



Ferrofluid-polyaniline magnetic-conducting nanocomposite synthesized through miniemulsion polymerization

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Resumen

La polimerización en miniemulsión fue usada para sintetizar un nanocomposito magnético-conductor polianilina-ferrofluido (PANI-FFe₃O₄ NC). El fluido magnético fue sintetizado por peptización química usando ácido oleico e Isopar M como surfactante y portador respectivamente. Monómero anilina, dodecil sulfato de sodio (SDS), etil benceno, persulfato de amonio (APS) y el fluido magnético se hicieron reaccionar a temperatura ambiente durante varias horas para sintetizar el nanocomposito magnético conductor PANI-FFe₃O₄ NC fue caracterizado por conductividad, VSM y STEM. Ambos el fluido magnético y el nanocomposito muestran n comportamiento superparamagnético con Ms de 21.3 y 2.83 emu/g respectivamente. Las micrografías de STEM indican que las fibras del nanocomposito tienen un diámetro uniforme de ~60 nm.

Abstract

Miniemulsion polymerization was used to synthesize a magnetic-conducting polyaniline-ferrofluid nanocomposite (PANI-FFe₃O₄ NC). The magnetic fluid was synthesized by chemical peptization using oleic acid and Isopar-M as surfactant and carrier, respectively. Aniline monomer, sodium dodecyl sulphate (SDS), ethyl benzene, ammonium persulfate

(APS) and magnetic fluid were reacted at room temperature for several hours to synthesize the magnetic-conducting nanocomposite. PANI-FFe₃O₄ NC was characterized by conductivity, VSM, and STEM. Both, the magnetic fluid and the nanocomposite show a superparamagnetic behaviour with MS of 21.3 and 2.83 emu/g, respectively. STEM micrographs indicate that the nanocomposite fibers have a uniform diameter of ~60 nm.

Keywords: ferrofluid nanocomposite, nanoparticles, magnetic conducting

Introduction

Magnetic fluids are stable colloidal dispersions of nanosized magnetic particles in a liquid carrier. Although the particles used in most commercial applications are iron oxides (magnetite, maghemite) because of their resistance to oxidation, transition metals have the benefit of higher saturation magnetisation. Magnetic fluids can be used in rotating shaft seals, exclusion seals, loudspeakers, dampers, inclinometers shock absorbers of DVD and CD actuators, medical applications, etc ⁽¹⁾.

Incorporation of a magnetic material, such as Fe₃O₄, into an organic material has attracted great attention due to the resulting electrical properties as well as the many different applications, such as: charge dissipation devices for computer

hard disks, batteries, electrochemical display devices, molecular electronics, non-linear optics, sensors and microwave absorption materials ^(2, 3). The use of polyaniline (PANI) as the organic material has attracted much attention due to its characteristics, such as air stability and good solubility in several solvents, besides it shows several changes in its electronic structure depending on its oxidation level. Also, multi-functionality of the PANI micro-nanostructures combined with optical or magnetic function has also attracted interests in order to match the requirements of the technology applications ⁽⁴⁾. Electro-magnetic functionalized conducting polymer micro/nanostructures have special attention because of their applications in stealth materials and electrical interfaced shielding ⁽⁵⁾. One of its main characteristics is that it can be

synthesized by different polymerization techniques such as suspension, emulsion, synthesize NCs by encapsulating inorganic particles, such as CaCO_3 and Fe_3O_4 , into different monomers, such as St and MMA^(6, 7). Wan et al.⁽⁸⁾ reported PANI composites containing Fe_3O_4 nanomagnets prepared by chemical polymerization. Deng et al.⁽⁹⁾ also reported the preparation of PANI/ Fe_3O_4 nanoparticles with core-shell via in situ polymerization of aniline monomer in an aqueous solution, which contained Fe_3O_4 nanoparticles and surfactant. Wang et al.⁽¹⁰⁾ synthesized Fe_3O_4 /PANI core-shell nanoparticles via a miniemulsion polymerization. Miniemulsion polymerization requires the use of surfactants and co-surfactants to achieve a good stabilization between aqueous and oleic phases and to get polymer particle or fiber sizes from 50 to 500 nm in diameter. Miniemulsion polymerization presents advantages as an encapsulation method because the inorganic particles upon the in situ polymerization of the miniemulsion droplets^(11, 12) The droplets are stabilized by an ionic surfactant and a co-surfactant; the function of the co-surfactant is twofold, it can act in

microemulsion and miniemulsion⁽⁶⁾. The later is a technique used to combination with the surfactant to create a barrier and avoid the drop-to-drop coalescence, and in can limit the diffusion of the oleic phase of small drops to larger drops of monomer by virtue of the low water solubility that allows for a delicate balance between the drops of different size and composition⁽¹³⁾. The magnetic fluids have been used to synthesize this kind of NCs, which have magnetic particles disperse in a carrier liquid, such as Isopar-M. Isopar-M has been used as a stabilizer in PANI particle synthesis by Marie et al.⁽¹⁴⁾.

Therefore, Isopar-M has a double function within PANI- FFe_3O_4 NCs, as miniemulsion stabilizer and FF carrier liquid⁽¹⁴⁾. A magnetic-conductive nanocomposite was synthesized, from aniline and Isopar-M based magnetic fluid, at 25 °C for 4 hours by miniemulsion polymerization. This PANI- FFe_3O_4 NC was characterized by conductivity, vibrating sample magnetometry (VSM) and scanning electron microscopy (SEM) in STEM mode.

Experimental Methodology

Materials and equipment

All chemicals used in this work were reagent grade and were used without

Methodology

Magnetic Fluid

Magnetite nanoparticles were synthesized by chemical co-precipitation using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and NH_4OH . A molar ratio of 1:2 [$\text{Fe}^{+2}:\text{Fe}^{+3}$] was used and nanoparticle precipitation was done at 70 °C under vigorous agitation by

Magnetic – Conductive Nanocomposite Synthesis

PANI- FFe_3O_4 nanocomposite was synthesized by miniemulsion polymerization using aniline monomer and Isopar-M based magnetic fluid. The miniemulsion system was prepared by sonicating a mixture of a 1/99 weight ratio of SDS (surfactant)/water, 0.5 g

Fe_3O_4 , FFe_3O_4 and PANI- FFe_3O_4 Nanocomposite Characterization

Magnetic measurements were carried out in a Lakeshore 7300 VSM instrument at room temperature up to an applied field

further purification. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 98%, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 99%, NH_4OH 28%, oleic acid 90%, aniline 98%, SDS, APS and ethyl benzene were provided by Aldrich; Isopar-M were industrial grade.

addition of NH_4OH . A peptization process at 80 °C and a mechanical stirrer rotating at a speed of 1000 rpm used to synthesize the magnetic fluid by mixing the precipitated magnetite, oleic acid and Isopar-M, all together. Oleic acid and Isopar-M were used as surfactant and carried liquid, respectively.

magnetic fluid, 125 mg ethyl benzene (co-surfactant) and 3 g aniline for 2 min at 0 °C. Later, the miniemulsion system was taken to room temperature and a solution of APS (initiator) was added to carry out the polymerization for a period of 4 h.

of 12,000 Oe. Transmission electron microscopy (TEM) was carried out with a TEM JEOL 1200 EXII coupled with an IMAGE-PRO image analyzer to process the micrographs in order to get the

particle size and particle size distribution of magnetic particles. SEM JEOL JSM-740-1F in STEM mode by drying a diluted colloidal solution drop in a copper grid. The conductivity of PANI- FFe_3O_4

NC was assessed using a standard four-probe method in a Metex multimeter at 2-V.

Results and Discussion

Magnetometry

Typical magnetization vs applied field curves of FFe_3O_4 and PANI- FFe_3O_4 NC (containing ~10.5 wt % Fe_3O_4) are shown in Figure 1. No hysteresis loop (zero remanence and coercivity) was observed for both materials, which means both materials show a superparamagnetic behavior. The saturation magnetization (M_S) of the magnetic fluid and PANI- FFe_3O_4 nanocomposite was found to be 21.3 and 2.83 emu/g, respectively. The

value of the maximum magnetization reached in the nanocomposite is related to the concentrations of the magnetic phase in the fluid, it was expected that the M_S of the magnetic-conducting nanocomposite should be lower than the M_S of the magnetic fluid, in the same proportion as that of the magnetic nanoparticles concentration in the nanocomposite. This confirms that the nanocomposite magnetic behavior is produced only by the presence of the magnetic fluid in the nanocomposite since PANI is not magnetic.

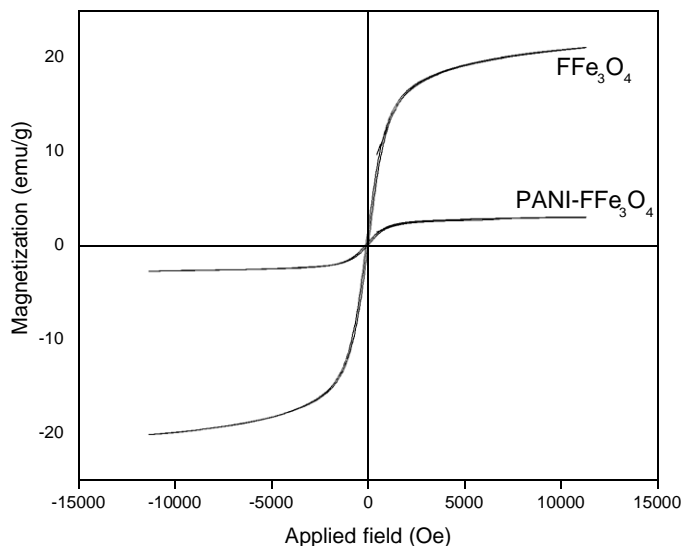
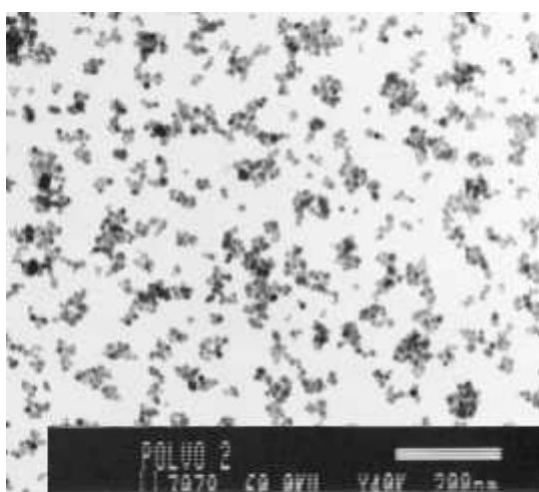


Figure 1. Magnetization curves of a) magnetic fluid and b) PANI- Fe_3O_4 nanocomposite.

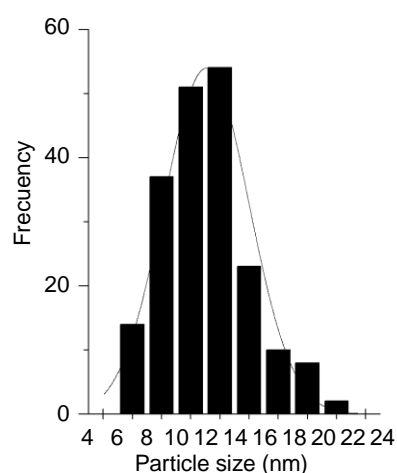
Scanning Electron Microscopy

Figure 2 a) y b) shows an electron micrograph of the magnetic particles and the particle size distribution obtained. Using TEM micrographs the particles size

distribution histograms were calculates as shown in Fig 2 b). Particle sizes between 6 and 22 nm are observed, with a mean size of 12 nm. The particles showed a spherical morphology.



a)



b)

Figure 2. a) Photograph of TEM of magnetite obtained by coprecipitation method, and b) particle size distribution of magnetic particles.

Figure 3 shows a micrograph of the magnetic fluid and nanocomposite obtained by STEM. We observed magnetic-conducting nanocomposite fibers with diameter and length sizes of about 60 and 400 nm, respectively.

The morphology and particle size of the magnetic fluid and nanocomposite were

determined by STEM. A micrograph of magnetic nanoparticles embedded in the magnetic-conducting nanocomposite. The particles are spherical with diameters below 12 nm. These particles are polydisperse and some of them agglomerated due to magneto-dipole interactions among them. The inset in

Figure 3 shows the magnetic-conducting nanocomposite fibers with diameter and

length sizes of about 60 and 400 nm, respectively

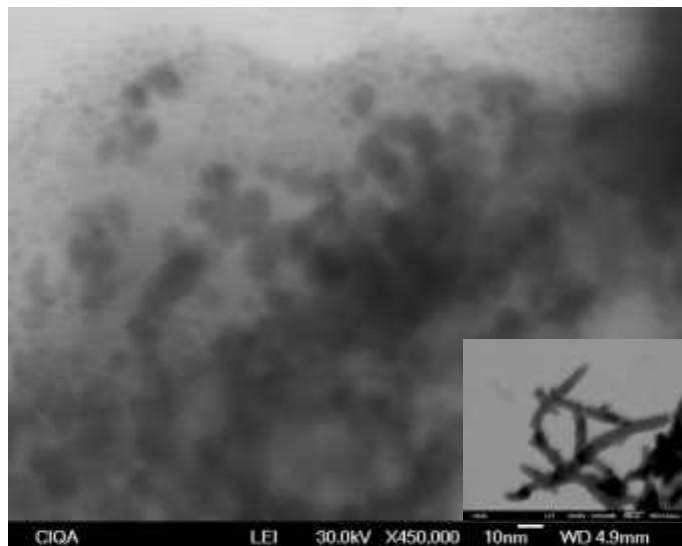


Figure 3. STEM micrographs of magnetic nanoparticles embedded into PANI-FFe₃O₄ nanocomposite and nanocomposite fibres (inset).

The distribution of magnetic fluid seems to be rather heterogeneous; some polymer fibers contain large amounts of magnetic fluid, where some others are practically void of magnetic particles. This effect can be explained by the ionic interaction between the surfactant, Isopar-M and co-surfactant. It is possible that these ionic interactions helped to maintain the magnetite within the monomer droplets once polymerization has initiated. It is important to mention that when a stable

magnetic fluid is incorporated into a nanocomposite, the magnetic fluid stabilization is lost and particles precipitate. This behavior was observed in synthesized PANI-FFe₃O₄ nanocomposite, and it can be assumed that this can be because the surfactant (SDS) used in the polymerization reaction and the magnetic fluid maintain some stability of the nanoparticles in the composite⁽¹⁴⁾.

PANI-FFe₃O₄ Nanocomposite Conductivity

The electromagnetic properties of nanostructured composites are strongly affected by the magnetic particle content. Conductivity at room temperature of 10.5 wt% Fe₃O₄ containing nanocomposite was 2×10^{-2} S/cm whereas PANI conductivity was 6×10^{-3} S/cm. The increase in conductivity of PANI-FFe₃O₄ nanocomposite with the incorporation of Fe₃O₄ could be due to an increase in the doping degree and type. This behavior is under further study.

CONCLUSIONS

Nanofibers of magnetic-conducting PANI-FFe₃O₄ composite containing Fe₃O₄ nanoparticles ($d < 20$ nm), with diameter of ~ 60 nm, length of ~ 400 nm, and conductivity of 2×10^{-2} S/cm, were

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Nanofibers of magnetic-conducting PANI-FFe₃O₄ composite containing Fe₃O₄ nanoparticles ($d < 20$ nm), with diameter of ~ 60 nm, length of ~ 400 nm, and conductivity of 2×10^{-2} S/cm, were successfully synthesized by a miniemulsion polymerization. PANI-FFe₃O₄ NC exhibited a superparamagnetic behavior due to nanosized Fe₃O₄ particles in the composite.

successfully synthesized by a miniemulsion polymerization. PANI-FFe₃O₄ NC exhibited a superparamagnetic behavior due to nanosized Fe₃O₄ particles in the composite.

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