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SYNTHESIS OF MICRO-SIZED POLYSTYRENE MAGNETIC PARTICLES

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Abstract - The present work illustrates the synthesis of spherical and micro-sized polystyrene magnetic particles by using a water-based suspension polymerization process to incorporate *in situ* surface modified superparamagnetic Fe₃O₄ nanoparticles. The crystallite size of Fe₃O₄ was determined to be equal to 7.7 nm, based on Scherrer's equation and XRD measurement. According to EDX analyses, Fe₃O₄ / polystyrene nanocomposites particles show strong characteristic peaks K α and K β of iron at the interval from 6.38 KeV to 7.04 KeV with an amount of iron in the samples equal to 98 %, indicating that the inorganic material dispersed in the polystyrene matrix is essentially Fe in the form of iron oxide (Fe₃O₄). The obtained polymeric materials presented good magnetic behavior, indicating that the modified Fe₃O₄ nanoparticles were successfully dispersed in the polystyrene particles.

Keywords: *Nanocomposites, superparamagnetic nanoparticles, polystyrene, suspension polymerization.*

Introduction

In recent years, nanotechnology has become an increasingly important field, attracting the attention of several researchers in both academia and industry. In this context, the concept nanotechnology is explored in order to produce new materials presenting improved final properties intended to be used in different technological branches, such as biomedical separation and purification, biotechnology, medicine, nanodevices, nanoelectronics, healthcare and energy [1, 2].

Although the diversity of magnetic nanoparticles synthesized based on different magnetic metals, special attention is given to superparamagnetic magnetite (Fe₃O₄) nanoparticles due to its remarkable features, such as biocompatibility, low toxicity, low susceptibility to changes due to oxidation, magnetic retention only when exposed to an external magnetic field and strong ferromagnetic behavior. In the field of biomedical research and technology, nanomagnetic particles are widely employed for *in vivo* and *in vitro* biomedical applications [3, 4].

Water-based process like suspension, dispersion, microemulsion, miniemulsion and emulsion polymerizations can be successfully utilized in the manufacture of magneto-polymeric materials [5-8]. Among them, suspension polymerization process deserves special recognition by presenting several advantages, such as low levels of impurities and additives in the polymer, easy separation of the polymer particles, avoiding undesirable problems of water wastage and contributing to the recycling of this process stream, easy removal of the heat of reaction, easy temperature control and formation of micro-sized spherical with very simple control of both the average size and the distribution of particle size .

The present work focuses on the production of micro-sized and spherical polystyrene / Fe₃O₄ particles with good morphological features consists of using a water-based suspension polymerization process to incorporate *in situ* surface modified superparamagnetic Fe₃O₄ nanoparticles.

Experimental

Styrene (Sigma-Aldrich), distilled water, nitrogen with 99.5% of purity (White Martins), poly(vinyl alcohol) with a degree of hydrolysis of 86 – 89 % (kindly supplied by DENKA) and benzoyl peroxide with a minimum purity of 99.4% (kindly donated by Arkema Química) were used in the polymerizations. Sodium hydroxide with purity of 97% (F. MAIA), ferric chloride hexahydrate with purity of 97% and ferrous sulfate heptahydrate with purity of 99% (VETEC), hydrochloric acid (ISOFAR) and oleic acid extra pure (Merck) were used in the synthesis of the magnetic nanoparticles. All chemicals were used as received, without further purification.

Synthesis of Magnetic Nanoparticles

Magnetite nanoparticles were prepared by chemical coprecipitation of aqueous Fe²⁺ and Fe³⁺ salt solution and NaOH solution, as described elsewhere.^[9] Basically, 6.1 g of FeCl₃.6H₂O and 3.1 g of FeSO₄.7H₂O were dissolved in 125 mL of distilled water and 5 mL of hydrochloric acid and heated to 60 °C with bubbling of nitrogen gas. Separately, 37.5 g of NaOH was dissolved in 625 mL of distilled water, followed by heating to 60 °C with bubbling of nitrogen gas. These solutions were mixed under vigorous stirring at 60 °C for 30 min, in atmosphere of nitrogen. The resulting black magnetic nanoparticles were isolated and washed with distilled water until neutral pH.

Surface Modification of Magnetic Nanoparticles

The surface of Fe₃O₄ nanoparticles was modified by using oleic acid as reported elsewhere.^[10] Basically, 5 g of magnetic nanoparticles were dispersed in 170 mL of distilled water under nitrogen and heated to 85°C. After that, 5.6 mL of oleic acid were added dropwise at a constant rate 0.5 mL·min⁻¹ under an inert nitrogen atmosphere. The resulting mixture was kept under mechanical stirring for 30 min at 85°C. The surface modified Fe₃O₄ magnetic nanoparticles were washed with distilled water, followed by washing with ethanol.

In-Situ Formation of Polystyrene Magnetic Microparticles

The polymerization reactions were carried out in a 500 mL glass reactor (Quickfit[®], England), equipped with a reflux condenser at 85 °C, with a total organic load of 25 wt-%, under an inert nitrogen atmosphere. Initially, the reactor was fed with 195 mL of distilled water, containing 0.98 g of poly(vinyl alcohol), DENKA POVAL B-24. The system was kept under isothermal conditions with a constant agitation of 1000 rpm. When the desired temperature was reached, 65 g of styrene, a

desired amount of surface modified Fe₃O₄ magnetic nanoparticles (normally in the range from 0 to 6.5 g) and 2.28 g of benzoyl peroxide (LUPEROX[®] 78) were added and the reaction performed for approximately 4.5 hours.

Material Characterization

The thermal stability of materials was determined by DTG measurements on a Shimadzu DTG-60 (Shimadzu Scientific Instruments) at heating rates of 10 °C·min⁻¹, under nitrogen atmosphere with a flow rate of 50 mL min⁻¹.

The XRD patterns of the polymeric materials were determined on a Bruker D8 FOCUS X-ray diffractometer (Bruker AXS), using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV and 30 mA) under the same conditions, in the angular range $2 \leq 2\theta \leq 80$ with steps of 0.05° at a rate of 0.25°·min⁻¹. Energy dispersive X-ray spectroscopy (EDX) measurements were carried out on an EDX-720 fluorescence spectrometer (Shimadzu Europa GmbH, Duisburg, Germany). The EDX spectra were acquired with steps of 0.02 and a live time of 100 s.

Magnetic force measurements were carried out by using a conventional analytical balance and a digital caliper, as illustrated elsewhere [11]. Magnetic susceptibility was measured as volume susceptibility using a Johnson Matthey magnetic susceptibility balance, as described elsewhere [12]. The surface morphology of polymer particles was analyzed through scanning electron microscopy (SEM). The images were recorded with a FEI Quanta 200 Scanning Electron Microscope (FEI Company).

Results and Discussion

Figure 1 illustrates the typical morphologies of polystyrene particles. It is observed that the polymeric particles present smooth surface and regular spherical morphology. The particle morphology plays a key role on the product application, exerting a strong effect on the processability of the final product. In this scenario, the suspension polymerization processes are most often employed due to the capacity of synthesizing spherical particles with good morphological features.

Table 1 shows different properties of the polymeric materials. The weight fraction of nanoparticles (ϕ_{NP}) determined by thermogravimetric measurements was 1.7, 4.8 and 10.1 wt-%, respectively. The crystallite size (ξ_{NP}) of the polymeric materials was estimated using the well-known Scherrer's equation, based on the XRD patterns of the pure magnetite nanoparticles and polymeric samples. The pure Fe₃O₄ presents average crystallite size equal to 7.7 nm, indicating that Fe₃O₄ nanoparticles present a superparamagnetic behavior, essential requirement for biomedical purposes [3, 13], which indicates that magneto-polymeric materials such as polystyrene / Fe₃O₄ produced in this work are very suitable for biological applications.

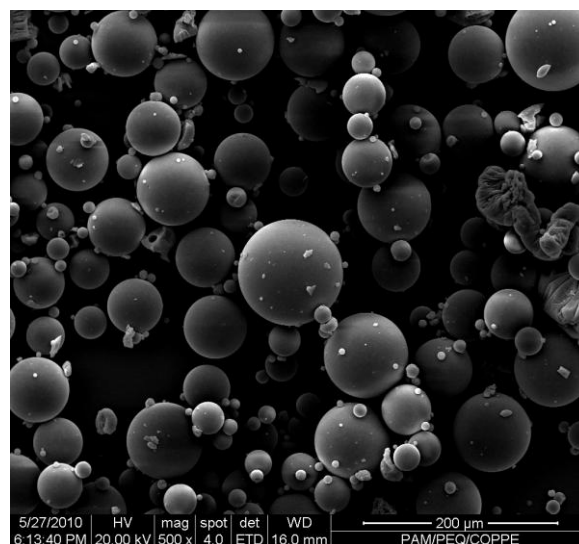


Figure 1 - SEM of Polystyrene Magnetic Particles with 4.8 wt-% of Fe₃O₄.

According to Table 1, polystyrene / Fe₃O₄ nanocomposites materials present crystallite sizes very similar to the one observed for Fe₃O₄ nanoparticles. It is noted that the crystallinity (\mathfrak{S}_{NP}) of the polymeric materials present a linear relationship with the content of Fe₃O₄ nanocomposites dispersed in the polystyrene matrix. One has to keep in mind that the crystallinity stated here regards to the Fe₃O₄ nanoparticles contribution, since the thermoplastic matrix of polystyrene is amorphous.

Based on the susceptibility classification, the polystyrene produced here presents a paramagnetic behavior since the magnetic susceptibility values are positive when a magnetic field is applied externally. As illustrated in Table 1, the magnetic susceptibility increases as the concentration of Fe₃O₄ nanoparticles dispersed in the polystyrene matrix is increased.

Table 1 – Nanoparticles Weight Fraction, Crystallite Size, Crystallinity and Magnetic Susceptibility of the Polymeric Materials.

Sample	Fe ₃ O ₄ (wt-%)	ξ_{NP} (nm)	\mathfrak{S}_{NP} (%)	χ_g (c.g.s)
I	0.0	0.0	0.0	0.00
II	1.7	4.2	2.6	0.15
III	4.8	4.6	10.3	0.31
IV	10.1	6.9	20.0	0.38

The energy dispersive X-ray spectra of the Fe₃O₄ / polystyrene nanocomposites particles show strong characteristic peaks K α and K β of iron at the interval from 6.38 KeV to 7.04 KeV, as illustrated in Figure 2. The average amount of iron in the samples was determined to be equal to 98 %. These results indicate that the inorganic material dispersed in the polystyrene matrix is essentially composed by Fe in the form of iron oxide (Fe₃O₄). EDX analyses also show small amounts of Si, Mn, S, and Cr, which could be attributed to typical contaminant species normally present in the reagents and glassware used in the synthesis of the magnetic nanoparticles.

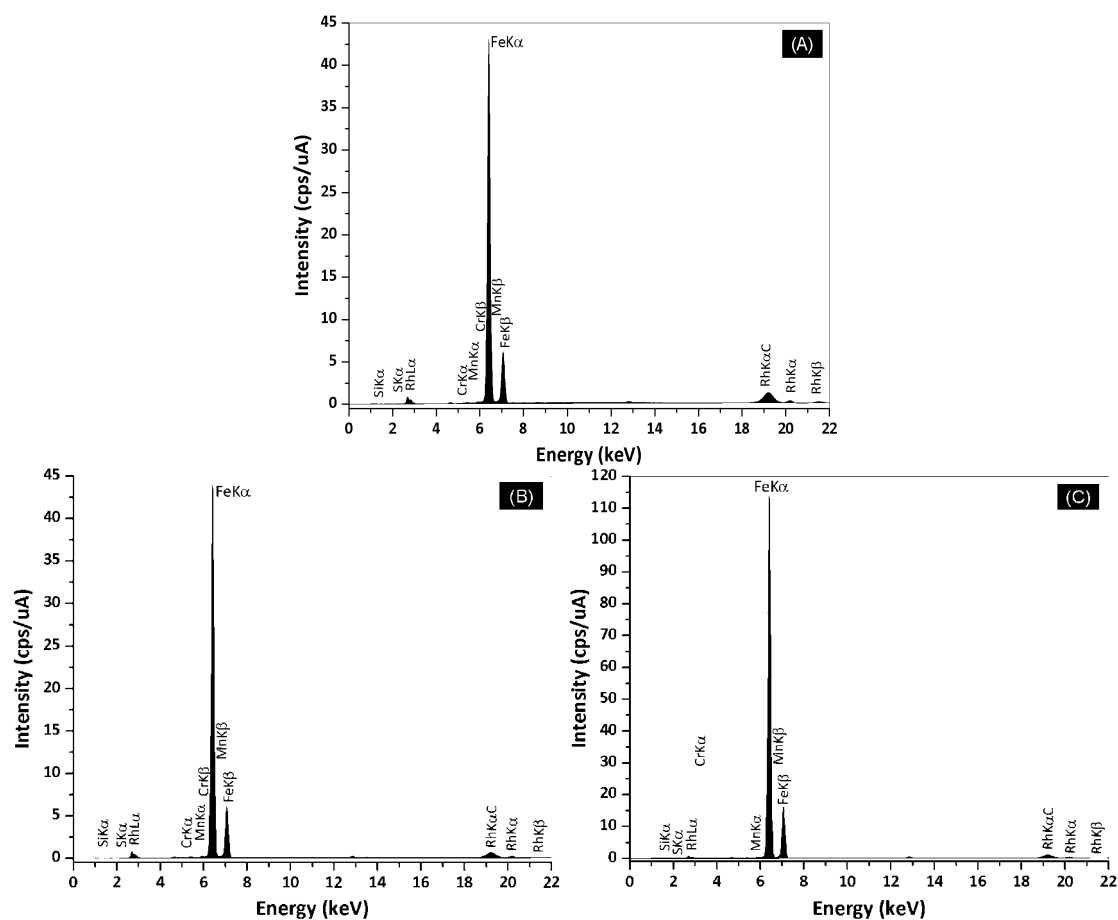


Figure 2 - EDX Spectra of the Polymer Particles. (A) Polystyrene / Fe₃O₄ (1.7 wt-%); (B) Polystyrene / Fe₃O₄ (4.8 wt-%); (C) Polystyrene / Fe₃O₄ (10.1 wt-%).

Figure 3 shows the magnetic behavior of the polymeric samples. According to the relative magnetic force, the polymeric sample with 1.7 wt-% of Fe₃O₄ nanoparticles presents the best response to the employed magnetic field. Although all magnetic polystyrene samples present the same magnetic profile, the maximum relative magnetic forces are relatively different, as depicted in Figures 12 A and B. The observed magnetic behavior can be attributed to the dispersion of the Fe₃O₄ nanoparticles in the styrene droplets during the polymerization, which can strongly depend on the amount of iron oxide nanoparticles.

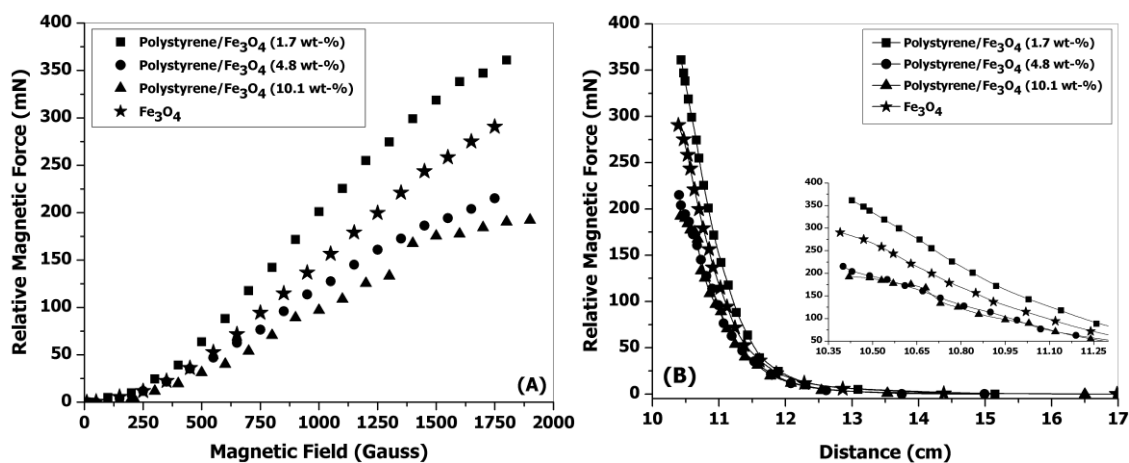


Figure 3 - Relative Magnetic Force of the Polymeric Material Samples.

Conclusion

This technique demonstrated to be very useful in the formation of magneto-polymeric particles, allowing for the proper dispersion of the nanomagnetic particles in the thermoplastic matrix of polystyrene, exhibiting good super paramagnetic response. This class of magnetic material might be used for in vivo biomedical applications, such as intravenous administration in vascular embolization procedures to the treatment of arteriovenous malformations, tumors and aneurysms. Additionally, this potential magnetic embolic agent might be successfully used for the hyperthermia treatment and prevention.

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References

1. P. M. Ajayan, L. S. Schadler, P. V. Braun, *Nanocomposite Science and Technology*, Weinheim: Wiley-VCH, 2003.
2. B. Bhushan, *Introduction to Nanotechnology*, in *Springer Handbook of Nanotechnology*, B. Bhushan, Editor, Springer: New York. p. 1, 2007.
3. A. Aqil, S. Vasseur, E. Duguet, C. Passirani, J. P. Benoit, A. Roch, R. Muller, R. Jerome, C. Jerome *Eur. Polym. J.* **2008**, *44(10)*, 3191.
4. C. T. Yavuz, A. Prakash, J. T. Mayo, V. L. Colvin *Chem. Eng. Sci.* **2009**, *64(10)*, 2510.
5. Z. Jia, W. Yujun, L. Yangcheng, M. Jingyu, L. Guangsheng *React. Funct. Polym.* **2006**, *66(12)*, 1552.
6. S. Lu, J. Ramos, J. Forcada *Langmuir* **2007**, *23(26)*, 12893.
7. A. Pich, S. Bhattacharya, A. Ghosh, H. J. P. Adler *Polymer* **2005**, *46(13)*, 4596.
8. J. X. Yang, T. Hasell, W. X. Wang, S. M. Howdle *Eur. Polym. J.* **2008**, *44(5)*, 1331.
9. H. T. Pu, F. J. Jiang, Z. L. Yang *Mat. Chem. Phys.* **2006**, *100(1)*, 10.
10. J. Huang, H. Pen, Z. Xu, C. Yi *React. Funct. Polym.* **2008**, *68(1)*, 332.
11. F. G. De Souza Jr., J. A. Marins, C. H. M. Rodrigues, J. C. Pinto *Macromol. Mater. Eng.* **2010**, *295(10)*, 942.
12. R. S. Davis *Meas. Sci. Technol.* **1993** *4(2)*, 141.
13. M. Arruebo, R. Fernandez-Pacheco, M. R. Ibarra, J. Santamaria *Nano Today* **2007**, *2(3)*, 22.