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# Preparation and Characterization of magnetic latexes using Styrene monomer

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## Summary

Preparation of magnetic latexes using styrene as monomer was carried out via miniemulsion polymerization. Magnetite ($Fe_3O_4$), with an average size of 12nm was used as magnetic particles. An organic phase is prepared dispersing the magnetite in styrene where bis(2-ethyl, hexyl) sulphosuccinate (AOT) is used as dispersant of the particles. The dispersion is miniemulsified in water using Cethyltrimethylammonium bromide (CTAB) as second emulsifier forming a stable emulsion. The miniemulsion polymerization was carried out at 60° C and was initiated with 2, 2 Azo-bis-iso-butyronitrile (AIBN). The latexes obtained were characterized by X-ray diffraction, Magnetometry and Transmission Electronic Microscopy.

## Introduction

The magnetic powders are inorganic materials that can be embedded in a polymeric matrix. The mechanical properties of the composite are dictated by the polymeric phase and the magnetic properties by the magnetic material. Magnetic powders include ferrites and intermetalic composites of rare earths. Magnetic materials have a wide range of applications in engineering and in medicine, such as, devices for automotive and communications systems, and thermosensitive magnetic particles for antibody purification [1].

The miniemulsion polymerization has been used to encapsulate inorganic particles to produce "polymer coated inorganic particles". This process requires a large amount of emulsifier and a co-surfactant, such as a long chain alcohol. This process can be defined as the polymerization of all monomer droplets present in the initial emulsion, where the final particle size distribution will correspond to the initial droplet size distribution [2]. Droplets generally range in size from 50 to 500 nm and the emulsion can be stable for as little as days or as long as months. The droplets are usually stabilized by the combination of an ionic surfactant and a co-surfactant [3].

Several works have been reported related to the encapsulation of inorganic particles. Hasegawa *et al.* encapsulated barium carbonate and calcium carbonate using methyl methacrylate as monomer via emulsion polymerization, finding that the encapsulation depends on the concentration of initiator [4]. The kinetics of emulsion polymerization using a MMA – $K_2S_2O_8$ – $H_2O$ system with barium sulfate powder has been studied by M. Konno *et al.* They found that the polymerization rate is greatly affected by the addition of the inorganic powder simply because the medium in which the polymerization is carried out changed considerably with the addition of powder [5]. The encapsulation of titanium dioxide has been investigated by B. Erdem *et al.* [6] using OLOA 370 as stabilizer in miniemulsion polymerization, they found that the inorganic particles are better encapsulated when they are dispersed in the oleic phase. D. Hoffmann *et al.* [7] used magnetite particles in a recent study, where they showed that these particles can be encapsulated into polystyrene through a miniemulsion process using oleoyl sarcosine acid for the magnetite-styrene interface and sodium dodecylsulfate for the styrene-water interface, creating a polymer coated ferrofluid.

Notwithstanding that the magnetic particles have been encapsulated by a polymer, the study of their magnetic properties and the use of different miniemulsion systems (surfactant, co-surfactant, initiator), has not been investigated. Therefore, the purpose of this work is to encapsulate magnetic particles with polystyrene, attaining nanometric dimensions, using miniemulsion polymerization with AOT as dispersing agent of magnetite in monomer, CTAB as surfactant of monomeric droplets in water in order to form the miniemulsion, and AIBN as initiator of the polymerization. The magnetic particles were prepared by chemical coprecipitation.

## Experimental

### *a) Chemicals*

For the preparation of magnetite, all chemicals were reagent grade and were used as received. $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, and $NH_4OH$ were from Aldrich. Styrene (St) from Aldrich was distilled at reduced pressure; bis(2 ethyl hexyl) sulphosucinate (AOT) from Fluka, and Hexadecane, Cethyltrimethylammonium bromide (CTAB), and 2,2-Azobisisobutyronitrile (AIBN) from Aldrich were used as received.

### *b) Preparation of magnetite.*

The magnetic particles were obtained by chemical coprecipitation, from a mixture of two aqueous solutions, one containing metallic salts and the other containing an alkali hydroxide. The chemical reaction is carried out using a molar ratio of 3:2 of $Fe^{3+}$:$Fe^{2+}$, at 70 °C and intense agitation; the alkali solution is added as fast as possible in order to get the smaller particle size. The magnetite was then thoroughly washed with distilled water to eliminate chloride ions and finally dried for use.

*c) Polymerization process.*

1 g of magnetite was dispersed in 15 g of styrene, with 1 g of AOT as surfactant, using a Branson sonifier W700 at 37% power, in three intervals of 5 min each; being this the oil phase in the polymerization system. 12.5 g of this dispersion were added to a solution of 50.5 g of water with 0.2519 g of CTAB as oil-water surfactant and 0.1209 g of initiator AIBN. The mixture was sonificated for 1 minute with a 37% power using a Branson sonifier W700 digital. After the mini-emulsion is formed it is added to a flask reactor under nitrogen to prevent oxidation. The reaction temperature was 60°C and usually it was completed after 3 hours.

*d) Characterization.*

Magnetite and magnetic polymer latexes were characterized with a JEOL 1200-EXII TEM to obtain the particle size distribution and see the encapsulation of magnetite with polymer by EDAX; they were also characterized by magnetometry using a Lakeshore 7300 vibrating sample magnetometer. The magnetite was characterized with a Siemens D-5000 X-Ray difractometer using $CuK_\alpha$ (25 mA, 35 kV).

## Results and Discussions

*Characterization of Magnetite*

*X-Ray Diffraction Studies*

Figure 1 shows the diffraction pattern of magnetic particles obtained by chemical coprecipitation. The presence of a magnetic phase associated to magnetite and maghemite is presented for the magnetic powders, according to standard patterns of magnetite and maghemite. The average particle diameter was determined through the Debye-Scherrer equation using the half maximum width $\beta$ of X-ray diffraction lines:

$$d = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

Where $\lambda$ is the radiation wavelength, which corresponds to 1.5406 Å and $\theta$ is the diffraction angle of the main peak. $\beta$ is calculated according to a Lorentz fitting of the main diffraction peak (311). For the prepared powder we found $d = 11.5$ nm.

The lattice parameter for the sample obtained from the main diffraction line (311) is $a = 8.368$ Å. This value lies between the lattice parameter corresponding to magnetite $a = 8.396$ Å and the one corresponding to maghemite $a = 8.35$ Å.

*Magnetic Measurements*

Magnetization measurements of magnetite and magnetic latexes were carried out at room temperature using a Lakeshore 7300 vibrating sample magnetometer (VSM). Figures 2 and

3 show a typical superparamagnetic behavior for magnetite and magnetic latexes, respectively.

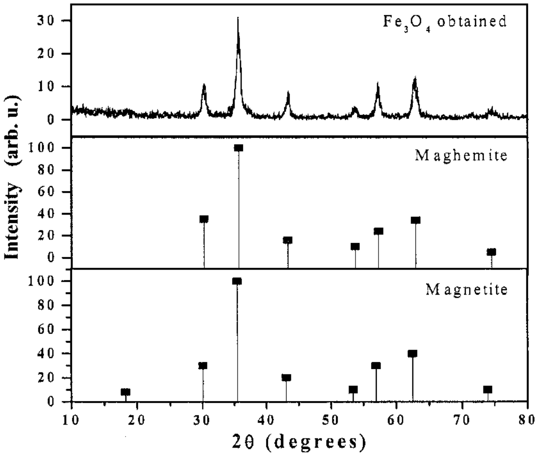

**Figure 1.** X-Ray diffraction patterns of the $Fe_3O_4$ obtained and of the magnetite and maghemite Standards

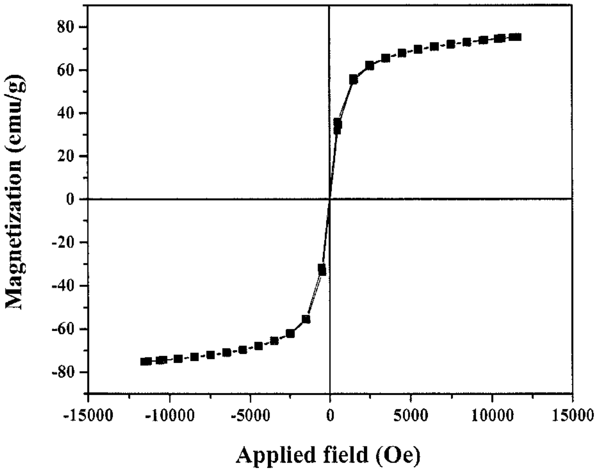

**Figure 2.** Magnetization curve of magnetite

From the magnetization curve and equations 2 and 3 [8], *where $\chi_i$ represents the initial susceptibility, and 1/Ho is the value of 1/H for M = 0, k is Boltzman constant and T absolute temperature*, the magnetite mean particle diameter (*Dv*) and its standard deviation were estimated *($\sigma$)*, using a log-normal distribution function; but in this case, we used the magnetization of the powders "ms" instead of "*$\varphi$ms*" because magnetite is not in a liquid medium. It is pointed out that the saturation of magnetization for magnetite is 75.2 emu/g, whereas the one in bulk is 92.5 emu/g which means that the magnetite obtained has sufficient magnetic properties to obtain magnetic latexes with similar characteristics.

$$D_v = \left[ \frac{18kT}{\pi m_s} \sqrt{\frac{\chi_i}{3\varphi m_s} \frac{1}{H_0}} \right]^{1/3} \tag{2}$$

$$\sigma = \frac{\left[ Ln\left( (3\chi_i H_0) / \varphi m_s \right) \right]^{1/2}}{3} \tag{3}$$

Applying this formula we obtained a mean particle size of 11.0 nm that corresponds with the size obtained by XRD. The standard deviation calculated with equation (3) was 0.42.

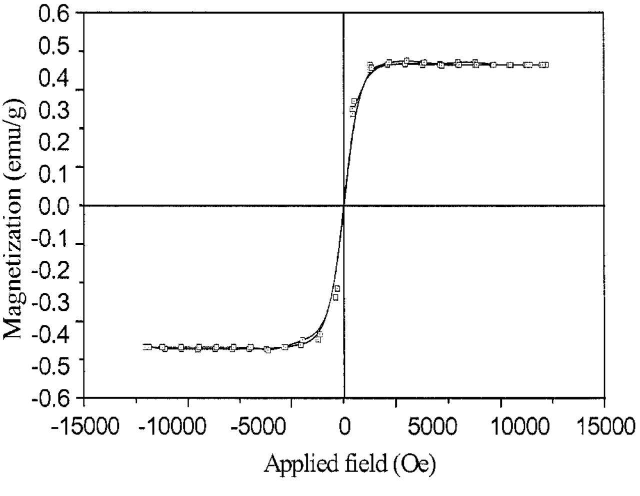

**Figure 3**. Magnetization curve of the magnetic latexes

The saturation of magnetization of magnetic latexes was found to be 0.42 emu/g, this value depends on the weight fraction of magnetite in the latex, and for our system corresponds to 0.0036. The negative slope at high fields is from the diamagnetic contribution of water.

### *Electronic Microscpy*

Figure 4 shows a TEM micrograph of magnetic latexes. Polymer particles containing magnetite of around 300 nm and particles of polymer with no magnetite of 100 nm are found.

The distribution of magnetite seems to be rather inhomogeneous, some polymer particles contain large amounts of magnetite, whereas some others are practically free of it. This effect can be explained considering the ionic interactions between the different surfactants; CTAB is a cationic surfactant to produces micelles and stabilizes the monomer droplets and AOT is the anionic surfactant that stabilizes the magnetite within the monomer. It is possible that these ionic interactions help to maintain the magnetite within the monomer droplets once polymerization has initiated.

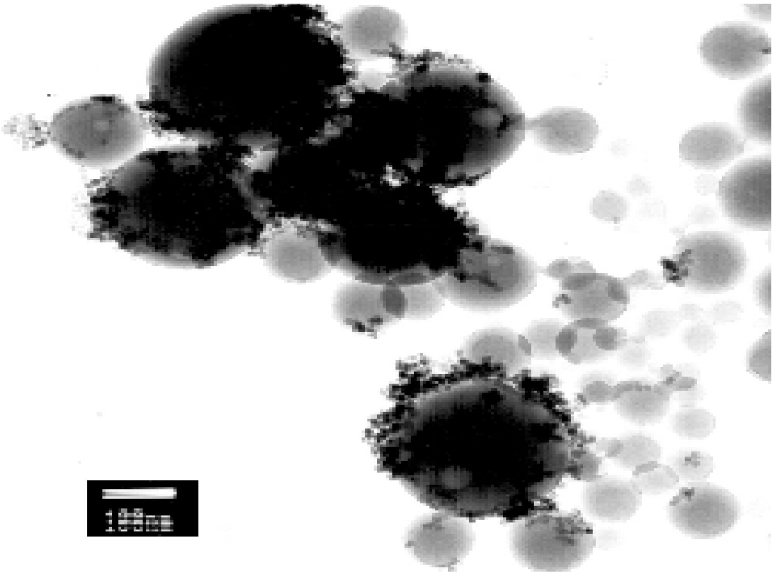

**Figure 4.** TEM Micrographs of magnetic latexes

Figure 5 shows the EDAX of a magnetic polymer-coated particle, where the main peak of FeK is 6.24 and C is 0.20 indicating that magnetite is within the particle.

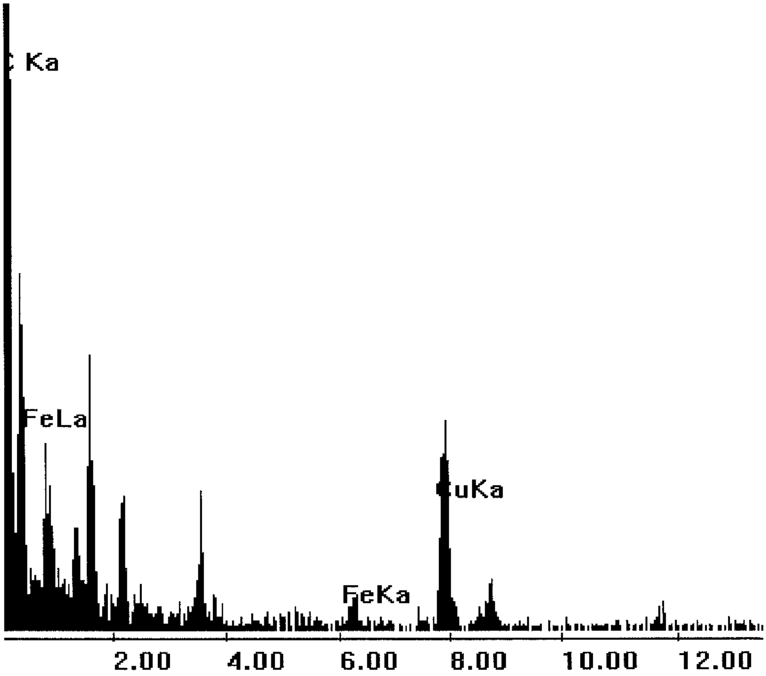

**Figure 5.** Elemental chemical analysis of one polystyrene magnetic particle (EDAX)

## Conclusions

Magnetic particles of nanometric size showing superparamagnetic behavior were encapsulated with polystyrene via miniemulsion polymerization. Ionic interactions between the surfactant used to stabilize the magnetic particles in the monomer and the one used to produce the miniemulsion are important in obtaining magnetic latexes.

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