

Synthesis and Characterization of Bulk and Colloidal Magnetic Polymer Nanocomposites

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ABSTRACT

The development of bulk and colloidal latex polymer nanocomposites of poly (methyl methacrylate) (PMMA) with embedded magnetic nanoparticles particles was investigated. The first approach consisted of the preparation of magnetic PMMA nanocomposites using oleic acid coated cobalt ferrite and magnetite nanoparticles for subsequent characterization of their magnetic properties. It was found that the cobalt ferrite nanocomposite had magnetic hysteresis at 2 and 300 K as well as the magnetite nanocomposite had magnetic hysteresis at 2 K and superparamagnetic behavior at 300 K. Both nanofillers had a similar effect in shifting the glass transition temperature from that of the neat polymer. The influence of cobalt ferrite nanofiller surface chemistry on the thermal, mechanical, and magnetic properties of PMMA nanocomposites was also studied by comparing nanofillers coated with oleic acid (OA, which does not covalently bond to the PMMA matrix) and 3-methacryloxypropyltrimethoxysilane (MPS, which covalently bonds to the PMMA matrix). The values of the degradation temperature (T_d) and glass transition temperature (T_g) increased relative to the neat amount polymery when the nanofillers were introduced into the nanocomposites. The greater increase in thermal stability of the nanocomposite with MPS-coated nanoparticles was due to chemical bonding between the acrylate group in MPS and the PMMA. The nanocomposite filled with nanoparticles functionalized with OA showed slightly higher values of magnetic saturation and coercivity compared with those grafted with MPS. Magnetic polymer nanospheres of PMMA with embedded CoFe_2O_4 nanoparticles were synthesized by magnetic miniemulsion polymerization. The average diameter of the CoFe_2O_4 /PMMA nanospheres was controlled by varying the amount of surfactant. Dynamic light scattering analysis (DLS) of the magnetic polymer nanospheres showed that the average hydrodynamic diameter increased from 145 nm to 225 nm due to the

increase in the concentration of the surfactant. The magnetic properties of nanospheres were investigated by measuring the magnetization curves and the complex susceptibility. The particles were found to respond to alternating fields by Brownian magnetic relaxation.

RESUMEN

El desarrollo de nanocompuestos poliméricos en forma coloidal (latex) y en forma de “bulk” de polimetacrilato de metilo con nanopartículas magnéticas incrustadas fue investigado. El primer acercamiento consistió en la preparación de nanocompuestos magnéticos de poli(metacrilato de metilo) (PMMA) usando nanopartículas de magnetita y de cobalto ferrita, recubiertas de ácido oleico (OA) en su superficie, los cuales fueron posteriormente caracterizados magnéticamente. Se encontró que los nanocompuestos con cobalto ferrita presentaron histéresis a temperatura de 2 a 300 K y los nanocompuestos con magnetita una histéresis a 2 K, además de comportamiento superparamagnético a 300 K. Ambos nanorrellenos demostraron similar efecto en el desplazamiento de la temperatura de transición vítrea comparada con la del polímero sin modificar. También se estudió la influencia de la superficie de las nanopartículas de cobalto ferrita utilizadas para la preparación de nanocompuestos de PMMA, funcionalizando las nanopartículas con ácido oleico (AO, el cual, no hace enlace con la matriz polimérica de PMMA) y 3-metacriloxipropiltrimetoxisilano (MPS, el cual hace enlace covalente con la matriz polimérica del PMMA). Las temperaturas de degradación (T_d) y temperatura de transición vítrea (T_g) incrementaron cuando las nanopartículas fueron introducidas dentro del nanocompuesto, comparadas con el polímero sin modificar. El mayor incremento en la estabilidad termal fue observado en los nanocompuestos con MPS, debido al enlace químico entre el grupo acrilato del MPS y el PMMA. Los nanocompuestos rellenos con nanopartículas funcionalizadas con OA mostraron un valor levemente mayor de saturación de magnetización y coercividad comparada con aquellos funcionalizados con MPS. Nanoesferas magnéticas de polímero de PMMA con nanopartículas incrustadas de CoFe_2O_4 fueron

sintetizadas por polimerización de mini emulsión magnética. El diámetro promedio de las nanoesferas de $\text{CoFe}_2\text{O}_4/\text{PMMA}$ fue controlado variando la cantidad de surfactante.

Análisis de dispersion de luz dinamica (DLS) de las nanoesferas poliméricas magnéticas mostró que el diámetro hidrodinámico promedio incrementa desde 145 nm hasta 225 nm debido al incremento en la concentración del surfactante. Las propiedades magnéticas de las nanoesferas fueron investigadas midiendo la curva de magnetización y la susceptibilidad. Las partículas respondieron a un campo magnético alternante mediante una relajación magnética Browniana.

To the memory of my mother . . .

To my family...

Esledy, Víctor and Wilson...for all the confidence, support and love they always give me, which makes me a better human being.

Andrea and Matías...for making my life meaningful, I love you.

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Chapter 1

1. Introduction

1.1 Magnetic properties

The magnetic properties of matter are fundamentally the result of the electrons of the atom, which have a magnetic moment by means of the electron motion. At the atomic level, there are two types of electron motion, spin and orbital, and each has a magnetic moment associated with it. The response of a material to a magnetic field, H , is called magnetic induction, B , and its relation is described by [1]:

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{M} \quad (1)$$

where M is the magnetization of the medium and depends of the properties of the material, and the ratio between them is given by the susceptibility χ :

$$\chi = \frac{M}{H} \quad (2)$$

The susceptibility refers to how a material responds to an applied magnetic field and the types of magnetism [2]. The types of magnetism are illustrated in Figure 1.

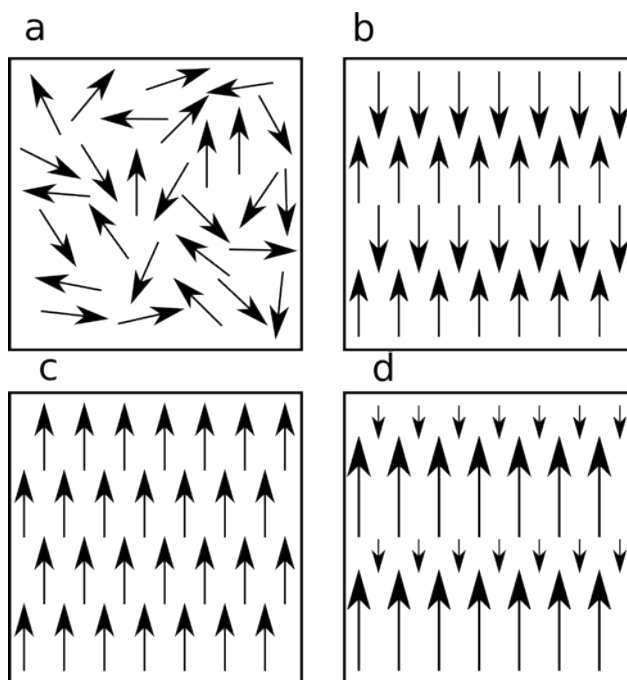


Figure 1. Types of magnetism a) Paramagnetic, b) Antiferromagnetic, c) Ferromagnetic and d) Ferrimagnetic

1.2 Types of magnetism

1.2.1 Diamagnetism

Diamagnetic materials have the direction of magnetization opposite to the field. They are constituted by atoms with zero net magnetic and negative susceptibility.

1.2.2 Paramagnetism

In this type of magnetism, the rotational movement of the electrons in the material is aligned in the same direction of external magnetic field. Consequently, the magnetic field inside becomes more intense, and the material tends to move to where the external magnetic field is stronger.

1.2.3 Ferromagnetic and Ferrimagnetic

These materials exhibit a spontaneous dipole moment in the absence of applied magnetic field, a magnetic phenomenon observed only below a given temperature. Their behavior is therefore different from paramagnetic materials whose elemental dipoles are oriented by a magnetic field to exhibit magnetic moment.

1.2.4 Antiferromagnetism

The materials with antiferromagnetism have zero net magnetic moment and their electron spins are opposite each other.

1.2.5 Superparamagnetism

The response of a superparamagnetic material in the presence of a magnetic field is similar to the response of a paramagnet but more intense.

The change in magnetization when magnetic nanoparticles are under an applied magnetic field can be described by a **magnetization curve** (Figure 2) [2]. The particles tend to align with the field direction either by particle rotation or by dipole moment rotation inside the particle until they achieve their **saturation magnetization** at high field. If the magnetization curve does not retrace its original path when the field is reduced from saturation, this phenomenon in the magnetization curve is called a **hysteresis** loop.

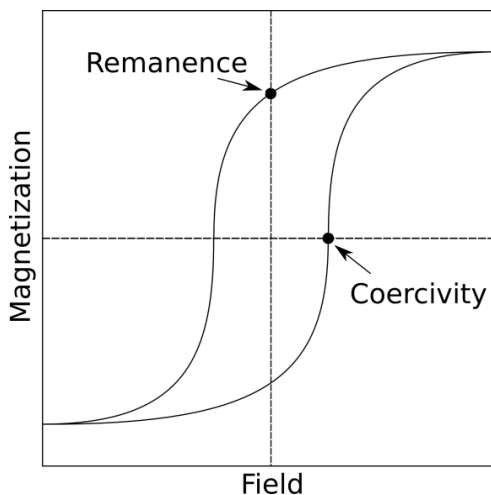


Figure 2. Magnetization curve showing remanence, and coercivity

When the field reaches zero, the magnetic particles remain magnetized because some particles are oriented in the former direction. This residual magnetization is called **remanence** M_r . To demagnetize the particles ($M_r = 0$), a field with opposite direction must be applied. The magnitude of field required to lower the nanoparticle magnetization to zero is called the **coercivity** H_C .

1.3 Ferrofluids

Ferrofluids are stable colloidal mixtures of a nonmagnetic liquid carrier, with dilute suspensions of surfactant/polymer coated magnetic nanoparticles, which undergo rotational and translational Brownian motion [3]. Magnetic nanoparticles used for the preparation of ferrofluids are permanently magnetizable with size range between 10-30 nm approximately and their surface is modified by means of different routes, avoiding the aggregation due to van der Waals and magnetic attraction [4].

Some factors related to the aggregation process or phase separation in ferrofluids are: a temperature lowering, steric and electrostatic stability, free surfactant, and free polymer chains

[5]. The magnetic nature of ferrofluids and their ability to respond to external magnetic and flow fields makes them attractive materials for novel research areas and applications.

The equilibrium magnetization behavior of ferrofluids can be described using the Langevin relation [3, 6].

$$M = M_s \left[\coth \alpha - \frac{1}{\alpha} \right]; \quad \alpha = \frac{\mu_o m H}{KT} \quad (3)$$

In this expression, M and H are the magnetization and magnetic field, and M_s is the saturation magnetization corresponding to all magnetic dipoles with moment m aligned with the local field.

The stability of a suspension of magnetic nanoparticles in a magnetic field requires that the thermal energy be large compared to the magnetic energy.

$$\frac{kT}{\mu_o M_d H \left(\frac{\pi D^3}{6} \right)} > 1 \rightarrow D < \left(6kT / (\mu_o M_d H)^{1/3} \right) \quad (4)$$

In the presence of a magnetic field, the magnetic nanoparticles align through Néel and Brownian relaxation. In the Néel mechanism only the internal magnetic dipole of the particle rotates and aligns in the direction of the applied field without physical particle rotation (equation 5), with characteristic time given by

$$\tau_N = \frac{1}{f_o} \exp \frac{KV}{k_B T} \quad (5)$$

In this expression, f_o is the Larmour frequency of the magnetization which has a value $\sim 10^9$, K the magnetic anisotropy constant, k_B is Boltzmann's constant, T is the absolute temperature, and V the magnetic core volume. On the Brownian relaxation mechanism the magnetic dipoles of the particles are fixed in a crystal direction generating physical rotation and alignment of the

particles in the direction of the applied magnetic field. The characteristic Brownian relaxation time is given by (equation 6).

$$\tau_B = \frac{3V_h\eta_0}{kT} \quad (6)$$

In this equation, V_h is the hydrodynamic volume of the particles, η_0 is the medium viscosity, and kT is the thermal fluctuation energy. The relaxation mechanism in a suspension will follow the process with the shortest relaxation time. For relatively small particles the Brownian relaxation time will be larger than the Néel relaxation time, and relaxation will take place by rotation of the internal moment of the particles (Néel mechanism).

when an oscillating magnetic field is applied to a ferrofluid, the magnetization considering the sinusoidal variation of field is described as:

$$M = \chi' H_0 \cos(\omega t) + \chi'' H_0 \sin(\omega t) \quad (7)$$

where χ' , χ'' are the real and imaginary components of the complex (dynamic) susceptibility.

The Debye model can be used to describe the response of the magnetization of a dilute suspension of spherical magnetic particles due to an alternating magnetic field when the dipole-dipole interaction energy is smaller than the thermal energy kT and the complex susceptibility of the magnetic fluid has the frequency dependence $\chi(\omega)$ [7].

$$\chi'(\omega) = \frac{\chi_0}{1+(\omega\tau)^2} \quad (8)$$

$$\chi''(\omega) = \frac{\chi_o \omega \tau}{1 + (\omega \tau)^2} \quad (9)$$

1.4 Ferrites

The spinel structure of ferrite [8] has the general formula MFe_2O_4 , where M corresponds to a divalent metal. Divalent ions such as Co^{2+} , Mn^{2+} , Ni^{2+} , and Zn^{2+} are commonly found in spinels. The spinel lattice is composed of a closed packed oxygen arrangement in which 32 oxygen ions form the unit cell in A and B sites. Tetrahedrally coordinated sites (A) are surrounded by four nearest oxygen atoms, and octahedrally coordinated sites (B) are surrounded by six nearest neighbor oxygen atoms. The unit cell contains 64 tetrahedral sites, only 8 being occupied. On the other hand, of the of octahedral sites half of them are occupied (see Figure 3).

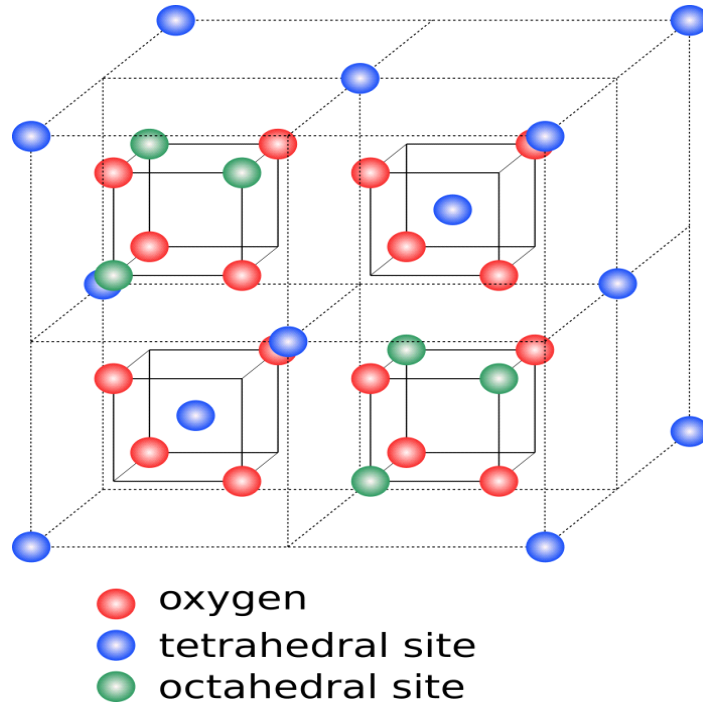


Figure 3. Spinel structure of ferrite

The cubic ferrites with paramagnetic behavior [1] have normal spinel in which Fe^{2+} ions are all on A sites and Fe^{3+} ions occupy B sites. Another type of spinel is the inverse; the divalent Fe^{2+} ions occupy only B sites while Fe^{3+} ions are located on both A and B sites equally. The magnetic moments of trivalent ions do not form net contribution to the magnetization of the solid. This is because the spin moments of all the trivalent ions on the octahedral sites are aligned parallel but in the opposite direction to the spin moments of the trivalent ions.

The cubic ferrites are desirable in many application field such as catalysis, biotechnology, biomedicine, magnetic fluids, magnetic recording, data storage and MRI [9]. Their properties such as high permeability and high electrical resistivity let high concentration of flux density inside the coil improve the inductance and reduce the formation of undesirable eddy currents. Both ferrites are attractive for uses as cores for induction coils with operations at high frequency due to their permeability, saturation magnetization and low electrical conductivity. The large magnetocrystalline anisotropy of the ferrites make them suitable for memory applications because of their square-shaped hysteresis loop (see Figure 2).

The hexagonal ferrites [1] have as general formula $\text{MO} \cdot 6\text{Fe}_2\text{O}_3$ and are easily synthesized by ceramic processing methods. They have a high coercivity and are used as permanent magnets. Also, they are formed by the spinel structure with the oxygen ions in close packing, but some layers include metal ions.

Cobalt ferrite has a large magnetocrystalline anisotropy, high coercivity, moderate saturation magnetization, a large magnetostrictive coefficient, chemical stability and mechanical

hardness, which have attracted considerable attention in many applications fields. It has an inverse spinel structure where oxygen atoms form an FCC lattice. Also, it has one half of Fe^{3+} ions occupying the tetrahedral A sites and the other half including its divalent ions are found in the octahedral B sites [10].

1.5 Nanocomposites Materials

Polymer nanocomposites are multi-phase materials typically composed of a polymer matrix (organic phase) loaded with reinforcing nanofiller (inorganic phase). Such systems have attracted attention because of the possibility of improving or tailoring the properties that are not obtained with traditional micro-scale fillers or the base polymer [11-13]. Nanocomposites have been loaded with a variety of nanoscale reinforcing fillers such as carbon nanotubes [14-16], silica [17-20], zinc oxide [21], and others. The nanofiller impart properties additional to conventional composites such as mechanical, thermal, magnetic, optical, thermo-mechanical, and electrical properties, among others.

Recently, attention has shifted to the incorporation of magnetic nanoparticles within polymeric matrices, which have shown various potential applications such as drug delivery and biomedical applications [22-25]. Recent studies indicate that the great challenge faced by the nanocomposites materials scientific community is how to successfully incorporate these inorganic particles into polymer matrices homogeneously at the nanometer scale [12]. One alternative to improve this is to modify the surface of the nanoparticles to improve their dispersion within the matrix.

1.6 Latex Polymer Nanocomposites

Other equally important composites are the colloidal latex polymer nanocomposites. Latexes are colloidal composites that combine inorganic and one or more polymers (organic) materials dispersed in liquids, commonly water, and which are present as drops of microscopic or nanoscopic size. Dispersed colloids are stabilized by agents that form films at the surface of the droplets or that impart to them mechanical stability [26,27]. There are several techniques used in the preparation of latex. The most common are the emulsion and mini-emulsion polymerization processes. These methods often use surfactants which for many applications are undesirable and need to be removed [28,29]. Other latexes that have been found to have importance are the magnetic polymer lattices (MPLs). The preparation of MPLs with uniform size distribution and high magnetization is challenging. We investigated in producing latex particles of controlled size so that we can get from micrometer to nanometer size. For this we used the emulsion technique and we studied the effect of the concentration of the surfactant on the size. The magnetic properties of latex were studied.

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Chapter 2

2. Synthesis and Characterization of Polymer Nanocomposites Containing Magnetic Nanoparticles

Magnetic poly(methyl methacrylate) nanocomposites were prepared using oleic acid coated cobalt ferrite and magnetite nanoparticles. Both nanofillers had a similar effect in shifting the glass transition temperature from that of the neat polymer. The cobalt ferrite nanocomposite had magnetic hysteresis at 2 and 300 K and the magnetite nanocomposite had magnetic hysteresis at 2 K and superparamagnetic behavior at 300 K. Surprisingly, zero field cooled magnetization measurements for the cobalt ferrite nanocomposite showed a peak at ~250 K, in contrast with measured hysteresis at 300 K. On the other hand, ac susceptibility measurements up to 400 K did not show any peaks for the cobalt ferrite nanocomposite. These measurements suggest the importance of ac susceptibility measurements in characterizing the magnetic properties of polymer nanocomposites.

2.1 Introduction

The present chapter focuses on the preparation of nanocomposites using as a matrix the polymer poly(methyl methacrylate) (PMMA) and as filler cobalt ferrite or magnetite nanoparticles. These nanoparticles were synthesized using the thermal decomposition method in the presence of oleic acid. The nanocomposites obtained were characterized magnetically through the magnetization versus field (MH) in addition to curves of zero field cooled (ZFC) and field cooled (FC). Finally, nanocomposites were investigated thermally to determine the influence of nanofiller.

2.2 Previous Work

Magnetics nanoparticles (MNPs) are currently used in a wide range of applications such as drug delivery [1], data storage [2], and biomedical applications [3, 4], among others. Magnetic iron oxide nanoparticles such as magnetite (Fe_3O_4) are especially applied because of their interesting magnetic properties, for which it is important to control the size and shape of the nanoparticles and to ensure these are well dispersed within the composite matrix [5, 6, 7]. Recently there has been increasing interest in polymer-based nanocomposites incorporating magnetic nanofillers. Two approaches are common: (i) *in situ* precipitation of the MNPs within the polymer matrix and (ii) addition of presynthesized nanoparticles to the prepolymeric solution, encapsulating the nanoparticles upon polymerization. As an example of the first approach, thin films of poly(vinyl alcohol) with magnetic properties were obtained by *in situ* precipitation and oxidation of Fe^{+3} and Co^{+2} within the polymer matrix [8]. Magnetic measurements revealed ferromagnetic behavior but with very small coercivity. Although *in situ* precipitation of the MNPs is promising, significant work is needed to obtain control of particle size and crystallinity achievable by wet chemistry methods of nanoparticle synthesis, such as the thermal

decomposition method [9]; hence, the interest in preparing nanocomposites by mixing the preformed MNPs into the prepolymeric mixture. As an example of such work, cobalt ferrite (CoFe_2O_4) nanoparticles have been capped with dimercaptosuccinic acid to obtain stable dispersions in poly(N-vinyl-2-pyrrolidone), resulting in a nanocomposite with ferromagnetic properties [10].

In this work, we report the preparation of polymeric magnetic nanocomposites in which the base polymer is PMMA and the magnetic nanofiller is either oleic acid coated magnetite or oleic acid coated cobalt ferrite. The thermal and magnetic properties of these nanocomposites are compared using differential scanning calorimetric (DSC) and static and dynamic magnetization measurements.

2.3 Experimental Section

2.3.1 Materials

Methyl methacrylate and cobalt (III) chloride hexahydrate, 98%, were purchased from Aldrich and used without further purification. Sodium oleate, 3-methacryloxypropyltrimethoxysilane and 1-octadecene were purchased from Tokyo Chemical Industry. Iron (III) hexahydrate 97% and 2,2-azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich.

2.3.2 Synthesis of Fe_3O_4 and CoFe_2O_4 Nanoparticles

Cobalt ferrite and magnetic nanoparticles were prepared by the thermal decomposition method [9, 11], which consists in the preparation of an iron-cobalt compound followed by thermal decomposition using a solvent such as octadecene. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0045

moles), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.016 moles) and sodium oleate (0.064 moles) were dissolved in a mixture consisting of 40 mL of deionized water, 80 mL of hexane, and 40 mL of ethanol. This mixture is heated to 70 °C with reflux for 4 h to allow the formation of the iron-cobalt oleate. Subsequently, the organic phase is separated from the aqueous phase and washed three times with 40 mL of deionized water and then dried in a vacuum oven for 48 h at 70°C. Then, 16.5 g of the iron-cobalt and 1.32 g of the oleic acid are dissolved in 66 mL of octadecene and mixed under nitrogen for 1 h to maintain an inert atmosphere. The mixture is heated to 320 °C at a heating rate of 3.5 °C/min, remaining at this temperature for 3 h. The resulting solution was washed with 100 mL acetone per 20 mL of mixture and the oleic acid coated nanoparticles were separated magnetically.

2.3.3 Preparation of Nanocomposites

Nanocomposites were prepared by mixing methyl methacrylate with selected amounts of oleic acid coated MNPs. The initiator AIBN was added and polymerization took place using a ramp from room temperature to 70 °C for 10 h to obtain nanocomposites.

2.3.4 Nanoparticle Characterization

The hydrodynamic diameter of the oleic acid coated nanoparticles was measured through dynamic light scattering (DLS) using a Brookhaven Instruments BI-90Plus particle size analyzer. Fourier transform infrared (FTIR) spectroscopy of the oleic acid coated nanoparticles was characterized using a Varian 800 spectrometer with ZnSe ATR plates. The mass percentage of inorganic material in the nanoparticles was determined through thermogravimetric analysis (TGA) using a TA-2950 from TA Instruments.

2.3.5 Nanocomposite Characterization

The effect of the MNP nanofillers on the glass transition temperature of the nanocomposites was determined using DSC, performed using a TA Instruments model Q2000. The samples were placed in aluminum DSC sample pans and scanned from 30 to 200 °C at a heating rate of 10 °C/ min. Magnetic properties of the nanocomposites were measured using a Quantum Design MPMS XL-7 SQUID magnetometer. Equilibrium magnetization measurements were made for fields of up to 7 T at 2 and 300 K. Temperature dependent magnetization was measured under zero field cooled (ZFC) and field cooled (FC) conditions using a field of 10 mT in the temperature range of 2 to 400 K. The temperature dependent magnetic properties of the nanocomposites were also studied in this temperature range through temperature dependent ac susceptibility measurements at various frequencies and with field amplitude of 0.1 mT.

2.4 Results and Discussion

2.4.1 Characterization of Nanoparticles

Figure 4 shows the hydrodynamic diameter of the oleic acid coated magnetite and cobalt ferrite nanoparticles suspended in hexane, which were found to be 15 and 10 nm, respectively. Figure 5 shows representative TEM images of the OA-coated nanoparticles of magnetite (Figure 5a), and cobalt ferrite (Figure 5b). It can be seen that the nanoparticles are not agglomerated as a result of OA coating.

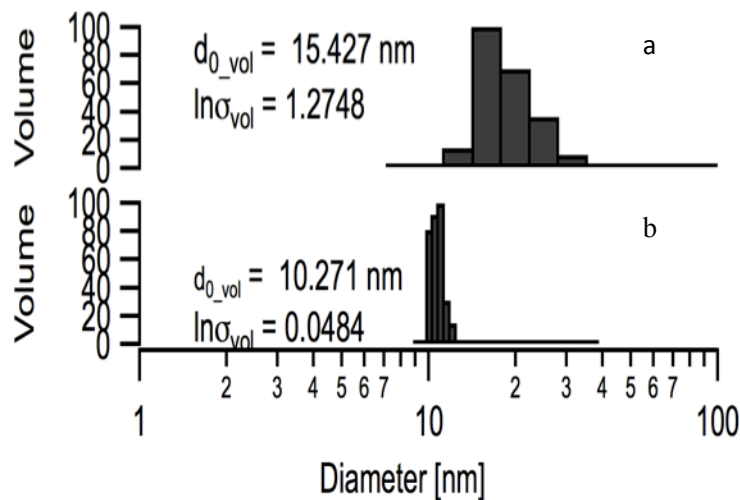


Figure 4. Volume size distribution obtained by DLS for nanoparticles of magnetite (Fe_3O_4) (a) and cobalt ferrite (CoFe_2O_4) (b) coated with oleic acid.

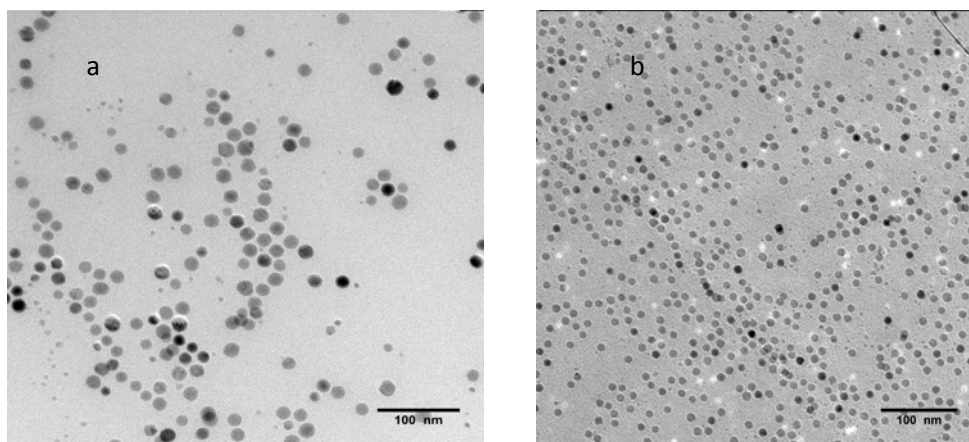


Figure 5. Representative TEM images of the nanoparticles of magnetite (Fe_3O_4) (b), and cobalt ferrite (CoFe_2O_4) (c) coated with oleic acid.

Analysis of the nanoparticle's FTIR spectra shows, among others, a band at 1705 cm^{-1} which is attributed to the ester bond $\text{C}=\text{O}$, characteristic of the vibration of the carbonyl group, indicating the presence of oleic acid coating the nanoparticles (Figure 6).

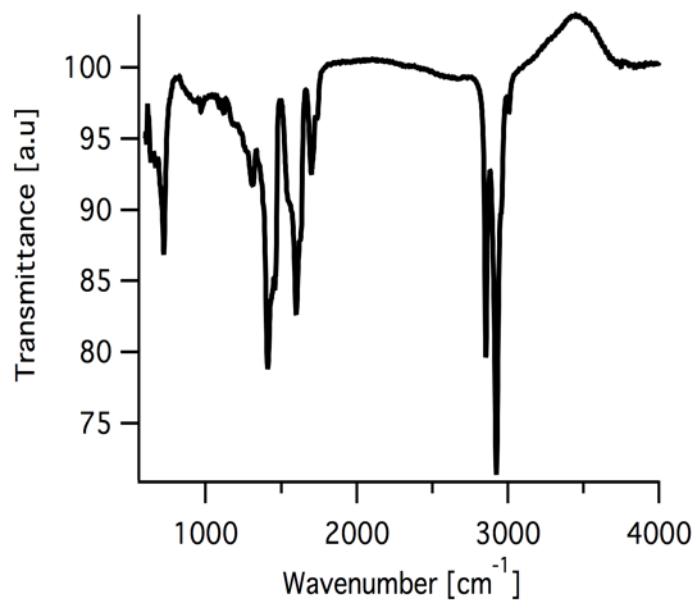
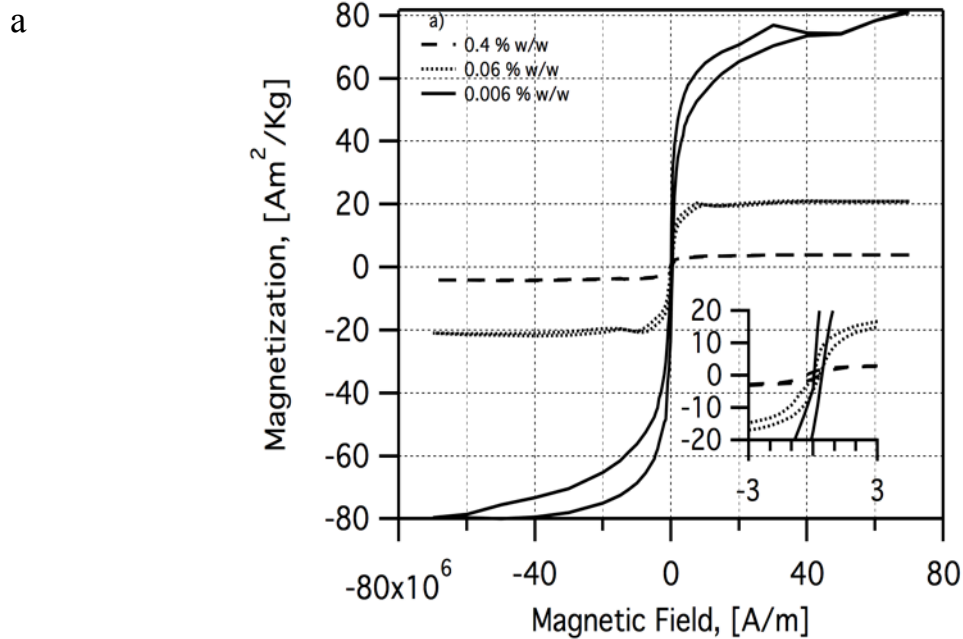


Figure 6. FTIR spectra of nanoparticles coated with oleic acid.

2.4.2 Magnetic Properties of the Nanocomposites

2.4.2.1 Magnetization curves



b

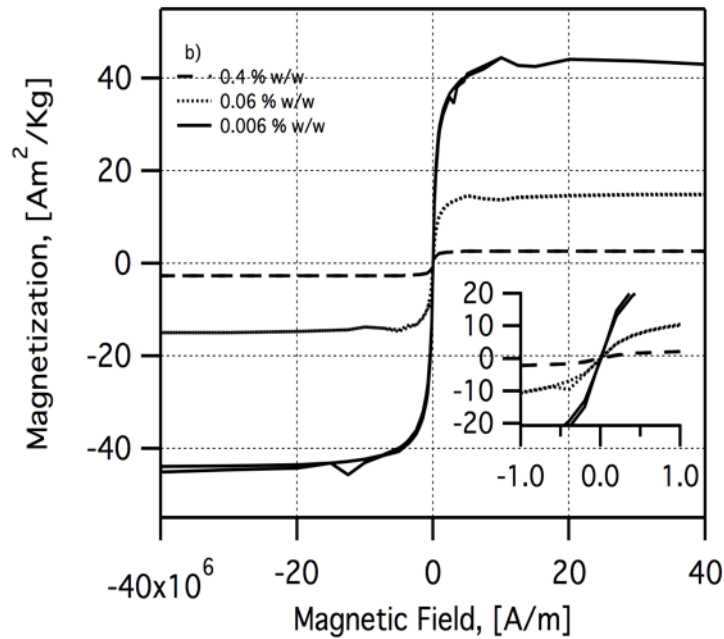


Figure 7. Equilibrium magnetization at 2 K (a) and 300 K (b) for 0.4 % w/w, 0.06 % w/w and 0.006 % w/w PMMA-Fe₃O₄ nanocomposites.

Equilibrium magnetization measurements for nanocomposites filled with magnetite nanoparticles with different percent w/w (0.4 %, 0.06 % and 0.006 %) at 2 K and 300 K are presented in Figure 7. The three types of nanocomposite displayed magnetic hysteresis at 2 K but at 300 K the magnetite nanocomposites were super paramagnetic. At 2 K, the coercivities (H_c) increased slightly with particles concentration giving values of 28 mT, 30 mT and 40 mT for 0.4 % w/w, 0.06 % w/w, and 0.006 % w/w nanocomposites, respectively. The saturations magnetization (M_s) values, normalized with respect to the magnetic core mass in the sample, were lower than the bulk values for all the nanocomposites at both temperatures. At 300 K, the saturation magnetization were $3 \text{ A m}^2 \text{ kg}^{-1}$, $15 \text{ A m}^2 \text{ kg}^{-1}$, and $43 \text{ A m}^2 \text{ kg}^{-1}$ for 0.4 % w/w, 0.06 % w/w, and 0.006 % w/w the magnetite nanocomposites respectively. At 2 K, the saturation

magnetization were $4 \text{ A m}^2 \text{ kg}^{-1}$, $21 \text{ A m}^2 \text{ kg}^{-1}$, and $81 \text{ A m}^2 \text{ kg}^{-1}$ for 0.4 % w/w, 0.06 % w/w, and 0.006 % w/w the magnetite nanocomposites, respectively. Similar reduced values of saturation magnetization have been reported by others and could be due to the following factors:

- 1- Slight errors in the inorganic core mass used to normalize the measured magnetization.
- 2- The presence of a magnetically dead layer on the nanoparticle surface due to interaction with the oleic acid ligand.
- 3- Magnetic dipole-dipole interactions between particles, which can effectively decrease the magnetization in the sample [12].

The saturation magnetization at 2 K and 300 K increased with decreasing particle concentration, which can be due to blocking caused by the opposition between particle-particle and magnetic anisotropy on the relaxation process [12,13]. The values obtained are summarized in Table 1.

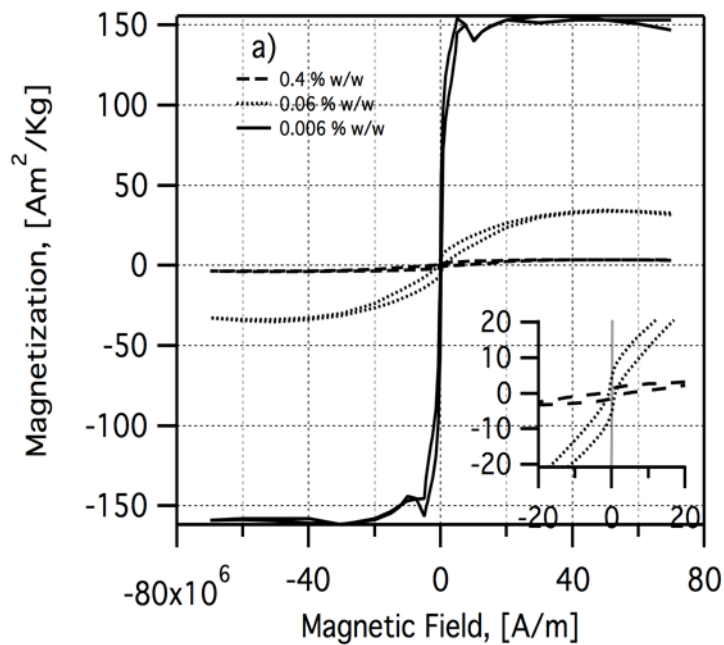
Table 1. Magnetic Properties for Nanocomposites with Fe_3O_4

	2 K	2 K	300 K	300 K
Fe_3O_4 % w/w	Hc (mT)	Ms ($\text{Am}^2 \text{ kg}^{-1}$)	Hc (mT)	Ms ($\text{Am}^2 \text{ kg}^{-1}$)
0.4	28	4.0	-	3.0
0.06	30	21	-	15
0.006	40	81	-	43

Equilibrium magnetization measurements for nanocomposites filled with cobalt ferrite nanoparticles with different percent w/w (0.4 %, 0.06 % and 0.006 %) at 2 and 300 K are presented in Figure 8. For both temperatures (2 K and 300 K), the three types of nanocomposites

displayed magnetic hysteresis. In addition when the particles concentration decreased the values obtained for coercivity also decreased. At 2 K, the coercivity was affected by particle concentration with values of 350 mT, 100 mT and 25 mT for 0.4 % w/w, 0.06 % w/w, and 0.006 % w/w nanocomposites, respectively. At 300 K, the values of the coercivity were 80 mT, 35 mT, and 3 mT for 0.4 % w/w, 0.06 % w/w, and 0.006 % w/w nanocomposites respectively. The saturation magnetization of the nanocomposites with cobalt ferrite at 2 K and 300 K decreased with increasing particle concentration (Table 2).

a



b

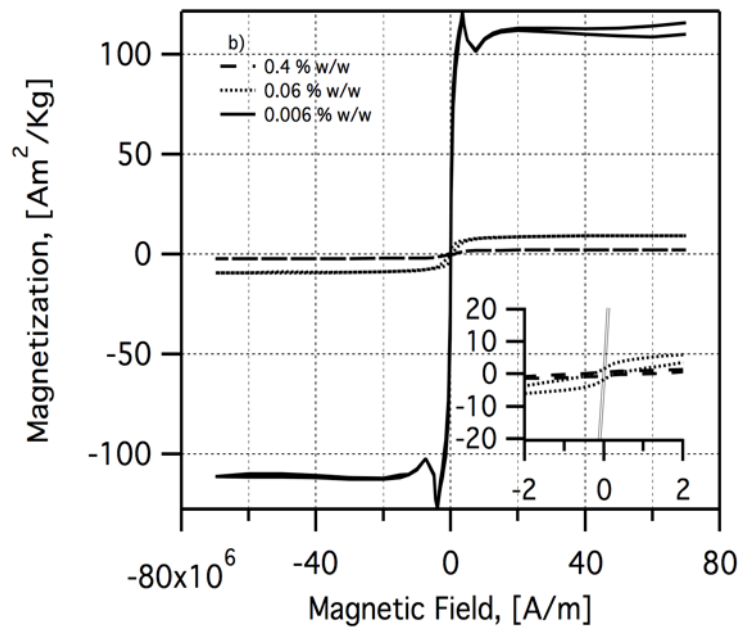


Figure 8. Equilibrium magnetization at 2 K (a) and 300 K (b) for 0.4 % w/w, 0.06 % w/w and 0.006 % w/w PMMA-CoFe₂O₄ nanocomposites.

Table 2. Magnetic Properties for Nanocomposites with CoFe₂O₄

	2 K	2 K	300 K	300 K
CoFe ₂ O ₄ %w/w	H _c (mT)	Ms (Am ² kg ⁻¹)	H _c (mT)	Ms (Am ² kg ⁻¹)
0.4	350	3.0	80	2.1
0.06	100	35	35	9
0.006	35	150	3	116

2.4.2.2 Anisotropy Constant Determination Using ZFC

Zero Field Cooled (ZFC) and Field Cooled (FC) temperature dependent magnetization curves for nanocomposites with magnetite nanofillers are shown in Figure 9. The anisotropy

constant can be determined by magnetic measurements such as zero-field-cooled (ZFC) magnetization curves in samples whereas magnetic relaxation is through the Néel mechanism. It is usual to identify the peak in the ZFC curve with the so-called blocking temperature T_B , interpreted as the temperature at which 50% of the nanoparticles transition from superparamagnetic to ferromagnetic behavior. As expected from the equilibrium magnetization measurements for the nanocomposite with magnetite nanofiller, which showed superparamagnetic behavior at 300 K, the blocking temperature for these nanocomposites determined from the ZFC curve was 209 K, 225 K, and 225 K for 0.4 % w/w, 0.06 % w/w, and 0.006 % w/w nanocomposites respectively.

The magnetic anisotropy constant K of the magnetite nanoparticles was estimated from these values of the blocking temperature according to the relationship:

$$K = 25k_B T_B / V_m \quad (10)$$

where k_B is the Boltzmann's constant and V_m is the volume of the magnetic cores, estimated using the particle diameter determined from DLS (which overestimates the magnetic core diameter) and subtracting 2 nm to account for the oleic acid coating. The resulting values are higher than the reported value of 13.5 kJ/ m³ for bulk magnetite [14], however, we observe that the peaks in the ZFC curve are broad, indicating polydispersity in magnetic properties and magnetic interactions between particles could be present, resulting in the perceived increase in anisotropy constant.

It was puzzling to find a blocking temperature of 257 K and of 289 K for the nanocomposite of 0.06 % w/w, and 0.006 % w/w respectively with the cobalt ferrite nanofiller, for which equilibrium magnetization measurements at 300 K showed hysteresis (Figure 10). The

magnetic anisotropy constant was estimated from this blocking temperature, obtaining a value of 330 kJ/ m^3 and 343 kJ/ m^3 , which is remarkably close to the reported value of 300 kJ/ m^3 for bulk cobalt ferrite [15] (Table 3).

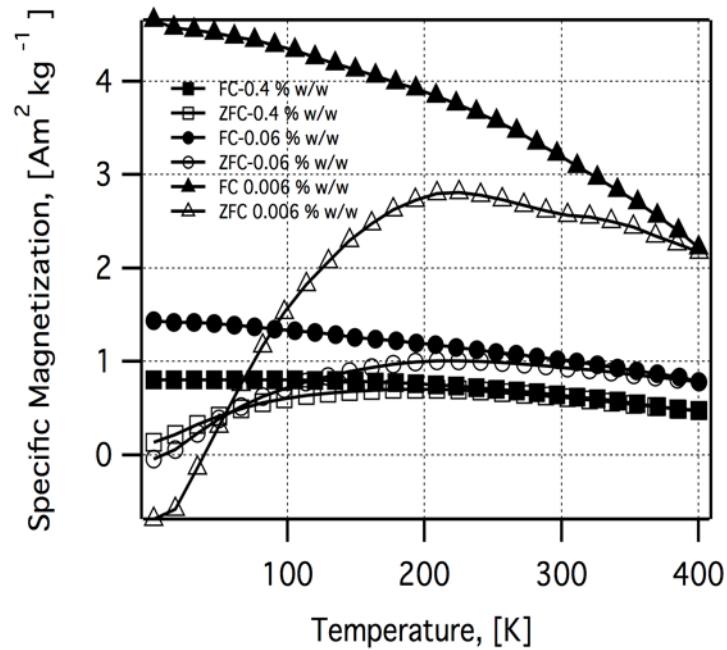


Figure 9. Field cooled (filled symbol) and Zero field cooled (open symbol) magnetization curves for 0.4 % w/w, 0.06 % w/w and 0.006 % w/w PMMA-Fe₃O₄ nanocomposites, obtained using 100 Oe.

Table 3. Anisotropy Constants for PMMA-Fe₃O₄ and PMMA-CoFe₂O₄ nanocomposites

	Fe₃O₄		CoFe₂O₄	
% w/w	T_B (K)	K (kJ/ m ³)	T_B (K)	K (kJ/ m ³)
0.4	209	83		
0.06	225	86	257	330
0.006	225	86	289	343

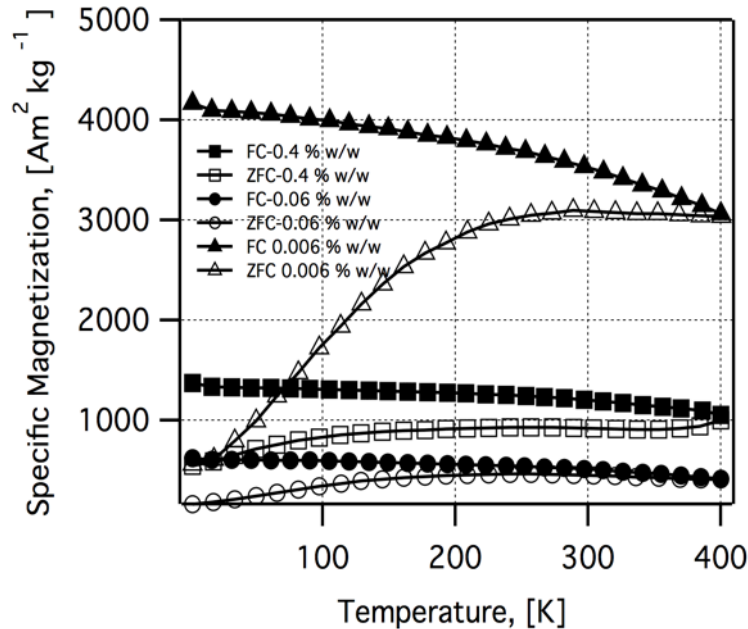


Figure 10. Field cooled (filled symbol) and Zero field cooled (open symbol) magnetization curves for 0.4 % w/w, 0.06 % w/w and 0.006 % w/w PMMA-CoFe₂O₄ nanocomposites, obtained using 100 Oe.

The ac susceptibility of both nanocomposites as a function of temperature was measured because of the discrepancy between the hysteresis at 300 K and the blocking temperature of 257 K observed for the cobalt ferrite nanocomposite. Two advantages of ac susceptibility measurements are that the time scale of the measurements is set by the applied field frequency (and hence is accurately known) and that only a small oscillating probe field is used, ensuring the estimated value of the anisotropy constant corresponds to the case of zero magnetic field. Unfortunately, the ac susceptibility signal was rather weak (Figure 11).

The curve for the magnetite nanocomposite has a broad peak at ~ 275 K, which is consistent with the blocking temperature determined from ZFC measurements. On the other hand, the cobalt ferrite nanocomposite did not show evidence of a peak below 400 K, in agreement with the observed hysteresis at 300 K. Further work is needed to improve the

accuracy of these measurements, however, the results indicate that ac susceptibility measurements may be more reliable in obtaining the blocking temperature of MNPs and in characterizing the magnetic properties of nanocomposites.

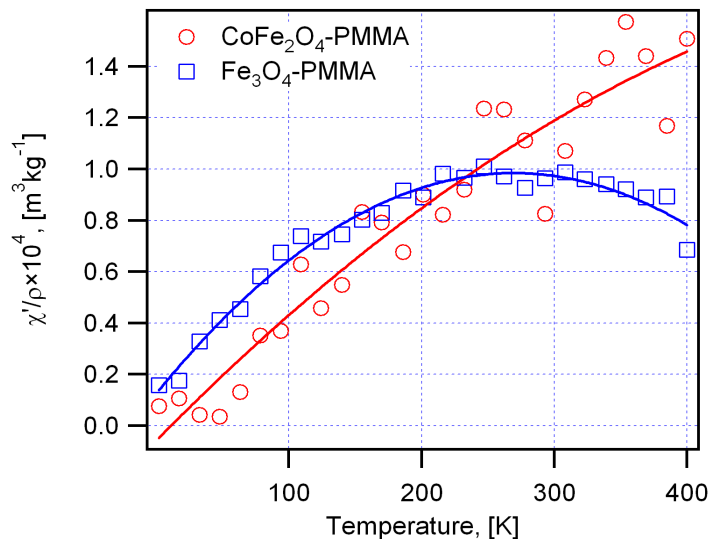


Figure 11. Temperature dependent measurements of the in-phase component of the complex susceptibility for 0.06% w/w CoFe₂O₄-PMMA and Fe₃O₄-PMMA nanocomposites.

2.4.2.3 Anisotropy Constant Determination Using AC Susceptibility Measurements

The in-phase component of the AC susceptibility χ' was measured as a function of temperature at various frequencies for the magnetite nanocomposite of 0.4 % w/w. The curve of in-phase component as a function of temperature presents a peak, which can be used to estimate the magnetic anisotropy. The Vogel-Fulcher model can be used to relate the dependence of the temperature with AC susceptibility data of interacting superparamagnetic nanoparticles [16-18]. This model assumes that the peak of the χ' vs. T curve corresponds to the condition $\Omega\tau = 1$,

therefore plotting $\ln(1/\Omega)$ vs. $1/T$ should yield to a linear relation in which the slope is an estimate for KV through the relation:

$$\ln(1/\Omega) = \ln \tau_0 + KV / k (T - T_0) \quad (11)$$

To use equation (11) to estimate K , it is necessary to set $T_0 = 0$. Also the value of τ_0 can be obtained from the infinite temperature intercept.

The in-phase χ' component of the dynamic susceptibility as function of temperature at various frequencies for the sample with 0.4% w/w PMMA-Fe₃O₄ is shown in Figure 12. The peak temperature increases with increasing frequency. Using the values of the peak, which were calculated by fitting of the dynamic susceptibility of the sample, Figure 13 was obtained.

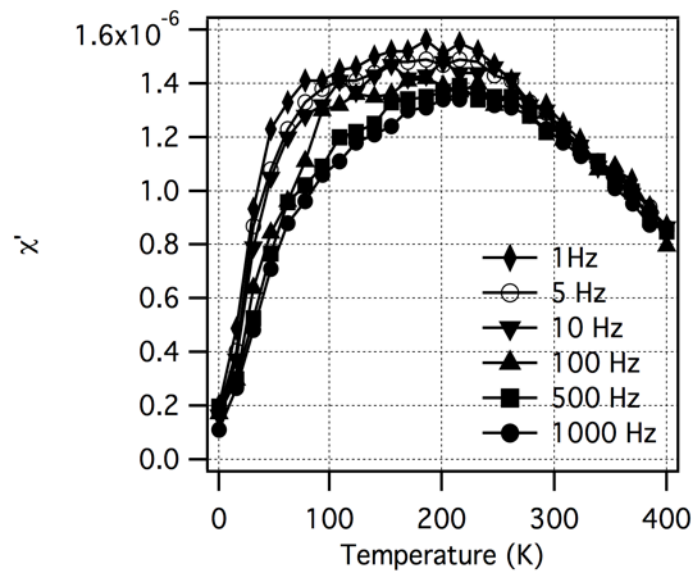


Figure 12. Variation of the in-phase component of the dynamic susceptibility with frequency for the sample with 0.4% w/w PMMA-Fe₃O₄ nanocomposites.

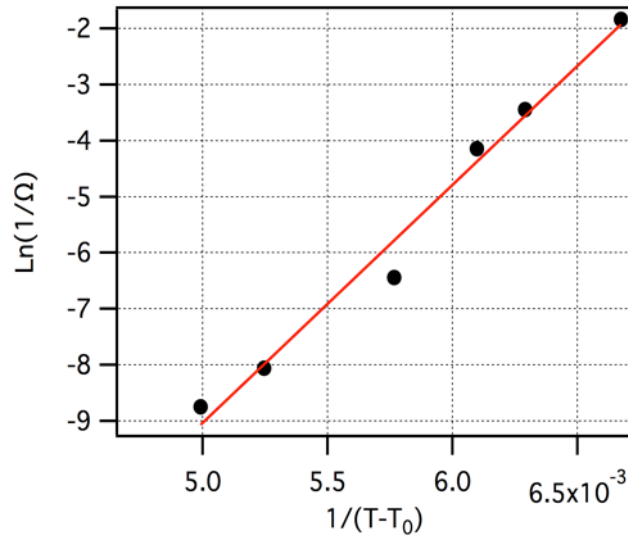


Figure 13. Plot of the inverse applied field frequency as a function of the inverse temperature corresponding to the peak of in-phase component of dynamic susceptibility using Neel's model for τ .

From equation (11) the anisotropy constant K and the characteristic time were τ_0 for the sample with 0.4% w/w PMMA-Fe₃O₄ nanocomposites were obtained. For the anisotropy constant, a value of 112.0 kJ/m³ was obtained for sample of 0.4% w/w magnetic nanocomposite using the Vogel-Fulcher model. This value is similar to that obtained through the ZFC (83 kJ/m³), and both are higher than the reported value of 13.5 kJ/m³ for bulk magnetite. Note above that the values of constant anisotropy calculated through ZFC and AC susceptibility measurement indicate polydispersity and magnetic interaction between particles.

2.4.3.4 Differential Scanning Calorimetry

Figure 14 shows the heat flow as a function of temperature obtained through differential scanning calorimetry (DSC) of the neat polymer and nanocomposites with a 0.4% mass percentage of the cobalt ferrite and magnetite nanofillers. A slight decrease in the heat flow curve is observed between 100 and 120 °C, which is identified as the glass transition of the

material. The neat PMMA polymer has a glass transition temperature (T_g) of 111.1 °C. The T_g is seen to increase upon addition of the MNPs to the polymer, to a value of 123.5 °C for both cobalt ferrite and magnetite nanofillers.

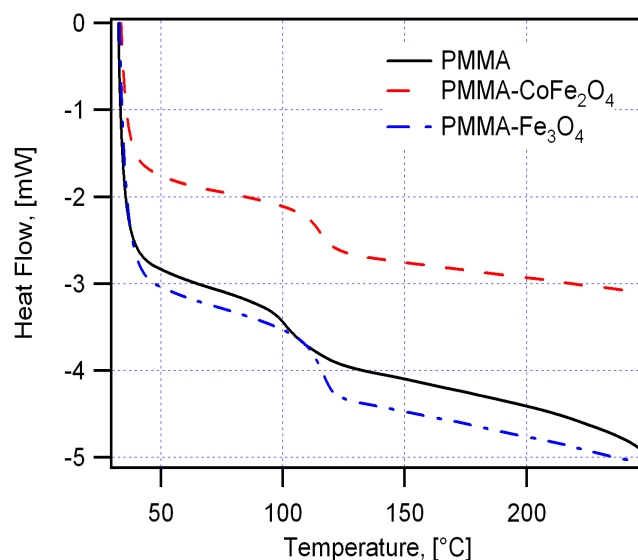


Figure 14. DSC of neat PMMA and 0.4% w/w PMMA-CoFe₂O₄ and PMMA-Fe₃O₄ nanocomposites.

2.5 Conclusions

Magnetic polymer nanocomposites were prepared using oleic acid coated cobalt ferrite and magnetite nanoparticles as nanofillers and PMMA as the polymer matrix. It was found that both nanofillers similarly affected the glass transition temperature of the nanocomposite, increasing it relative to the neat polymer. The magnetite nanocomposite displayed superparamagnetic behavior at 300 K whereas the cobalt ferrite nanocomposite displayed magnetic hysteresis at 2 and 300 K. ZFC magnetization measurements in both samples showed peaks below 300 K, which is in contrast with the hysteresis observed for the cobalt ferrite nanocomposite at 300 K. Temperature dependent ac susceptibility measurements, on the other hand, did not show a peak at up to 400 K for the cobalt ferrite nanocomposite. These

observations demonstrate the importance of ac susceptibility measurements in determining the magnetic properties of magnetic polymer nanocomposites.

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Chapter 3

3. Influence of Nanoparticle Surface Chemistry on the Thermomechanical and Magnetic Properties of Ferromagnetic Nanocomposites

The effect of nanoparticle surface chemistry on the thermal, mechanical, and magnetic properties of poly(methyl methacrylate) (PMMA) nanocomposites with cobalt ferrite nanofillers was studied by comparing nanofillers coated with oleic acid (OA; which does not covalently bond to the PMMA matrix) and 3-methacryloxypropyltrimethoxysilane (MPS, which covalently bonds to the PMMA matrix). Thermogravimetric analysis revealed an increase in the thermal degradation temperature of the nanocomposites compared with the neat polymer. The effect of cobalt ferrite nanofiller on the glass transition temperature (T_g) of the nanocomposite was evaluated by differential scanning calorimetry. The T_g value of the material increased when the particles were introduced. Dynamic mechanical analysis indicated an increase in the storage modulus of the nanocomposite because of the presence of nanofiller and a shift in the peak of loss tangent toward higher temperature. Magnetic measurements indicated that both nanocomposites had a small hysteresis loop at 300 K and no hysteresis at 400 K. However,

estimates of the nanofiller's rotational relaxation times and measurements of the zero field cooled temperature-dependent magnetization indicate that the observed lack of hysteresis at 400 K is likely because of particle rotation in the polymer matrix.

3.1 Introduction

The present chapter presents the influence of surface modification on the thermomechanical and magnetic properties of the PMMA nanocomposite. The process was carried with two different molecules: oleic acid (OA) and 3-methacryloxypropyltrimethoxysilane (MPS), which coated the surface of the nanoparticles of cobalt ferrite, used as nanofiller. Afterwards, the materials were tested through thermogravimetric analysis, differential scanning calorimetry, dynamic mechanical analysis, and magnetic measurements.

3.2 Previous Work

Polymer nanocomposites are multiphase materials typically composed of a polymer matrix loaded with a reinforcing nanofiller. Such systems have attracted attention because of the possibility of improving or tailoring their mechanical and thermal properties beyond those of the base polymer. Also, the nanofiller may impart additional optical, thermomechanical, electronic, and magnetic properties. A wide range of nanoparticles have been used as fillers, the most common being carbon nanotubes [1–4], ZnO [5], ZnS [6], CdTe [7], BaTiO₃ [8], Au [9], Ag [9,10] and TiO₂ [11]. A significant challenge in the field of nanocomposites is incorporating these inorganic particles into polymer matrices homogeneously at the nanometer scale, to minimize factors such as poor alignment and poor interfacial load transfer to the filler, problems which limit the benefits of nanocomposites [12]. It is currently believed that filler morphology is

a determining factor of the mechanical properties of nanocomposites and of load transfer from the polymer to the filler. One alternative to improve this is to modify the surface of the nanoparticles to facilitate their dispersion within or modulate interactions with the matrix.

Magnetic nanocomposites have been prepared using different matrices such as silicon dioxide [13], aluminum oxide [14] and porous glass [15]. Recently, attention has shifted to the incorporation of magnetic nanoparticles within polymeric matrices. Iron oxide nanoparticles have been melt-mixed with Nylon 66 to obtain a magnetic polymer nanocomposite [16]. Transmission electron microscopy (TEM) and field emission scanning electron microscopy (SEM) of the nanocomposites showed that the nanofiller was highly aggregated, possibly because the surface of the nanoparticles were not modified to be made compatible with the polymer.

The influence of surface modification of magnetic metallic nanoparticles of iron, cobalt, and nickel on the properties of (PMMA) and polystyrene has been studied by modifying the nanoparticles by irradiation-induced polymerization [17]. Although surface modification of the nanoparticles seemed to affect the properties of the resulting nanocomposites, TEM did not show a significant improvement in the dispersion of the nanoparticles within the polymer matrix. Studies of the magnetic properties of cobalt ferrite–poly(N-vinyl-2-pyrrolidone) and cobalt ferrite–polyvinyl alcohol nanocomposites have been reported, and ferromagnetic behavior was observed in both nanocomposites [18, 19]. Cobalt ferrite nanoparticles have also been synthesized in situ in poly(styrene-*b*-ethylene/butylene-*b*-styrene) block copolymers, with differential scanning calorimetry (DSC) indicating that the nanoparticles are likely embedded in the styrene blocks [20]. However, TEM of these nanocomposites indicated that relatively large and polydisperse particles had been formed.

Core shell Fe-FeO nanoparticles have been dispersed in epoxy resins with observed changes in the thermomechanical, magnetic, and electric properties of the nanocomposites with nanoparticle loadings of 1–20% [21]. In other work, iron oxide nanoparticles coated with oleic acid (OA) were well dispersed in PMMA matrix by in situ polymerization, resulting in a bulk transparent polymeric and magnetic nanocomposite with enhanced thermal stability in comparison to neat PMMA [22].

Schmidt and coauthors [23] reported functionalized magnetite nanoparticles with different alkoxysilanes on the particle surfaces and reported that the Fe_3O_4 nanoparticles coated with 3-methacryloxypropyltrimethoxysilane (MPS) showed good dispersion in a PMMA nanocomposite, but the resulting materials were not characterized with respect to their thermomechanical and magnetic properties. We have also reported preparation of magnetic polymer nanocomposites consisting of OA-coated magnetite nanoparticles dispersed in PMMA [24].

As noted above, the preparation of nanocomposites with magnetic fillers has attracted considerable recent attention. However, in most cases the nanoparticles were poorly dispersed within the polymer matrix or had a rather wide size distribution. Poor dispersion and polydispersity in the nanofiller can result in nanocomposites with suboptimal properties; as such there is still a need for methods to prepare magnetic nanocomposites with finely dispersed nanoparticles possessing a narrow size distribution. Here, we report a study of the influence of surface functionalization on the thermal, mechanical and magnetic properties of ferromagnetic PMMA nanocomposites with cobalt ferrite (nominally of composition CoFe_2O_4) nanofillers by comparing samples prepared with nanoparticles coated with OA and MPS. Both surface molecules promote dispersion in the prepolymeric mixture but differ in their interaction with the

polymer. OA does not chemically bond with the PMMA whereas the acrylate group in MPS can covalently bond to the PMMA matrix. Cobalt ferrite particles were synthesized by the thermal decomposition method [25], which produces nanoparticles with a narrow size distribution.

Nanocomposites were prepared by mixing the MMA monomer with OA- or MPS-coated particles, followed by polymerization of the monomer. The thermal, mechanical and magnetic behavior of the PMMA/CoFe₂O₄ nanocomposites was investigated to determine the influence of surface modification on the properties of the nanocomposite.

3.3 Experimental Section

3.3.1 Materials

Methyl methacrylate (MMA) and cobalt (III) chloride hexahydrate, 98%, were purchased from Aldrich and used without further purification. Sodium oleate, MPS and 1-octadecene were purchased from Tokyo Chemical Industry. Iron (III) hexahydrate 97% (ACS reagent) and 2,2-azobisisobutyronitrile (AIBN) were purchased from Sigma-Aldrich.

3.3.2 Synthesis of CoFe₂O₄ Nanoparticles

Cobalt ferrite nanoparticles were prepared by the thermal decomposition method [25, 26], which consists of the preparation of an iron-cobalt oleate compound followed by thermal decomposition using a solvent such as octadecene. CoCl₂·6H₂O (0.0045 moles), FeCl₃·6H₂O (0.016 moles), and sodium oleate (0.064 moles) were dissolved in a mixture consisting of 40 mL of deionized water, 80 mL of hexane and 40 mL of ethanol. This mixture was heated to 70 °C with reflux for 4 h to allow the formation of the iron-cobalt oleate. Subsequently, the organic phase was separated from the aqueous phase and washed three times with 40 mL of deionized water and then dried in a vacuum oven for 48 h at 70 °C. Afterward, 16.5 g of the iron-cobalt

oleate and 1.32 g of OA were dissolved in 66 mL of octadecene and mixed under nitrogen for 1 h. The mixture was heated to 320 °C at a heating rate of 3.5 °C/min, remaining at this temperature for 3 h.

The resulting solution was washed with 100 mL acetone per 20 mL of mixture and the OA-coated nanoparticles were separated magnetically. A ligand exchange procedure [27] was used to obtain MPS coated nanoparticles. The OA-coated nanoparticles were redispersed in 150 mL of hexane, then 20 mL of MPS and 50 L of acetic acid were added and the solution was agitated in a shaker for 72 h. The particles were again recovered by magnetic precipitation and used for the preparation of nanocomposites.

3.3.3 Preparation of Nanocomposites

Nanocomposites were synthesized by mixing the MMA monomer with OA- or MPS-coated nanoparticles. The initiator AIBN was added and polymerization took place using a ramp from room temperature to 70 °C for 10 h to obtain nanocomposites with 1.5 wt % of magnetic nanoparticles in PMMA.

3.3.4 Nanoparticle Characterization

For TEM of functionalized magnetic nanoparticles, OA-coated nanoparticles were suspended in hexane, and MPS-coated nanoparticles were suspended in acetone. Samples were prepared by placing a drop of the particle suspension on formvar-coated copper grids, followed by solvent evaporation. All TEM images were obtained using a Zeiss LEO 922 at an accelerating voltage of 200 kV. The average particle diameter and distribution were determined from measurements of the diameters of 200 particles, using the software ImageJ. Fourier transform infrared (FTIR) spectra were recorded in a Varian 800 FTIR ZnSe ATR holder operating from

600 to 4000 cm^{-1} . Hydrodynamic diameter of nanoparticles was measured through dynamic light scattering (DLS) using a Brookhaven Instruments BI-90 Plus particle size analyzer and 0.1% w/w suspensions of nanoparticles in the MMA monomer. The organic/inorganic percentages in synthesized nanoparticles were determined by thermogravimetric analysis (TGA) using a TA Instruments TA-2950 at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from room temperature to 400 $^{\circ}\text{C}$ with continuous purge of air at 60 mL/min.

3.3.5 Nanocomposite Characterization

The morphology of the nanocomposites was characterized using a Zeiss LEO 922 TEM operated at an accelerating voltage of 200 kV. Samples of the nanocomposites with thickness of about 50 nm were obtained using a LEICA EM UCGrT microtome. The thermal degradation temperature (T_d) of the nanocomposites was determined by TGA using a TA Instruments TA-2950 at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from ambient temperature to 400 $^{\circ}\text{C}$, with continuous purge of air at 60 mL/min. The glass transition temperature (T_g) of the nanocomposites was determined by DSC using a TA Instruments model Q2000. The samples were placed in aluminum DSC sample pans and scanned from 30 to 200 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Dynamic mechanical analysis (DMA) was performed using a Mettler Toledo DMA/SDTA8861. Samples were analyzed in tension mode at a frequency of 1 Hz, and temperature was ramped up from ambient temperature to 200 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C}/\text{min}$. The sample dimensions were 16 mm x 4.5 mm x 0.5 mm. A quantum design MPMS XL-7 SQUID magnetometer was used to measure the magnetic properties of the nanocomposites.

Magnetization measurements were normalized using the nanocomposite mass. Equilibrium magnetization measurements were made for fields of up to 7 T at 300 and 400 K. The diamagnetic background of the PMMA and sample holder was estimated from the high field

slope of the magnetization curve and was subtracted to obtain the magnetization response of the nanofiller. The temperature dependence of magnetization was characterized by zero field cooled (ZFC) and field cooled (FC) magnetization measurements between 2 and 400 K. Samples were first heated to 400 K, held at that temperature for 15 min, and then cooled to 2 K in zero field. A magnetic field of 100 Oe was applied, and the sample magnetization was measured at temperature intervals as the sample was heated to 400 K, corresponding to the ZFC curve. The FC curve was obtained by cooling the sample again from 400 to 2 K under the 10 m T magnetic field, making magnetization measurements at regular temperature intervals.

3.4 Results and Discussion

Figure 15 a shows a representative TEM image of the OA coated nanoparticles with an average diameter of 10 ± 1 nm. It can be seen that the nanoparticles are not agglomerated as a result of the OA coating. TEM of the nanoparticles functionalized with MPS indicated a slight diameter increase to an average of 14 ± 1.5 nm [Figure 15 b]. The slight increase in size visible in the TEM for the MPS-coated nanoparticles could be due to formation of a surface layer of silica due to the silane.

FTIR spectra are shown in Figure 16 for (a) nanoparticles coated with OA and (b) coated with MPS. Infrared spectrum (a) shows a band at 1705 cm^{-1} that is attributed to the ester bond $\text{O}=\text{C}-\text{O}$, a band at 1620 cm^{-1} that corresponds to the $\text{C}=\text{C}$ stretch, a band at 1320 cm^{-1} that corresponds to $\text{C}-\text{O}$ stretch, two bands around $2800\text{--}2900\text{ cm}^{-1}$ corresponding to $\text{C}-\text{H}$ stretch, and a band at 1465 cm^{-1} characteristic of the vibration of the carboxyl group, indicating the presence of OA in the particles of cobalt ferrite. Spectrum (b) shows a band at 1600 cm^{-1} that corresponds to $\text{C}=\text{C}$, a band at 1715 cm^{-1} assigned to the $\text{C}=\text{O}$ stretch of the ester group, and a band at 1087 cm^{-1} corresponding to the vibration of $\text{Si}-\text{O}$, providing an indication of the presence of MPS. The

analysis of the IR spectra provides clear evidence that the composition of the surface of the nanoparticles has been chemically modified from OA coated to MPS coated.

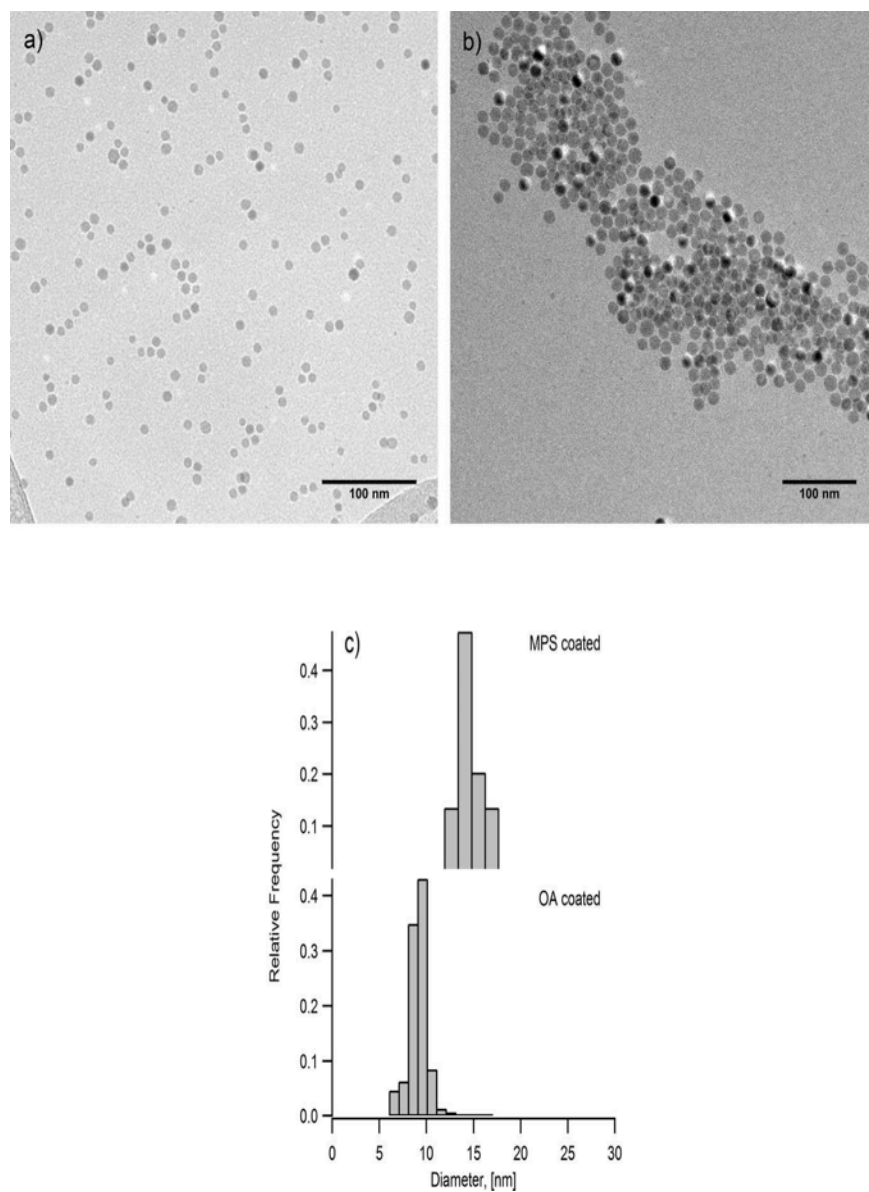


Figure 15. Representative TEM images of nanoparticles coated with oleic acid (a), MPS (b), and corresponding size distributions (c).

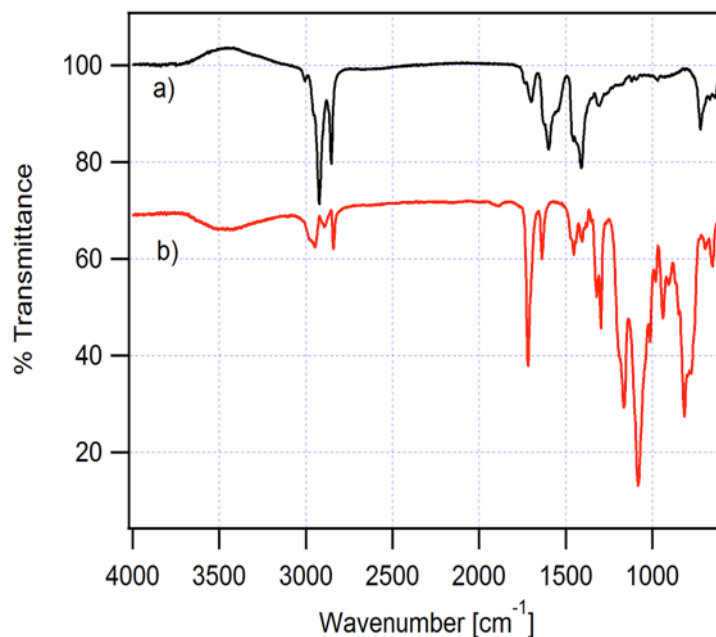


Figure 16. FTIR spectra of nanoparticles coated with oleic acid (a) and MPS (b).

Dynamic light scattering of the OA- and MPS-coated nanoparticles suspended in the MMA monomer, shown in Figure 17, indicates good dispersion of both types of particles with a narrow size distribution. The hydrodynamic diameters are slightly larger than those determined by TEM due to the organic particle coating, which cannot be observed by TEM. The volume-weighted distributions obtained from the DLS are shown in Figure 17. The intensity-weighted distributions show similar size, with a fraction of aggregates of around 100 nm in both samples. These measurements indicate that both types of particles disperse well in the monomer prior to polymerization to MMA.

Figure 18 shows representative TEM images of microtomed nanocomposites with nanoparticles coated with OA (Figure 18a) and with MPS (Figure 18b). It can be seen that the nanoparticles coated with MPS are dispersed much more uniformly in the polymer matrix,

without formation of aggregates. This indicates that the grafted MPS improves the dispersion of the magnetic nanoparticles in the nanocomposite whereas the OA coating does not, even though both particles seemed to disperse well in the monomer. To make a quantitative comparison, the number of aggregates visible by TEM is represented as an aggregate size distribution in Figure 19. To construct this figure, several images of single particles and particle aggregates were obtained throughout the microtomed nanocomposite sample and the number of particles in each aggregate was counted. Figure 18 illustrates the significant improvement in dispersion of the nanoparticles in the nanocomposite for the MPS-coated nanoparticles, which are seen as mostly single particles and dimers. On the other hand, a wide range of cluster sizes are seen for the OA coated nanoparticles.

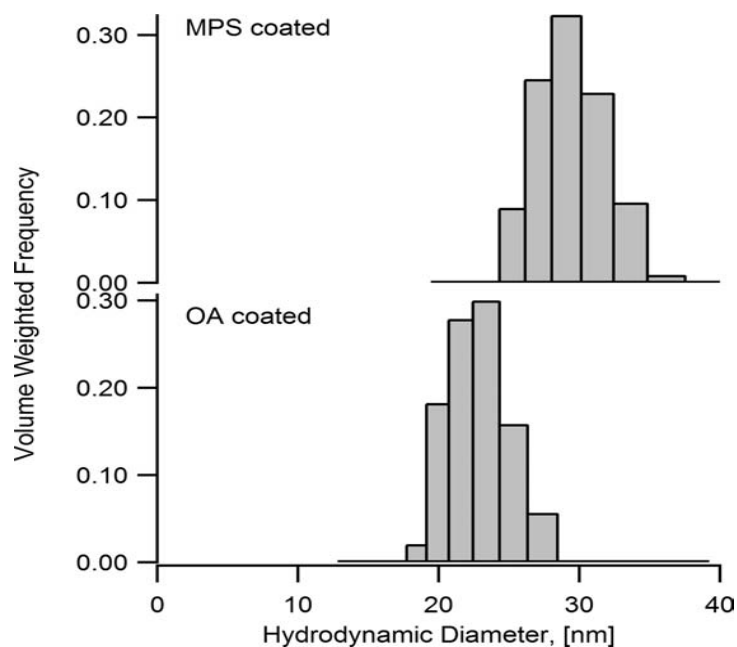


Figure 17. Volume-weighted size distribution obtained by DLS for nanoparticles coated with 3-methacryloxypropyltrimethoxysilane (MPS) and oleic acid and suspended in the MMA monomer.

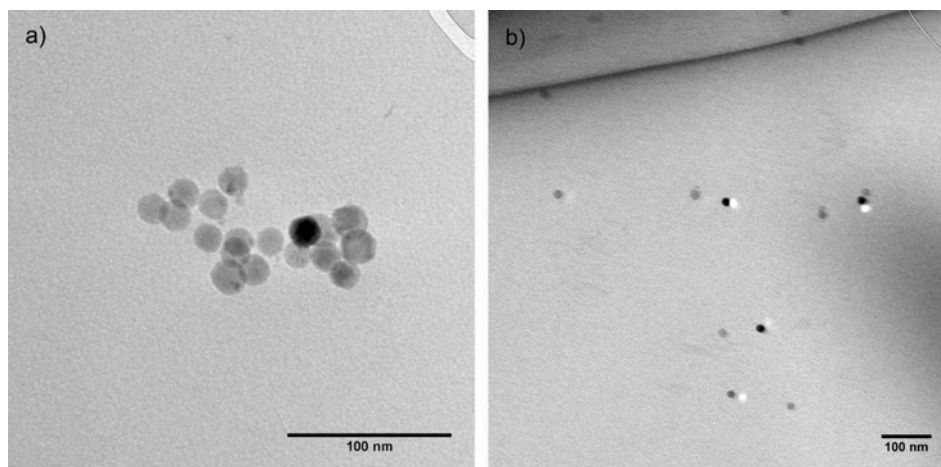


Figure 18. Representative TEM images of the nanocomposites with nanoparticles coated with (a) oleic acid and (b) 3-methacryloxypropyltrimethoxysilane (MPS).

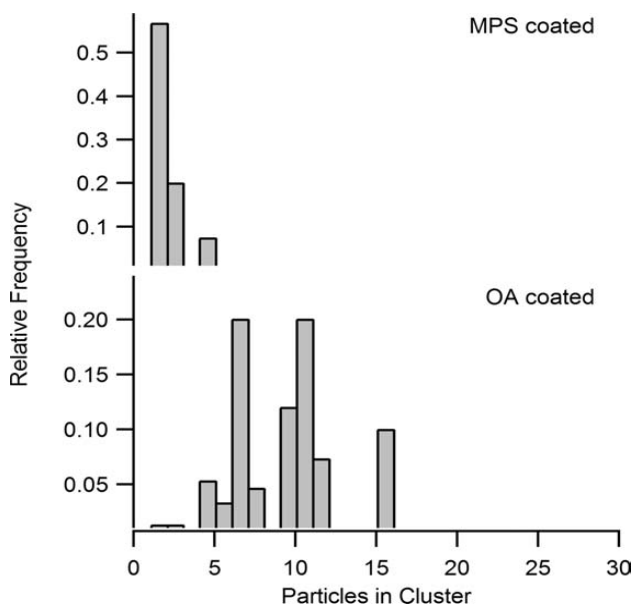


Figure 19. Aggregate size distribution obtained from TEM imaging of microtomed nanocomposites with nanoparticles coated with MPS and oleic acid.

Figure 20 shows the effect of the nanofiller on the T_d of the PMMA nanocomposites, revealing an increase in T_d compared to neat PMMA when adding OA- and MPS-functionalized nanoparticles. The neat PMMA shows a T_d of 249 °C. When the OA-coated particles are

introduced into the polymer matrix, the T_d of the resultant nanocomposite shows a slight increase to 252 °C. On the other hand, the nanocomposite with the MPS-coated nanoparticles shows an increase to 282 °C (Table 4).

Recently Li et al. [22] reported enhanced thermal stability of a nanocomposite consisting of PMMA/ iron oxide-coated with OA. The greater increase in thermal stability of the nanocomposite with MPS-coated nanoparticles may be explain by the improved interactions between the particles with MPS and the polymer matrix owing to their improved dispersion and because of the chemical bonding between the acrylate group in MPS and the PMMA. It has been suggested that strong interactions between the surface of the particles and the polymer matrix can cause a decrease in the thermal motion of the molecules in the polymer, improving thermal stability [4].

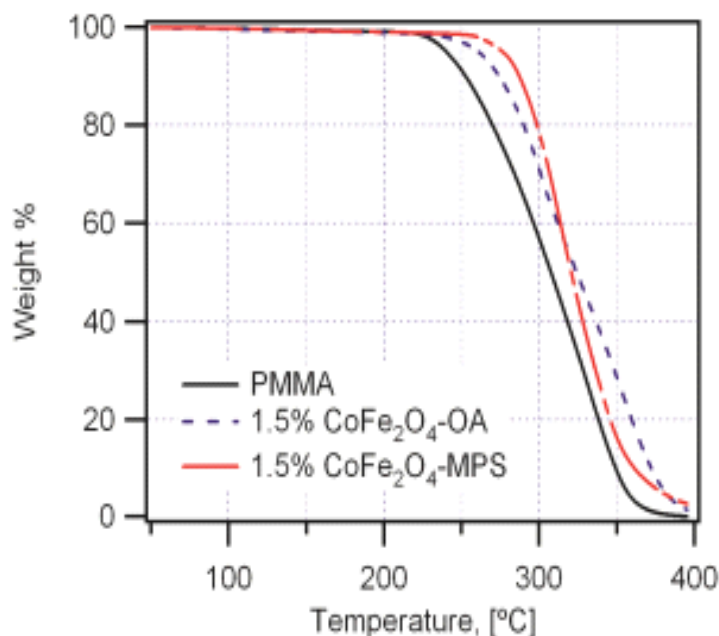


Figure 20. TGA analysis of neat PMMA and PMMA nanocomposites with oleic acid- and MPS-coated nanoparticles.

Table 4 Values of T_g and T_d for Nanocomposites Determined using Different Methods of Analysis

	Neat PMMA	OA-Coated Nanofiller	MPS-Coated Nanofiller
TGA, T_d ($^{\circ}\text{C}$)	249	252	282
DSC, T_g ($^{\circ}\text{C}$)	100.1	111.3	117.0
DMA, T_d ($^{\circ}\text{C}$)	95.5	111.2	116.5

Poly (methyl methacrylate) (PMMA), Oleic acid (OA), 3-methacryloxypropyltrimethoxysilane (MPS), Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC), and Dynamic mechanical analysis (DMA).

Figure 21 shows the results of DSC, which demonstrates a difference in the glass transition temperature T_g of the various samples. The neat PMMA polymer has a T_g of 100.1 $^{\circ}\text{C}$. This value increases when the particles are introduced into the nanocomposites with 1.5% CoFe_2O_4 –OA. The nanocomposites with 1.5% w/w of OA-coated nanofiller had a T_g of 111.3.

On the other hand, the nanocomposites with 1.5% w/w of MPS-coated nanofiller had a T_g of 117.0 $^{\circ}\text{C}$. There was a greater increase in the T_g of nanocomposites containing particles functionalized with MPS compared to nanocomposites where the particles are only covered with the OA surfactant. Again, this is possibly due to the greater dispersion of the MPS coated nanoparticles in the polymer matrix and the formation of chemical bonds between the MPS and MMA during polymerization of the latter. Previous work on nanocomposites using nanofillers of iron-oxide coated with OA has suggested that the increase of T_g could be due to the influence of molecules on the surface of the nanoparticles in the polymerization process [6, 22].

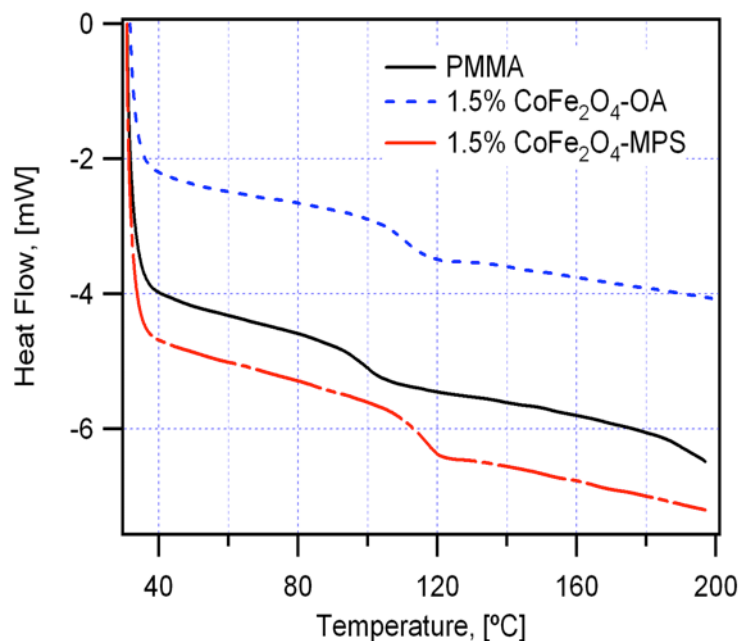


Figure 21. DSC of neat PMMA and nanocomposites with oleic acid- and MPS-coated nanoparticles.

Dynamic mechanical analysis of the nanocomposites was used to evaluate the influence of the two nanofillers on the thermomechanical properties of the nanocomposites. Figure 22 shows the damping factor ($\tan \delta$) as a function of temperature. The peak of this curve provides another indication of the T_g , albeit one that is different from that determined by DSC as it is influenced by both the heating rate and load frequency used in the measurement. Although a direct comparison with the T_g determined from DSC is not rigorous, the T_g determined from the DMA measurements allows us to confirm that improved dispersion of the nanofiller using an MPS coating results in a shift in the thermomechanical properties of the nanocomposite. The T_g shifted from 95.5 °C for neat PMMA to 111.2 °C for the nanocomposite with 1.5% w/w of the OA-coated nanofiller and to 116.5 °C for the nanocomposite with 1.5% w/w of the MPS-coated nanofiller. These values follow the same trend of increase in T_g observed by DSC when the particles are introduced into the polymer.

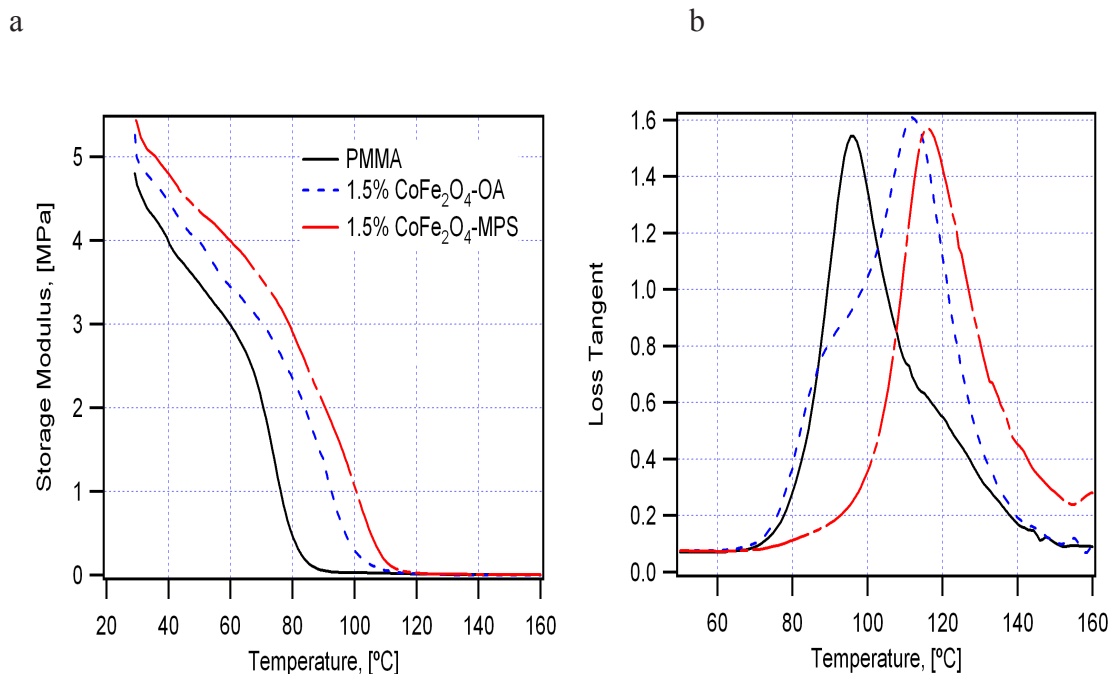


Figure 22. Storage modulus (a) and damping factor, $\tan \delta$, (b) versus temperature for neat PMMA and nanocomposites.

Figure 22 also shows the storage modulus versus temperature curves for the PMMA and the nanocomposites. The storage modulus at room temperature changes from 4.6 MPa for neat PMMA to 4.9 MPa for nanocomposites reinforced with 1.5% w/w of the OA-coated nanofiller, and to 5.3 MPa for nanocomposites reinforced with 1.5% w/w of the MPS-coated nanofiller. Note that these values correspond to 6% and 15% increase in storage modulus on dispersion of only 1.5% of the OA- and MPS-coated nanofillers. The largest increase in storage modulus was observed in the nanocomposites with nanoparticles coated with MPS. This is consistent with the observations made by TGA and DSC of a greater improvement in thermomechanical properties when MPS is used to promote nanoparticle dispersion in the polymer matrix (Table 4).

The equilibrium magnetization response of the nanocomposites with OA-coated and MPS-coated nanoparticles was measured at 300 K and 400 K. The values of saturation

magnetization and coercivity of the two nanocomposites obtained at 300 K were $1.60 \text{ Am}^2/\text{kg}$, and $47,958 \text{ A/m}$ for the nanocomposite with the OA-coated nanoparticles and $1.11 \text{ Am}^2/\text{kg}$ and $12,000 \text{ A/m}$ for the nanocomposite with the MPS-coated nanoparticles, indicating ferromagnetic behavior at room temperature (Figure 23) in both samples. Both values are slightly lower for the nanocomposites with nanofiller coated with MPS. This may be due to the formation of the silane layer on the particle surface contributing to the total particle mass but not contributing to the magnetization of the particle. The magnetization response of the nanocomposites at 400 K showed values of saturation slightly lower than those obtained at 300 K and zero coercivity (Figure. 23). However, it is possible that this observation is not due to an actual transition from intrinsic ferromagnetism to intrinsic superparamagnetism by the embedded nanoparticles but rather is due to physical rotation of the nanoparticles in the polymer matrix at high temperature.

To investigate this possibility, we estimated the rotational (Brownian) relaxation time of the nanoparticles in the polymer matrix and compared this to the characteristic measurement times of our experiments.

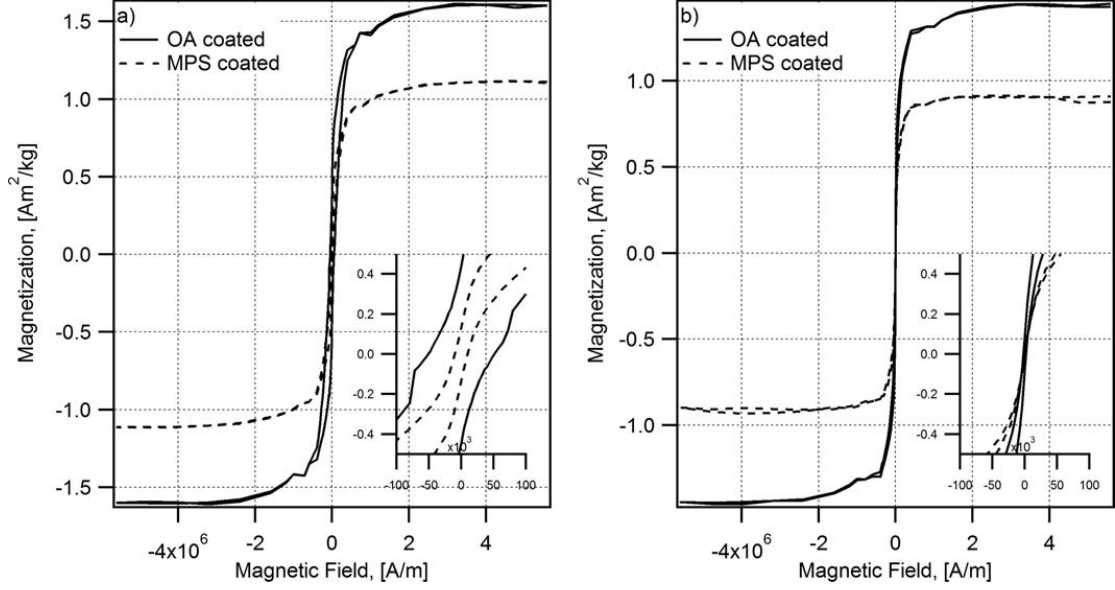


Figure 23. Magnetization versus field for PMMA/CoFe₂O₄-OA and PMMA/CoFe₂O₄-MPS nanocomposites at (a) 300 K and (b) 400 K.

We will consider that although the particles are embedded in a polymer matrix they may still physically rotate due to thermal effects, that is, that the particles still possess a Brownian magnetic relaxation time. For particles suspended in a fluid the Brownian relaxation time can be estimated from

$$\tau = \frac{3\pi\eta d^3}{8kT} \quad (12)$$

where η is the viscosity of the surrounding fluid, d is the particle diameter, and k is Boltzmann's constant. To use equation 12, we must obtain an estimate for the viscosity of the polymer matrix in the nanocomposites. This may be estimated from the DMA measurements according to [28].

$$\eta = \frac{E' [1 + (\tan \delta)^2]^{1/5}}{\Omega} \quad (13)$$

where E' is the Young's (storage) modulus and $\tan \delta$ is the loss tangent at the temperature of interest, obtained using an oscillating load of radian frequency. Actually, the viscosity given by equation 13 is the so-called dynamic viscosity.

The dynamic viscosity is equal to the shear viscosity used in equation 12 if the semiempirical Cox-Merz rule applies, which is a good assumption for many polymers [29]. With the estimates for the viscosity given by equation 13, the rotational relaxation times for the nanofillers coated with OA and MPS were calculated, using the diameter determined from TEM measurements (10 nm for the OA nanofiller and 14 nm for the MPS nanofiller). Arguably, this is a very crude estimate of the nanoparticle's rotational relaxation time in the polymer matrix. The sources for error in this estimate include the fact that equation 12 is valid only for nanoparticles in a Newtonian fluid whereas the polymer has elastic character, the fact that η as given in equation 13 is not rigorously the shear viscosity of the polymer surrounding the particles (i.e., it was assumed that the Cox-Merz rule applies), and the fact that the core diameter was determined from TEM measurements, rather than the average aggregate size. Still, these calculations serve to obtain order-of-magnitude estimates of the rotational relaxation time of the nanoparticles. With these limitations in mind, the rotational relaxation time of the OA-coated nanofiller in the nanocomposite is estimated to be of the order of 200 s at 300 K and of the order of 0.1 s at 400 K.

On the other hand, the rotational relaxation time of the MPS-coated nanofiller in the nanocomposite is of the order of 600 s at 300 K and of the order of 1 s at 400 K. However, the TEM of microtomed nanocomposite samples indicated that the MPS-coated nanofiller was found

primarily as singlets and dimers in the nanocomposite, whereas the OA-coated nanofiller consisted of a wide range of aggregate sizes. Considering that the aggregates of the MPS-coated nanofiller are at most twice the core particle size this would indicate an eightfold increase in the rotational relaxation time. On the other hand considering that the aggregates in the OA-coated nanofiller were up to 10 times larger than the core particle size this would indicate up to a 1000-fold increase in the rotational relaxation time. Thus, the rotational relaxation time of the OA-coated nanoparticles in the PMMA nanocomposite lies in the range of 200–200,000 s at 300 K and in the range of 0.1–100 s at 400 K. On the other hand, the rotational relaxation time of the OA-coated nanoparticles in the PMMA nanocomposite lies in the range of 600–6000 s at 300 K and in the range of 1–10 s at 400 K.

During the equilibrium magnetization measurements at 300 and 400 K shown in Figure 23, hysteresis was observed in both samples at 300 K and no hysteresis in either sample at 400 K. The hysteresis was more open (larger coercivity) for the nanocomposite with the OA-coated nanoparticles than for the nanocomposite with the MPS-coated nanoparticles. Our MPMS XL-7 SQUID magnetometer took roughly 1200 s to sweep the range from 100,000 to -100,000 A/m, shown in the insets of Figure 23. First, we consider the equilibrium magnetization curves at 300 K. As noted above, the relaxation time of the OA-coated nanoparticles at 303 K is of the order 200 s if the particles were singly dispersed, but could be up to 1000 times larger; hence the hysteresis response is reasonable.

The time scale of the magnetic measurements is shorter than the time scale for rotational realignment of the nanoparticles in the polymer matrix, and the sample appears thermally blocked. Similarly for the MPS-coated nanoparticles, however, here the relaxation time for singly dispersed nanoparticles is of the order of 600 s and because the aggregates are seen to be

smaller at most a 10-fold increase in relaxation time is expected. Thus, in this case the rotational relaxation time is expected to be of the same order as the experimental measurement time. This is consistent with the observation of a narrower hysteresis curve for this sample even though both the OA- and MPS-coated nanoparticles used in these nanocomposites were prepared from the same synthesis batch. Next, the magnetization response at 400 K is considered. Under these conditions a rotational relaxation time in the range of 0.1–100 s for the OA-coated nanoparticles is expected. For the MPS-coated nanoparticles, a rotational relaxation time in the range of 1–10 s was calculated. In both cases, the rotational relaxation time of the nanoparticles is much shorter than the characteristic time for the magnetization measurements (1200 s to sweep the range from 100,000 to -100,000 A/m), consistent with the observation of no hysteresis in the samples.

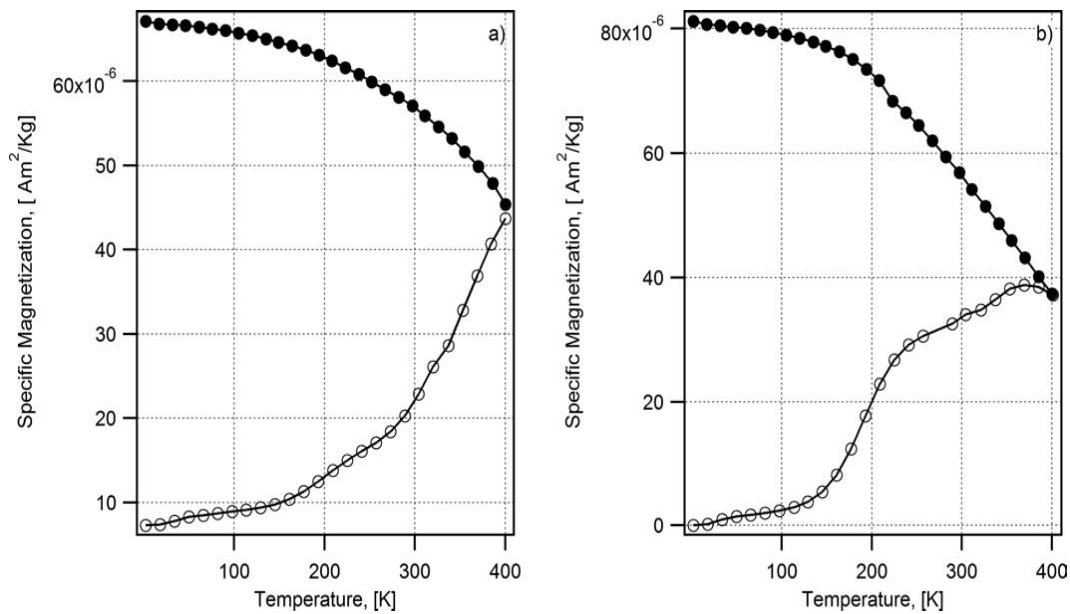


Figure 24. Zero field cooled (open symbols) and field cooled (closed symbols) temperature-dependent magnetization curves at 100 Oe for the nanocomposite with (a) OA-coated nanofiller and (b) MPS-coated nanofiller.

To confirm these observations and estimates, the ZFC/FC magnetization response of both nanocomposites in the range of 2–400 K was measured using an applied field of 10 m T. In this case, the characteristic measurement time is of the order of 300 s, as determined from the time logged for each measurement. When interpreting ZFC/FC curves one feature of interest is the appearance of a peak in the ZFC curve, commonly interpreted as the blocking temperature of the sample. The blocking temperature is supposed to represent the temperature which separates ferromagnetic behavior (below the blocking temperature) from superparamagnetic behavior (above the blocking temperature) of the sample. Arguably this is an ill-defined concept; however, it still holds value in interpreting temperature dependent magnetization measurements.

Based on the relaxation times calculated above, we would expect the OA-coated nanoparticles to not show a blocking temperature even at 400 K, as their rotational relaxation time at this temperature is estimated to be of the same order as the characteristic measurement time of 300 s, especially for the larger aggregates. This is consistent with the experimental measurements, shown in Figure 24, where the ZFC curve for the nanocomposite with the OA-coated nanofillers does not show a peak. On the other hand, for the MPS-coated nanoparticles, a rotational relaxation time at 400 K was estimated, which is in the range of 1–10 s, much shorter than the characteristic measurement time of 300 s. Thus for this sample, a peak in the ZFC curve below 400 K is expected.

This prediction is in agreement with the experimental observation of a peak in the ZFC curve close to 370 K for the nanocomposite with the MPS-coated nanoparticles. This value seems fortuitously close to the T_g of the neat PMMA polymer matrix and is below the T_g observed for the nanocomposite with the MPS-coated nanofiller. It is interesting to note that using the Young's modulus and loss tangent at this temperature, a rotational relaxation time of

the order 100 s was estimated, which is of the same order as the characteristic measurement time of the ZFC measurements. This indicates that the observed peak in the ZFC does not correspond to a transition from intrinsic ferromagnetic to superparamagnetic behavior of the embedded nanoparticles, but rather it corresponds to the particles being able to thermally rotate within the polymer matrix at the same time scale as the magnetization measurements.

3.5 Conclusions

In this work, the influence of nanofiller surface chemistry on the thermomechanical and magnetic properties of PMMA nanocomposites with embedded cobalt ferrite nanoparticles coated with OA or MPS was studied. Although both types of nanoparticles suspended well in the MMA monomer, TEM of microtomed samples of the nanocomposites indicated that the MPS-coated particles were better dispersed in the nanocomposites. The values of the T_d and T_g increased relative to the neat polymer when the nanofillers were introduced into the nanocomposites at a concentration of 1.5% w/w. There was a greater increase for nanocomposites containing nanoparticles functionalized with MPS compared to nanocomposites where the particles were covered with OA. DMA of the nanocomposites showed a shift in the peak of the damping factor ($\tan \delta$) and an increase and shift in the storage modulus, the effect again being greater for MPS-coated nanoparticles.

The nanocomposite filled with nanoparticles functionalized with OA showed slightly higher values of magnetic saturation and coercivity compared with those grafted with MPS. Because the MPS is attached covalently to the nanoparticles and because the resulting silane layer adds to the particle mass, there may be a decrease in magnetization per unit mass of particles. Both nanocomposites were found to have hysteresis at 300 K but not at 400 K.

However, on the basis of estimates of the rotational relaxation times of the embedded nanoparticles in the polymer matrix, compared to the characteristic times for the equilibrium magnetization measurements, we believe that this observation of superparamagnetism at 400 K is rather indicative of particle rotation in the polymer matrix rather than intrinsic superparamagnetism of the nanoparticles. ZFC/FC measurements support this view, as a peak in the ZFC curve was not observed for the nanocomposite prepared with the OA-coated nanoparticles, which, due to their larger aggregate size are expected to have a characteristic rotational relaxation time larger than the characteristic measurement time of the ZFC curve even at 400 K. On the other hand, a peak was observed for the nanocomposite prepared using the MPS-coated nanoparticles. This peak occurred at a temperature (370 K) for which the estimated rotational relaxation time of the nanoparticles is of the same order of magnitude as the characteristic measurement time of the ZFC curve. These results illustrate that surface functionalization to promote covalent bonding results in improved nanocomposite thermomechanical properties, and that the embedded particles seem to be able to rotate in the polymer matrix in response to applied magnetic fields, especially at elevated temperatures and even when the nanoparticles are chemically crosslinked with the polymer matrix. This fact could be used to prepare permanently magnetized polymer nanocomposites by aligning the particles in an applied field at elevated temperatures and then lowering the nanocomposite temperature to lock-in the particle dipoles in a desired direction.

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Chapter 4

4. Preparation of Magnetic Polymer Nanospheres with Brownian Magnetic Relaxation

Magnetic polymer nanospheres (MPNS) consisting of CoFe_2O_4 embedded in poly(methyl methacrylate) (PMMA) were synthesized by magnetic miniemulsion polymerization. CoFe_2O_4 nanoparticles were modified with 3-trimethoxysilylpropylmethacrylate (MPS) and directly emulsified with different concentrations of sodium dodecyl sulfate (SDS) under ultrasonication for subsequent miniemulsion polymerization. The average diameter of the CoFe_2O_4 /PMMA nanospheres was controlled by varying the amount of surfactant. Thermogravimetric analysis indicated that magnetic content of the magnetic polymer nanospheres was in the range of 44 % to 73 %. The magnetic properties of the dispersions were investigated by measuring the magnetization curves and the complex magnetic susceptibility as a function of frequency. The nanospheres were found to follow the Debye model for the complex susceptibility, with a characteristic time given by the rotational hydrodynamic resistance and thermal energy through the Stokes-Einstein relation. This demonstrates that the magnetic nanospheres respond to applied magnetic fields by rotating. Due to their uniform size and high magnetic loading these magnetic

nanospheres could be suitable in a variety of applications, including nanoscale mechanical probes and actuators in complex fluids and biological systems.

4.1 Introduction

The present chapter focuses on the synthesis of magnetic polymer nanospheres of poly(methyl methacrylate) (PMMA) with embedded CoFe_2O_4 nanoparticles coated with 3-methacryloxypropyltrimethoxysilane (MPS) by utilizing the miniemulsion magneto template polymerization technique. The magnetic properties were studied by measuring the equilibrium magnetization curves and the complex magnetic susceptibility.

4.2 Previous Work

Latexes are colloids of one or more polymers dispersed in liquids, commonly water, and of microscopic or nanoscopic size [1, 2]. There are several techniques used in the preparation of latexes. The most common are the emulsion and miniemulsion polymerization processes. These methods often use surfactants, which are undesirable in some applications and must be removed [3, 4]. The most widely used polymers in the synthesis of polymer colloids are poly(methyl methacrylate) (PMMA) and polystyrene (PS) [5-7]. Recent research has been directed to develop polymer nanocomposite colloids, which contain inorganic nanoparticles embedded in a polymer matrix. Controllable synthesis of hybrid inorganic/organic polymer latexes is pursued for applications in various fields, such as in electrochemical sensors, drug carriers, and in biochemical applications [8-10]. Some of the challenges in preparing these materials include achieving high and uniform loading of the inorganic nanoparticles in the polymer, maintaining colloidal stability and controlling size.

Core-shell polymer-inorganic hybrid nanospheres have been prepared by various methods. Core-shell magnesium hydroxide (MH) and polystyrene (PS) nanoparticles were prepared through ultrasonic wave-assisted in-situ copolymerization [11]. Magnesium hydroxide nanosheets were vinylated with 3-trimethoxysilylpropylmethacrylate (MPS) in order to improve their dispersion and enhance their interaction with the polymer matrix. Similarly, zinc oxide nanoparticles were encapsulated in polystyrene using in situ emulsion polymerization in the presence of MPS as coupling agent, improving dispersion stability in the polymer matrix [12]. In another work, MPS was used to modify flaky aluminum surfaces, which were encapsulated in PMMA by in situ emulsion polymerization of methyl methacrylate [13].

Magnetic polymer lattices (MPLs) are attractive in a variety of applications. The preparation of MPLs with uniform size distribution and high magnetization is challenging. Magnetic polymer latex of Fe_3O_4 /polystyrene have been developed with high magnetite content of around 86.0 %. Fe_3O_4 nanoparticles were produced by the coprecipitation method, followed by addition of a surfactant mixture of oleic acid (OA) and undecylenic acid (UA). This system possessed superparamagnetic properties [14]. Another approach to the synthesis of magnetic latex colloids uses magnetic nanoparticles, treated with MPS, leading to a particle-stabilized emulsion. Poly (methyl methacrylate) (PMMA) latex was prepared according to a standard emulsion polymerization in the presence of such an emulsion. This synthesis gave uniform size distribution PMMA latex-core-shell spheres with a magnetite core [15,16].

Hybrid polymeric nanospheres consisting of Fe_3O_4 nanoparticles embedded in a poly (styrene-co-divinylbenzene) P(St/DVB) were synthesized using a magnetic template miniemulsion [17]. First, iron oxide nanoparticles were prepared according to the precipitation method introducing oleic acid as stabilizer. These nanoparticles were dispersed in octane to form

a ferrofluid. Subsequently, the ferrofluid was directly emulsified in the presence of sodium dodecyl sulfate under ultrasonication and applied as a magneto template. The hydrodynamic diameter of the magneto template was measured by dynamic light scattering DLS, showing a mean particle size of 99 nm [17].

Zhang et al [18], obtained magnetic polymer nanospheres of P(St-MMA)/Fe₃O₄ with high magnetic content which, subsequently surface functionalized with carboxyl and amino groups by hydrolysis and ammonolysis of the ester group. Similarly, Lan et al [19], used miniemulsion polymerization to synthesize superparamagnetic Fe₃O₄ /PMMA. Fe₃O₄ nanoparticles were modified with n-octadecyltrimethoxysilane (C18TMS) and MPS, and the effect of surface modification on the preparation of Fe₃O₄/PS via miniemulsion polymerization was studied. The Fe₃O₄ /PS composite particles were obtained using Fe₃O₄ modified with C18TMS were shown to be polydisperse, with a PDI greater than 0.1, compared with the composite particles obtained when the nanoparticles were modified with MPS [20].

Oleic acid coated magnetite were dispersed in octane to obtain a ferrofluid and miniemulsified using sodium dodecylsulfate (SDS) [21]. Then another miniemulsion with monomer MMA was added into the ferrofluid emulsion to carry out polymerization, and finally a brown magnetic emulsion was obtained. The average diameter of the magnetic PMMA nanospheres increased slightly with increasing weight ratio of MMA to magnetic particles. Magnetic properties of magnetic PMMA spheres showed typical superparamagnetic behavior. However, the saturation magnetization of magnetic PMMA was smaller than that of Fe₃O₄ nanoparticles, which was attributed to oxidation during polymerization, which leads to formation of some nonmagnetic iron oxide [21].

Scheiber et al [22], showed the encapsulation of hydrophobic metal (iron) complexes into polymer particles using a miniemulsion process. By choosing different amounts of surfactant, they could adjust the particle size between 100 and 260 nm. To obtain particles of up to 370 nm they used a seeded polymerization technique. Monodisperse latex could be arranged on the surface of a substrate and subsequently the polymer was removed by plasma etching obtaining ordered arrays of these metal nanoparticles with catalytic applications [22]. Miniemulsion methods have been used to prepare hybrid nanobeads of polystyrene with either a manganese oxo $\text{Mn}_{12}\text{O}_{12}(\text{L})_{16}(\text{H}_2\text{O})_4$ or magnesium-iron-oxo cluster $\text{Mn}_8\text{Fe}_4\text{O}_{12}(\text{L})_{16}(\text{H}_2\text{O})_4$ (where L= 4-vinylbenzoate). The use of ligand conferred hydrophobicity to the clusters allowing greater solubility in the monomer and hence to be firmly grafted into the polymer latex. Magnetic susceptibility studies confirmed that the nanobeads had magnetic properties and have the potential for functionalization for biomedical applications [23].

Multifunctional composite particles were designed with fluorescence and magnetic properties [24]. First, monodisperse and fluorescent submicron particles of poly(styrene-co-2-naphthyl methacrylate) (poly(St/MAA/NMA)) were prepared using emulsifier-free emulsion polymerization and second, Fe_3O_4 nanoparticles were immobilized onto the Poly(St/MAA/NMA) surfaces to give rise to multifunctional latex. These iron oxide nanoparticles were functionalized with pyrrolidone that provide $-\text{NH}$ to the surface which were absorbed onto the $-\text{COOH}$ functional surface of poly(St/MAA/NMA). The photoluminescence spectra show that the nanoparticles possess good luminescent characteristics with blue emission at around of 450 nm. A method to obtain bifunctional nanoparticles with fluorescence and magnetic properties was used. This method consists of modifying a fluorescent monomer (9-(4-vinylbenzyl)-9H carbazol) (VBK) on the surface of magnetic nanoparticles by directly mediated atom-transfer radical polymerization

(ATRP) with activators generated by electron transfer (AGET). In addition, after grafting of poly(ethylene glycol) methyl ether methacrylate (PEGMA) was synthesized giving as result hydrophilic nanoparticle with possible applications in biotechnology and nanomedicine [25].

The CoFe_2O_4 nanoparticles present permanent magnetic dipole moment since to the nanoparticles acquire magnetization when an external magnetic field is applied and lose magnetization when the field is removed giving a characteristic frequency that correspond to the Brownian rotation. This property was exploited using spheres of silica embedded with cobalt ferrite nanoparticles for the fundamental study of rotational diffusion through measurement of the complex magnetic susceptibility [26-28].

Rotational diffusion motion of CoFe_2O_4 magnetic nanoparticles is related to mechanical properties of complex fluid where they are suspended, and can be determined measuring their response to a magnetic field through magnetic susceptibility. In this work, the synthesis of magnetic polymer nanospheres of poly(methyl methacrylate) (PMMA) with embedded CoFe_2O_4 nanoparticles coated with 3-methacryloxypropyltrimethoxysilane (MPS) is described. For this the miniemulsion magneto template polymerization technique was used [29, 30, 27]. The magnetic properties were studied by measuring the equilibrium magnetization curves and the complex magnetic susceptibility as a function of frequency and field amplitude. The particles were found to respond to alternating fields by Brownian magnetic relaxation.

4.3 Experimental

4.3.1 Materials and Methods

Methyl methacrylate and cobalt (III) chloride hexahydrate, 98 %, were purchased from Aldrich and used without further purification. Sodium oleate, 3-

methacryloxypropyltrimethoxysilane (MPS), and 1-octadecene were purchased from Tokyo Chemical Industry. Iron (III) hexahydrate 97% (ACS reagent), potassium persulfate (KPS) 99.99%, sodium dodecyl sulfate (SDS), and inhibitor removers were purchased from Sigma-Aldrich. Double distilled and deionized water was used throughout the experiments.

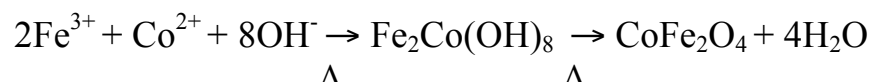
For transmission electron microscopy (TEM) experiments CoFe_2O_4 -OA nanoparticles were suspended in hexane and for CoFe_2O_4 -MPS, nanoparticles were suspended in acetone. Samples were prepared by placing a drop of the particle suspension on copper grids coated with Formvar, followed by solvent evaporation. A similar procedure was used for TEM of magnetic polymer nanospheres of CoFe_2O_4 /poly(methyl methacrylate) (PMMA). All TEM images were obtained with a Zeiss LEO 922, using an accelerating voltage of 200 kV. The morphology of the magnetic polymer nanospheres was observed by using field-emission scanning electron microscopy (FE-SEM, JSM 6500F, JEOL) and scanning electron microscopy (SEM, JSM, 6390, JEOL). The hydrodynamic diameter of the nanoparticles was measured through dynamic light scattering (DLS) using a Brookhaven Instruments BI-90 Plus particle size analyzer. The organic/inorganic mass fractions of the synthesized nanoparticles were determined by thermogravimetric analysis (TGA) using a TA Instruments TA-2950 at a heating rate of 10 °C/min from room temperature to 400 °C with continuous purge of air at 60 mL/min.

A Quantum Design MPMS XL-7 SQUID magnetometer was used to measure the magnetic properties of the colloidal dispersions. Equilibrium magnetization measurements were made for fields of up to 7 T at 300 and 400 K. Dynamic susceptibility measurements were made with a drive field of 4 Oe in a frequency range of 0.1- 1000 Hz.

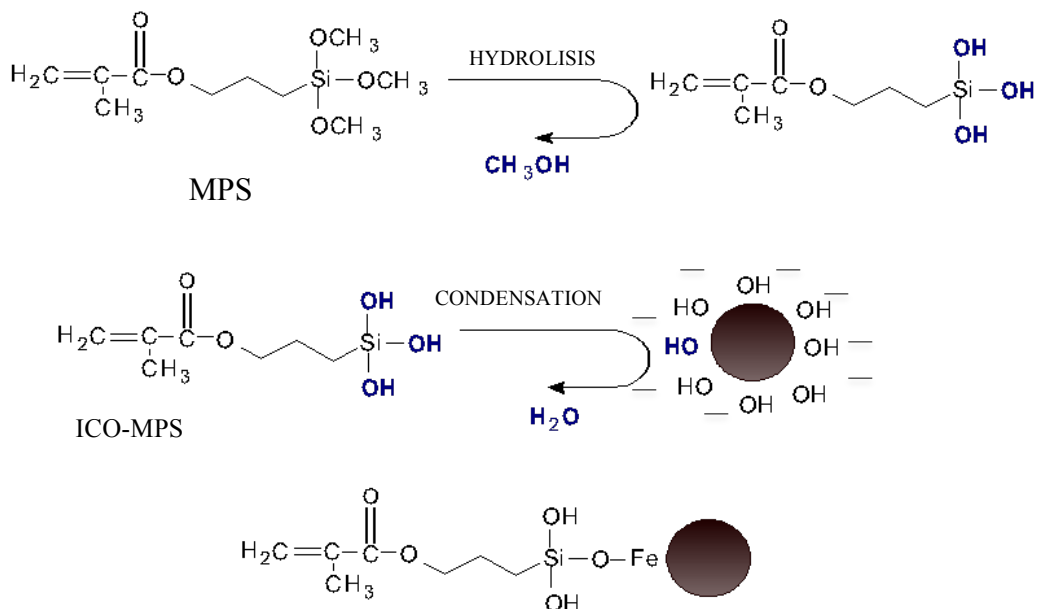
4.3.2 Preparation of Magnetic Nanoparticles

4.3.2.1 Synthesis of CoFe₂O₄ Nanoparticles by Co-precipitation

The cobalt ferrite nanoparticles were synthesized by a co-precipitation method [31]. An aqueous solution of 0.055M Co(II) and 0.11M Fe(III) was rapidly added to a boiling alkaline solution with excess of hydroxide OH⁻ ions. The hydrolysis reaction in the presence of an excess of OH⁻ ions leads to the formation of a paramagnetic Fe-Co Hydroxide, undergoing dehydration and atomic rearrangement producing a ferrite structure, according to:



A functionalization procedure [32] was used to obtain MPS coated nanoparticles (Scheme 1). The peptized nanoparticles were re-dispersed in a mixture of 120 mL of ethanol and 44 mL of water, then 10 mL of MPS and 5.5 mL ammonium hydroxide were added and the solution was agitated in a shaker for 72 h. The particles were again recovered by magnetic precipitation and used for the preparation of magnetic polymer nanospheres of CoFe₂O₄/poly(methyl methacrylate) (PMMA).

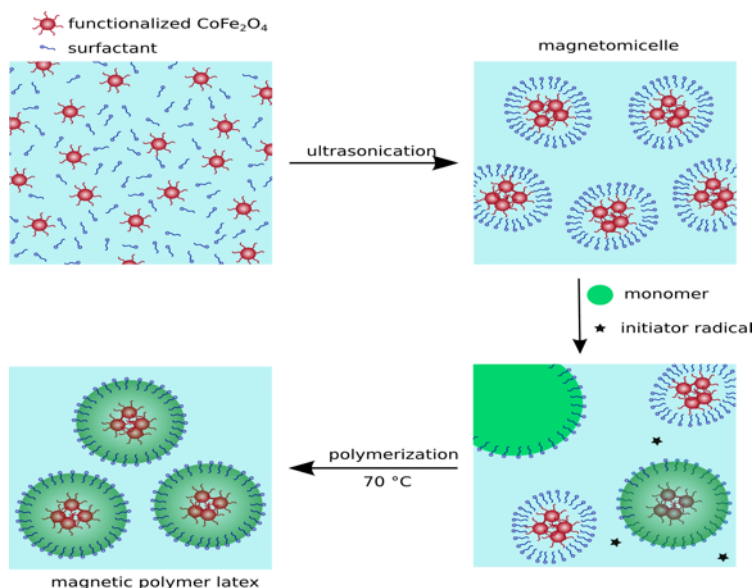


Scheme 1. Illustration of the functionalization process to obtain MPS coated nanoparticles.

4.3.3 Preparation of Magnetic Polymer Nanospheres of CoFe₂O₄/poly(methyl methacrylate) (PMMA)

Inhibitor hydroquinone was removed from the monomer using a packed column with silica. The glass material used for the synthesis was washed and rinsed with aqua regia and deionized water. Magnetic miniemulsions were prepared as follows: the MPS coated nanoparticles were mixed with an aqueous solution containing various amounts of SDS and emulsified under ultrasonication in an ice bath to form magnetic miniemulsions. These solutions were transferred to a three-neck reactor and mechanically stirred under nitrogen. The purified monomer was added dropwise and the emulsion was formed in about 2 hours. During this time the monomer diffused to and swelled the micelles. The magnetic miniemulsions were heated to 70 °C and 0.149 g of the initiator KPS was added. At this point the water soluble initiator underwent decomposition, producing a radical which enters the swollen micelles, starting the

polymerization of primary particles. Polymerization took place over 6 hours. This is illustrated in Scheme 2.



Scheme 2. Illustration of the experimental polymerization process for preparing magnetic polymer nanospheres.

4.4 Results and discussion

4.4.1 Synthesis of CoFe_2O_4 Nanoparticles

Transmission electron microscopy image (Figure 25 a) shows the MPS coated nanoparticles forming aggregates of roughly spherical particles with an average primary particle size of about 23 ± 0.1 nm. High-resolution TEM images (Figure 25 b) show a group of atomic planes within a single crystal of CoFe_2O_4 nanoparticles. Dynamic light scattering (Figure 26) indicates the MPS-coated particles have a diameter of 37 ± 0.1 nm, whereas the synthesized particles had a diameter of 24 ± 0.1 nm. Hence, MPS coating led to some aggregation. The TGA thermogram shown in Figure 26c indicates that 33 % of the mass of the MPS coated cobalt ferrite nanoparticles corresponds to MPS.

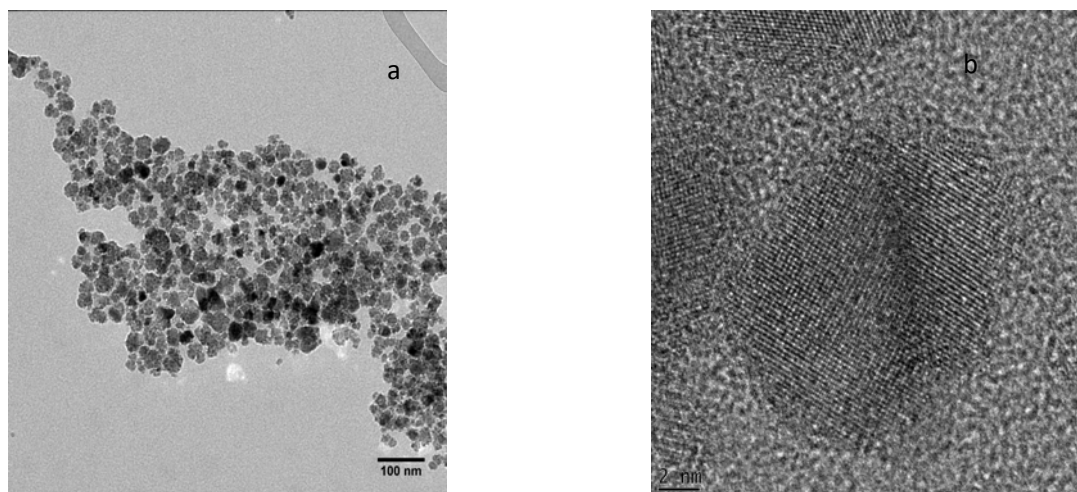


Figure 25. a) TEM of magnetic cobalt-ferrite nanoparticles coated with MPS and b) HR-TEM image of $(\text{CoFe}_2\text{O}_4)$ nanoparticles.

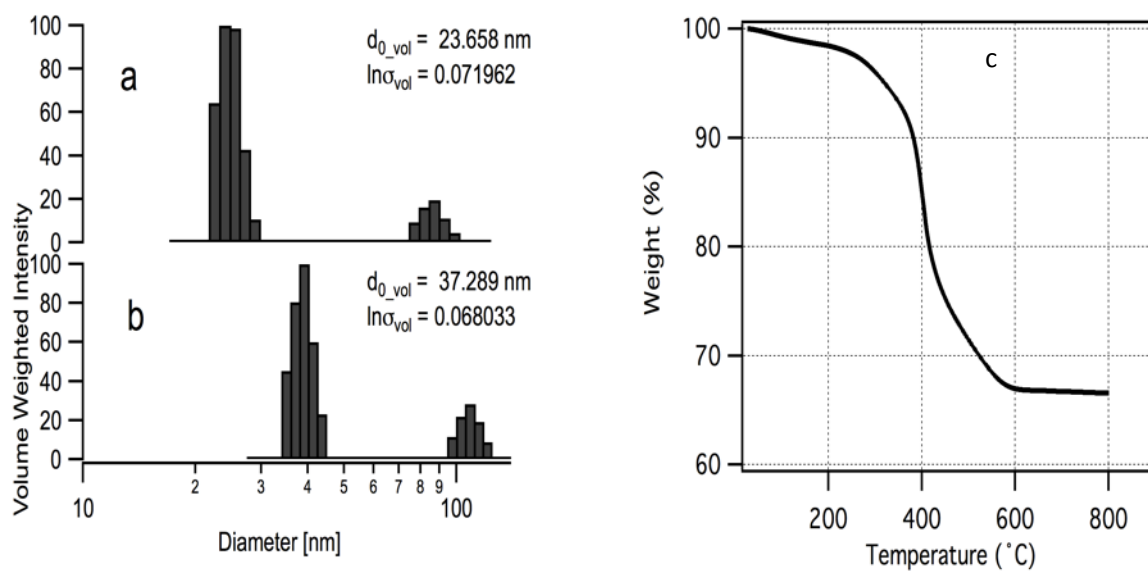


Figure 26. (a) Volume weighted hydrodynamic diameter of $(\text{CoFe}_2\text{O}_4)$ nanoparticles prepared by coprecipitation, (b) Volume weighted hydrodynamic diameter of MPS coated nanoparticles (CoFe_2O_4 -MPS) and (c) thermogravimetric analysis curve.

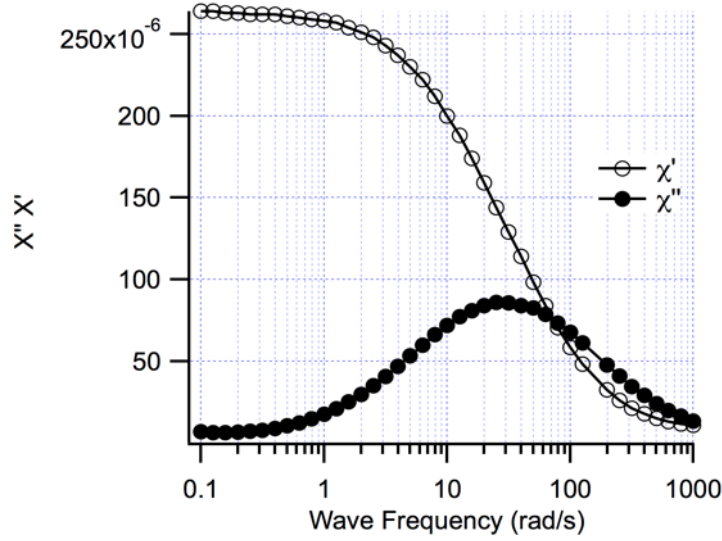


Figure 27. Complex magnetic susceptibility spectra at 283 K of peptized CoFe_2O_4 magnetic nanoparticles. The particles show almost ideal Debye relaxation with relaxation time given by the Brownian mechanism.

When a suspension of magnetic nanoparticles is subjected to an alternating magnetic field, the Debye model describes the dynamic response of these particles in terms of the complex susceptibility χ as a function of applied field frequency Ω ,

$$\chi = \chi' - j\chi''; \quad \chi' = \chi_0 / [1 + (\Omega\tau)^2]; \quad \chi'' = \chi_0 \Omega\tau / [1 + (\Omega\tau)^2] \quad (14)$$

where χ_0 is the initial susceptibility of the sample and τ is the characteristic magnetic relaxation time.

There are two accepted mechanisms by which the magnetization of a suspension of magnetic nanoparticles relaxes after the applied magnetic field has changed. In the mechanism of relaxation where there is a rotation, the nanoparticles themselves in the liquid is referred to as Brownian relaxation. The characteristic time τ_B for Brownian relaxation is given by

$$\tau_B = 3\eta V_H / k_B T \quad (15)$$

where η is the viscosity of surrounding fluid, V_H is hydrodynamic volume of the particles, and thermal fluctuation energy $k_B T$ where k_B is Boltzman's constant and T is the temperature. In the second mechanism, relaxation is due to rearrangement of the magnetic dipole vector within the particle along the magnetic easy axis to achieve alignment with the applied field without nanoparticle rotation, and is referred to as Néel relaxation. The characteristic time τ_N for Néel relaxation may be estimated from

$$\tau_N = 1/f_0 \exp (KV / k_B T) \quad (16)$$

where f_0 is an attempt frequency having an approximate value of $f_0 \sim 10^9$ Hz. In general both mechanisms occur in parallel with an effective relaxation time τ given by [33-40].

$$\tau = \tau_B \tau_N / \tau_B + \tau_N \quad (17)$$

Dynamic magnetic susceptibility of a dispersion of the synthesized nanoparticles in a 20:80 w:w mixture of water-glycerol is show in Figure 27. The dynamic susceptibility peak seen corresponds to the Brownian relaxation mechanism. The hydrodynamic diameter of the nanoparticles was determined by fitting the dynamic magnetic susceptibility to the Debye model, with a result of 24 nm ($\ln = 0.1$); in good agreement with the hydrodynamic diameters measured from dynamic light scattering DLS.

4.4.2 Size Distribution and Morphology

Transmission electron microscopy images of magnetic polymer nanospheres prepared with different amounts of SDS and a fixed concentration of the monomer MMA are presented in Figure 28. Inorganic nanoparticles are embedded in the polymer matrix. The CoFe_2O_4 –MPS nanoparticles appear as dark spots due to their higher electron density, in contrast to the PMMA polymer, which appears lighter. Figure 28a (MPNS-1) shows that the magnetic polymer nanospheres obtained by adding 70 mg of SDS are somewhat irregular. These particles had a hydrodynamic diameter of 225 nm according to DLS (Figure 29) and an inorganic content of 44% according to TGA (Figure 32). As the amount of SDS used increased we observed a decrease in physical and hydrodynamic diameter of the resulting magnetic polymer nanospheres. Figure 28 b for MPNS-2 shows a better distribution of magnetic nanoparticles inside the polymer nanospheres. These MPNS were obtained by adding 140 mg of SDS, and had a hydrodynamic diameter of 203 nm with a magnetic content of 52 %. On the other hand, when 280 mg of SDS were added (MPNS-3) the hydrodynamic diameter of the magnetic polymer nanospheres was 160 nm with a magnetic inorganic content of 63 % (Figure 28c). Finally when 420 mg of SDS were used (MPNS-4) the hydrodynamic diameter was 145 nm and the inorganic content was 62 %.

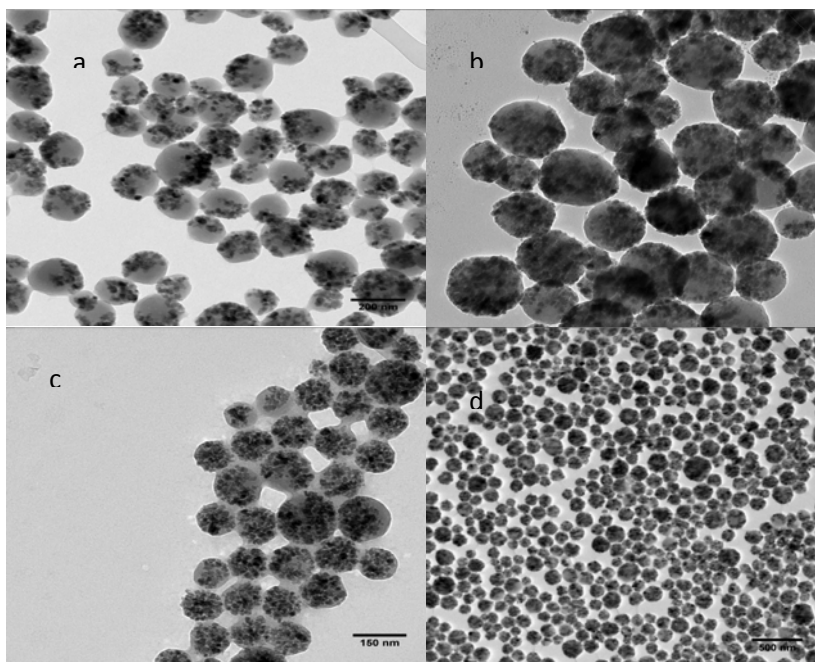


Figure 28. Transmission electron microscopy images of $\text{CoFe}_2\text{O}_4/\text{PMMA}$ nanospheres prepared with different amounts of SDS: (a) MPNS -1, (b) MPNS -2, (c) MPNS -3, and (d) MPNS -4.

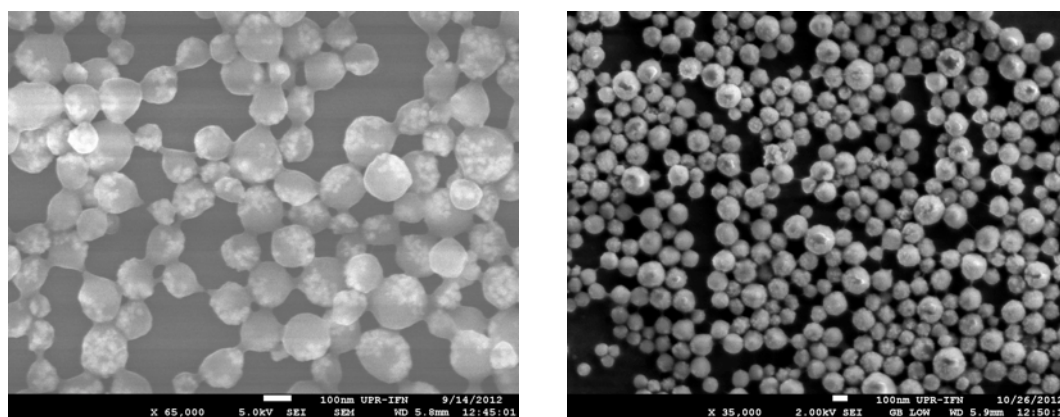


Figure 29. Field scanning electron microscopy images of $\text{CoFe}_2\text{O}_4/\text{PMMA}$ nanospheres prepared with different amounts of SDS: (a) MPNS -2 and (b) MPNS -4

Scanning electron microscopy images of magnetic polymer nanospheres with diameters of 203 and 145 nm respectively are shown in Figure 29. The FE-SEM images reveal the morphology of the nanospheres, which have a smooth surface. Figure 30 shows scanning

electron microscopy of magnetic polymer nanospheres with diameters of 225 and 160 nm, respectively. The SEM image does not allow observe the nanoparticles that are embedded; however it is possible to see their surface, which is smooth for both sample.

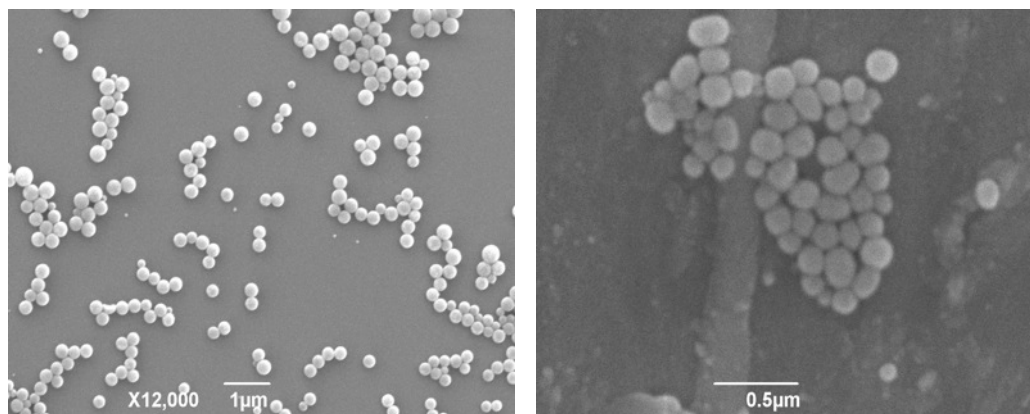


Figure 30. Scanning electron microscopy images of $\text{CoFe}_2\text{O}_4/\text{PMMA}$ nanospheres prepared with different amounts of SDS: (a) MPNS -1 and (b) MPNS -3

Figure 31 shows dynamic light scattering of the magnetic polymer nanospheres. This study showed that the average hydrodynamic diameter increased from 145 nm to 225 nm as the concentration of the surfactant decreased.

TGA was used to measure the magnetic content of magnetic polymer nanospheres. Figure 32 shows the thermal degradation T_d curves for nanospheres and pure PMMA. The curve in Figure 32 (e) reveals that neat PMMA has a T_d of 250 °C. The magnetic polymer nanospheres show an increase in T_d between 280 and 300 °C. Additionally, TGA allowed us to estimate approximately the amount of CoFe_2O_4 -MPS embedded in the MPNS (Table 5).

Table 5. Synthesis conditions, hydrodynamic diameters, and inorganic content of hybrid magnetic polymer nanospheres

Sample	MMA (mg)	NP's (mg)	SDS (mg)	Size Fitting magnetic susceptibility (nm)	Size DLS (nm)	PDI	% Magnetic filler
MPNS-1	2.0	300	70	222	225	0.095	44.4
MPNS-2	2.0	300	140	200	203	0.098	51.8
MPNS-3	2.0	300	280	160	160	0.097	62.8
MPNS-4	2.0	300	420	145	145	0.078	62.4

Methyl methacrylate (MMA), Nanoparticles (NP's), Sodium dodecyl sulfate (SDS), Dynamic light scattering (DLS), Polydispersity index (PDI), and Magnetic nanospheres (MPNS).

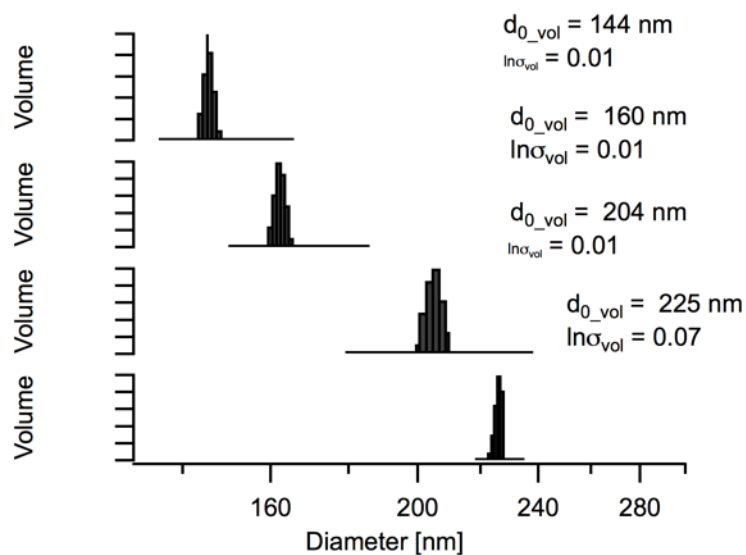


Figure 31. Hydrodynamic diameter distributions of CoFe₂O₄/PMMA nanospheres prepared with different amounts of SDS: (a) MPNS-1, (b) MPNS-2, (c) MPNS-3, and (d) MPNS-4.

4.4.3 Magnetic Properties

4.4.3.1 Dynamic Magnetic Susceptibility Spectra and Magnetization Curves

Figure 33 shows the dynamic magnetic susceptibility spectra of magnetic polymer nanospheres obtained under the synthesis conditions described in Table 5. The curves show characteristic behavior of particles having Brownian relaxation. Fitting of the dynamic susceptibility of the samples to the Debye model, weighted using a lognormal size distribution, resulted in hydrodynamic diameters of 222 nm for MPNS-1, 200 nm for MPNS-2, 160 nm for MPNS-3 and 145 nm for MPNS-4, in excellent agreement with the hydrodynamic diameters determined from DLS measurements.

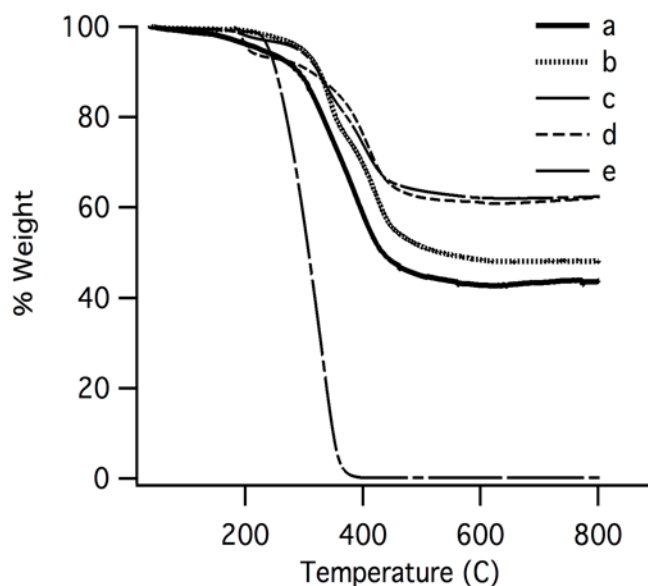


Figure 32. TGA curves of CoFe₂O₄/PMMA nanospheres prepared with different amounts of SDS: (a) MPNS-1, (b) MPNS-2, (c) MPNS-3, (d) MPNS-4, and (e) PMMA.

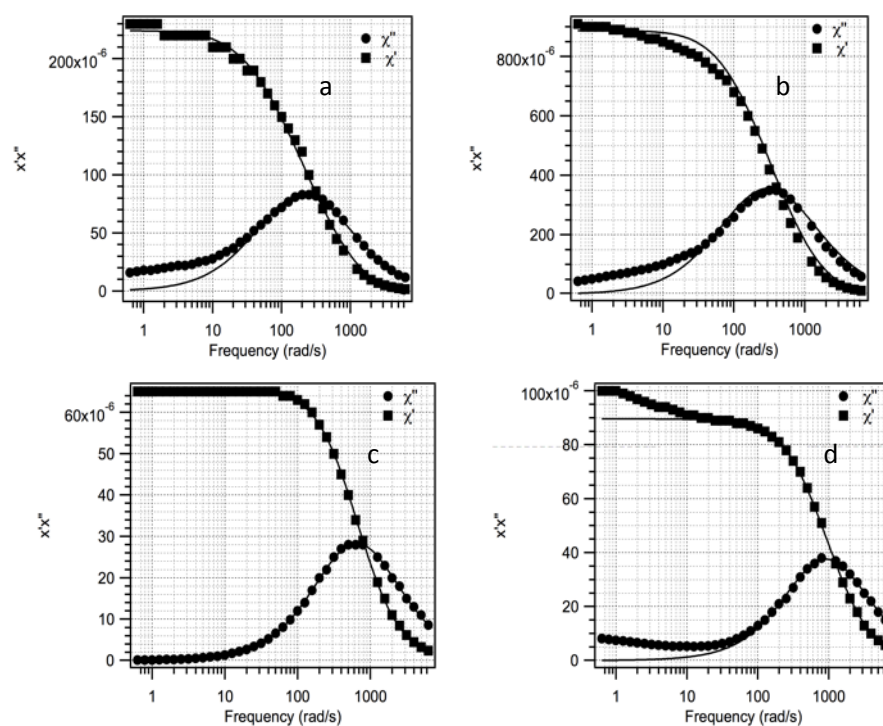


Figure 33. Dynamic magnetic susceptibility of magnetic polymer nanospheres prepared with different amounts of SDS: (a) MPNS-1, (b) MPNS-2, (c) MPNS-3, and (d) MPNS-4. The solid lines are least-squares fits of the spectra.

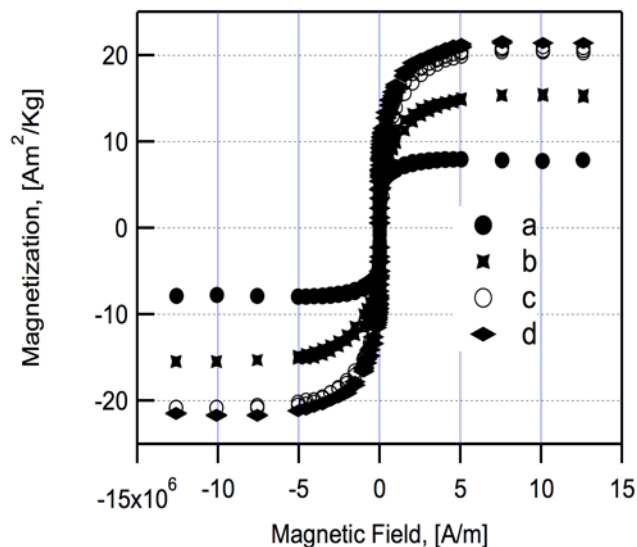


Figure 34. Magnetization curves of magnetic polymer nanospheres prepared with different amounts of SDS: (a) MPNS-1, (b) MPNS-2, (c) MPNS-3, and (d) MPNS-4.

Equilibrium magnetization curves were measured for the various magnetic polymer nanospheres at 295 K and are shown in Figure 34. The saturation magnetization M_s values, normalized with respect to the inorganic content of the MPNS, were of 7.84 Am²/Kg, 15.1 Am²/Kg, 20.3 Am²/Kg, and 21.4 Am²/Kg for MPNS-1, MPNS-2, MPNS-3, and MPNS-4. This is much lower than the value (87.0 Am²/Kg) for bulk cobalt ferrite.

4.5 Conclusions

The miniemulsion technique reported here can be used to produce magnetic polymer nanospheres with embedded cobalt ferrite nanoparticles that have a permanent magnetic moment and with Brownian magnetic relaxation. The amount of surfactant used influenced the particle size, which decreased with increasing surfactant amount. The physical and hydrodynamic diameters of the magnetic polymer nanospheres were in the range of 145-225 nm. The magnetic

content of the magnetic nanospheres was in the range of 44–62 wt %. Such particles could be suitable as probes and actuators in complex fluids and biological systems.

4.6 References

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Chapter 5

5. Concluding remarks

The main purpose of this work was to contribute to the development of bulk and colloidal latex polymer nanocomposites of poly (methyl methacrylate) (PMMA) with embedded magnetic nanoparticles particles. First, magnetic polymer nanocomposites were prepared using oleic acid coated cobalt ferrite and magnetite nanoparticles as nanofillers. It was demonstrated that both nanofillers similarly affected the glass transition temperature and the magnetic properties of the nanocomposite, increasing it relative to the neat polymer. These bulk nanocomposites are new magnetic materials that have potentially magneto-optic applications. A significant challenge in the field of nanocomposites is incorporating inorganic nanoparticles into polymer matrices homogeneously. One alternative to improve this is to modify the surface of the nanoparticles to facilitate its dispersion within or modulate interactions with the matrix. To this end we were able to obtain a material with a nanofiller modified surface. The process was carried comparing cobalt ferrite nanofillers coated with oleic acid (OA; which does not covalently bond to the PMMA matrix) and 3-methacryloxypropyltrimethoxysilane (MPS, which covalently bonds to the PMMA matrix). Our results suggest that nanofiller surface chemistry influences the thermomechanical and magnetic properties of PMMA nanocomposites.

Magnetic nanoparticles with Brownian magnetic relaxation have been used as sensors taking advantage of the hydrodynamic size dependence of the dynamic magnetization response that they have in solution. The principle is based on binding of a magnetic nanoparticle to an analyte, with a resulting change in hydrodynamic radius and Brownian relaxation time. The change of the hydrodynamic size can be measured, then indicating the detection of the analyte. On other hand, magnetic nanoparticles offer an alternative to obtain nanoscale mechanical properties of fluids complexes such as gelatin and biological fluids. For the case of gelatin, it was found that nanoscale measurements of gelation temperatures and melting points show features similar to those observed in macroscopic measurements.

Actually, there are researches focused on obtaining information on the physicochemical properties of human biological fluid. Physicochemical properties such as viscosity that change are directly related to a symptom of a disease, and could be determined through measurement of the rotational diffusivity of magnetic nanoparticles. The magnetic nanoparticles commonly used in these studies are in the range of 10-100 nm.

We reported a way to obtain particles of larger sizes of magnetic polymer nanospheres of poly(methyl methacrylate) (PMMA) with embedded CoFe_2O_4 nanoparticles. For this were used the miniemulsion magneto template polymerization technique which allowed to obtain magnetic polymer nanospheres in the range of 145-225 nm. Such particles can be suitable as probes and could allow systematic studies of complex fluids and biological systems because they have Brownian magnetic relaxation.