J Mater Sci (2011) 46:2123–2134
DOI 10.1007/s10853-010-5048-5

Bi-layered polymer–magnetite core/shell particles: synthesis and characterization

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Received: 27 July 2010 / Accepted: 1 November 2010 / Published online: 16 November 2010

Abstract Polymer magnetic core particles receive growing attention due to these materials owing magnetic properties which are widely used in different applications. The prepared composite particles are characterized with different properties namely: a magnetic core, a hydrophobic first shell, and finally an external second hydrophilic shell. The present study describes a method for the preparation of bi-layered polymer magnetic core particles (diameter range is 50–150 nm). This method comprises several steps including the precipitation of the magnetic iron oxide, coating the magnetite with oleic acid, attaching the first polymer shell by miniemulsion polymerization and finally introducing hydrophilic surface properties by condensation polymerization. The first step is the formation of magnetite nanoparticles within a co-precipitation process using oleic acid as the stabilizing agent for magnetite. The second step is the encapsulation of magnetite into polyvinylbenzyl chloride particles by miniemulsion polymerization to form a magnetic core with a hydrophobic polymer shell. The hydrophobic shell is desired to protect magnetite nanoparticles against chemical attack. The third step is the coating of magnetic core hydrophobic polymer shell composites with a hydrophilic layer of polyethylene glycol by condensation polymerization. Regarding the miniemulsion polymerization the influence of the amount of water, the mixing intensity and the surfactant concentration were studied with respect to the formation of particles which can be further used in chemical engineering applications. The resulting magnetic polymer nanoparticles were characterized by particle size measurement, chemical stability, iron content, TEM, SEM, and IR.

Introduction

Nanoencapsulation received considerable increasing attention by providing the possibility of combining the properties of different material types (e.g., inorganic and organic) on the nanometer scale (<1 µm in diameter) having a spherical or irregular shape. Capsules can be divided into two parts, namely the core and the shell. The core (the intrinsic part) contains the active ingredient (e.g., a hardener, magnetite, or a biocide), while the shell (the extrinsic part) protects the core permanently or temporarily from the external environment.

Compatibility of the core material with the shell is an important criterion for enhancing the efficiency of encapsulation [1]. Pretreatment of the core material is very often carried out to improve such compatibility. The size of the core material also plays an important role for diffusion, permeability or controlled release applications [2], paints [3], cell separation [4], and tissue engineering [5].

The presence of chloromethyl groups on the surface of magnetic particles coated with polymer gives actively to be used in various industrial and medical applications. To apply magnetic polymer in various potential fields, it is very important to control the size and shape, and to design the thermal and chemical stability by surface modification [6]. However, these nano-sized magnetite particles tend to aggregate because of their high specific surface area and

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strong interparticle interaction. Therefore, it is essential to develop strategies for the chemical stabilization of the magnetic nanoparticles against aggregation.

The preparation of magnetite/polymer particles can be generally classified in three categories. First is the most simple one which is the separately performed synthesis of the magnetic particles and polymer materials and then mixing them. During mixing adsorption (physical or chemical) of either the magnetic particles onto the polymer spheres [7] or vice versa occurs. The second technique to obtain magnetic polymer dispersions is based on in situ precipitation of magnetic material in the presence of polymer, where the magnetic particles are surrounded by a hydrophilic polymer shell [8]. The third way is to polymerize monomers in situ in the presence of magnetic particles, including miniemulsion polymerization [9].

To prepare magnetite nanoparticles with a coating the application of fatty acids such as oleic acid is state of the art. Oleic acid acts as surfactant since oleic acid has high affinity to the surface of superfine magnetite (10–20 nm) and hence makes the particles compatible with monomer. However, the complexity of the particle nucleation mechanism and the difficulties in controlling the dispersion stability of inorganic particles in the continuous or disperse phase during emulsification and encapsulation polymerization appear to be the main problems in preparing magnetic polymer. Miniemulsions are relatively stable oil-in-water dispersion with droplets in the nanometer range. The main advantage of emulsion-based polymerization methods consists in the control of the molecular weight and molecular weight distribution, using parameters such as the initiator and/or surfactant concentrations.

A miniemulsion is typically obtained by shearing a system containing monomer, water, surfactant, costabilizer, and initiator. The droplet diameter is adjusted by the type and amount of surfactant and costabilizer, the volume fraction of the disperse phase, and the homogenization process. One of the characteristic features of the miniemulsion polymerization technique may be an advantageous encapsulation method.

Magnetic polymer cores functionalized with chloromethyl groups are more important in applications such as magnetic separations, solid phase syntheses, immunodiagnostics, etc. Their chlorine groups are easily displaced by nucleophiles to produce anion exchange polymers, solid state synthesis (Merrifield) resins and electron beam negative resists [10–13].

One of the modifications magnetic polymers functionalized with chloromethyl groups can be used for is the preparation of a second layer of polyethylene glycol (PEG). This results in an additional hydrophilic shell.

In this work optimum condition are described to prepare magnetite nanoparticles by studying the effect of addition of oleic acid at room temperature and at higher temperature as stabilizing agent. A direct method is suggested where the formation of one solution mixture is formed of magnetite and monomer for the preparation of chlorinated magnetic polymer core nanoparticles based on miniemulsion polymerization technique. The effect of water and surfactant were measured as function of emulsion stability. Vinylbenzyl chloride was chosen as a monomer because it offers the possibility to anchor additional functional groups for active site attachment. The resulting magnetic polymer nanoparticles were characterized by particle size measurement (Malvern Zeta Sizer), iron content (elemental analysis by wet chemistry), and morphology (transmission electron microscopy (TEM) and scanning electron microscopy (SEM)). The binding of iron and oleic acid was investigated by infrared spectroscopy. Finally acid treatment (hydrochloric acid) was used to evaluate chemical stability.

Experimental part

Material

Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), ammonium hydroxide (26% NH_3 in H_2O), hexane, dichloromethane (DCM), vinylbenzyl chloride (VBC 95%), hexadecane, polyethylene glycol (PEG 600), sodium dodecyl sulfate (SDS), potassium peroxodisulfate (KPS), and oleic acid (90%) were purchased from Fluka AG and used as received.

Preparation of magnetite nanoparticles

The magnetite nanoparticles are produced by co-precipitation of an aqueous solution of iron (III) chloride hexahydrate and iron (II) sulfate heptahydrate with a molar ratio of $Fe^{3+}/Fe^{2+} = 2:1$. The iron solution is precipitated with concentrated ammonium hydroxide in excess. 24.05 g $FeSO_4 \cdot 7H_2O$ and 47 g $FeCl_3 \cdot 6H_2O$ are dissolved in 1000 mL distilled water and heated to 70 °C. 60 mL of ammonium hydroxide is added quickly to the resulting solution, producing deep black magnetite precipitate at once. The magnetite yield is 20 g/L. The suspension has been stirred for another 30 min at 70 °C in order to evaporate any trace ammonia. Otherwise, ammonium salts adsorb after precipitation onto the particle surface and the transfer into the organic phase is obstructed.

Coating of the magnetite with oleic acid and transfer of the magnetite to the organic phase

In a previous paper we described a method for this task [14, 15] which is now modified to make the procedure easier in handling according to the literature [16, 17]. The comparison of both methods is also given here for the same amount of oleic acid.

At room temperature

After cooling to room temperature, the magnetite particles are transferred directly without drying from the aqueous phase into a mixture of dichloromethane or hexane 500 mL and oleic acid 10 mL which serves as a steric stabilizer. A minimum amount of about 0.3 g oleic acid/g magnetite is needed to transfer all the particles into the organic phase. Otherwise an intermediate phase consisting of non-stabilized particles, which shows a different wetting behavior, may disturb the transfer procedure [18].

At elevated temperature

The magnetic iron nanoparticles formation at high temperature was done without the addition of hexane. Only oleic acid was added at a temperature of 70–90 °C. High stirrer speed was adjusted to ensure evaporation of any excess of ammonia and water. This was done for 30 min. Iron oxide coated with oleic acid formed and became a separated phase from the water phase going to the bottom of the vessel. Then a cooling step followed by washing with water for several times and finally drying was done.

Synthesis of magnetic polyvinylbenzyl chloride nanoparticles by using miniemulsion polymerization

In the literature the coating with styrene was described [16, 17]: We evaluated if this method is suitable for other monomers which are more attractive due to functional groups, as monomer vinylbenzyl chloride was used. For the formation of a homogeneous mixture 1 g iron oxide coated with oleic acid (after organic solvent evaporation), 3.0 g vinylbenzyl chloride (VBC), 0.15 g hexadecane, and surfactant solution according to Table 1 were mixed well by an US-sonotrode. We used an ultrasonic homogenizer from Bandelin, Germany (Sonopuls HD 200 with sonotrode UW 200) with the following settings: 2 min treatment time, power output 50%, 90% cycle in an ice-cooled bath to form the miniemulsion solution. Then the polymerization was started by the addition of potassium peroxodisulfate (KPS) solution (0.0015 g in 5 mL water) and heating to 80 °C. This temperature was kept for 24 h. The result is a stable dispersion of polymer coated magnetite.

Synthesis of magnetic polyvinylbenzyl chloride nanoparticles (double magnetic amount) by using miniemulsion polymerization

The procedure is same as described above for preparation of magnetic polyvinylbenzyl chloride nanoparticles. The only difference is the addition of iron oxide coated with oleic acid is 2 g.

Synthesis of bi-layered polymer magnetic core by condensation polymerization

The formation of a hydrophilic shell on a commercial Merrifield resin is described in the literature [19]. We adopted this method to particles resulting from a miniemulsion polymerization. Well mixing of 0.4 g of the magnetic polyvinylbenzyl chloride nanoparticles and an excess of PEG of 44.5 g is done using an US-sonotrode. The magnetic polyvinylbenzyl chloride nanoparticles are dispersed in PEG, then KOH solution is added (1.2 g in 5 mL water) and heated to 80 °C for 24 h.

Characterization

Particle size measurements were performed by photon correlation spectroscopy (PCS, Malvern Instruments Nanosizer ZS), the content of magnetite is quantified with a spectrophotometer (Hach Company, DR 4000) using the 1.10 phenanthroline method [20].

The morphology and diameter were measured by transmission electron microscopy (TEM) on Jeol JEM 2100 electron microscope and by scanning electron microscopy (SEM) on ZEISS DSM 982 GEMINI. The binding of iron and oleic acid was investigated by infrared spectroscopy (IR) FT-IR spectrometer from Bruker IFS 66v with Raman module FRA 106, Bruker Optik GmbH. The samples were prepared by mixing with KBr and pressing into a compact pellet. Finally acid treatment was done by concentrated hydrochloric acid.

Table 1 Effect of water and SDS on emulsion stability

Sample	Water (wt%)	Monomer (wt%)	SDS (wt%)	Composition	Sedimentation
1	76.74	23.02	0.23	3 g VBC + 10 g H_2O + 0.03 g SDS	Hours
2	88.79	11.09	0.11	3 g VBC + 24 g H_2O + 0.03 g SDS	1 day
3	97.02	2.91	0.06	3 g VBC + 100 g H_2O + 0.07 g SDS	2 days
4	97.90	1.96	0.137	3 g VBC + 150 g H_2O + 0.21 g SDS	Month

Results and discussion

Preparation of magnetite nanoparticles coated with oleic acid

In our method hydrophobic magnetite nanoparticles are produced. The particle size of magnetite iron nanoparticles in a water phase (~50 nm) is bigger than in an organic phase (~30 nm) were measured by PCS (Zetasizer). That is attributed to the type and amount of solvent which plays an important role in the control of magnetite iron nanoparticles size.

Supermagnetic Fe_3O_4 nanoparticles (magnetite iron nanoparticles) with mean diameter (10–20 nm) were prepared by co-precipitation process. Precipitation of an aqueous Fe^{3+}/Fe^{2+} solution with a base of concentrated ammonium solution takes place, then followed by coating these particles with an adsorbed layer of oleic acid, which acts as surfactant layer on magnetite particles to give hydrophobic character to the particles. Additionally, the oleic acid layer helps in decreasing the aggregation between particles and in increasing the concentration of monodispersed magnetite iron nanoparticles.

Formation step

The formation of magnetite nanoparticles by quick addition of concentrated ammonium hydroxide solution to an iron solution with intensive stirring at a temperature of 70 °C occurs according to the following equation:

$$2Fe^{3+} + Fe^{2+} \xrightarrow{8OH^-} Fe_3O_4 + 4H_2O$$

Stabilization step

After the formation of magnetite nanoparticles oleic acid is added at room temperature or at higher temperature to give a first hydrophobic shell to the nanoparticles. This was done with dichloromethane or hexane at room temperature or by the addition of oleic acid directly during the heating and stirring at a temperature of 70 °C.

At room temperature The magnetic iron nanoparticles were transferred to the organic phase by addition of an organic phase to the mixture. The mixture consisted of hexane or dichloromethane (DCM) and oleic acid. Mixture addition was done at room temperature. Then waiting until the complete transfer of the particles to the organic phase is accomplished was done. Then the water phase could be separated easily.

At elevated temperature Stabilization is reachable by addition of oleic acid directly at a heating temperature of 70 °C with intensive stirring to get excess of ammonia and water evaporated. No hexane was added to simplify the method. Iron oxide coated with oleic acid is formed and become separated from water. A consequent washing step is necessary for several times to wash out the non-adsorbed oleic acid. The particles are dried and then dispersed in an organic solvent for further reactions.

A minimum amount of about 0.4 $g_{\text{oleic acid}}/g_{\text{magnetite}}$ is needed to transfer all the particles into the organic phase. Otherwise an intermediate phase consisting of non-stabilized particles will occur. Comparing the transfer of magnetite coated with oleic acid in DCM and hexane the latter resulted in better stabilization than with DCM. The reason is the lower polarity of the solvent hexane compared to DCM.

Preparation and properties of bi-layered polymer with a magnetic core

The following steps are the formation of two polymer layers: the first hydrophobic one and the second hydrophilic one.

1. Preparation of the first (hydrophobic) layer by miniemulsion polymerization.
   The formation of the first hydrophobic layer is depicted in Fig. 1. The binding of oleic acid to the polymer is discussed in our previous paper [14].
2. Preparation of the second (hydrophilic) layer by polycondensation reaction with PEG.
   By addition of an excess of PEG to magnetic polyvinylbenzyl chloride nanoparticles condensation polymerization starts by addition of KOH as catalyst as shown in Fig. 2.

Emulsion stability as function of water and surfactant

In the literature [17] it is reported that the ratio of water to monomer and SDS to monomer should be 75 and

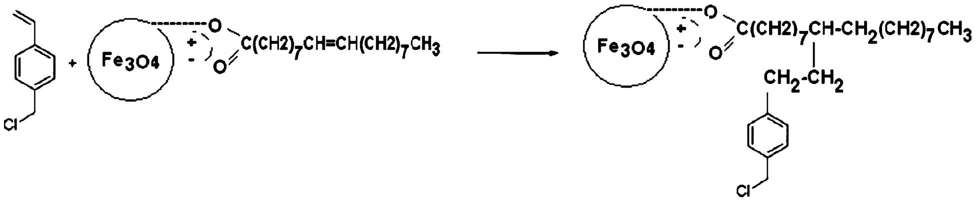
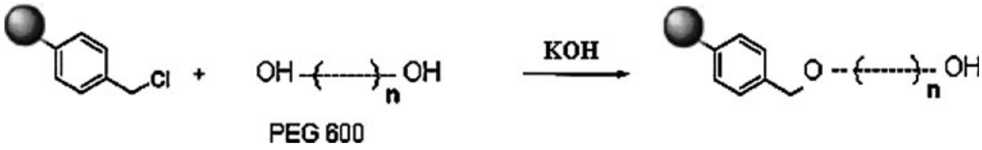
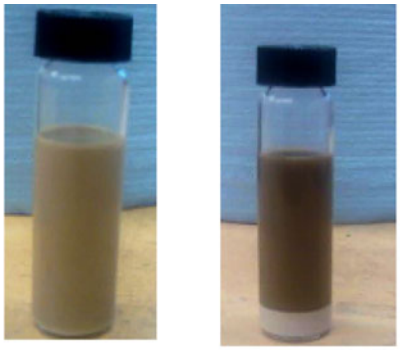


Fig. 1 Polymerization of vinylbenzyl chloride with oleic acid coated magnetite

Fig. 2 Formation of the hydrophilic second layer on hydrophobic coated





Freshly prepared emulsion Emulsion within 1-2 days

Fig. 3 Comparison of literature recipe (the ratio of water to monomer and SDS to monomer should be 75 and 1.1%, respectively, for styrene as monomer) applicability to vinylbenzyl chloride monomer with respect to emulsion stability magnetite

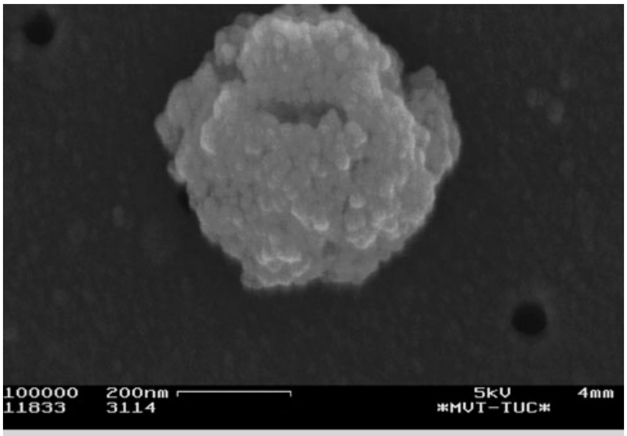


Fig. 4 SEM picture of magnetic polymer formed by the miniemulsion process (ratio of water and SDS 76.74 and 0.23%, respectively) using 3 g VBC as monomer

1.1%, respectively, for an effective synthesis of magnetic polymers with styrene as monomer. However, we found that the amount of water and SDS given in the literature are not sufficient for the preparation of a stable emulsion for our monomer (stable droplets of vinylbenzyl chloride monomer), as after 1–2 days the emulsion gets separated as shown in Fig. 3. So the amount of water and surfactant play a main role in the stabilization of the emulsion strongly dependant on the monomer. This fact is confirmed by the patent literature [21, 22], e.g., the polymer/liquid mixture during emulsion polymerization must be within the range of 75–95%, by the weight of the liquid, defined in terms of water. The amount of surfactant or inherent surface stabilizing groups required to form polymerizable miniemulsion is 5–25% relative to the monomer phase.

In Table 1 different amounts of water and SDS were used to investigate the stability of the emulsions. As a result the minimum ratio of water and SDS should be 97.90 and 0.137%, respectively, for the monomer VBC. This ratio was found to be an optimum and used for all consecutive experiments.

One sample to check the literature information was prepared using ratios of water and SDS of 76.74 and 0.23%, respectively, in the miniemulsion process. As a finding the magnetic polymer particles are rougher with higher agglomeration than for the optimum given above. They have flower-like shapes (Fig. 4). This is attributed to the non-sufficient amount of water and SDS to get a stable emulsion as discussed above.

Properties of magnetic particles and magnetic polymer composites

The magnetite nanoparticles prepared at room temperature and at elevated temperature of 70 °C were evaluated by measuring magnetite content and stability of nanoparticles against concentrated hydrochloric acid.

Table 2 presents the resistance of magnetite nanoparticles prepared at both room and elevated temperature against concentrated hydrochloric acid. It can observe that the magnetite nanoparticles coated with oleic acid which

Table 2 Resistance of magnetite nanoparticles and magnetic polymer composites against HCl

Sample	Magnetite content Fe_3O_4 (wt%) [19]	Resistance to HCl
Magnetite in DCM (room temperature)	23	Seconds
Magnetite in hexane (room temperature)	24.2	Seconds
Magnetite (higher temperature)	67.3	Minutes
Magnetic polyvinylbenzyl chloride	30.5	Days
Magnetic polyvinylbenzyl chloride (double magnetic amount)	85.5	Days
Bi-layered polymer with magnetite core	41.8	Days

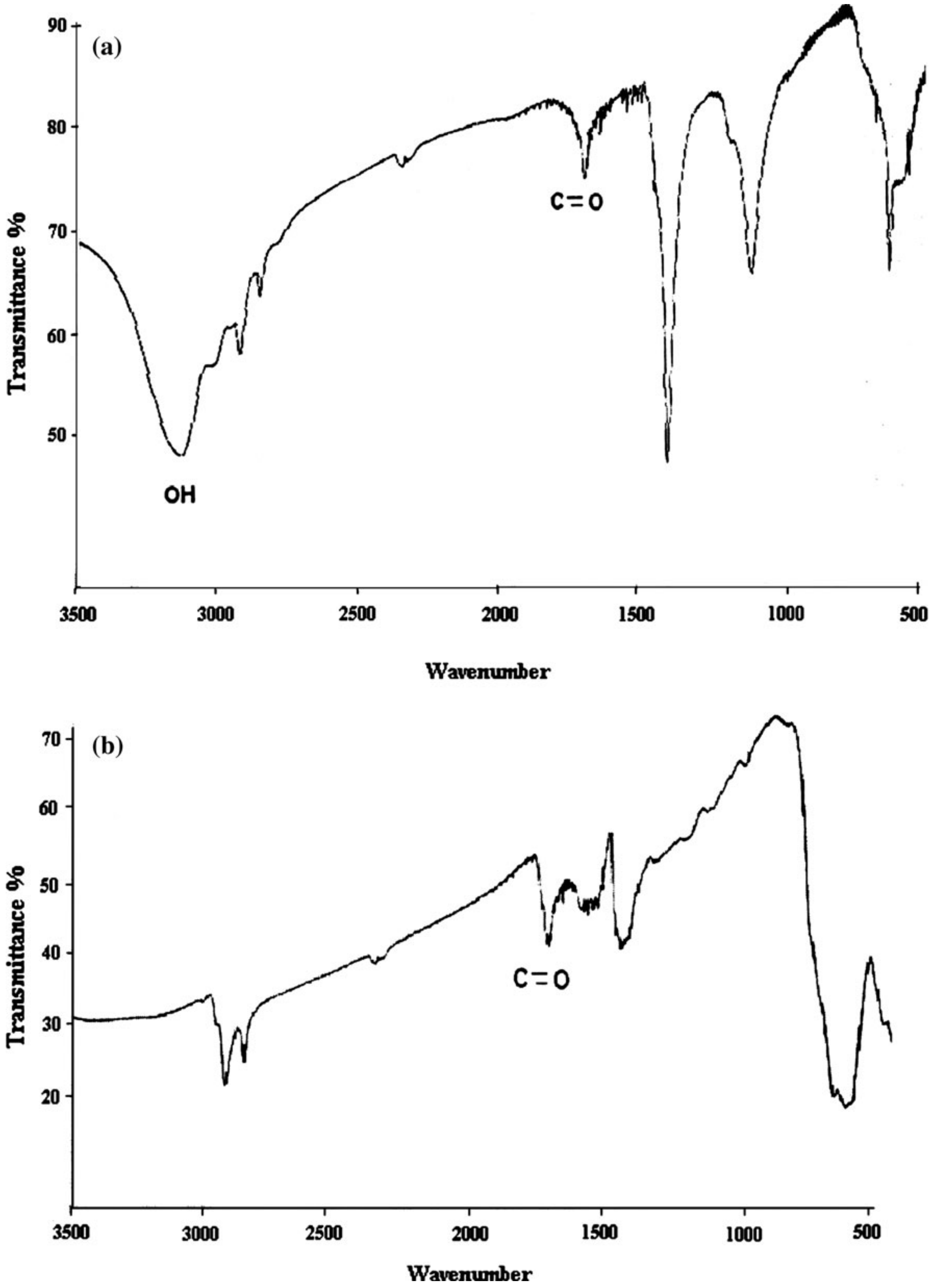


Fig. 5 IR spectra of magnetite covered with oleic acid: **a** prepared at room temperature, **b** prepared at higher temperature of 70 °C

prepared at room temperature in DCM and in hexane loose within seconds its black color to yellow and also the magnetic properties. On the other hand, the sample of magnetite which was prepared at higher temperature show more resistance by minutes when treated with concentrated hydrochloric acid. It is the reason that magnetic nanoparticles are so tightly coated by oleic coating that few H^+ can enter the interior to dissolve them.

The resistance against concentrated HCl of all samples made of magnetic polyvinylbenzyl chloride, magnetic polyvinylbenzyl chloride (double magnetic amount), and bi-layered polymer with magnetite core is in the range of several days. After this time most of the iron oxide is dissolved and magnetic properties are lost. This indicates that magnetite indeed is covered by the polymer, but some “holes” or gaps must be in the coating, allowing slow access of the acid. It should be mentioned that this test happens at very severe conditions which are far beyond regular applications. As a consequence the stability in neutral more weakly acidic environment should be high.

Also the magnetite content of magnetite nanoparticles which were formed at higher temperature is much higher than for the samples prepared at room temperature. The difference between the two samples in magnetite content was likely due to the originals starting sample consisting not only of magnetite, but also some maghemite (γ-Fe_2O_3).

$$2Fe_3O_4 + 0.5O_2 \rightarrow 3Fe_2O_3$$

Particle size measurement was performed by PCS photon correlation spectroscopy (Zetasizer). The measurements show that the mean diameter of the magnetic nanoparticles is almost 30 nm. The bigger diameter of all samples prepared at room temperature or at elevated temperature is higher than expected due to agglomeration of magnetic particles as result of higher surface energy between nanoparticles.

Measurement of size of the prepared samples of magnetic polymer by PCS photon correlation spectroscopy (Zetasizer) shows that the particle diameter is approximately 50–100 nm. This value is higher than expected due to the agglomeration of particles from strong interparticle interaction and hence particles are agglomerates.

Infrared spectroscopy (IR)

In Fig. 5 the presence of magnetite is characterized by two absorption bands at 632 and 585 cm^{-1}, which correspond to the Fe–O. The bands at 1430 and 1590 cm^{-1}, which correspond to the symmetric and antisymmetric stretching

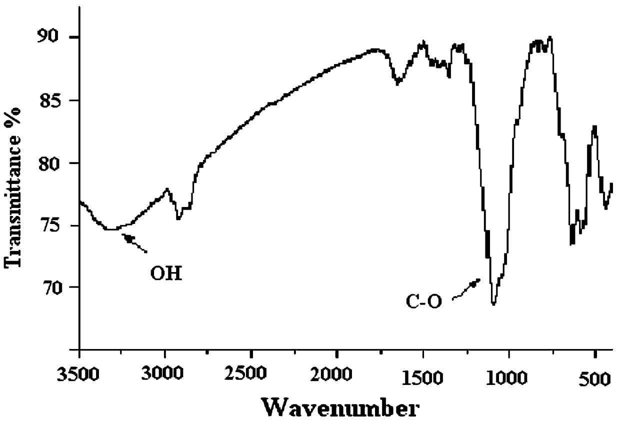


Fig. 7 IR spectrum of bi-layered polymer magnetic core particles

Fig. 6 IR spectrum of magnetic polyvinylbenzyl chloride coated particles

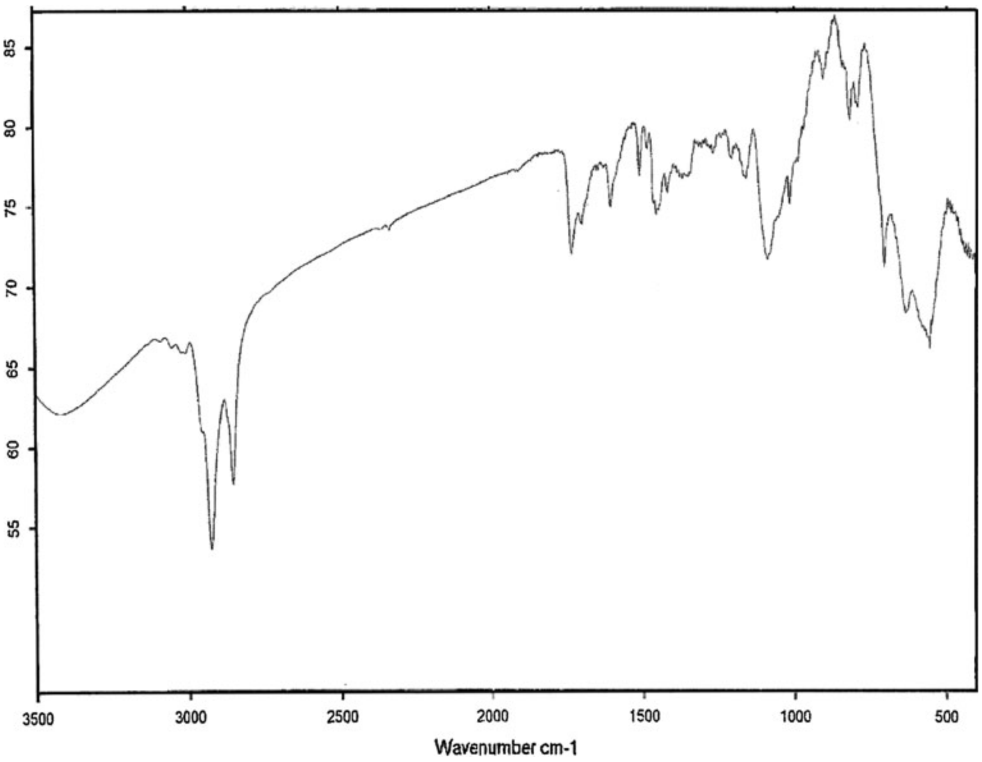
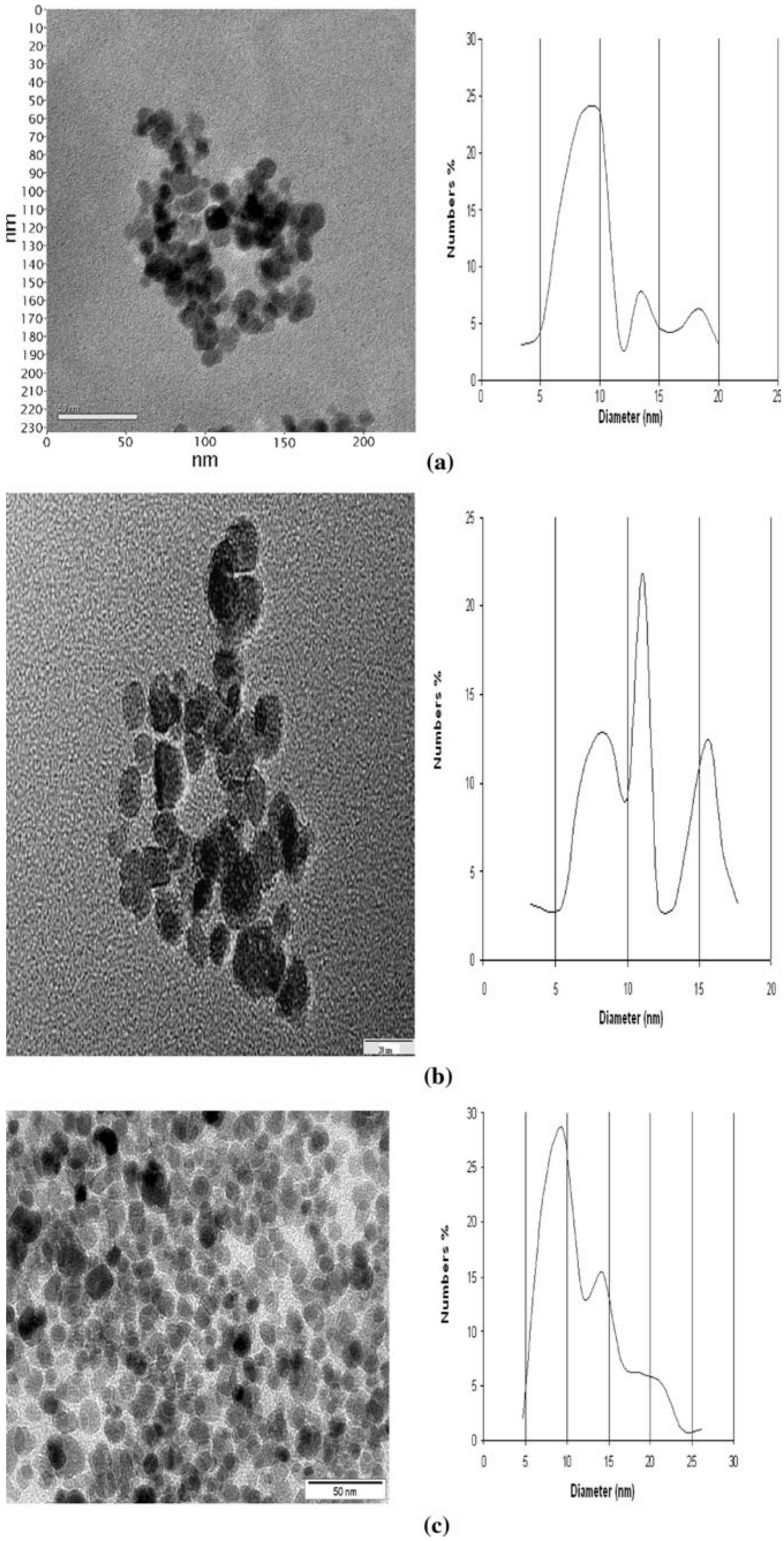
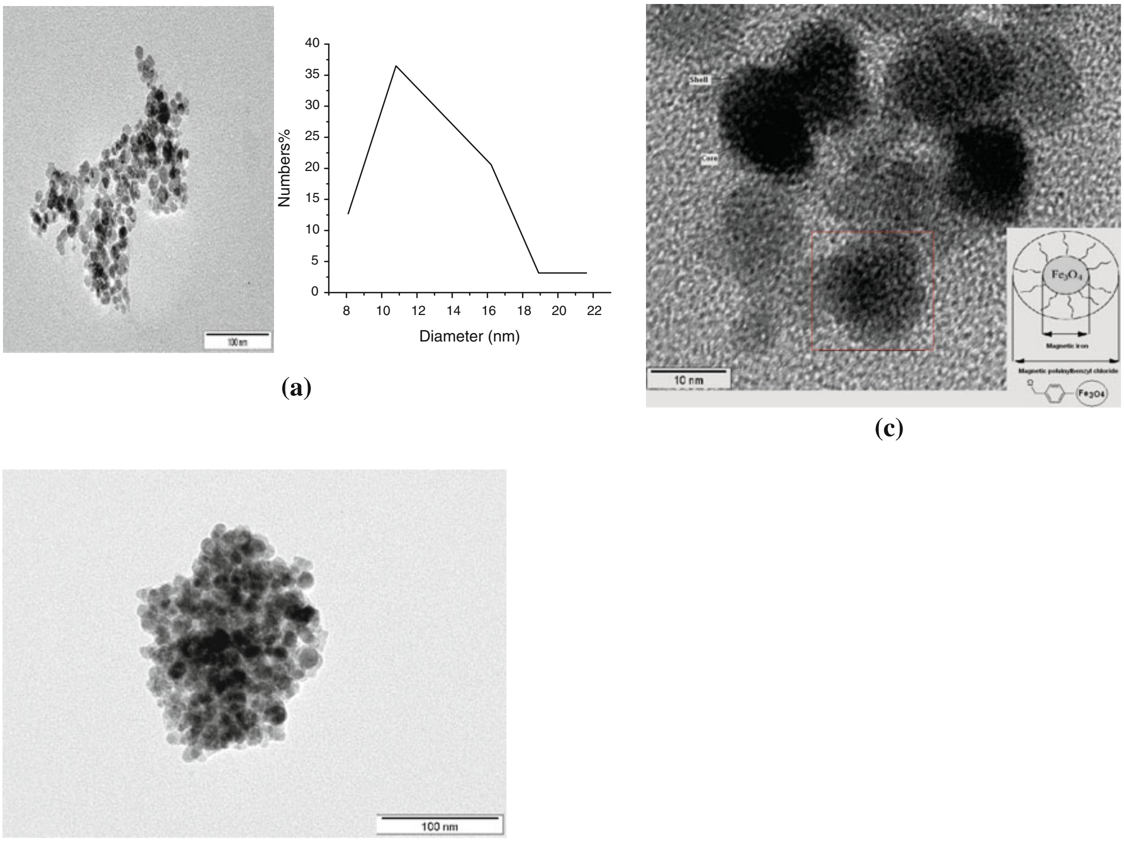


Fig. 8 TEM images and particle size distributions of magnetite particles coated with oleic acid: **a** into DCM, prepared at room temperature, **b** into hexane, prepared at room temperature, **c** without organic solvent, prepared at higher temperature





(a)

(c)

(b)

Fig. 9 TEM pictures of polyvinylbenzylchloride coated magnetite particles after different treatments. **a** TEM image and particle size distributions of polyvinylbenzylchloride coated magnetite particles dispersed in acetone without drying, **b** TEM image of polyvinylbenzylchloride coated magnetite particles dried by heating, **c** TEM image of polyvinylbenzylchloride coated magnetite particles dispersed in acetone without drying

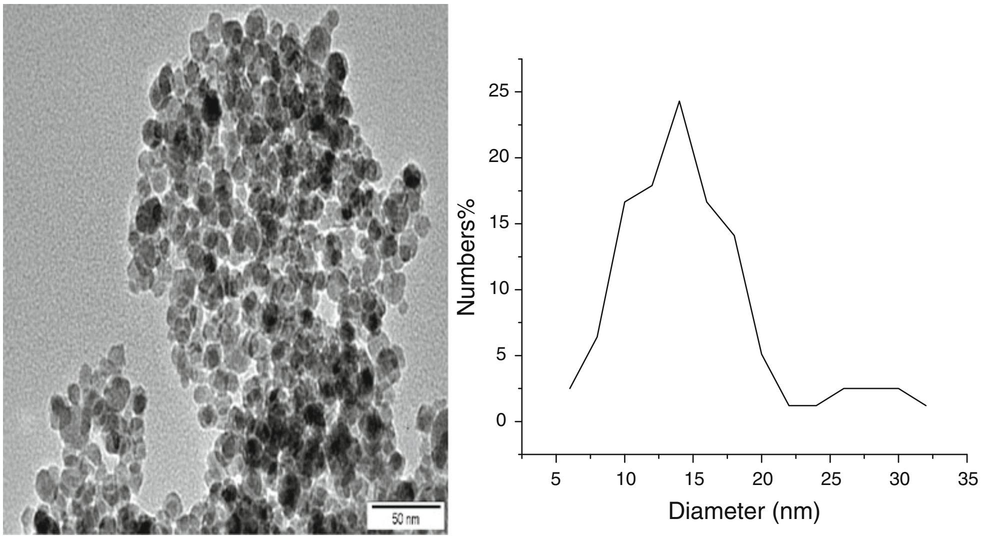


Fig. 10 TEM image and particles size distribution for magnetic polyvinylbenzyl chloride nanoparticles (double magnetic amount) dispersed in acetone without drying

vibration of oleate (–COO) appeared as well and the band at 1720 cm^{-1} which corresponds to the (C=O) group. This implies that oleic acid is bonded with iron oxide.

The presence of hydroxyl groups on the surface of the magnetite is noticed by a band at 3200 cm^{-1} and strong band for C–O–H bending at 1401 cm^{-1}. The intensity is

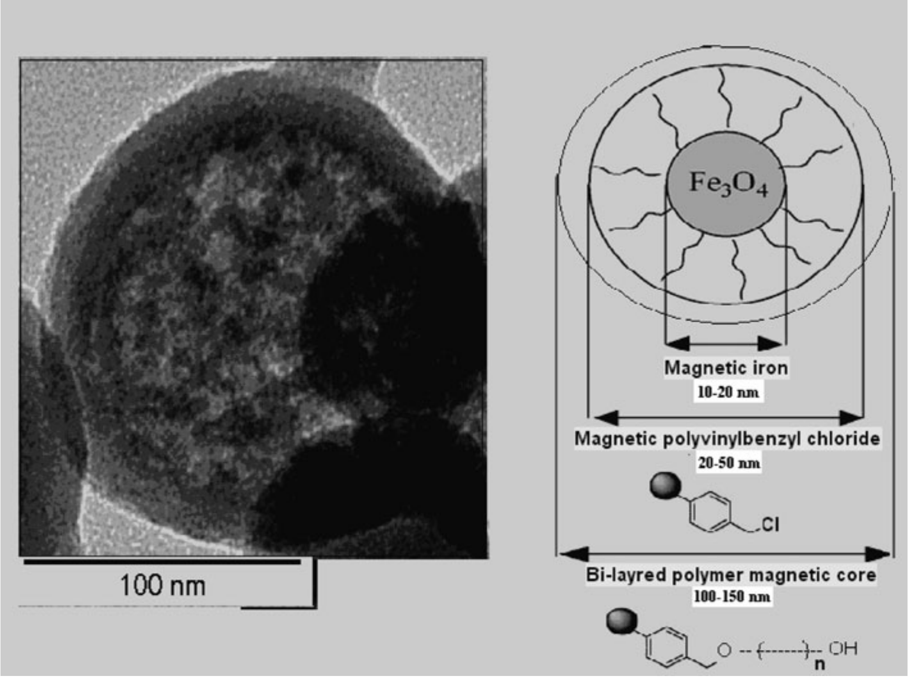


Fig. 11 TEM picture of one composite magnetite polymer bi-layered particle dispersed in acetone, showing the core–shell structure

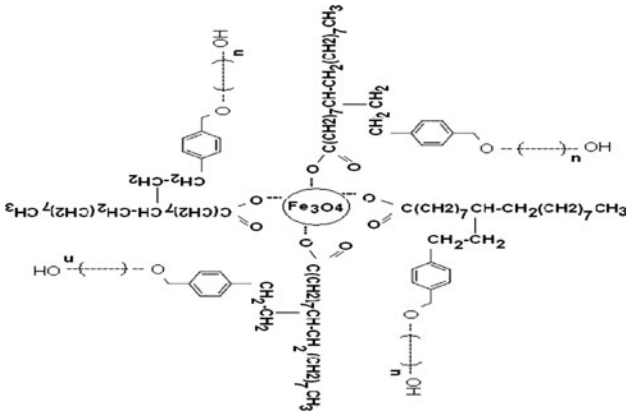


Fig. 12 Composite of magnetite and polymer with a bi-layered shell structure based on the performed characterization

more pronounced for samples prepared at room temperature than for those prepared at high temperature.

This is due to the fact that most of the hydroxyl groups are consumed during the formation of the ester group with oleic acid at higher temperature, which is also reported in the literature [23].

In Fig. 6 the IR spectrum shows two absorption bands at 632 and 585 cm^{-1}, which correspond to the Fe–O bond. Also C–H stretching vibration with absorption bands between 2900 and 3000 cm^{-1} appear [24, 25]. This proves the presence of magnetite in the polymer. The absorption bands at 1500–1600 cm^{-1} stand for the aromatic ring with di-substitution C=C (ring, two bands). These findings together with the previous measurement indicate that the oleic acid treated iron oxide is encapsulated by the polymer.

In Fig. 7 the IR spectrum for the ethylene glycol coated sample is given. The strong absorption bands at 1100 cm^{-1} for the C–O bond indicate that in the bi-layered polymer magnetic core particles PEG is bonded by the formation of an ether bond by reaction with the chlorine atom of the polyvinylbenzyl chloride on the surface of the composites.

Transmission electron microscopy (TEM)

Figure 8a, b shows TEM images and particles size distributions of iron magnetite samples in DCM and hexane. In this figure it can be seen that the average particle diameters are between 10 and 20 nm. Also it is noticed that there are agglomerated particles due to large free surface energy of each nanoparticle. Further, less agglomeration is observed in the case of magnetite nanoparticles prepared at elevated temperature (Fig. 8c). This may be attributed to the better coating of particles by oleic acid which is more complete at higher temperature. It is supposed that all surface iron oxide molecules have reacted with oleic acid, forming a layer of chemically bonded oleic acid.

In Fig. 9a, b TEM pictures of the magnetic polyvinylbenzyl chloride particles are given. The average particles diameter ranges from 20 to 50 nm. Particles have spherical shape with considerable polydispersion. The effect of drying is also noticed on the morphology of the heated sample as the agglomeration is found to increase by drying.

The core–shell structure where the outer shell is polymer and magnetite is the inner core is shown in Fig. 9c.

It can be seen that both diameter and polydispersity of magnetic polymer particles increase with increasing concentration of the Fe_3O_4 used for the preparation as shown in Figs. 9 and 10. Probably the content of the magnetic Fe_3O_4 nanoparticles in the composite particles has a remarkable effect on product morphology caused by the existence of static magnetic attraction, which is also reported in the literature [26]. Another reason for increasing the magnetite aggregate size by increasing magnetite concentration could be that with rising iron oxide concentration agglomeration is favored compared to encapsulation inside the polymer particles. It seems that with increased agglomeration of the iron oxide some polymer particles form without iron oxide inside. These particles are smaller than the agglomerates and contribute by this to a broader particle size distribution. This decreases monodispersity and increases polydispersity.

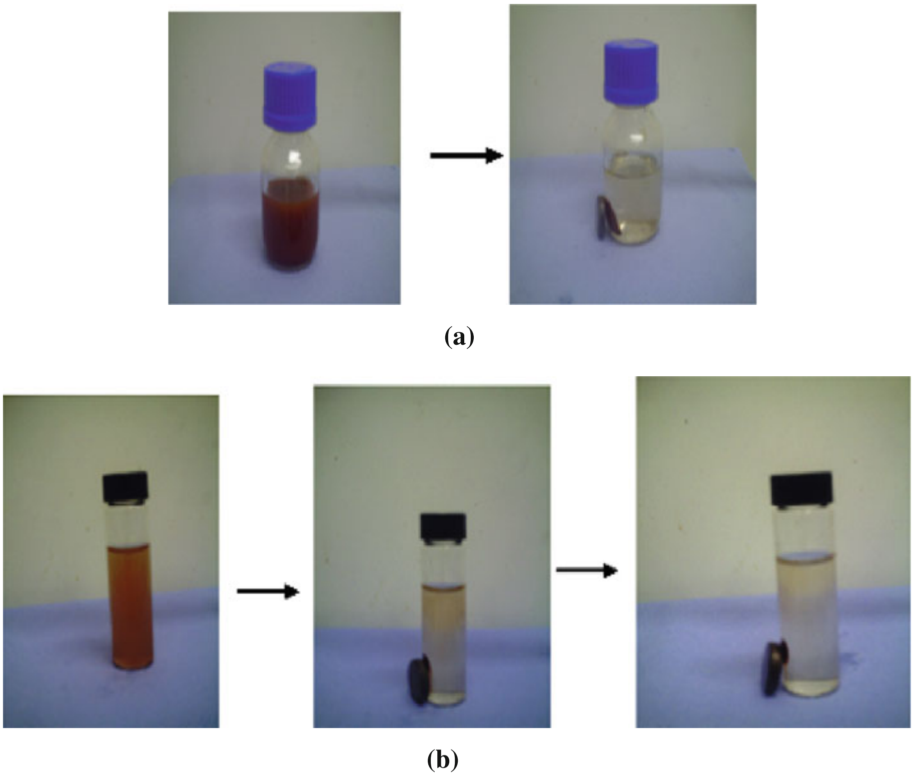
The morphology of the bi-layered polymer magnetic core particles with an average particle diameter ranging from 50 to 150 nm can be observed. Particles have spherical shape with considerable polydispersion. Also it can be noticed that the effect of drying by heating has a size increasing effect on the morphology of the sample, caused by agglomeration.

In Fig. 11 a single particle clearly showing the core–shell structure of the magnetic composites is depicted. Agglomerated magnetite nanoparticles covered by oleic acid can be seen in the center. A layer of polyvinylbenzylchloride surrounds this particle. The outer shell of brighter appearance is the shell of PEG. In the right part of the picture, the schematic structure derived by our investigation is depicted.

In Fig. 12 the core–shell structure with the two polymer shells is given. This picture is based on the synthesis steps and the performed characterization. There are free OH groups which allow dispersion in aqueous medium and which can be used for further reactions which makes them suitable, e.g., for binding enzymes on these functionalized surface sites.

Dispersion of magnetic polymer nanoparticles

Samples of magnetic polyvinylbenzyl chloride and magnetic polyvinylbenzyl chloride with a double amount of magnetite as well as the hydrophilic bi-layered materials were investigated with respect to their dispersion behavior. Acetone (40 mL) was used as the organic phase for the hydrophobic sample (0.5 g); water (15 mL) was used for the hydrophilic sample (0.25 g). All samples could be dispersed easily in the mentioned dispersion phases. They can be attracted to a magnetic bar in a few seconds; also they can easily be re-dispersed as shown in Fig. 13a, b.


(a)

(b)

Fig. 13 Dispersion of magnetic polyvinylbenzyl chloride and bi-layered magnetic polymer in different solvents. **a** Polyvinylbenzylchloride coated magnetite dispersed in acetone and after influence of a magnetic bar after 3 s demonstrating easy separation by magnetic force. **b** Bi-layered magnetic polymer dispersed in water and after influence of magnetic bar after 2 and 10 s

Conclusion

- The stabilization of magnetite nanoparticles (10–20 nm) by addition of oleic acid at higher temperature without organic solvent results in higher stability with higher magnetite content compared to that formed by addition of oleic acid at room temperature. This was confirmed for DCM and hexane as dispersion liquids.
- The formation of magnetic polyvinylbenzyl chloride nanoparticles (20–50 nm diameter) by a method given in the literature can be used, but the ratio of water, SDS, and monomer needs adaptation with respect to the monomer properties. For vinylbenzylchloride the optimum values for water and SDS should be 97.90 and 0.137%, respectively.
- The formation of the hydrophobic first shell protects the iron oxide core against concentrated hydrochloric acid for several days.
- A hydrophilic second shell can be attached by base catalyzed polycondensation with PEG.
- Bi-layered polymer magnetic core nanoparticles (50–150 nm) show better resistance against concentrated HCl than magnetite, which gives evidence that the magnetic composite has a dense core/shell structure.

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