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Encapsulation of ferromagnetic iron oxide particles by polyester resin

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Abstract: Magnetic iron oxide (maghemite, Fe_3O_4) particles were encapsulated with polyester resin. The resulting magnetic powders were characterized by Fourier transform infrared spectroscopy (FTIR), thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC), Fritsch particle sizer, scanning electron microscopy (SEM), X-ray diffractometer (XRD) and vibrating sample magnetometer (VSM) measurements. FTIR and XRD confirmed the presence of iron oxide in polymer phase. The TGA and DSC measurements indicated the magnetic polymer particles have more than 50% iron oxide content and high thermal stability. SEM revealed that all maghemite particles were embedded in the polymer phase. The size distribution analysis of prepared magnetic particles has shown that the mean diameter of the bare iron oxide particles slightly increased with encapsulation. According to our magnetometry data, shape of the loops evidences the ferromagnetic character of the material and no evidence of superparamagnetism was seen.

Keywords: magnetic polymer particle; iron oxide; encapsulation; polyester; polymerization

Introduction

Composite particles consisting of an inorganic core and a polymer shell, due to the possibility of combining the advantages of different materials, have attracted much attention of material scientists and researchers. For instance, composite particles are designed to enhance the overall performance of composites in mechanical, electrical and photonics properties [1-3]. Besides, functional composite particles can be prepared from inorganic particles and a polymer containing functional groups such as carboxylic acid, hydroxyl, amine, and sulfate [4, 5]. As a consequence of its encapsulation with the polymer, particle surface will be changed, and its compatibility with other polymers and dispersion stability in the blending system can be improved [6]. In fact, this type of composite particles have received some interest in a wide range of industrial fields, such as adhesives, textiles, pesticides, drugs, diagnosis, toner and paints [7-11].

Although a lot of methods exist, conventional emulsion polymerization is the most frequently used technique for the encapsulation reaction of inorganic particles with polymer. Luna-Xavie et al. [12] used an emulsion polymerization approach along with a cationic initiator system to encapsulate silica particles modified with a nonionic polyoxyethylenic surfactant. Yu et al. [13, 14] studied encapsulation of titania particles by dispersing them in water using emulsifiers (sodium dodecyl sulfate (SLS) and Triton X-100). Yu et al. [15] modified the surface of silica particles with (hydroxypropyl)methyl cellulose (HPMC) coupling agents in studies of their encapsulation by conventional emulsion polymerization. Viala et al. [16] tried to encapsulate inorganic pigments such as TiO2 or FexOy (black, yellow or red), using nonylphenol ethoxylated mole 30 (NP30) as surfactants. Choi et al. [17] investigated the encapsulation of cadmium sulfide particles with polyacrylonitrile by γ-irradiation and emulsion polymerization. Tan et al. [18] studied the polymerization of methyl methacrylate on the surface of pigment particles by using soap less emulsion polymerization method. Alternative polymerization techniques, as suspension or dispersion, have also been employed to encapsulate inorganic particles. Duguet et al. [19] modified the surface of alumina through the condensation of 3-(trimethoxysilyl)propyl methacrylate in studies of their encapsulation by aqueous suspension polymerization. Dispersion polymerization was also employed for encapsulation of submicron size titania particles within different polymers such as poly[(styrene-co-divinylbenzene)-methacrylic acid] [20, 21] and poly[(methyl methacrylate-co-ethylene glycol dimethacrylate)- methacrylic acid] [22].

Recently, miniemulsion polymerization was developed to encapsulate inorganic particles [10, 27–34] because its characteristic feature, the monomer droplets nucleation, provides advantage on encapsulation of inorganic solid [10]. Generally, the encapsulation of inorganic particles via miniemulsion polymerization has three steps, two dispersion steps and one polymerization step. First, inorganic particles are dispersed in the monomer phase with the aid of stabilizer. Secondly, the monomer phase and the aqueous phase are mixed by a dispersion device with a high shear force to prepare the miniemulsion. Third, miniemulsion polymerization is carried out [10, 27–32].

The goal of this work was to obtain iron oxide/ polyester composite particles with a high magnetic content by miniemulsion polymerization like technique. The composite particles were characterized by means of FTIR, TGA, DSC, Fritsch Particle Sizer, SEM, XRD and VSM.

Results and discussion

In conventional emulsion polymerization [10], the principal site of particle nucleation is either in the aqueous phase or in the swollen monomer micelles. In the presence of inorganic particles dispersed in the aqueous phase, an additional site can be the surface of the particles. However, the competition between these mechanisms can lead to both polymer particles containing no inorganic particles and unencapsulated particles, besides the encapsulated ones.

Unlike conventional emulsion polymerization in miniemulsion polymerization, the principal site of particle nucleation is monomer particles. So using this technique, in the presence of inorganic particles, dispersed in the monomer phase, can only lead to encapsulated inorganic particles. In the present work, the technique similar to miniemulsion polymerization was used. So, the homogenized monomer phase containing unsaturated polyester resin, styrene, AIBN, Span 80, Tween 80 and iron oxide particles was dispersed in water phase, and the polymerization was carried out at 80 ˚C for 8 h.

FTIR and XRD methods were used to identify and characterize iron oxide particles before and after encapsulation. FTIR spectra and powder XRD pattern of bare iron oxide are shown in Fig. 1a and 2a respectively. Presence of double peak of 473 and 582 cm^{-1} in the FTIR spectra (Fig. 1a) and presence of intensive sharp peaks at

33.15, 33.55, and 62.72° in the powder XRD pattern (Fig. 2a) indicate maghemite structure of bare iron oxide particles [35-36].

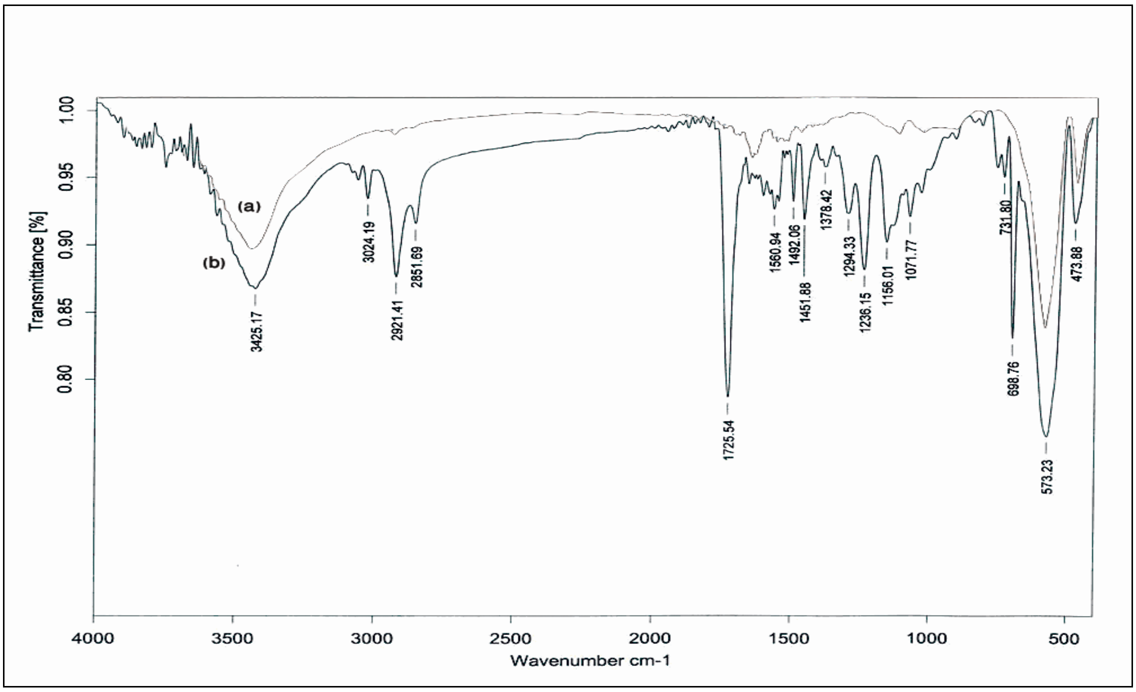


Fig. 1. FTIR spectra of iron oxide (a) and encapsulated iron oxide (b).

FTIR spectra and powder XRD pattern of encapsulated iron oxide particles are shown in Fig. 1b and 2b respectively. Reiteration characteristic peaks of maghemite in FTIR spectrum and XRD pattern of synthesized powder have shown the existence of an iron oxide in the synthesized particles and that the structure of iron oxide after encapsulation has not changed. The following were observed in the spectrum of Figure 1b:

-The peak with wave number of 1725 cm^{-1} in the FTIR spectra which is the characteristic peak of polyester resins.

-The bands in the region 2800-3000 cm^{-1} corresponded to the CH_2 and CH_3 group of polymer backbone.

-The peak with wave number of 3025 cm^{-1} and 3060 cm^{-1} corresponded to the C-H stretching of benzene ring.

-A broadband region of 3200-3600 cm^{-1} associated to the hydroxyl groups of iron oxide particles.

Thermal behavior of the synthesized particles was studied by TGA and DSC. The TGA results can quantify iron oxide content and the thermal stability of polyester/iron oxide composite particles. Figure 3 shows the TGA results of synthesized particles. As it is seen, loss of weight in TGA thermogram at between 200-300°C is related to the presence of adsorbed water, and dehydroxylation reaction ($2OH^{-} \rightarrow O^{2-} + H_2O$) of structural OH in the iron oxide and loss of weight between 300-500 °C is due to degradation of polymer matrix. So the TGA measurements indicated the synthesized particles have more than 50% iron oxide content and high thermal stability.

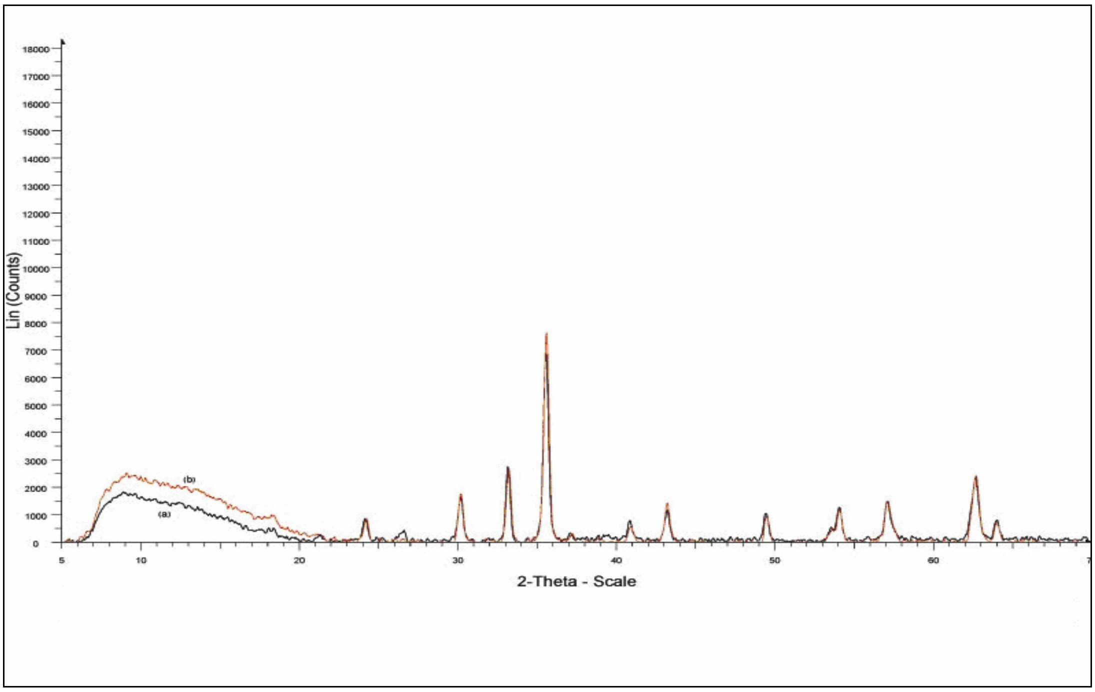


Fig. 2. Powder XRD pattern for iron oxide (a) and encapsulated iron oxide (b).

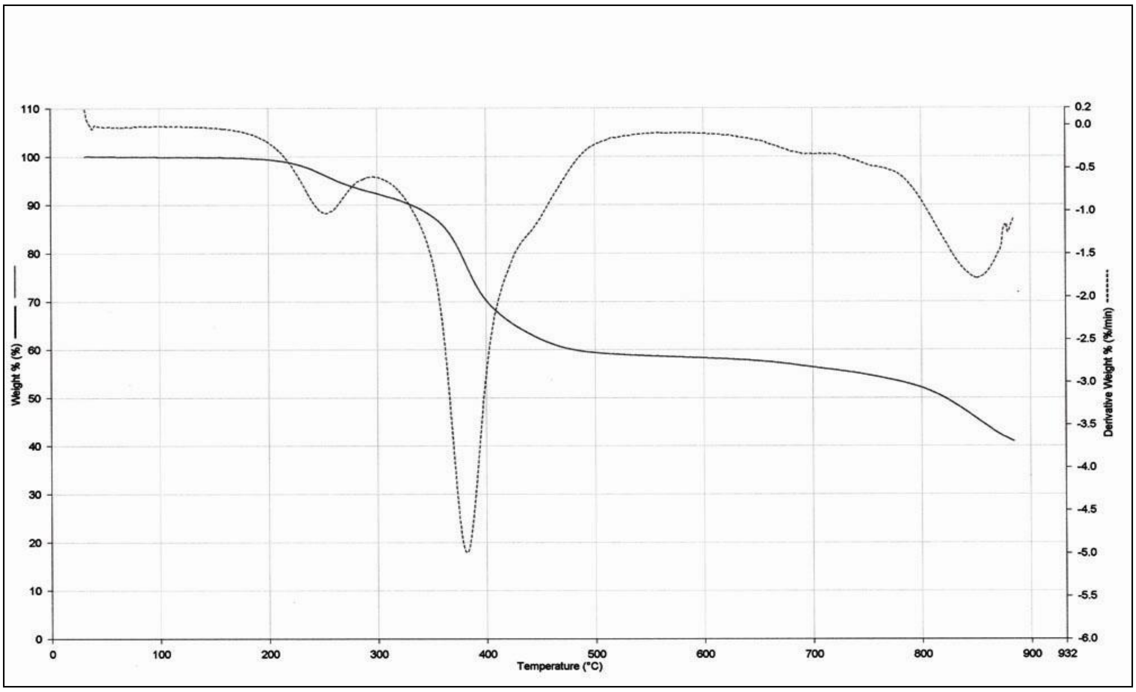


Fig. 3. TGA thermogram of encapsulated iron oxide, in N_2, at heating rate of 10 ˚C/min.

Fig. 4 shows the DSC thermogram of polyester/iron oxide composite particles. It can be seen that the glass transition temperature (T_g) of polyester/iron oxide composite particles is about 163 ˚C. As it is seen, there are two endothermic peaks in DSC thermogram between 200-300 ˚C and 300-500 ˚C. First endothermic peak is related to the release of adsorbed water, and dehydroxylation reaction ($2OH^- \rightarrow O^{2-} + H_2O$) of structural OH in the iron oxide and the second endothermic peak is due to degradation of polymer phase. Absence of exothermic peak in DSC curve, before degradation indicates the absence of the residue monomer in the synthesized particles.

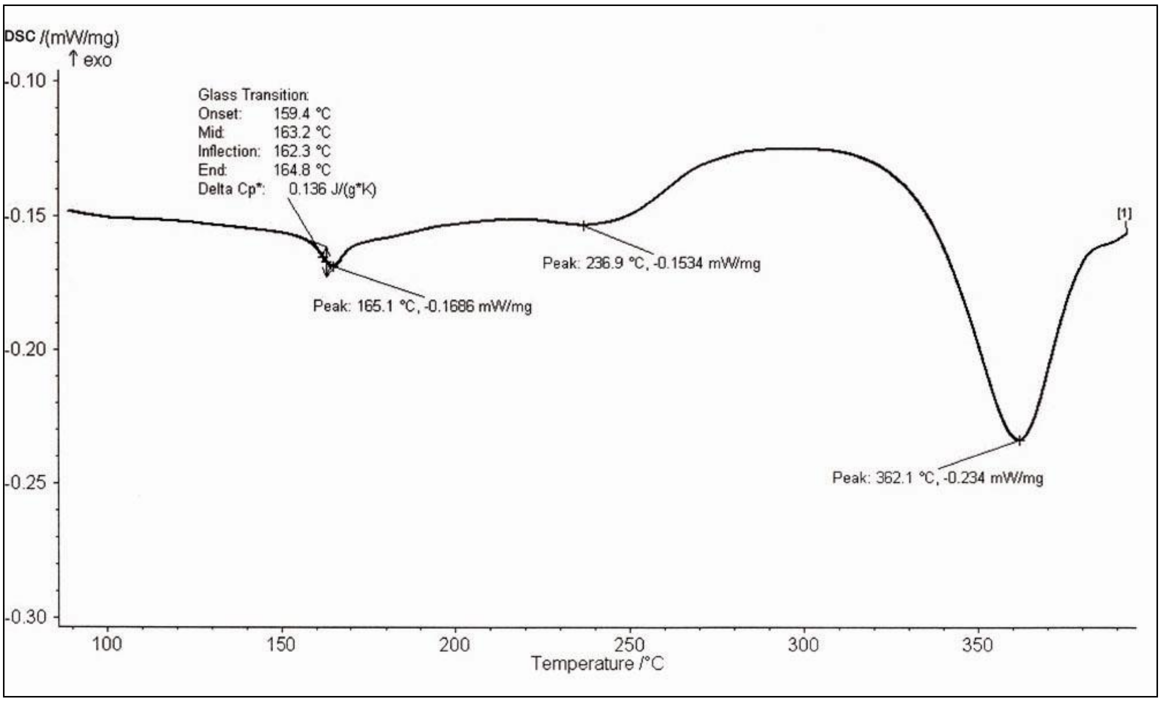
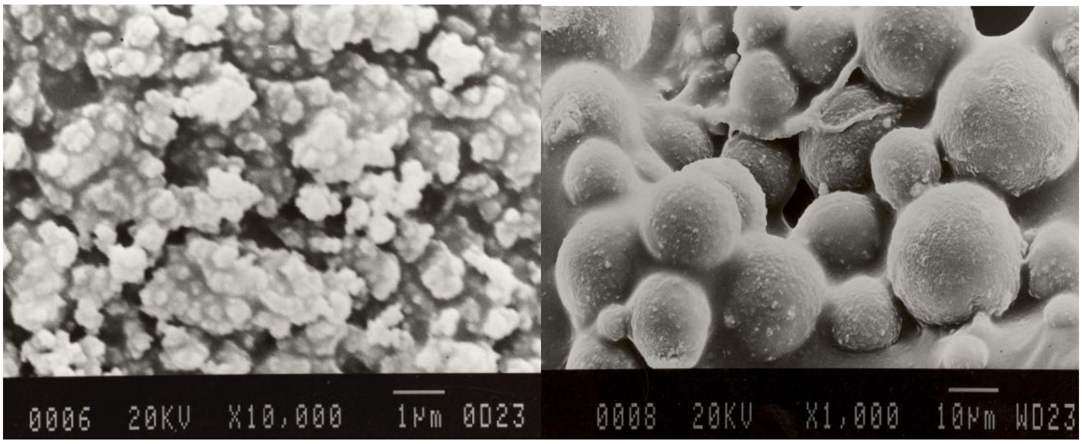


Fig. 4. DSC thermogram of encapsulated iron oxide, in N_2, at heating rate of 10 ˚C/min.

To study the morphology of synthesized particles, before and after encapsulation of iron oxide, SEM was used. SEM micrographs (Fig. 5 (a) & (b)) indicate that the iron oxide particles have irregular shape but after encapsulation exhibited spherical forms.



(a) (b)

Fig. 5. SEM micrograph of (a) iron oxide (10 000×) and (b) encapsulated iron oxide (1000×).

Particle size measurements in the range 0.5-100 micrometer were performed with Fritsch particle sizer. The size distribution analysis (Fig. 6) has shown that the means diameter of iron oxide particles after encapsulation slightly increases. It can be seen, that the particle size distribution of iron oxide particle after encapsulation was shifted to larger size.

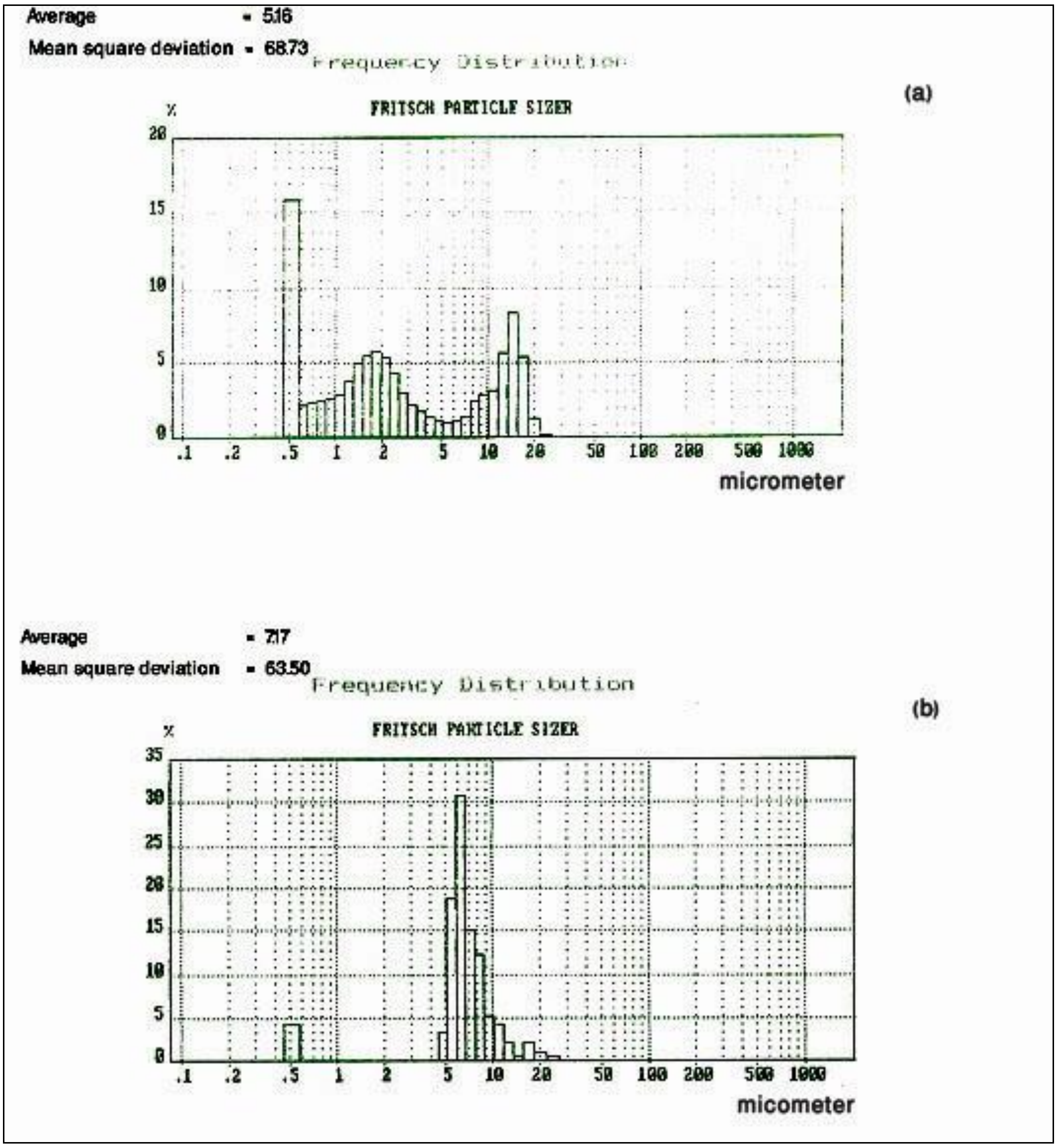


Fig. 6. Particle size distribution of (a) iron oxide and (b) encapsulated iron oxide.

And it can be said that at first stages of the process due to high viscosity of monomer phase and high content of iron oxide powder in the monomer phase, formation of particles less than one micrometer is not permitted.

The hysteresis loops were recorded at room temperature, using vibrating sample magnetometer (VSM), as shown in Fig. 7. The loops are closed and symmetrical versus origin of coordinate system. Shape of the loops evidences the ferromagnetic character of the material. No evidence of superparamagnetism was seen. Coercivity and remanence of the synthesized particles in comparison to the bare iron oxide particles slightly decrease. But their magnetic permeability considerably decreases. These variations may be due to encapsulation of iron oxide particles with a polymer phase.

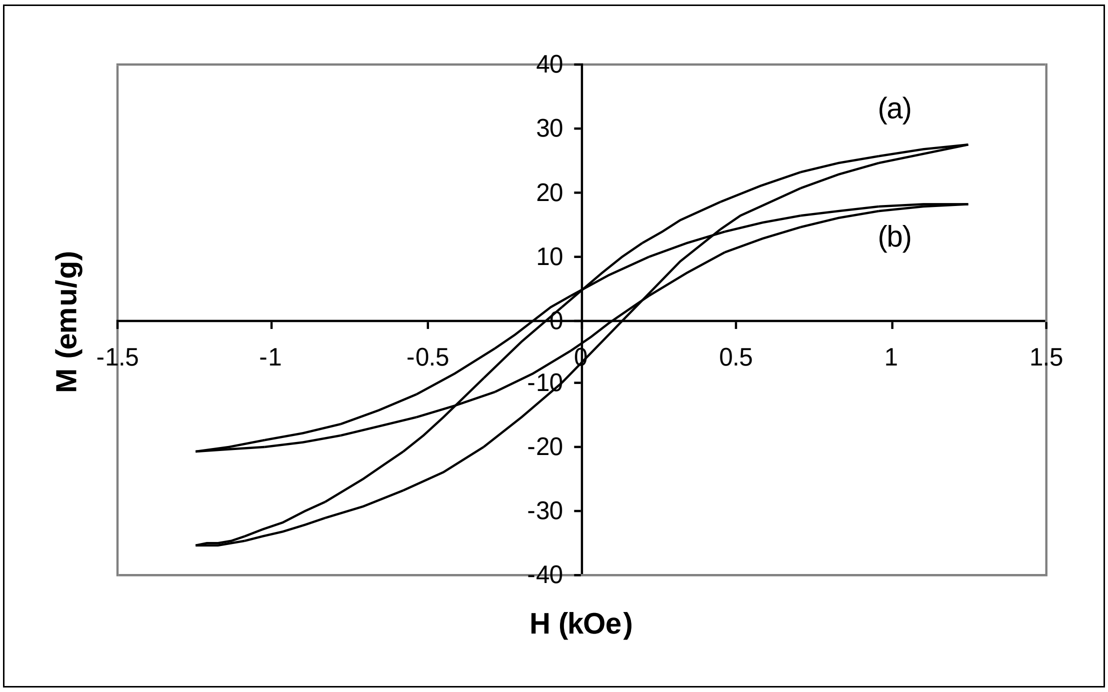


Fig. 7. Hysteresis loops for the iron oxide (a) and composite particles (b).

Conclusions

The maghemite core and polyester shell composite particles were prepared by miniemulsion polymerization like technique. SEM and particle size analysis of the resulting composite particles showed that these particles were regularly spherical core-shell morphology and have narrower size distribution. The average particle diameter of composite particles was 7.17 µm. The TGA measurements indicated the synthesised particles have more than 50% iron oxide content and high thermal stability. DSC thermogram shows, that the glass transition temperature (T_g) of polyester/iron oxide composite particles is about 163 ˚C. The hysteresis loops recorded at room temperature using vibrating sample magnetometer (VSM) have shown the ferromagnetic character of the material.

Experimental part

Materials

The following chemicals were used: styrene(St; Merck), unsaturated polyester resin (BUSHEPOL 81715) was purchased from Emam Petrochemical Company (I.R. IRAN), azobisisobutironitrile (AIBN; Fluka); iron oxide pigment (Bayer, brown 686); sodium hydroxide (Merck); Tween 80 (Merck) and Span80 (Merck) were all used as received.

Apparatus

The magnetic particle was examined using Fourier transform infrared spectroscopy (FTIR), Bruker, Equiker 55. Morphology and particle size measurements in the range of 0.5-100 micrometers were performed with scanning electron microscopy (SEM) Jeol JXA-840 and Fritsch particle sizer, Analystte 22. The iron oxide content of the magnetic polymer particle, the glass transition temperature and degradation temperature of polymer phase were investigated by thermogravimetry analysis

(TGA), Perkin Elmer and differential scanning calorimetry (DSC), Netzsch DSC 200 F3. X-ray difractometer (XRD) with Siemens D500 instrument and vibrating sample magnetometer (VSM) with Princeton Applied Research VSM 155 instrument were taken to study structural and magnetic properties of the prepared particles respectively.

Procedure of encapsulation

A 250-cm^3 four-neck round-bottom flask was equipped with a mechanical stirrer, thermometer, reflux condenser and a nitrogen gas inlet and outlet. The flask initially charged with 160 ml deionized water and 0.87 g of sodium hydroxide. Then, at room temperature the homogenized monomer phase containing unsaturated polyester resin, styrene, iron oxide, Span 80, Tween 80 and AIBN (Table 1) was added into the reaction flask, with continuous stirring. The stirring speed was fixed to 1000 rpm. After 30 minutes, the reaction flask was immersed into an 80˚ C oil bath and the nitrogen gas was bubbled through the reaction mixture for deoxygenation. The polymerization was carried out at 80˚ C for 8 hr. Then the reaction product was separated from the slurry by vacuum filtration. The filter cake was washed with deionized water for five times. Finally, the particles were dried at room temperature and it was used to obtain the specimens for characterizations.

Tab. 1. Typical recipe used for the encapsulation of iron oxide.

Water	160 ml
NaOH	0.87 g
Polyester resin	17.74 g
Styrene	10.6 g
Iron oxide	42.28 g
Span 80	3.71 g
Tween 80	1.5 g
AIBN	0.9 g

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References

[1] Xie, X. L.; Li R. K.; Liu, Q. X.; Mai, Y. W. *Polymer* **2004**, 45, 2793.
[2] Rupali, G.; Amitabha, D. *Chem. Mater* **2000**, 12, 608.
[3] Vollath, D.; Szabo, D. V.; Schlabach, S. *J. nanoparticle research* **2004**, 6, 181.
[4] Srikanth, H.; Hajndl, R.; Chirinos, C.; Sanders, J.; Sampath, A.; Sudarshan, T. S. *Appl. Phys. Lett.* **2001**, 79, 3503.
[5] Sung, J. H.; Jang, I. B.; Choi, H. J.; Chin, I. J. *Polym. Prepr.* **2004**, 45, 970.
[6] Chen, J.; Wang, G.; Zeng, X.; Zhao, H. *J. Appl. Polym. Sci.* **2004**, 94, 796.
[7] Abboud, M.; Casaubieilh, L.; Morvan, F.; Fontanille, M.; Duguet, E. *J. Biomed. Mater. Res., Part A* **2000**, 53, 728.
[8] Bauer, F.; Glasel, H. J.; Hartmann, E.; Bilz, E.; Mehnert, R. *Nuclear Instruments and Methods in Physics Research B* **2003**, 208, 267.
[9] Norio, S.; Makoto, F.; Yoshinari, T.; Masato, T. *J. Chem. Eng. Jpn.* **2004**, 37, 731.

[10] Erdem, B.; Sudol, E. D.; Dimonie, V. L.; Mohamed, S. *J. Polym. Sci. Part A* **2000**, 38, 4441.
[11] Caruso, F. *Adv. Mater.* **2001**, 3, 1.
[12] Luna-Xavie, J. L.; Guyot, A.; Bourgeat-Lami, E. *J. Colloid Interface Sci.* **2002**, 250, 82.
[13] Yu, D. G.; An, J. H.; Bae, J. Y.; Lee, Y. E. *J. Appl. Polym. Sci.* **2004**, 92, 2970.
[14] Yu, D. G.; An, J. H.; Bae, J. Y.; Ahn, S. D.; Kang, S. Y.; Suh, K. S. *J. Appl. Polym. Sci.* **2005**, 97, 72.
[15] Yu, H. Y.; Gu, J. S.; Guan, M.Y.; Wu, Z. C.; Sun, Y. M.; Du, J. *Chin. J. Chem.* **2003**, 21, 1297.
[16] Viala, P.; Bourgeat-Lami, E.; Guyot, A.; Legrand, P.; Lefebvre, D. *Macromol. Symp.* **2002**, 187, 651.
[17] Choi, S. H.; Choi, M. S.; Lee, K. P.; Kang, H. D. *J. Appl. Polym. Sci.* **2004**, 91, 2335.
[18] Tan, D. S.; Yan, N. X.; Xue, Q. *Journal of Shanghai University* **1998**, 2, 67.
[19] Duguet, E.; Morvan, F.; Maheu, P.; Fontanille, M.; Abboud, M. *Macromol. Symp.* **2000**, 151, 365.
[20] Dong-Guk, Y.; Jeong, H. A. *Colloids Surf. A: Phisicochem. Eng. Aspects* **2004**, 237, 87.
[21] Yu, D. G.; An, J. H. *Polymer* **2004**, 45, 4761.
[22] Yu, D. G.; An, J. H.; Bae, J. Y.; Kim, S.; Lee, Y. E.; Ahn, S. D.; Kang, S. Y.; Suh, K. S. *Colloids Surf. A: Phisicochem. Eng. Aspects* **2004**, 245, 29.
[23] Wu, R.; Wei, Y.; Zhang, Y. F. *Materials Research Bulletin* **1999**, 34, 2131.
[24] Corcos, F.; Bourgeat-Lami, E.; Novat, C.; Lang, J. *Colloid. Polym. Sci.* **1999**, 277, 1142.
[25] Zeng, Z.; Yu, J.; Guo, Z. X. *Macromolecular chemistry and physics* **2005**, 206, 1558.
[26] Odian, G. *Principles of Polymerization,* John Wiley & Sons, Inc., New York **1981**, 452.
[27] Wormuth, K. *J. Colloid. Interf. Sci.* **2001**, 241, 366.
[28] Hoffmann, D.; Landfester, K.; Antonietti, M. *Magnetohydrodynamics* **2001**, 37, 217.
[29] Zhang, S. W.; Zhou, S.X.; Weng, Y.M.; Wu, L.M. Langmuir **2005**, 21, 2124.
[30] Xie, G.; Zhang, H.P.; Zhang, Q.Y.; Li, T.H. *Acta Polym. Sin.* **2003**, 5, 626.
[31] Liu, X.; Guan, Y.; Ma, Z.; Liu, H. Langmuir **2004**, 20, 10278.
[32] Csetneki, I.; Faix, M.K.; Szilagyi, A.; Kovacs, A.L.; Nemeth, Z.; Zrinyi, M. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, 42, 4802.
[33] Zheng, W.; Gao, F.; Gu, H. *J Magn. Magn. Mater.* **2005**, 288, 403.
[34] Ramirez, L.P.; Landfester, K. *Macromol. Chem. Phys.* **2003**, 204, 22.
[35] Poling, G.W. *J. Electro-Chem. Soc.* **1969**, 116, 958.
[36] Taylor, R.M.; Schwertmann U. *Clay Min.* **1974**, 10, 299.