Magnetic nanoparticles covalently functionalized with oleoyl chloride

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ABSTRACT— In this work, different conditions for the synthesis of magnetic iron oxide nanoparticles (P) covalent functionalized are presented. These modifications were made in order to fix the magnetic material in an organic matrix by copolymerization reaction. A simple strategy of acid chloride chemistry for the modification of nanoparticles surface (FP_i) is proposed. The process includes an ultrasound-supported addition in non-aqueous media to obtain iron oxide nanoparticles with organic chains covalently bonded to its surface coated. The structure and morphology of the prepared P and composite materials were characterized by transmission electron microscopy (TEM), x-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and the thermal stability (TG). The magnetic functionalized nanoparticles (FP_i) can be easily included in a co-polymerization with styrene to prepare composite materials (FP_i-PS). Morphological analysis of these composites confirms a homogeneous dispersion of the functionalized nanoparticles attached to the organic matrix.

Index Terms— *magnetic nanoparticles, covalent functionalization, ferrofluids*

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1 INTRODUCTION

Magnetic nanoparticles and their surface modifications have attracted great attention in oil industry, and in environmental and biomedical applications. When these surface modifications were made through covalent bonding, the corresponding composite material acquires several desirable characteristics. Covalent functionalization is an important key to give stability to the material in drastic conditions such as high salinity, temperature, extreme pH, etc. This behavior would allow that these nanomaterials can be used in hard conditions, without the decomposition of the nanoelement.

In the past years, there have been several researches in nanoparticles surface modification. In 2007, Zhang et al.[1] used 3-(2-bromo-2-methylacryloxy) propyltrethylsilane to build a macroiniciator for Atom Transfer Radical Polymerization (ATRP) on silica nanoparticles surface, and obtained monodisperse nanospheres with silica *core* and polystyrene *shell*. During the same year, Sun et al.[2] used a 2-bromo-2-methyl-N-(3-(triethoxysilyl)propyl) propanamide for surface covalent functionalization of magnetic nanoparticles *via* ligand exchange. These functionalized nanoparticles were used for ATRP macroiniciator and obtained magnetic nanoparticles coated with polystyrene, hybrid materials with excellent dispersion in organic solvents. The options of that kind of functionalization, with homo or copolymers, with different way of growth control, are still producing new materials [3].

These hybrid materials constitute the starting point that opens innumerable possibilities of applications in many different fields of technological application. Phuong Huu Do et al. reported the synthesis of magnetic composite nanoparticles enveloped in copolymers for oilfield applications [4]. In a more recent study [5], Atta et al. analyzed the chemical surface modification of nanoparticles to be used as crude oil collector.

In other field of interest, magnetite nanoparticles were functionalized with carboxymethyldextran (CMDx) covalently attached to the magnetic nanoparticles in order to prevent polymer desorption in biomedical applications [6]. Early clinical evidences have suggested that functionalization of nanoparticles with specific recognition chemical moieties, indeed yields multifunctional nanoparticles with enhanced efficacy, while simultaneously reducing side effects, due to properties such as targeted localization in tumors and active cellular uptake [7]. Recently, magnetic nanoparticles have attracted attention because of their potential as contrast agents for magnetic resonance imaging (MRI) and heating mediators for cancer therapy (hyperthermia). Since magnetic nanoparticles are attracted to a high magnetic flux density, it is possible to manipulate cells labeled with magnetic nanoparticles using magnets; this feature has been applied in tissue engineering [8]. Besides, in the field of polymers, Lakouraj *et al*. [9] prepared a high-performance epoxy resin with excellent thermal, chemical and corrosion stability using amino functionalized Fe_3O_4 nanoparticles as curing agent. In this work, we explore the surface functionalization of maghemite nanoparticles with oleic acid residues, *via* the acyl chloride approach in order to fix them in organic matrix by a copolymerization reaction.

1. Experimental

2.1 Synthesis of Nanoparticles (P)

For the synthesis of magnetic nanoparticles a variation of a procedure reported by Vergés et al. was used [10]. Shortly, two solutions were prepared, A and B. Solution A was prepared by dissolving 20.57 g of $FeSO_4.7H_2O$ in 300 mL distilled water in a three-neck round bottom flask. The solution was heated with magnetic stirring to 80 ºC for 30 minutes under an inert atmosphere of nitrogen. Solution B was prepared by dissolving 1.70 g of KNO_3 and 14.56 g of KOH in 100 mL distilled water under nitrogen atmosphere for 5 minutes in a separate container. Then, solution B was slowly added to solution A reaching pH 12. After 45 minutes, the three-neck round bottom flask was cooled in the refrigerator. 1.5 hours later, the system was placed on a magnet for 2 minutes, so the supernatant was discarded. The separated precipitate was washed 4 times with distilled water, 2 with ethanol and 1 with acetone. In each case, the suspension was centrifuged before discarding the supernatant. Finally, the precipitate was left to dry in a vacuum oven for 24 hours.

2.2 Functionalization of Nanoparticles (FP_i)

The functionalization of the nanoparticles (P) prepared in 2.1 was carried by a modification of the method reported by Brzozowska et al [11]. 300 mg of magnetic nanoparticles were suspended in 55 ml of toluene in a flask with a septum inlet. The resultant mixture was stirred under nitrogen and 2.5 ml of triethylamine and 5 ml of oleoyl chloride were added to the flask using a syringe. The system was left 24 hours under nitrogen with continuous stirring. The functionalized nanoparticles were washed 4 times with acetone, 2 with ethanol, 2 with distilled water and 2 with acetone, using the centrifuge to separate the supernatant. The precipitate was left to dry in a vacuum oven for 24 hours. Samples nominations are presented in Table 1.

Table 1. Samples nomination and experimental conditions

MNP_s SAMPLE	mol OC/mg Part. ($.10^{-6}$)	TEA (ml)	AN (ml)	Composite Sample
P	---	---	---	P-PS
FP_1	7.75	0.45	---	---
FP_2	38.8	2.5	---	FP_2-PS
FP_3	38.8	2.5	1	---

Where MNPs: magnetic nanoparticles; AN: acetonitrile; OC: oleoyl chloride;
TEA: triethylamine; P: nanoparticles; FP_i: functionalized nanoparticles;
P-PS: nanoparticles polymerized with styrene; FP_2-PS: functionalized nanoparticles FP_2, polymerized with styrene.

2.3 Characterization of samples

The crystallinity of P was studied using X-ray diffraction (XRD). The spectra were obtained on a Siemens XRD instrument, using filtered Cu Kα radiation with accelerating voltage of 40 kV, current of 30 mA and scanned at 2Θ from 10º to 80º. Samples profiles were analyzed with X-Pert program for phase's identification and with the Powder cell program for structural parameters. For structural characterization transmission electron microscopy (TEM) was performed. A vibrating sample magnetometer Lakeshore 7300 was used to measure magnetic properties at room temperature. Hysteresis loops M vs H were measured with a maximum applied field of 15 kOe. Thermogravimetric analysis (TG) of the functionalized samples was carried on a thermalgravimetric analyzer (Shimadzu, DTG-50) under a linear heating of 10 K min^{-1}, in air atmosphere. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet FT-IR Instrument 510P. For this purpose, KBr and powder samples pellets were prepared. All experiments in this study were performed at room temperature.

2.4 Polymerization of nanoparticles (P-PS and FP-PS)

60.6 mg of magnetic nanoparticles and 18 mg of AIBN (azobisisobutyronitrile) as radical initiator were weighted in a test tube. Then, 2.2 ml of styrene were added under magnetic stirring. The tube was placed in a glycerin bath at 80 ºC during 4.25 hours, and after that, the composite material was obtained.

2.5 Dissolution of composite in toluene

500 mg of the above mentioned composite were dissolved in 3 ml of toluene with sonication, during 1.5 hours. Then, an additional 1 ml of toluene was added heating the system at 45 ºC during 15 minutes. On this suspension, a magnetic separation was performed, and the magnetic material was washed 3 times with 1 ml toluene. Finally, the solid sample and the liquid sample were left to dry in a vacuum oven for 12 hours.

3 Results and Discussion.

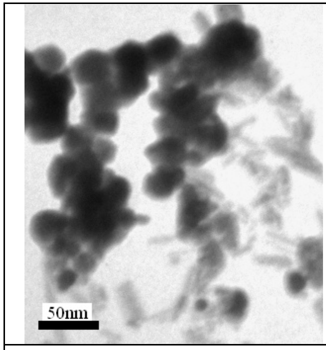
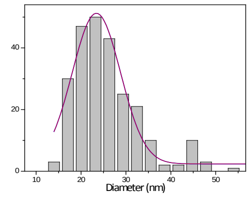
	

Fig.1 a) Microphotography of sample P	Fig.1 b) Histogram of sample P

TEM images (Fig.1a) show faced particles with homogeneous size distribution near 23 nm while XRD (inset of Fig.2) confirm spinel phase.

Prepared nanoparticles (P) were analyzed by transmission microscopy. TEM images (Fig.1) show faced particles with homogeneous size distribution near 23 nm

To achieve a covalent functionalization of magnetic nanoparticles (Table 1), we transform some surface hydroxyl groups into esters, by treatment with oleic acid chloride. In order to find favorable reaction conditions at room temperature, we performed the transformation in three different ways:

a.- Suspension of nanoparticles (300 mg) in toluene (25 mL) with addition of oleoyl chloride (1 mL) and TEA (0.45 mL) (FP_1).

b.- Suspension of nanoparticles (300 mg) in toluene (55 mL) with addition of oleoyl chloride (5 mL) and TEA (2.5 mL) (FP_2).

c.- Idem b) where P are previously treated with acetonitrile in order to deployed surface hydroxiles (FP_3).

Fig. 2 shows the magnetic behavior of the prepared as (P) and the corresponding functionalized (FP_i) nanoparticles. All samples show a superparamagnetic profile related to the small size of nanoparticles. It is remarkable that after each chemical functionalization the magnetic properties are conserved. Saturation magnetization of P is lower than the characteristic bulk values (near 80 emu/g). Ms of FP_i correspond to a fraction P, as it is functionalized with a non-magnetic chain.

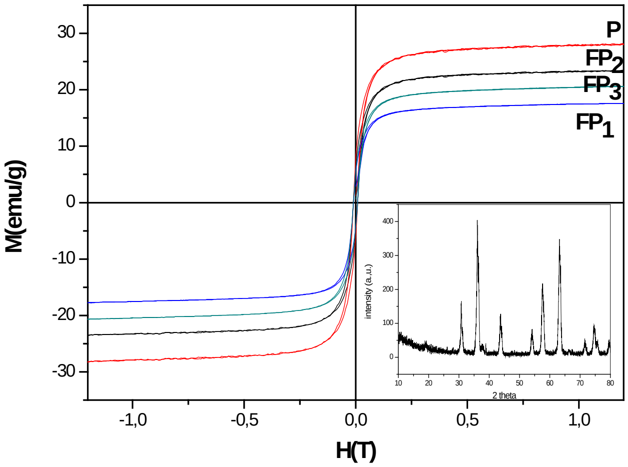


Fig.2. Magnetic profiles of the as prepared (P) and the functionalized (FP_i) nanoparticles. The inset shows the diffraction pattern of P.

Structural pattern (inset) corresponds to a monophasic sample (P) indexed as magnetite. No extra phases were detected in the DRX pattern.

In order to get evidence of surface functionalization, we performed the corresponding FT-IR on FPi samples and compared them with the corresponding non functionalized nanoparticles. As it was logical, spectra of all FP_i samples were very similar and showed evidences of the presence of water, but they are completely different to that of non-functionalized P, so, we can conclude that some modifications took place. Fig. 3 shows the spectra of FP_2 and P, but the evidences were not conclusive. Even when FPi were cleaned with different solvents and dried in vacuum, them retains some water and the absorption band O-H stretching is so broad that the contribution of C-H stretching may go unnoticed if the degree of functionalization was low. Despite that, a shoulder is visible around 3000 cm^{-1}, which could be assigned to C-H bonds. Besides, the bending band for water at 1644 cm^{-1} could interfere with the observation of C=O stretching band. In order to get a higher functionalization, we performed the third synthesis with the same conditions than b.-, including a previous treatment of nanoparticles with acetonitrile (FP_3). This previous treatment was made in order to expose the surface hydroxyl groups by means of interaction with a more polar solvent, promoting a higher degree of functionalization.

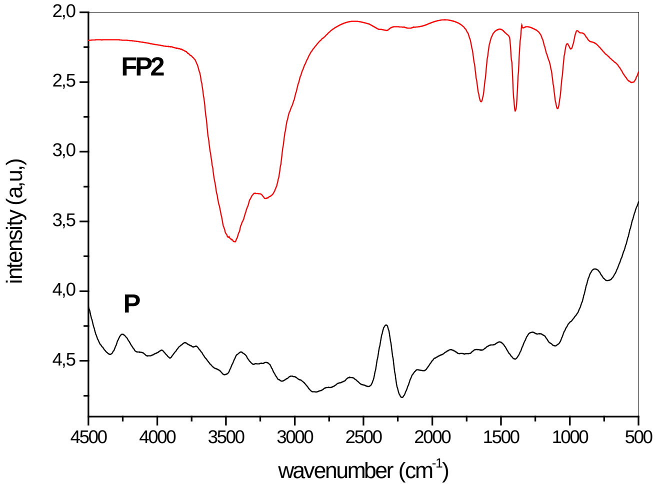


Fig.3. FTIR spectra of magnetic nanoparticles as prepared (P) and one of the functionalized nanoparticles (FP_2) as example.

To verify the presence of organic material associated to FPi, the new materials were analyzed by TGA, as it is presented in Fig. 4.

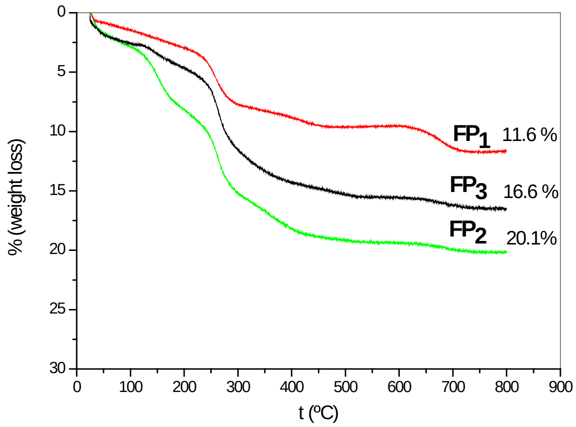


Fig. 4. Thermogravimetric profiles of the functionalized samples

For each different material, an initial loss of weigh were observed, which could be attributed to a variable amount of water (1.9% for FP_1; 3.2% for FP_2). Thermograms show that, even using excess of chloride in both cases, FP_1 has a lesser loss of weight than FP_2 (11.61% vs 19.48%) indicating that the last one incorporate a higher proportion of organic mass, so better results were obtained when a large excess of reagent was used. To determine if the low percentage of functionalization is related with a limited availability of surface hydroxyls (which could lost their activity

during de drying process), we treated the MNPs with acetonitrile (FP_3), previously to the functionalization, using the same conditions than for FP_2.

The resulting material (FP_3) showed a higher loss of mass than FP_1 (15.88% vs 11.61%), but lesser than FP_2. This can be attributed to a strong interaction between hydroxyl groups and acetonitrile, which probably act building a solvent shell around the superficial functional group, preventing their functionalization. Taking into account the average surface, the composition of magnetic nanoparticles, and the results of TGA we can conclude that the functionalization includes an average of one oleic molecule by magnetic nanoparticle.

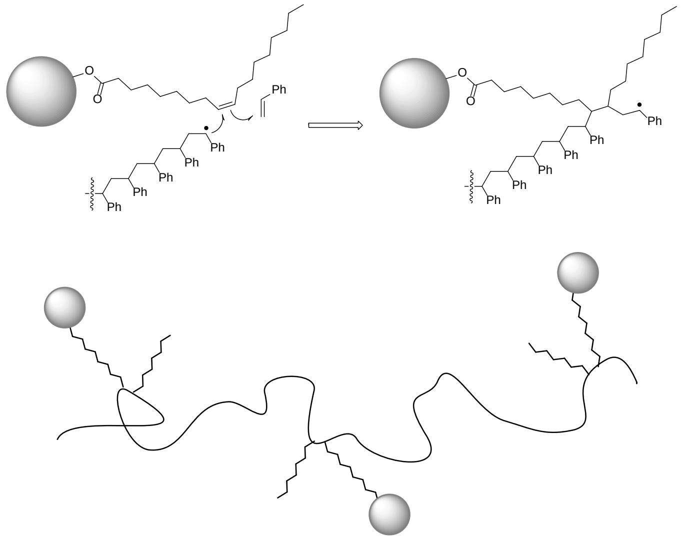
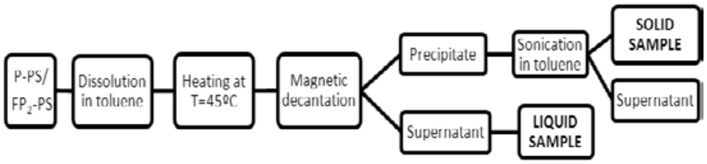


Fig. 5. Incorporation of FP_i to PS growing chain.

As it is well known, 1,2-disubstituted double bond cannot self- polymerize, but they are appropriate substrates for copolymerization. In order to confirm covalent attachment between oleic acid and particle surface, we decided to perform two polymerizations of styrene (S), one in presence of FPi and the other with P without functionalization. So, with the existence of covalent bonding nanoparticles they would be incorporated to the polymer chain as a backbone decoration (see Fig. 5), meanwhile if the presence of organic matter in nanoparticles was due to simple chemisorption, it could be removed by dissolution of polymer followed by magnetic separation.

In order to determine if the magnetic element was covalently incorporated to polymeric matrix, we followed the procedure detailed in Scheme 1.(at the end of the paragraph)



Scheme 1. Experimental procedure to explore polymerized nanoparticles (P-PS and FP_2-PS)

From 2.4 and 2.5, if a homogeneous material is supposed, it can be calculated that the amount of P or FP_2 is about 15mg.

As result of the procedure showed in Scheme 1, 18 mg of nanoparticles were recovered from P-PS. This value is very close to the theoretical one. The same workup carried out on FP_2-PS, yield 50 mg of magnetic material, which indicates that around 35 mg of organic material still remains attached to FP_2 after solvent washing as they were covalently incorporated.

Optical microscopy of materials P-PS and FP_2-PS are shown in Fig.6 (a and b). The later presents a more homogeneous surface, meanwhile P-PS seems to be a more discontinuous material.

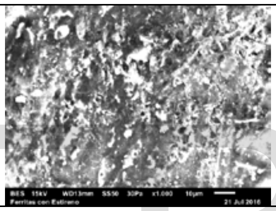
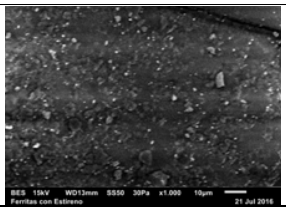
	

Fig.6 a) Micrograph of P-PS	Fig.6 b) Micrograph of FP_2-PS

4 Conclusion

As result of this work we can conclude that our proposed modification of the acyl chloride treatment is a valid strategy for covalent surface modification of magnetic nanoparticles. A previous treatment with a polar non protic solvent was not effective in order to increase the degree of modification, but even with a low degree of functionalization, the FPi were able for covalent incorporation into polymeric matrices. Further experiments are in progress for magnetic films preparation.

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