Formation of polymer microcapsules with encapsulated Fe₃O₄ magnetic nanoparticles

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Abstract – Surface functionalized iron oxide magnetic nanoparticles (MNPs) are a kind of novel functional materials, which can be widely used in biotechnology and catalysis as magnetic separation systems. Therefore the goal of our work was to study preparation of encapsulated MNPs by elaborated extraction-coacervation technique using synthesized heterofunctional acrylate copolymer. Magnetic MNPs modified by oleic acid were synthesized and used in encapsulation process. Developed encapsulation technique allowed to obtain microcapsules with Fe₃O₄ nanoparticles encapsulated in paraffin core possessing magnetic properties and covered by heterofunctional copolymer shell.

Key words – heterofunctional acrylate copolymer, magnetite, magnetic nanoparticles, encapsulation, microcapsules.

I. Introduction

MNPs have many unique magnetic properties such as superparamagnetic, high coercivity, low Curie temperature, high magnetic susceptibility, etc. MNPs are of a great interest for researchers from a broad range of disciplines, including magnetic fluids, data storage, catalysis, and bioapplications [1–5]. Currently, MNPs are also used in important bioapplications, including magnetic bioseparation and detection of biological entities (cell, protein, nucleic acids, enzyme, bacterials, virus, etc.), clinic diagnosis and therapy (such as MRI (magnetic resonance image) and MFH (magnetic fluid hyperthermia)), targeted drug delivery and biological labels. However, it is crucial to choose the materials for the construction of nanostructure materials and devices with adjustable physical and chemical properties.

In the last decade, increased investigations with several types of iron oxides have been carried out in the field of MNPs. Magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) are the very promising and popular candidates since their biocompatibility have already proven.

However, it is a technological challenge to control size, shape, stability, and dispersibility of MNPs in desired solvents. Iron oxide MNPs have a large surface-to-volume ratio and therefore possess high surface energies. Consequently, they tend to aggregate so as to minimize the surface energies. Moreover, the naked iron oxide MNPs have high chemical activity, and are easily oxidized in air (especially magnetite), generally resulting in loss of magnetism and dispersibility. Therefore, providing proper surface coating and developing some effective protection strategies to keep the stability of iron oxide MNPs is very important. These strategies comprise grafting of or coating with organic molecules, including small organic molecules or surfactants, polymers, and biomolecules.

Oleic acid (OA) is a commonly used surfactant to stabilize the magnetic nanoparticles with strong chemical bond between the carboxylic acid and the amorphous iron oxide nanoparticles [6]. Practically, it is worthy that in many cases the protecting shells not only stabilize iron oxide MNPs, but can also be used for stabilization during the encapsulation process.

Generally preparation of MNPs for biochemical applications as bio catalytic magnetic separation systems involved three steps. Firstly, the preparation of magnetic nanoparticles of required size, secondly, the encapsulation of the nanoparticles using suitable polymer with active functional groups and lastly attachment of a desired functional group such as anhydride which is suitable to bind a targeted active component such as enzyme for biochemical applications. In our work we studied two stages of magnetic separation system formation.

II. Results and Discussion

The main goal of this paper was to study the formation of MNPs encapsulated in paraffin core by developed “extraction-coacervation” technique in the presence of heterofunctional shell-forming copolymer.

Our work was conventionally divided into two stages: 1. synthesis of modified by oleic acid Fe₃O₄ nanoparticles; 2. capsule formation of modified Fe₃O₄ MNPs in paraffin core using synthesized heterofunctional acrylate copolymer under various conditions and studying the properties of the formed microcapsules (MCs).

Synthesis and modification of the Fe₃O₄ MNPs

The magnetite nanoparticles were prepared by a co-precipitation method [7] under optimal conditions. FeCl₃·6H₂O (about 0.046 mol) and FeSO₄·7H₂O (about 0.023 mol) were dissolved in deionized water in a 80 mL three-necked flask and heated to 318 K. The solution was bubbled with nitrogen gas to prevent unwanted oxidation. Then ammonium hydroxide (25%) was added quickly into the iron solution under vigorous stirring (800 rpm.)

\[2\text{FeCl}_3\cdot6\text{H}_2\text{O} + \text{FeSO}_4\cdot7\text{H}_2\text{O} + 8\text{NH}_4\text{OH} \rightarrow \text{Fe}_3\text{O}_4 + 6\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{SO}_4 + 23\text{H}_2\text{O}\]

After 30 min oleic acid (OA, 3 mL) was added into the mixture to modify the Fe₃O₄ MNPs and the mixture was heated to 353 K.

After 1 h, the resulting Fe₃O₄ MNPs (black precipitate) were collected from the solution by magnetic separation and washed several times with deionized water and ethanol and then the suspension of the MNPs in ethyl acetate (EA) was prepared.

Encapsulation of Fe₃O₄ MNPs

Synthesized heterofunctional copolymer (HFC) of acrylonitrile (AN), butyl methacrylate (BMA), styrene
(ST), maleic anhydride (MA) with the composition AN:BMA:ST:MA = 50:28:14:8 mol% was used as dispersion stabilizer and shell-forming agent during microcapsule formation. Encapsulation of MNPs was carried out by developed “extraction-coacervation” technique [8].

Encapsulation was carried out in three-necked flask with propeller stirrer. The suspension of NMPs in solution of paraffin and HFC in ethyl acetate (Fe3O4:paraffin:HFC = 1:7:22 wt ratio) was added to the solution of EA in water with 1% polyvinyl alcohol (used as surfactant) at 313-323 K and different [organic phase]:[water] ratios under vigorous stirring (400, 450 rpm). After formation of stable dispersion, water was dropwise added and brown particles were formed. Formation of the microcapsules occurred due to the process of phase separation that passes as a result of EA solvent extraction with gradually forming of the solids MC which are filled with hydrocarbon and MNPs.

After finishing of the encapsulation the reaction medium was loaded into the glass and finely was washed with 400 mL of water for flushing particles from surfactant and EA. The resulting MCs with Fe3O4 MNPs were separated by filtration through a nylon sieve (sieve pore size was 10 microns) and repeatedly was washed with water. The resulting wet MCs were dried at room temperature and atmospheric pressure to constant weight.

As a result, we obtained spherical MCs with MNPs in paraffin core and polymer functional shell Fig. 1.

![Fig. 1. Micrographs of MCs with encapsulated Fe3O4 MNPs of synthesis: a) №1; b) №3; c) №4](image)

Formation conditions and size characteristics of synthesized MCs are presented in Table 1.

<table>
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<th>No</th>
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<th>Stirring rate, rpm</th>
<th>d_n, μm</th>
<th>d_w, μm</th>
<th>k</th>
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<tr>
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<td>1.32</td>
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<td></td>
<td>38.1</td>
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</table>

In accordance to obtained results (Table 1), the increasing of the stirring rate leads to formation of particles with smaller size and at the same time the polydispersity index also reduces. The increasing of surfactant amount in the system leads to decreasing number-average (d_n) and weight-average (d_w) diameter of MCs and reduces their coefficient polydispersity (k).

As it is shown in photos (Fig. 2) MCs with encapsulated Fe3O4 MCs possess magnetic properties (they are collected by neodymium magnet).

![Fig. 2. MCs of synthesis №3 with encapsulated Fe3O4 MNPs: a) dried MCs after synthesis; b) MCs in water (left position) and MC in 1.5% water solution of HCl (right position)](image)

It should be noted that obtained MCs are stable in solution of 1.5 % HCl and after 1 month MNPs still possess magnetic properties (see Fig 2b) that proves the encapsulation of magnetic particles in paraffin core.

**Conclusion**

Thus, the developed “extraction-coacervation” technique provides the encapsulation of Fe3O4 magnetic nanoparticles into paraffin microcapsules. Synthesized MCs possess magnetic properties and are covered with heterofunctional copolymer shell. Depending on formation conditions spherical MCs with size from 24 to 110 μm and polydispersity index 1.32-1.60 were synthesized. Obtained MCs possess magnetic properties after treatment by water solution of HCl during 1 month.

**References**


