al*. 2005). The most common strategy that has been implemented is to change the oxidizing agent employed in the chemical polymerization reaction. Magnetite (Fe_3O_4) is one of the famous magnetic materials in common use. Due to strong magnetic property and low toxicity, theirs applications in biotechnology and medicine has gained significant attention (Dresco *et al*. 1999). Many bioactive substances such as enzymes, proteins, antibodies, and anticancer agents

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have been bound to it (Tong *et al*. 2001 and Chen *et al*. 2002). The binding is commonly accomplished through the surface coating with polymers, the use of coupling agents or cross-linking reagents, and encapsulation. α–Fe_2O_3 (hematite) is a semiconductor (Eg=2.1 eV) which is environmentally friendly–nontoxic and corrosion-resistant (Wen *et al*. 2005). Various iron oxide structures, such as nanocrystals, particles, cubes, spindles, rods, wires, tubes, and flakes, have been successfully fabricated (Zhong *et al*. 2006). In addition, recent work has shown that Ostwald ripening does not adequately describe the kinetics of the particle growth for many systems (Huang *et al*. 2003). The preparation of Ni–Zn ferrite nanocomposites using mechanical milling method and magnetic, conductive, and microwave absorption properties of polythiophene nanofibers layered on $MnFe_2O_4$/Fe_3O_4 core–shell structures were reported in the recent years (Raju *et al*. 2013 and Hosseini *et al*. 2014). Deng and co-workers prepared magnetite/polyaniline (Fe_3O_4/PANI) nanocomposites with core-shell structure (Deng *et al*. 2002). Synthesis and microwave-absorbing properties of polypyrrole/$MnFe_2O_4$ nanocomposites was reported with high conductivity and saturated magnetization (Hosseini *et al*. 2012). The theoretical foundation of this method was common ion absorption effect. Fe_3O_4 nanoparticles were treated with $FeCl_3$ aqueous solution. Because of common ion absorption effect, Fe^{3+} ions were absorbed onto the surface of Fe_3O_4 nanoparticles to form a positively charged (Fe^{3+}) shell. In this article, we have reported a class cross linked polyaniline then prepared its magnetic nanoparticle by Fe_3O_4 shelled by PEG.

The preceding work, we prepared chemical and electrochemical synthesis of cross-linked aniline sulfide resin and its mechanism and kinetic polymerization studies (Hosseini *et al*. 2010). In this work, we have synthesized conducting and magnetic nanocomposite of cross-linked aniline sulfide resin with core-shell structure.

2. Experimental

2.1 Reagents and instrumentation

Aniline monomer (reagent grade, Merck) was distilled under the reduced pressure and stored below 0 ^oC. All the other reagents were analytical grade, and used without further purification, including polyethylene glycol (PEG Mw=4000), ferrous sulfate ($FeSO_4.7H_2O$), ammonia persulfate (APS), sulfur dichloride, sodium hydrate (NaOH), HCl (37%), hydrogen peroxide (H_2O_2, 30%), and ethanol. Water was double distilled and bubbled for 30 min with N_2.

Conductivity changes were measured with four-probe device (ASTM Standards, F 43-93). ^1H, ^{13}C-NMR spectra were recorded on a BRUKER 250 NMR spectrometer at 400 MHz in deuterated dimetylsulfoxide-d_6 with TMS as an internal standard. NMR data are reported in the following order: chemical shift (ppm), spin multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), and integration. The PHILIPS XL30 was used for scanning electron microscopy (SEM). The DME, Dualscope C 26 were used for Atomic Force Microscopy (AFM) and Vibrating Sample Magnetometer (VSM). The Philips-EM 208 was used for Transmission Electron Microscopy (TEM). FT-IR spectrum was recorded on a 8101-M-Shimadzu and BRUKER-IF-66.5 spectrometer. Vibrational transition frequencies are reported in wave number (cm^{-1}). The UV-Visible spectra were obtained using an UV-Vis recording spectrophotometer (Perkin-Elmer Lambda 15).

2.2 Preparation of Fe_3O_4 nanoparticles

A mixture of 7 g of PEG and 0.3 g of $FeSO_4.7H_2O$ dissolved in 20 mL of distilled water was placed in a 150 mL four-necked round bottom flask equipped with a condenser, a nitrogen inlet and a mechanical stirrer. The mixture was stirred under nitrogen for 30 min, followed by adding 5 mL of an aqueous solution containing 0.1 mL 40% H_2O_2. The reaction was allowed to proceed for 6 h at 50 ^oC at pH13. The pH of reaction mixture was regulated with 3 M NaOH solution. The produced magnetic fluid was dialyzed and purified repeatedly by magnetic fluid separation, decantation, and re-dispersed in water.

2.3 Preparation of Fe_3O_4-PEG core-shell nanoparticles

Monolayer PEG coated on Fe_3O_4 nanoparticles was prepared by ultrasonic irradiation. 2 g of Fe_3O_4 nanoparticles was dispersed in 150 ml of 2 vol.% PEG solution by ultrasonic treatment for 30 min and subsequent vigorous stirring for 1 h. The suspension was allowed to stand for more than 6 h, and then the PEG aqueous solution was decanted, leaving only PEG adsorbed on Fe_3O_4 nanoparticles to obtain the modified- Fe_3O_4 (Fe_3O_4-PEG).

2.4 Synthesis of aniline-sulfur resin (ASR) (Hosseini et al. 2010)

ASR was synthesized by reacting sulfur dichloride to aniline. In a 100 mL three necked flask equipped with a stir, a condenser and an inlet of nitrogen, 0.2 mL sulfur dichloride in 5 mL diethylether was added to a mixture of 0.5 g of aniline and 0.1 mL pyridine in 10 mL diethylether by drop wise. Condensation was carried at 25 ℃ for 1 h. The resin was filtered and washed with warm water three times. The resin was kept at 80 ℃ under a reduced pressure of 10 kPa for 1 h to remove any unreacted aniline and/or sulfur dichloride.

2.5 Synthesis of aniline-sulfur cross-linked copolymer (ASC)

In a 150 mL reaction vessel, 0.5 g ASR and 0.1 g aniline monomer were dissolved in 50 mL of 1 M HCl aqueous solution with varying ratios. A trace amount of $FeSO_4$ was added to the solution as a catalyst. Then 3 mL of 30% H_2O_2 was added drop wise to the solution with stirring vigorously. After polymerization for 6 h at 25 ℃, a dark polymer powder was obtained. The powder was washed with 1 M HCl until the washing solution became clear. Lower molecular weight oligomers were removed by further washing with copious amounts of acetonitrile. The doped ASC was obtained by acidification with 1 M HCl. The base form of the polymers was obtained by mixing the polymers with aqueous 1 M NH_3OH.

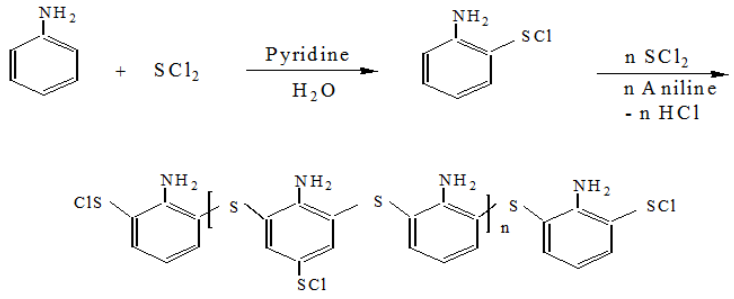
2.6 Synthesis polyaniline-sulfur cross-linked Fe_3O_4 nanocomposite (ASC-Fe_3O_4)

Fe_3O_4-PASC magnetic particles were prepared via an in situ emulsion polymerization in aqueous solution containing Fe_3O_4 magnetic fluid and PEG. The polymerization was carried out in a 250 mL round bottomed four necked flask equipped with a mechanical stirrer, an inlet of nitrogen and a condenser. The 0.5 g ASR, 0.2 g aniline, 0.15 g Fe_3O_4-PEG and 0.01 g $FeSO_4$ were dissolved in 50 mL of 1 M HCl. Then 4 mL H_2O_2 30% was added drop wise to solution; as a result, polymerization was allowed to proceed for 12 h at 0-5 ℃ under stirring. The products were

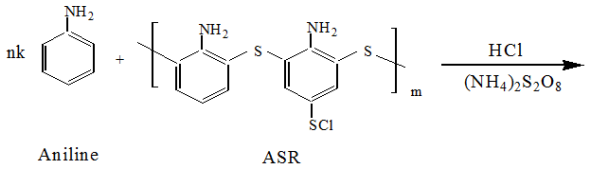
dialyzed and purified by magnetic field separation and decantation. This purification procedure was repeated four times. The microspheres were then immersed in a 0.1 M of HCl solution. The produced Fe_3O_4-PEG powder was removed by magnetic separation and washing with distilled water for three times. The products were dried under vacuum at 80 ℃ for 24 h.

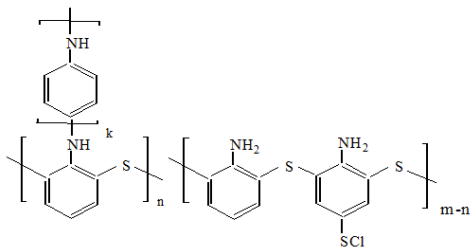
3. Results and discussion

ASC copolymer can be synthesized by chemically oxidizing of ASR in presence of aniline and an initiator. The Fe_3O_4-PASC nanocomposite can be synthesized by chemical oxidation of aniline, Fe_3O_4, and ASR mixtures, too. By controlling the ratio of ASR to aniline prior, Mw of ASC can be controlled. As a result, it is possible to change the molecular weight, solubility, and conductivity of the cross-linked polymer. Under appropriate conditions, high molecular weight polymers, with



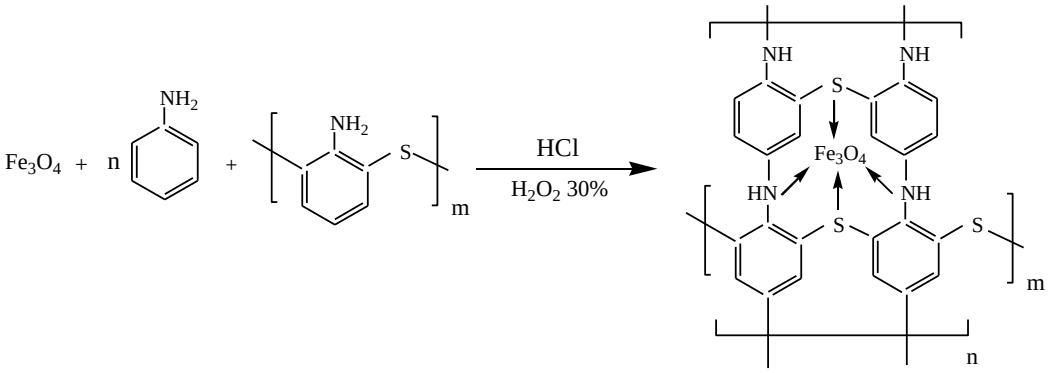
Scheme I





Aniline - Sulfur Crosslinked (ASC)

Scheme II



Scheme III

conductivity, flexibility and solubility similar to pure polyaniline, can be obtained. Uniform- sized Fe_3O_4-PASC nanocomposite containing different amount of magnetic nanoparticles has been prepared through modified polymerization.

The condensation and the chemical structure of ASR are shown in Scheme I, where the resulted polymer has alternatively substituted aniline and sulfur units.

ASR can be oxidatively polymerized in the presence of aniline, so copolymer is result with incorporate polyaniline and ASR (Scheme II). The fact that copolymerization occurs quite readily is attributed to the fact that the resulting structures allow ASR chains to be further apart, thereby reducing steric interactions. The proposed mechanism for the polymerization, role of ASC on the rate of polymerization and the influence of ASR on each step of polymerization are explained in preceding work (Hosseini *et al*. 2010). The synthesis procedures for Fe_3O_4 nanoparticles and Fe_3O_4-PASC nanocomposites are shown in Scheme III.

3.1 Structure characterization of Fe_3O_4-PASC nanocomposite, NMR

Figs. 1 and 2 show ^1H and ^{13}C-NMR spectra of Fe_3O_4-PASC nanocomposite, respectively. As shown in Fig. 1, ASC spectrum is similar to pure polyaniline but the peak at 2.4 ppm corresponds to trace proton of NMR-solvent and the peaks around 7-9 ppm are assigned to protons on the benzene ring. Therefore in Fig. 2, peaks at 36-40 ppm correspond to carbons of DMSO and the peaks around of 123-145 ppm are assigned to carbons on the benzene ring, too.

3.2 Structures and morphology

Fig. 3(a,b) shows the SEM images of the surfaces of Fe_3O_4-PASC nanocomposite. Based on the characterization of SEM, we can find that the morphology of final nanospheres changed from irregular to spherical at the same time. The prepared nanocomposite nanospheres in cross-linked resin are quite uniform in size just as SEM images. Transmission electron micrograph (TEM) proved that nanometer-sized Fe_3O_4-PEG in the composites was responsible for the ferromagnetic behavior of the composites.

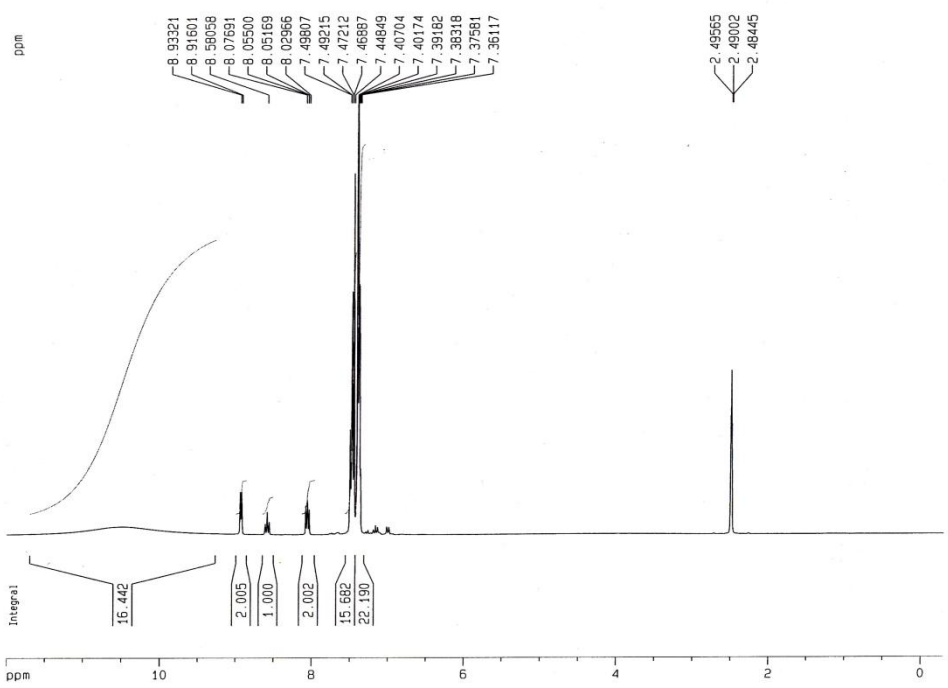


Fig. 1 FT-1HNMR of Fe3O4-PASC nanocomposite

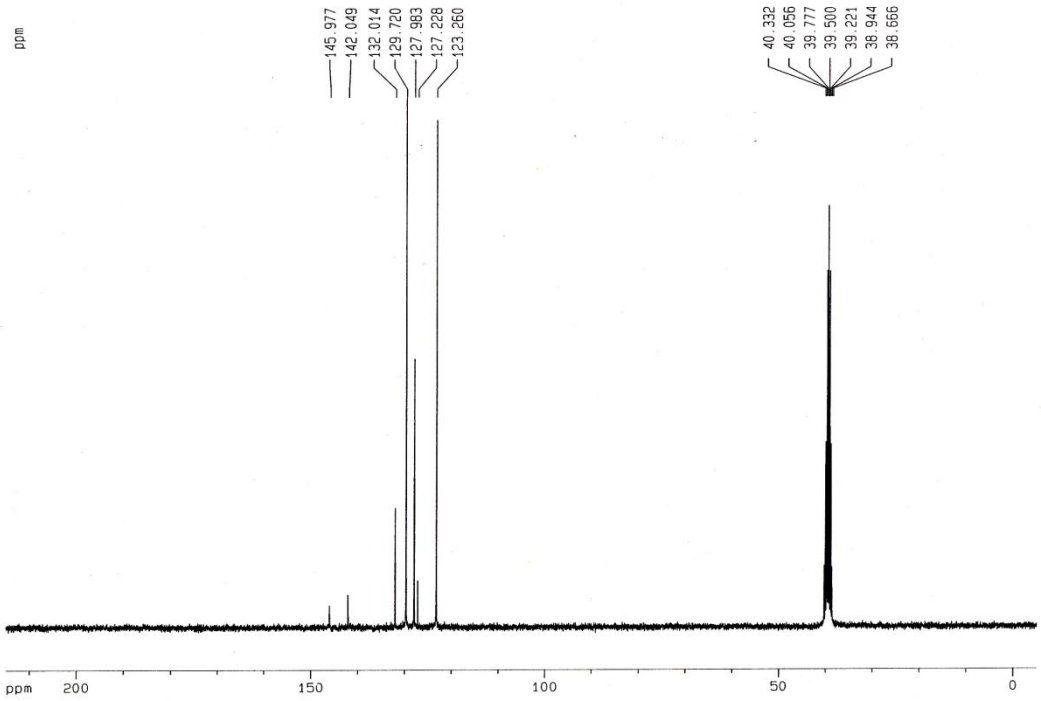
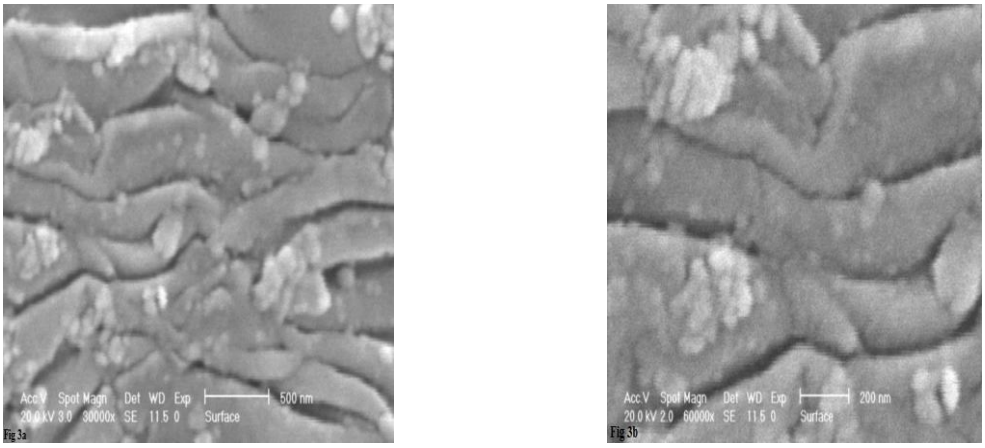


Fig. 2 FT-^{13}CNMR of Fe_3O_4-PASC nanocomposite



a b

Fig. 3 FT-^{13}CNMR of Fe_3O_4-PASC nanocomposite

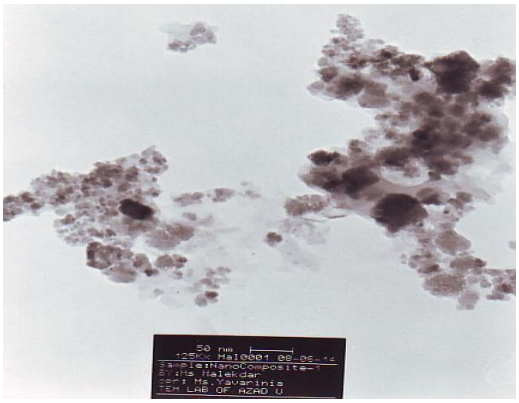


Fig. 4 The TEM photograph Fe3O4-PASC nanocomposite containing 15%wt nanoparticle

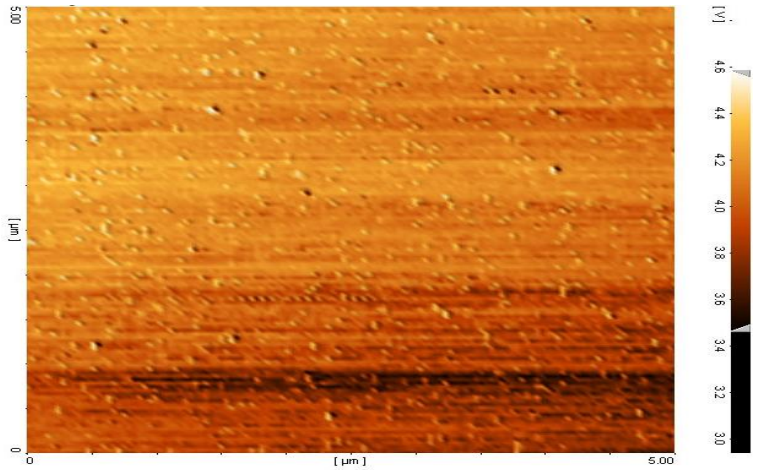


Fig. 5 Microcopy images of Fe3O4-PASC nanocomposite 15%wt a) optical microscopy and b) AFM topography

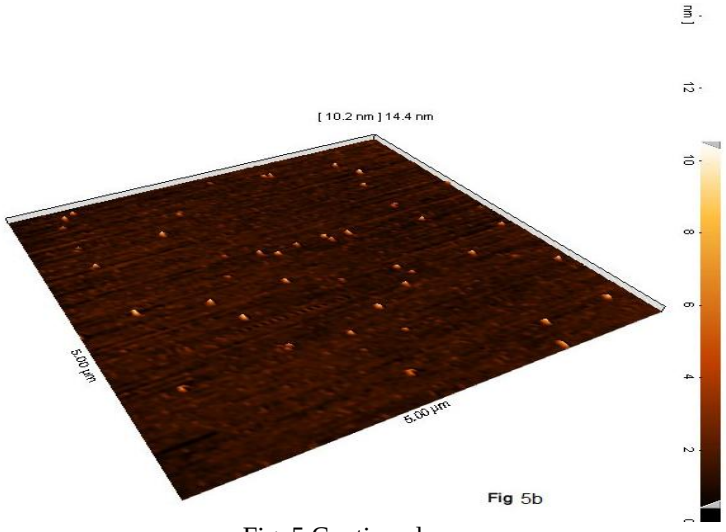


Fig. 5 Continued

The TEM photographs of Fe_3O_4-PASC nanocomposite was shown in Fig.4. In images, Fe_3O_4 nanoparticles in this composite were not dispersed and Fe_3O_4 nanoparticles were aggregated, while in other TEM photograph, Fe_3O_4 nanoparticles were not aggregated after ultrasonic system. In this case, Fe_3O_4 nanoparticles were encapsulated in the PASC chains. In Fig. 4, the magnetic shell formed in PEG solution had a relatively narrow particle size distribution with an average diameter of 20-30 nm and was small enough to exhibit ferromagnetic behavior. Ferromagnetism signifies that the magnetite particles have essentially single domains and these nanoparticles may be ideal components vehicles for magnetic field-directed delivery of therapeutic agent. In this system, PEG acted as an effective surfactant which can stabilize the magnetite particles in the system with lowest iron concentration and decrease the value of the saturation magnetization of the shell particles.

It is well known that the magnetic properties can be affected by both the magnetite size and the adsorption of a surfactant (Hosseini *et al*. 2014).

In this preparation, since the surfaces of nanoparticles were coated with a monolayer PEG, they were hydrophobic and readily dispersed under ultrasonic. AFM topographies of Fe_3O_4-PASC nanocomposite with 15%wt Fe_3O_4 are shown in Fig. 5(a,b). At nanoscopic scale, AFM images reveal Fe_3O_4 nanoparticles being uniform dispersed in PANi matrix. The polymeric shell of the magnetic composite sphere is important for the effective distance of neighboring magnetic grains. This polymeric shell can be weaken or eliminated coupling between them.

3.3 Magnetic properties

The magnetite particles were analyzed in room temperature by VSM with an applied field of -7.5 to 7.5 KOe. Plot of magnetization vs applied magnetic field for Fe_3O_4-PASC nanocomposite is presented in Fig. 6.

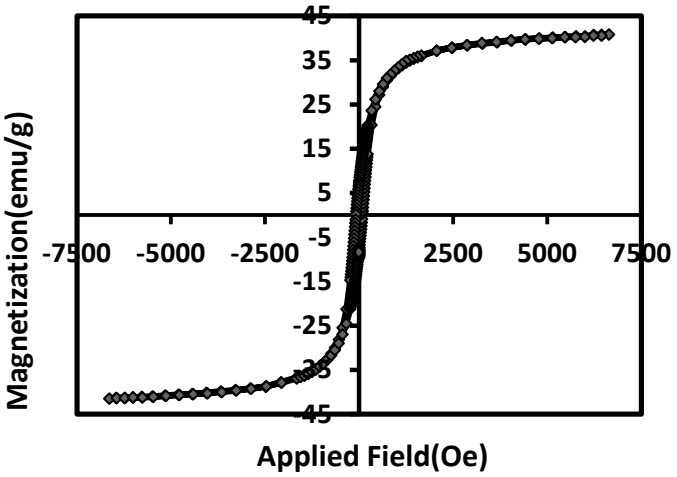


Fig. 6 Magnetization vs. applied magnetic field for of Fe_3O_4-PASC nanocomposite

The saturation magnetization (Ms) changes with the content of the Fe_3O_4 nanoparticles in the composite spheres were investigated. Its Ms was 41.46 emu/g and its magnetic content is 15wt%. The hysteresis loop which is the unique characteristic of the ferromagnetic behavior is clearly observed (*Hc=1.5* T) in Fig. 6. It can be inferred from the hysteresis loops that the composite magnetic spheres are magnetically soft at the 300 ^oC.

Uniform- sized Fe_3O_4-PASC nanocomposite containing different amount of magnetic nanoparticles has been prepared by modified polymerization. The resulting Fe_3O_4-PASC nanocomposite with core-shell structure showed ferromagnetic and electric properties. The saturated magnetization was increased by increasing of Fe_3O_4 content and decreased by increasing aniline ratio.

4. Conclusions

The resulting Fe_3O_4-PASC nanocomposite with core-shell structure showed ferromagnetic and electric properties. The saturated magnetization was increased by increasing of Fe_3O_4 content and decreased by increasing aniline ratio. The conductivity of the composites at room temperature depended on the Fe content and doping degree. Transmission electron micrograph (TEM) proved that nanometer-sized (about 20-30 nm) Fe_3O_4 in the composites was responsible for the ferromagnetic behavior of the composites. Fe_3O_4-PASC nanocomposite has been flexible structure with electrical and magnetic properties.

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