

New nanostructures derived from magnetic polymer hybrids and functional silanes

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This work describes the possibility of obtaining latexes derived from hydrophobic modified magnetite nanoparticles (MNPs). The hydrophobic modification was achieved by functionalizing Fe_3O_4 particles with different monofunctional alkoxy silanes (methyl, octyl, octadecyl and phenyl). Polymerizations were performed through ultrasonic initiated miniemulsion in the presence of sodium dodecyl sulfate (SDS). The hydrophobic ferrite was dispersed in monomer (styrene) with hexadecane and decaethylene glycol oleyl ether (Brij 96 V). The resulted new materials were analyzed by DLS, FT-IR, SEM and TGA. The data show the influence of the hydrocarbon chain length of the alkoxy silanes on the final magnetic hybrids.

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1. Introduction

In recent years nanoscience has made much progress in the synthesis of nanostructured materials based on magnetic particles. Nanoparticles of magnetic materials have numerous applications in biomagnetic separation, magnetic biosensing, magnetic resonance imaging, (MRI) and hyperthermia treatment. To apply nanoparticles in this field, it is important to accurately control the size, shape, and chemical coating and to retain the thermal and chemical stability of the particles [1-3]. Magnetic nanoparticles homogenously encapsulated in a hydrophobic polymer are of high interest. [4]

A large number of experiments for the preparation of the magnetic nanocomposites particles have been used to encapsulate magnetic nanoparticles inside polymers by various polymerization methods.

This work describes the preparation process of magnetic polymeric composites which consists in three steps: a) the preparation of the colloidal dispersion of magnetic particles, b) condensation of Fe_3O_4 with mono and trialkoxysilanes (Fig. 1) and c) encapsulation of the resulting ferrite with polymer.

Magnetite, Fe_3O_4 , is the most common material [5, 6] used, and it is usually prepared by chemical coprecipitation of an aqueous of $\text{Fe}^{3+}/\text{Fe}^{2+}$ solution ($\text{Fe}^{3+}/\text{Fe}^{2+}=2:1$ (mol)) with a base.

To obtain a successful encapsulation and to avoid the primary cross-linking processes, the magnetite aggregates were functionalized with mono and trialkoxy-silane. Alkoxysilanes are among the most frequently used surface coating materials for inorganic materials, especially iron oxide particles. They are bifunctional molecules with the general formula $[X(CH_2)_n]_mSiR(OR')_{3-m}$ where X represents the headgroup functionality, $(CH_2)_n$ a flexible spacer, and Si(OR)_n the anchor groups by which they can

attach to free SiOH or FeOH surface groups after hydrolysis of the alkoxy group [7]

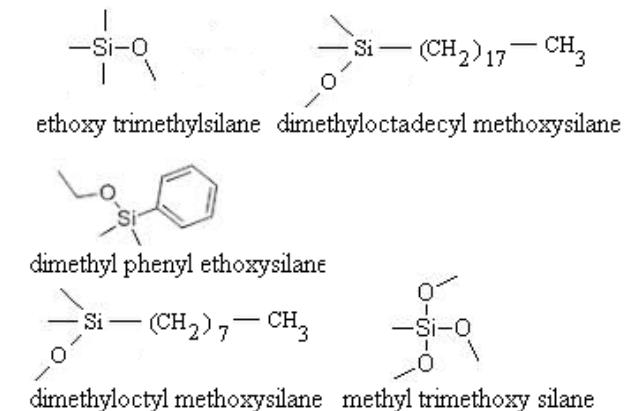


Fig. 1 Chemical structures of different precursors used in the surface modification of magnetic particles

Ultrasonically initiated emulsion polymerization has many advantages, such as chemical-free initiation and low reaction temperature. The preparation of hydrophobic magnetic polymeric composite, in which a hydrophobic polymer such as polystyrene is used, ultrasonic initiated miniemulsion is an effective technique for modified magnetite encapsulation [8-10].

A mixture of modified magnetite particles and styrene was miniemulsified in water, and after polymerization, polymer-encapsulated magnetite particles were obtained.

In the second part of this work, we present new results relating to the preparation of the nanocomposite particles through ultrasonic initiated miniemulsion, chemical initiator free, with styrene as monomer, Brij96V as stabilizer, sodium dodecyl sulfate as an ionic surfactant and hexadecane as hydrophobic agent [11-22].

2. Experimental

2.1 Materials

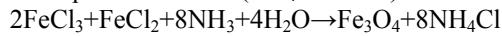
Ferrous chloride (II) ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride (III) ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ammonium hydroxide NH_4OH (25% aqueous solution) were purchased from Merck. Silanes: ethoxy trimethylsilane (Me_3MeSi) (Merk-Schuchardt), methyl trimethoxy silane (MeMe_3Si), dimethyl phenyl etoxysilane (PhMe_2ESi), dimethyloctadecyl methoxysilane (Fluka), dimethyloctyl methoxysilane ($\text{C}_8\text{Me}_2\text{MeSi}$) (Aldrich) were used as received.

Monomer styrene (St) was purified through rectification; the surfactant, sodium dodecylsulphate (SDS, Fluka), decaethylene glycol oleyl ether (Brij96V) (Fluka) and hexadecane (HD) (Aldrich) were used as received.

2.2 Procedures

I. Magnetite functionalization

The ferroferric dispersion was prepared by Massart method, through classic coprecipitation of FeCl_2 and FeCl_3 , in 1:2 molar ratio, by addition of concentrated alkaline aqueous solution (NH_4OH 25%) at 75°C .



The alkoxy silanes: ethoxy trimethylsilane, methyl trimethoxy silane, dimethyl phenyl etoxysilane, dimethyloctadecyl methoxysilane, dimethyloctyl methoxysilane, were added on the synthesized magnetic particles and ultrasonicated at 40°C , for six hours. Resulted particles were dried, and a part of them were dispersed in propylbenzene and dichloromethane for DLS measurements.

II. Miniemulsion polymerization initiated through ultrasonication

The procedure for miniemulsion preparation follows. Miniemulsion was prepared by mixing the styrene monomer (5 g) and the modified ferrite (0.1 g) with Brij96V (0.143 g), the mixture is ultrasonicated (Ultrasonic Processor CPX750, Cole Parmer) for 5 minutes and then hexadecane (0.25 g) is added. SDS (0.15 g) was dissolved in water and then added over the mixture. Oil and aqueous phases were ultrasonicated for 30 min in ice bath under nitrogen inlet. The resulted miniemulsion was transferred into a 100 ml three neck flask equipped with a mechanical stirrer, nitrogen inlet and reflux condenser. The miniemulsion was purged with nitrogen for 15 min while it was heated to the reaction temperature. The polymerization temperature and the stirring speed were kept constant at 70°C and 280 rpm, respectively.

2.3 Measurements

Dynamic light scattering (DLS) and Zeta Potential.

The surface charge of modified magnetic particles was determined by measuring the Zeta potential using a Zetasizer, Nano ZS instrument (Malvern). The same instrument measured the average size of the synthesized particles. All measurements were carried out at 25°C .

Fourier transform infrared spectroscopy

FT-IR analysis was performed on a Brucker Tensor instrument employing a KBr pellet method. Each FTIR spectrum was measured with 4 cm^{-1} resolution in a range between 4000 and 500 cm^{-1} .

Thermal Gravimetric Analyses

TGA was performed on a TA instruments Q5000 IR under N_2 atmosphere. The samples were heated to 700°C at $10^\circ\text{C}/\text{min}$ to determine the amount of the organic coating on the nanoparticle surface.

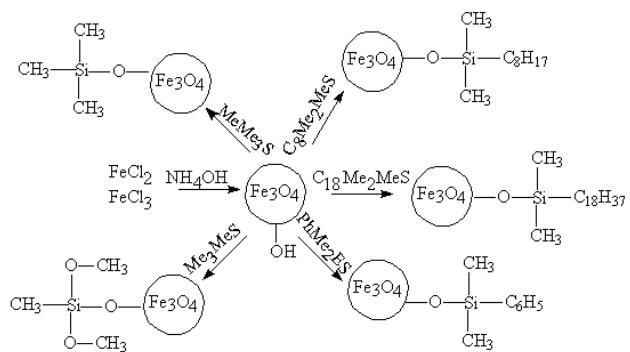
X-ray Photoelectron Spectroscopy

XPS measurements were performed on XPS Spectrometru K-ALPHA (Thermo Scientific) equipped with a $\text{AlK}\alpha$ source.

3. Results and discussion

3.1 Magnetite functionalization

It is well known that, in general, inorganic particles have hydroxyl groups on their surface, which can react with alkoxy silanes. Therefore, silane coupling agent is suitable for the introduction of functional groups onto the surface of inorganic particles. In this work 5 monoalkoxysilanes were engaged in order to obtain hydrophobic particles (Scheme 1). Methoxy and ethoxy groups bonded to silane can easily react with ferrite at 40°C temperature. This reaction takes place better yield as the length of the carbon chain is shorter and the alkoxide group's number bonded to the silicon atoms is higher. The hydroxyl groups from the surface of the magnetite particles reacts with monoalkoxysilanes, but side reactions also may occur resulting in a siloxane grafted layer. Core-shell magnetic particles have a magnetic core and a hydrophobic shell induced by the octadecyl, octyl, methyl, phenyl and trimethyl groups from the alkoxy silanes.



Scheme 1 The scheme of the modified magnetic particles with alkoxy silanes

Particle size distributions of alkoxy silanes modified magnetite were determined by dynamic light scattering (DLS) technique and have been showed in Figure 2. The mean sizes of the magnetic particles are 10 times higher in

propylbenzene than in dichlormethane. It is clear that in propylbenzene, average size of modified magnetite particles are decreased than blank magnetite particles. In dichloromethane, the average size of the particles increases with the increase of the hydrocarbon chain.

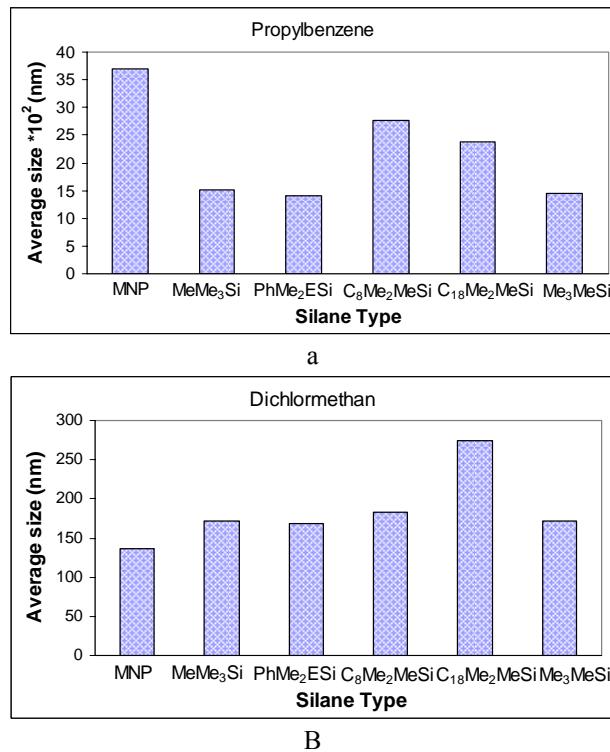


Fig. 2 DLS measurements of the modified magnetite particles dispersed in two solvents: a) propylbenzene and b) dichlormethane

The length of the alkyl chain of the alkoxy silanes influences the final particles dimensions and also the associating character of the particles. For both solvents, the modified magnetite with the highest particle size is C₈ and C₁₈, the monoalkoxy silanes which have the longest hydrocarbon chain.

TGA provided additional quantitative evidence on the structure of the nanoparticles' coating before and after grafting the alkoxy silanes, and allowed us to calculate the monoalkoxy silanes grafting density (Table 1). The highest value of the grafted density occurred for the MNPs modified with MeMe₃Si and the lowest for the MNPs modified with C₁₈Me₂MeSi. This fact can be explained by the grafting density dependence on the monoalkoxy silanes chain length.

Monoalkoxy silanes modified magnetite had a weight loss up to 180°C for water, and between 200 - 600°C the alkyl groups decompose. The magnetite modified with phenyl group had the smallest residue and MeMe₃Si had the highest residue, this alkoxy silane was also the most reactive and its reactivity influenced the final compound which had the highest thermal stability from all the modified magnetite compounds.

Blank magnetite particles had a weight loss of 2.7% between 25-180°C, specific to the hydroxyl groups -OH and 3.43% in the range 180-700°C characteristic to ferro-ferric oxide transformation in ferrous oxide. TGA curves indicated an increase in the residual blank magnetite particles compared with modified magnetite particles, which contain a higher organic component.

Table 1 Termogravimetric analyses of the alkoxy silanes modified magnetite and the resulted grafting density

Samples type	Weight loss intervals	Temp. [°C]	Residual [%]	Grafting amount mol/100 g Fe ₃ O ₄ *10 ⁻²
MNP	I	0-400	93.9	0
	II	500-600		
Me ₃ MeSi	I	100-400	90.4	5.5
	II	500-600		
C ₈ Me ₂ MeSi	I	100-400	89.9	2.7
	II	500-600		
C ₁₈ Me ₂ MeSi	I	0-400	91	1.3
	II	500-600		
PhMe ₂ ESi	I	100-400	89	2.7
	II	500-600		
MeMe ₃ Si	I	0-400	92	16
	II	500-600		

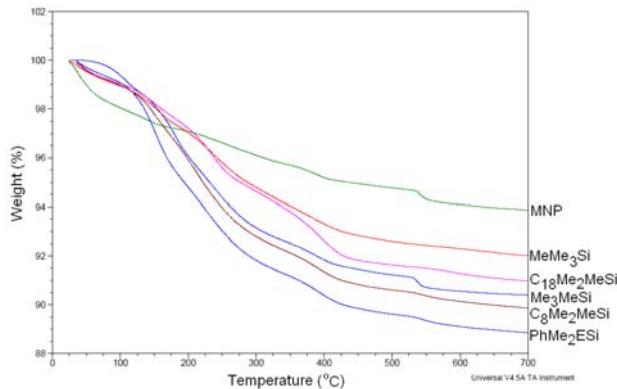


Fig. 3 Thermogravimetric curves of magnetic modified particles with different alkoxy silanes.

Fig. 4 are FT-IR spectra of blank Fe_3O_4 particles and modified Fe_3O_4 particles, respectively. Furthermore, the two band around 2850 and 2918 cm^{-1} are assigned to the asymmetric and symmetric CH_2 stretching, respectively. For silane-magnetic nanoparticles the peaks between 1055-1073 cm^{-1} are assigned to Si-O stretching.

The IR spectrum (Fig. 4) have shown a shoulder at 1036 cm^{-1} , which was assigned to Fe-O-Si stretching vibrations.

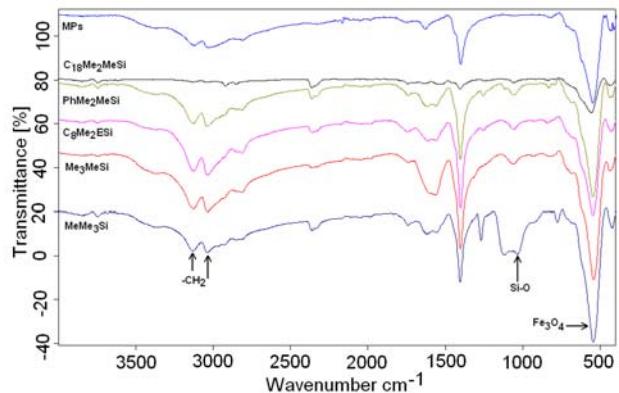


Fig. 4 The FTIR spectrum of magnetic particles and modified magnetic particles by different alkoxy silanes

The bands from 541 to 550 cm^{-1} confirms the presence of Fe_3O_4 magnetic particles, as a result of silane functionalization. IR results confirm the successful surface silanes functionalization of Fe_3O_4 MNPs.

XPS measurements were also performed to get more quantitative data on the structure of the silane layers. The surface elemental concentrations determined via XPS are presented in Tab.2.

Table 2 XPS measurements: the atomic concentrations for the elements at the surface of the synthesised compound

Functionalized magnetite	Surface elemental concentrations (%)					
Element	N	C	O	Fe	Si	Cl
MNP	1.2	11.4	37	48.3	0.0	1.9
Me ₃ MeSi	3.7	16.3	42.5	28.8	3	5.7
C ₈ Me ₂ MeSi	1.5	15.5	46.5	32.4	0.0	4.1
C ₁₈ Me ₂ MeSi	1.	27.2	39.9	25	4.3	2.6
PhMe ₂ ESi	1.9	14.4	47.4	32.2	0.0	4
MeMe ₃ Si	1.8	17.6	47.8	24	5.2	3.6

After silane grafting, the appearance of characteristic atoms, unreacted, such as nitrogen and chlor could be observed. The silanes with an increased amount of Si were found to have a decreased Fe concentration. The increase in Si can be explained by the deposition of a Si-rich silane layer, whereas the decrease in Fe is dedicated to the attenuation of Fe2p photo electrons through the silane layer.

II Miniemulsion polymerization initiated through ultrasonication

Particle size distributions of magnetic nanocomposite particles have been listed in Table 3. The smallest particles are the magnetite particles around 90 nm.

Table 3 DLS measurements of the synthesised latex

No.	Latexes of magnetite modified with alkoxy silanes:	Average size (nm)
M9	Polystyrene	136.6
M10	Magnetic particles	90.7
M11	MNP-Dimethyloctylmethoxysilane Latex	109.9
M12	MNP-Trimethylmethoxysilane Latex	93.5
M13	MNP-Dimethyloctadecylmethoxysilane Latex	102.5
M14	MNP-Dimethylphenylethoxysilane Latex	93.3
M15	MNP-Methyltrimethoxysilane Latex	92.7

The particle sizes of the final latexes are evidently higher for the magnetite modified with dimethyloctyl methoxy silane and dimethyl octadecyl methoxysilane, accordingly to Fig. 2, where the ferrite particles modified with these two alkoxy silanes have also the highest values. The highest particles are for the magnetite latex (Tab. 3). It can be noticed that the latexes with modified magnetite decrease in the particle size. The latex of magnetite modified with trimethyl methoxysilane, dimethylphenyl ethoxysilane, methyl trimethoxysilane has particles with the diameters in the same range of values with the particles of magnetite modified with alkoxy silanes (Figure 2), showing that the miniemulsion polymerization does not increase the final size of the particles.

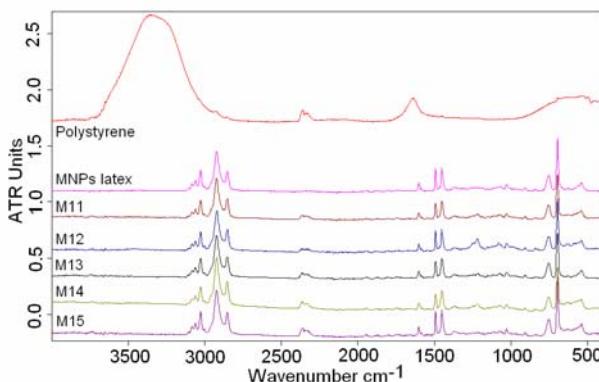


Fig. 5 The FTIR spectrum of latexes of magnetic particles unmodified and modified with alkoxy silanes

The key step is how to anchor the alkoxy silanes molecules onto the surface of magnetic particle for the subsequent miniemulsion polymerization of styrene onto the surface of magnetic particles. To prove that the alkoxy silanes are anchored onto the surface of the magnetic particle, FTIR spectroscopic was used (Fig. 5).

The adsorption peaks at 583 cm^{-1} corresponds to Fe-O groups vibrations from the magnetite morphology and the peaks at 2960 cm^{-1} for CH_2 groups, at 1260 cm^{-1} for $\text{Si}-\text{CH}_3$, at $1000\text{-}1100\text{ cm}^{-1}$ for Si-O, from the attachment of the alkoxy silanes groups on the magnetite surface of particles [11, 14]. Also, FTIR spectra reveal the appearance of $\text{C}=\text{C}$ aromatic groups from styrene between $1500\text{-}1600\text{ cm}^{-1}$. The band at 1625 cm^{-1} is the characteristic for bending mode of Fe-OH groups.

Fig. 6 shows the ESEM micrographs of samples obtained by miniemulsion polymerization from modified magnetite and styrene. It is clear that the particles have spherical shape and their sizes are around 100 nm, exactly like the sizes determined by DLS.

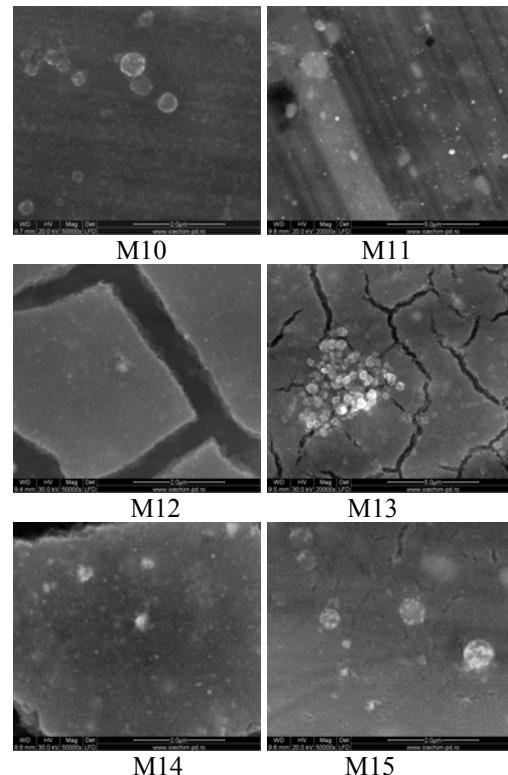


Fig. 6. SEM images of the PS-coated Fe_3O_4 modified .

It is also clear that the particles are agglomerated, with a modified magnetite core and encapsulated by the polymer.

4. Conclusions

Magnetite nanoparticles (Fe_3O_4) were synthesized by chemical coprecipitation and modified by condensation on the surface with alkoxy silanes compounds. The silanes with an increased amount of Si were found through XPS measurements to have a decreased Fe concentration. The increase in Si can be explained by the deposition of a Si-rich silane layer, whereas the decrease in Fe is dedicated to the attenuation of Fe2p photo electrons through the silane layer.

TGA measurements demonstrated that the hydrocarbon chain length influence the alkoxy silanes grafting on the surface of magnetite nanoparticles, the alkoxy silane with the longest polymer chain has the lowest grafting density. FTIR results confirm the successful surface silanes functionalization of Fe_3O_4 magnetic nanoparticles.

PSt polymer was formed on the surface of magnetite nanoparticles through miniemulsion polymerization. FTIR and SEM revealed that magnetite have been incorporated into the polymeric phase.

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