Revista Internacional de Investigación e Innovación Tecnológica

Página principal: www.riiit.com.mx

# 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-$FFe_3O_4$ 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-$FFe_3O_4$ 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, maguemite) 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 $Fe_3O_4$, 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, muli-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, microemulsion and miniemulsion [6]. The later is a technique used to 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 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-F$Fe_3O_4$ 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 ºC for 4 hours by miniemulsion polymerization. This PANI-F$Fe_3O_4$ 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 further purification. $FeCl_3\cdot 6H_2O$ 98%, $FeCl_2\cdot 4H_2O$ 99%, $NH_4OH$ 28%, oleic acid 90%, aniline 98%, SDS, APS and ethyl benzene were provided by Aldrich; Isopar-M were industrial grade.

## Methodology

### Magnetic Fluid

Magnetite nanoparticles were synthesized by chemical co-precipitation using $FeCl_3\cdot 6H_2O$, $FeCl_2\cdot 4H_2O$ and $NH_4OH$. A molar ratio of 1:2 [$Fe^{+2}$:$Fe^{+3}$] was used and nanoparticle precipitation was done at 70 ºC under vigorous agitation by 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 – 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 magnetic fluid, 125 mg ethyl benzene (co-surfactant) and 3 g aniline for 2 min at 0 ºC. 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.

### $Fe_3O_4$, $FFe_3O_4$ 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 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.

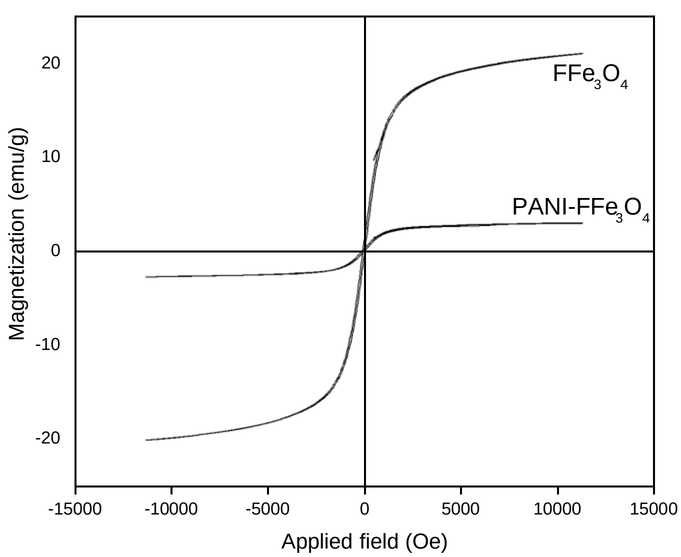
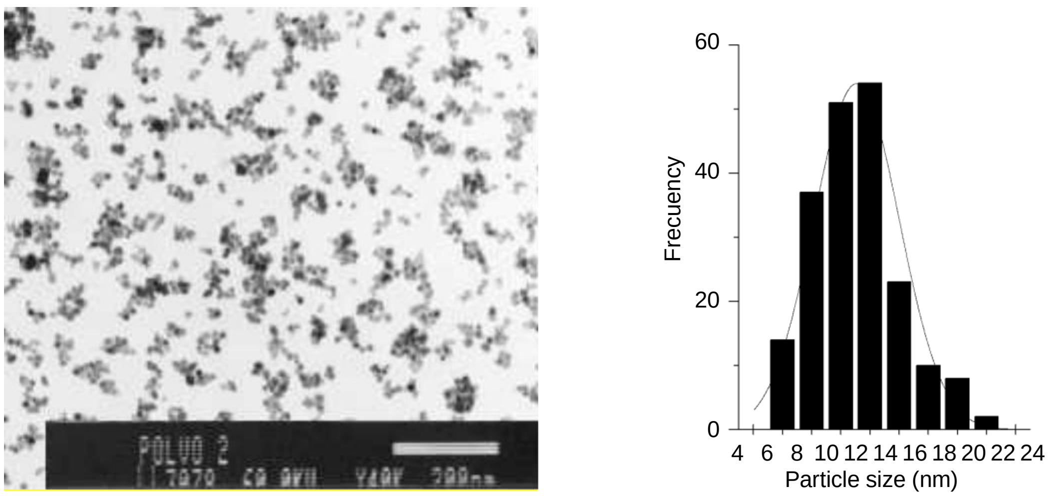


**Figure 1.** Magnetization curves of a) magnetic fluid and b) PANI-F$Fe_3O_4$ nanocomposite.

**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

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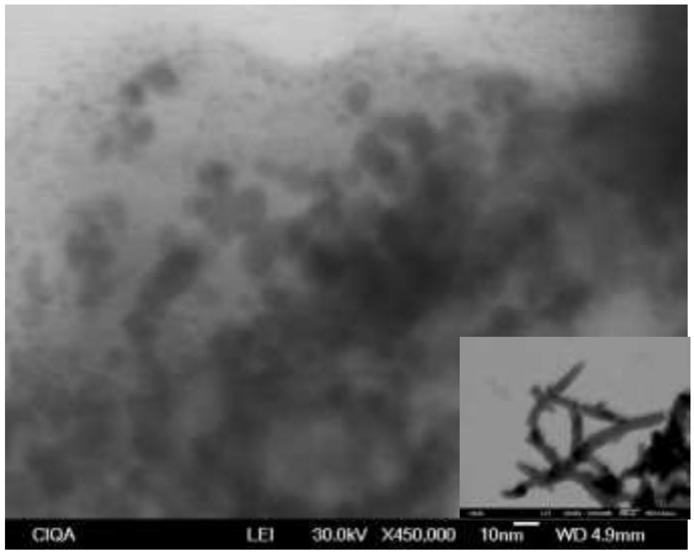


**Figure 3**. STEM micrographs of magnetic nanoparticles embedded into PANI-FFe$_3$O$_4$ nanocomposite and nanocomposite fibres (inset).

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-FFe$_3$O$_4$ 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-F$Fe_3O_4$ Nanocomposite Conductivity

The electromagnetic properties of nanostructured composites are strongly affected by the magnetic particle content. Conductivity at room temperature of 10.5 wt% $Fe_3O_4$ containing nanocomposite was $2x10^{-2}$ S/cm whereas PANI conductivity was $6x10^{-3}$ S/cm. The increase in conductivity of PANI-F$Fe_3O_4$ nanocomposite with the incorporation of $Fe_3O_4$ could be due to an increase in the doping degree and type. This behavior is under further study.

Nanofibers of magnetic-conducting PANI-FFe3O4 composite containing $Fe_3O_4$ nanoparticles (d < 20 nm), with diameter of ~60 nm, length of ~400 nm, and conductivity of $2x10^{-2}$ S/cm, were successfully synthesized by a miniemulsion polymerization. PANI-F$Fe_3O_4$ NC exhibited a superparamagnetic behavior due to nanosized $Fe_3O_4$ particles in the composite.

## CONCLUSIONS

Nanofibers of magnetic-conducting PANI-FFe3O4 composite containing $Fe_3O_4$ nanoparticles (d < 20 nm), with diameter of ~60 nm, length of ~400 nm, and conductivity of $2x10^{-2}$ S/cm, were successfully synthesized by a miniemulsion polymerization. PANI-F$Fe_3O_4$ NC exhibited a superparamagnetic behavior due to nanosized $Fe_3O_4$ particles in the composite.

**Acknowledgments** We thank CONACyT-México for the economic support through CONACyT project CB-2007/80159.

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