



# Synthesis and magnetic properties of inverted core-shell polyaniline–ferrite composite

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## ABSTRACT

The present paper studies the effect of polyaniline grafting on magnetite functionalized with aminopropyltrimethoxysilane. All the compounds were characterized by analytical techniques (X-ray fluorescence, X-ray diffraction, Fourier transform infrared spectroscopy, thermal analysis, Transmission electron microscopy), as well as by determining their magnetic properties. The electron microscopy analysis of the hybrids shows similar morphologies for all the samples. The presence of the iron atoms on the surface of the final product supports the idea of the existence of an inverted core-shell type structure, the more polar ferrite orienting itself towards water. The correlation between the maximum grafting probability and the maximum magnetization is evidenced, demonstrating the importance of the polymer grafting method on the magnetic properties.

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## 1. Introduction

The polyaniline–magnetite (PANI–Fe<sub>3</sub>O<sub>4</sub>) composites are recommended for obtaining magnetic composites with epoxy resin [1], polyurethanes [2] or polymethacrylic acid [3]. The hybrid aqueous dispersions PANI–Fe<sub>3</sub>O<sub>4</sub> are efficient reactives for the removal of dyes [4–6] or heavy metals from waste water [7,8]. Also, the PANI–magnetite composites can serve as support for the immobilization of enzymes [9–11] or antibodies [12], as well as for the development of biosensors [13] or as magnetic resonance imaging (MRI) contrast agents [14]. Due to their inductive heating properties, these types of composites are used for local treatment of cancer by hyperthermia [15]. Other applications for PANI–Fe<sub>3</sub>O<sub>4</sub> composites, such as for the development of supercapacitors [16] or microwave absorbent materials [17] have been studied.

The presented applications represent, of course, only a minor part of the possible uses of the selected composites; several review papers exhaustively present their properties and possible applications [18–22].

The final properties of the PANI–Fe<sub>3</sub>O<sub>4</sub> hybrids are strongly affected by the interactions between the two partners [23]. Literature data suggests a small probability of interaction between the filler and the polymeric matrix: Fe<sub>3</sub>O<sub>4</sub> is very polar [24] and the PANI macromolecules are strongly aggregated due to hydrogen and  $\pi$ – $\pi$  bonds [14,25]. The changes in the infrared spectra of the composites compared to those of the components show some electrostatic/hydrogen bond interactions [26].

The magnetic properties of PANI–Fe<sub>3</sub>O<sub>4</sub> composites are also in a strong connection with the final morphology and crystallinity of the composite and the synthesis methods followed: Patil et al. [27] obtained polyaniline–magnetite composites through self-polymerization of monomer aniline showing weak ferromagnetic behaviour, with hysteresis; the PANI–Fe<sub>3</sub>O<sub>4</sub> nanocomposites obtained by a surface initialized polymerization method by Gu et al. [28] show a strong correlation between the dielectrical properties and the Fe<sub>3</sub>O<sub>4</sub> loading; also the composites show a larger positive magnetoresistance compared with pure PANI.

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Kumar and Jain [29] obtained superparamagnetic nanocomposites using a reverse microemulsion technique. Elsayed et al. [30] obtained, by in situ precipitation method, polyaniline-magnetite and polyaniline-cobalt ferrite nanocomposites with ferromagnetic behaviour. For the initial phase of the ANI polymerization, an electrostatic interaction between the monomer cation and the ferrite nanoparticles is considered [31]. The existence of special electrical and magnetic properties at a certain gravimetric ratio between partners also show some limited interactions [25]. A method of increasing the interactions between PANI and the magnetic nanofillers is to create covalent bonds between the two partners. This bond can be obtained by functionalizing the magnetite with aminopropyl-trialkoxysilane [24,26]. The amino group fixed on the ferrite can take part in the reaction by copolymerization with the monomer during its oxidative polymerization, in most cases with alkaline persulfates [24,26]. Ferrites functionalized with amino groups represent the subject of several studies aiming for further functionalization with enzymes or other biological substrates. The papers of Bruce et al. [32,33] prove that, if the reaction of the magnetite takes place in aprotic organic solvents, the resulted APTES (aminopropyltriethoxysilane) concentration on the ferrites is greater than if the reaction is done in the presence of water [32]. By repeated washing, a part of APTES is removed, due to the presence of an absorption phenomenon and not a grafting one. In presence of water this phenomenon is not noticed [32]. Several studies regarding the synthesis of core-shell polymer particles highlight the existence of two parameters, thermodynamic and kinetic, affecting the final morphology [34–38]. The thermodynamic parameters affect the final morphology according to the principle of surface free energy change. Thus, if the core particles are more hydrophilic than the polymer formed in the second stage, it is possible to obtain different structures and even inverted core-shell particles [34]. This is also the case of the PANI-magnetite synthesis: ferrite is more polar than the polymer. If literature data presents the PANI containing core-shell composites with polymer coating [5,6,9,10], we present a simple method of functionalization of ferrite with APTES by adding the functionalizing agent in the reaction mixture in which the magnetic filler was synthesized, obtaining an inverted core-shell structure, with polymeric core and magnetic shell. Existing papers mention that the iron atoms in the PANI-Fe<sub>3</sub>O<sub>4</sub> composites [11] or in the magnetite functionalized with amino trialkoxysilane [39] can influence the activity of some biological substances. To avoid these effects, magnetite was coated with a silica protective layer and then the aminosilanes were grafted [39,40]. Also, we synthesized magnetite that was covered with silica shell by the sol-gel process of the tetraethoxysilane (TEOS), and then APTES was grafted using the same simple method. The two stages that follow the Fe<sub>3</sub>O<sub>4</sub> synthesis were also done in the initial Massart-type reaction medium, using FeCl<sub>2</sub> and FeCl<sub>3</sub> [3,24,26,32].

Two types of synthesis pathways (polymerization of ANI in the presence of magnetite or firstly the polymerization of ANI followed by the formation of magnetite), are considered when discussing the final morphology of the composites. In the present work it is also studied the possibility of obtaining inverted core-shell composites when PANI is synthesized in the presence of more polar ferrite. For comparison, composites in which the ferrite is synthesized after ANI polymerization were also obtained. The properties comparison of the obtained composites, using the two syntheses pathways, offer important information for selecting the materials considering their intended applications.

From the current state-of-the art, it can be concluded that the possibility of obtaining inverted core-shell PANI-ferrite hybrids was not demonstrated so far. The present paper aims to investigate this type of composites.

## 2. Materials and methods

### 2.1. Reactives

Aniline hydrochloride (ANIHCl) (Sigma-Aldrich), ammonium persulfate (APS) (Sigma-Aldrich), FeCl<sub>3</sub>·6H<sub>2</sub>O and FeCl<sub>2</sub>·4H<sub>2</sub>O (Merck), aminopropyltriethoxysilane (APTES) (Aldrich), tetraethoxysilane (TEOS) (Merck-Schuchardt), N-methylpyrrolidone (NMP) (Sigma-Aldrich), NH<sub>4</sub>OH (25%) (Chimreactiv) have been used without further purification.

### 2.2. Synthesis conditions

#### 2.2.1. Ferrites

The synthesis of the magnetite was performed by adapting a previously used method [24–26,31,41].

In a three-neck flask provided with mechanical stirring, a mixture of 120 ml NH<sub>4</sub>OH (25%) and 130 ml water was introduced. The whole mixture was purged with nitrogen. A mixture formed by (2g FeCl<sub>2</sub>·4H<sub>2</sub>O + 10 ml HCl 1N) and (5,4 g FeCl<sub>3</sub>·6H<sub>2</sub>O + 20 ml water) was added. The reaction took place at 25 °C. A black precipitate appeared immediately after the addition of the iron salts. After one hour of reaction the stirring was stopped and the magnetite was separated using a magnet. The precipitate was washed twice with 200 ml water each time, and was filtered and dried in vacuum (method A, Table 1).

The functionalization of magnetite was done by adding 0.42 g APTES in three different ways. In method B presented in Table 1, APTES was added simultaneously with the iron salts dissolved in water. In method C, the same amount of aminosilane was added after the precipitation of magnetite, as in method A.

In method D (Table 1), 0.42 g APTES were added after the precipitation of magnetite as in method A and then it was functionalized with 2 g TEOS. The goal of method E (Table 1) was the synthesis of Fe<sub>2</sub>O<sub>3</sub>, in order to compare the differences between the composites with different iron oxides. In this synthesis method, 5.4 g FeCl<sub>3</sub>·6H<sub>2</sub>O dissolved in 20 ml of water were added to a mixture formed by 80 ml NH<sub>4</sub>OH (25%) and 100 ml water. The precipitated was formed during 1 h, was decanted and washed with 200 ml water. Finally it was dried in vacuum.

#### 2.2.2. PANI and magnetic composites

The PANI synthesis was carried out by the polymerization of ANIHCl with APS and using sonication [26,30]. In a glass flask with mechanical stirrer were introduced 1.3 g ANIHCl and 45 ml water. The whole mixture was purged with nitrogen and sonicated for 30 min, while the flask was kept in water and ice. Then 2.8 g APS dissolved in 5 ml water were dripped.

The reaction mixture was kept in a water and ice bath, under ultrasonication for 4 h. It was left overnight at rest and then decanted, washed twice with 100 ml water each time, filtered and dried in vacuum. In this way the PANI-emeraldine salt (PANI-ES) was obtained (sample 1, Table 2). To obtain the PANI-emeraldine base (PANI-EB), the same procedure was followed and finally the mixture polymer-water was treated with a mixture of 35 ml NH<sub>4</sub>OH 25% and 38 ml water. The obtained mixture was washed and dried as described above (sample 2, Table 2).

The synthesis of PANI hybrids was carried out in two ways. In the first method, the ANIHCl was polymerized in the presence of different amounts of ferrite, as mentioned in Table 2. The A-type ferrite samples have been named A-3 (PANI-ES) and A-4 (PANI-EB). The samples resulted from the synthesis of the other hybrids with different ferrite types were denoted indicating the inorganic component type followed by the current number (Table 2).

The second synthesis method was carried out by firstly polymerizing the ANIHCl. Then ferrite precursors (FeCl<sub>2</sub>, FeCl<sub>3</sub>) and a

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