

XRD AND SEM ANALYSIS OF IRON OXIDE NANOPARTICLES FORMATION IN POLYAMIDE TEXTILE MATERIAL

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Abstract: Functional textile materials with magnetic properties were prepared by synthesis of magnetite nanoparticles using ferric chloride, ferrous sulphate and sodium hydroxide. The morphology, crystal phase, magnetization properties and chemical structure of the textile materials were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), vibrating sample magnetometry (VSM) and energy dispersive X-ray spectroscopy (EDX). It was found that Fe_3O_4 nanoparticles with average crystal sizes of about 12.5 nm. The uniform distribution of the iron oxide nanoparticles on the fiber surface was confirmed by SEM and EDX. The magnetite treated samples showed reasonable saturation magnetization values of about $7.5 \text{ emu}\cdot\text{g}^{-1}$. Interestingly, the tensile properties of the treated samples were enhanced compared with the untreated polyamide textile materials.

Key words: iron oxide nanoparticles, textile material, fiber, scanning electron microscopy, X-ray diffraction.

1 INTRODUCTION

Over the past decade, there is increased interest in multi-functional textiles with potential technological application. Development of textile products that contain magnetic nanoparticles will provide the new properties for various applications [1-12]. The search for new approaches and methods for the creation of textile materials that contain nanoparticles of iron-oxide compounds is connected with the possible development of nanocomposite textile materials with a set of specified properties (magnetic and protective). Obtaining and investigation of properties of iron-oxide nanoparticles compounds are the subject of many studies, but to the questions of obtaining of the magnetic textile materials are devoted only a few works [13-15].

The purpose of the study: The investigation of morphological and structural characteristics the starting materials and of the magnetic nanocomposites based on them using XRD and SEM, determination of the chemical composition the surface of the textile material before and after the modification, determination of a particle size of the iron oxide inside and on the surface of the obtained composite materials.

2 EXPERIMENTAL

For studies was used polyamide comprehensive thread with a linear density of 15.6 tex and polyamide knitted fabric, which is obtained from this polyamide thread. There investigated of magnetite powder form synthesized without fiber under the same technology [13, 15].

Polyamide textile material containing particles of synthetic magnetite was obtained of using the mechanism *in situ*. As reagents were used chemical substances without further purification: iron chloride (FeCl_3), ferrous sulphate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$) and ammonium hydroxide (NH_4OH).

Prior to the treatment polyamide fiber material washed with 1 g/l non-ionic detergent at 60°C for 20 minutes and then washed with distilled water to remove any impurities. Iron oxide particles were synthesized in the bath, in the presence of polyamide fiber material, that contains reagents FeCl_3 , $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ in amounts previously calculated ($\text{Fe}^{2+}/\text{Fe}^{3+}$ molar ratio = 2) and NH_4OH (pH = 11-12), total volume manufacturing bath is brought to 100 ml with distilled water. The process was carried out at 100°C for 1 h, resulting in the preparation of magnetite particles. Finally, the treated samples were washed with distilled water for 10 min and dried at room temperature.

X-ray diffraction analysis (XRD) was performed with a DRON-UM1 X-ray diffractometer using a Co K α radiation source ($I = 1.5418 \text{ \AA}$) operating at 40 kV to investigate the crystalline size and phases of the synthesized iron oxide nanoparticles in the polyamide fiber. The angular range was of $10\text{--}80^\circ$, in increments of 0.05° . Diffraction patterns are recorded digitally in a file format 2θ ($^\circ$) – I (intensity, s^{-1}) and shown in Figure 1.

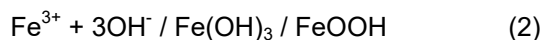
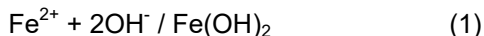
The surface morphology of the treated polyamide materials were characterized by scanning electron microscopy MIRA 3 LMU, Tescan, with a resolution of $\pm 1 \text{ nm}$ and energy-dispersive spectroscopy (EDX)

with chemical analysis Oxford X – MAX 80 mm² with appliance uncertainty ±1%.

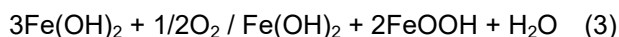
3 RESULTS AND DISCUSSION

Synthesis of iron oxide nanoparticles

In the preparation method, the iron oxide nanoparticles were formed after mixing the iron salts with NaOH solution. The end product is a black precipitate of Fe₃O₄ nanoparticles or red-brown hematite nanoparticles, depending on the applied temperature. The following reactions may proceed resulting in the nanoparticle compound:



FeOOH can be also formed by the partial oxidation of ferrous hydroxide by oxygen in dissolved air according to reaction (3).



In this study, the Fe²⁺/Fe³⁺ molar ratio was more than the stoichiometric ratio, guaranteeing a sufficient amount of Fe²⁺, complete consumption of FeOOH and the formation of pure magnetite nanoparticles. According to the applied preparation procedure, the synthesis proceeded at high pH value, during which hydroxylation of Fe²⁺ and Fe³⁺ species occurred simultaneously (reactions (1) and (2)). Under the applied conditions as the reaction mixture contained an excess of OH⁻ ions and sufficient amount of iron ions, a large amount of particle seeds instantaneously formed. One hour duration of the process at boiling point allowed enough time for complete growth of the magnetite nucleus. Although the conventional pH for the preparation of magnetite nanoparticles is ~11, herein we adjusted the pH at 12 for simultaneous synthesis of particles in the polyamide fiber. It has been reported that the growth of Fe₃O₄ nuclei happens more easily when the solution pH is higher than 11. Therefore, the mean diameter of Fe₃O₄ nanoparticles increases with the increase of pH to higher than 11.

According to the heterogeneous nucleation process it can be postulated that the local concentration of hydrolyzing ions (Fe³⁺ and Fe²⁺) at the solid/water interface is higher than that in the aqueous bulk phase, thus the iron oxide nanoparticles were more nucleated in the textile materials.

3.1 XRD investigation

Figure 1 shows the XRD spectra of the synthesized iron oxide nanoparticles (a) and the treated polyamide textile materials (b).

By comparison to the XRD pattern of the synthesized magnetite nanoparticles with diffraction peaks at 2θ angles 30°, 35° (major), 43° the successful synthesis of Fe₃O₄ nanoparticles in

the treated polyamide sample can be confirmed by the characteristic peak at 2θ angle 35° in addition to the main peak of the original polyamide fiber at 2θ=17°–25°.

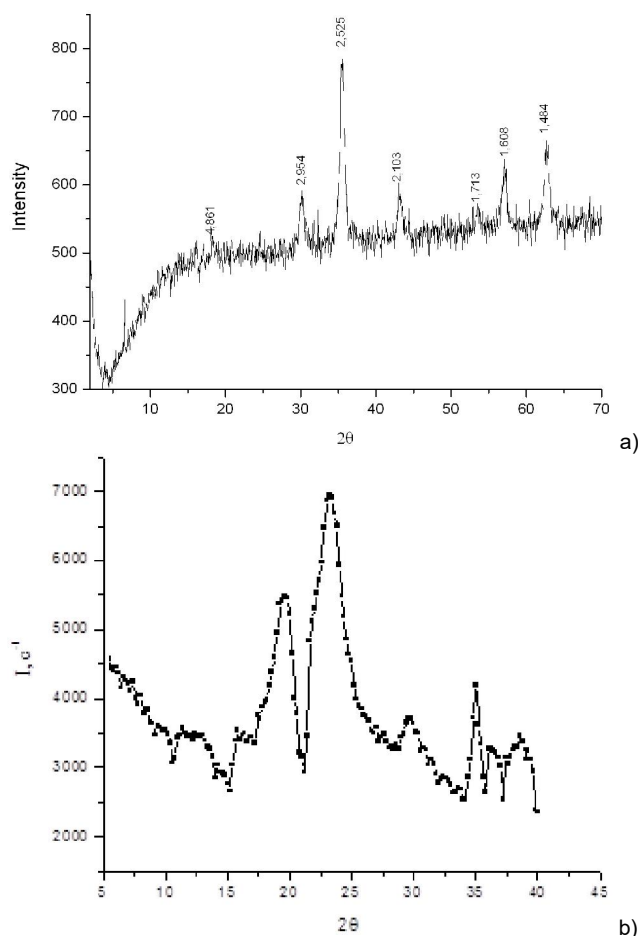


Figure 1 XRD spectra of the a) synthesized iron oxide nanoparticles and the b) treated polyamide textile materials

Using Scherer's equation and from the widths of the peaks at 30°, 35° and 43° the crystallite sizes of the Fe₃O₄ nanopowders and the synthesized nanoparticles in the treated textile materials were calculated to be 11.8 nm, 12.8 nm and 12.9 nm, respectively. The average size of nanoparticles is 12.5±0.47 nm.

For composite polyamide/nanomagnetite average size of the crystals of inorganic phase is 10.0±1.42 nm. For this composite systems also decrease the average size of magnetite crystals during their formation in the volume of polyamide matrix. It can be concluded that the synthesis of nanoparticles in the textile materials inhibited the further growth of the prepared iron oxide crystals resulting in smaller crystal sizes. The crystal structure of the textile materials in the processing did not change, indicating the placing nanomagnetite on the surface of microfibrils or amorphous areas of polyamide structure.

3.2 SEM and EDX analyses

The deposition of nanomagnetite particles in the volume of polyamide textile materials and particle size determination was studied by XRD. However, it is appropriate to consider and explore the surface of the textile materials after treatment with the use of SEM. The SEM images of the untreated polyamide textile materials and polyamide with nanoparticles of the Fe_3O_4 are shown in Figure 2. These micrographs show that there are areas with a continuous layer nanomagnetite and areas where nanomagnetite is in the form of individual particles Fe_3O_4 /aggregates.

This composite system is characterized by coverage of the surface polyamide textile materials slightly higher than 60%, which is possibly due to the relative chemical inertness polyamide as substrate. During the deposition of the nanomagnetite on the surface of polyamide textile materials the layer the Fe_3O_4 nanoparticles with an average thickness of 360 ± 56 nm is formed.

In other parts of the surface covered with a layer of polyamide textile materials can be seen the individual particles of Fe_3O_4 of about 25 nm, the size of their aggregates 100-300 nm and micron size particles. Analysis of surface nanocomposite shows that the average size of individual particles of nanomagnetite is 54 ± 30 nm.

With all things being equal can assume that the low reactivity of polyamide surface slightly affects the stability of the dispersion of magnetite nanoparticles and as a result the aggregation processes are expressed weakly. Formation of large-sized aggregates though it is, but is atypical for this composite system.

The structure of the surface layer of a large quantity identified small in size (about 20 nm) particles of nanomagnetite. Nanocomposites polyamide-nanomagnetite characterized by sufficient iron content in the surface layer, which reaches 22 wt.%.

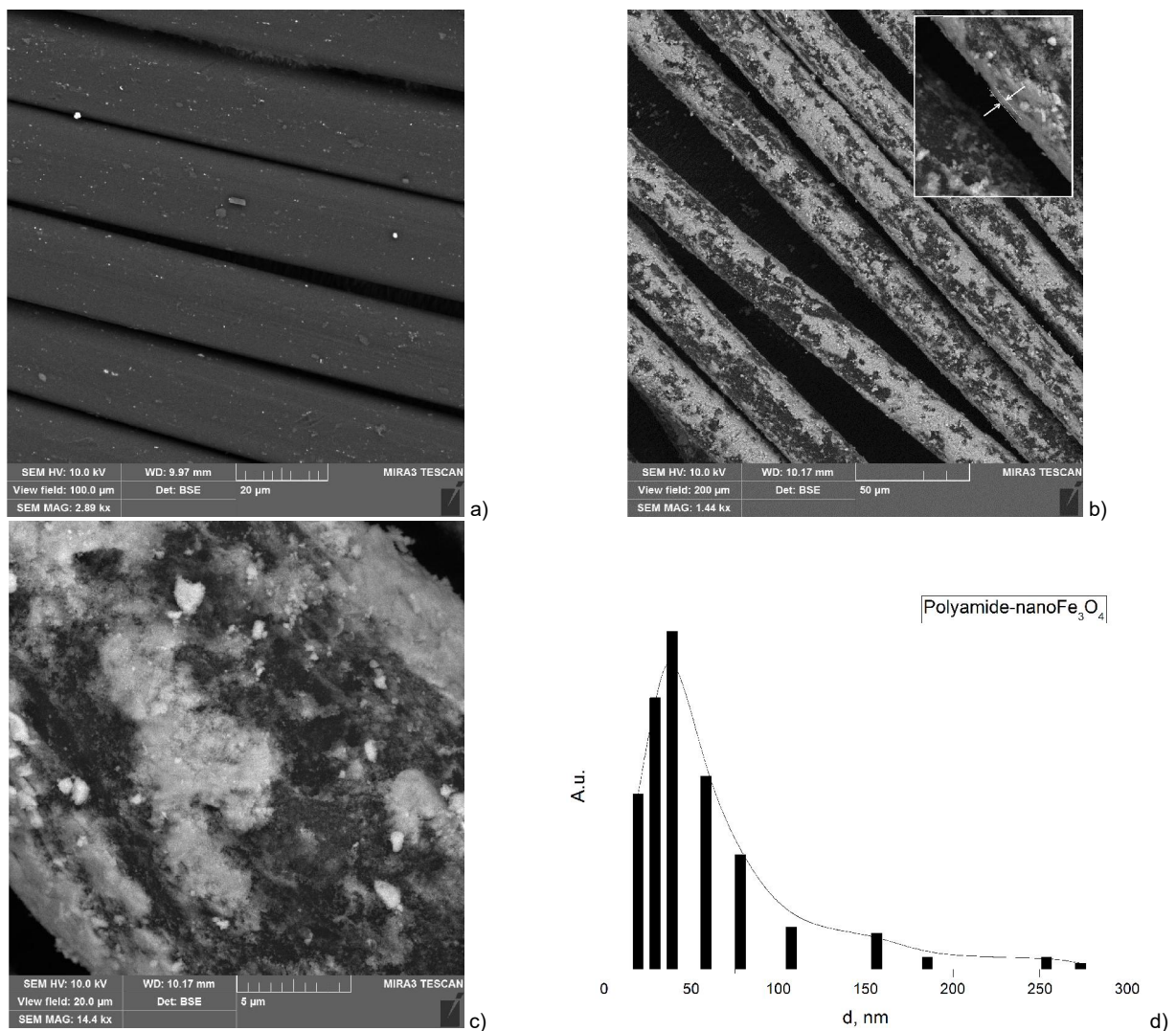


Figure 2 The SEM images of the a) untreated polyamide materials; b, c) polyamide with nanoparticles of the Fe_3O_4 ; and d) the histogram of distribution Fe_3O_4 in size

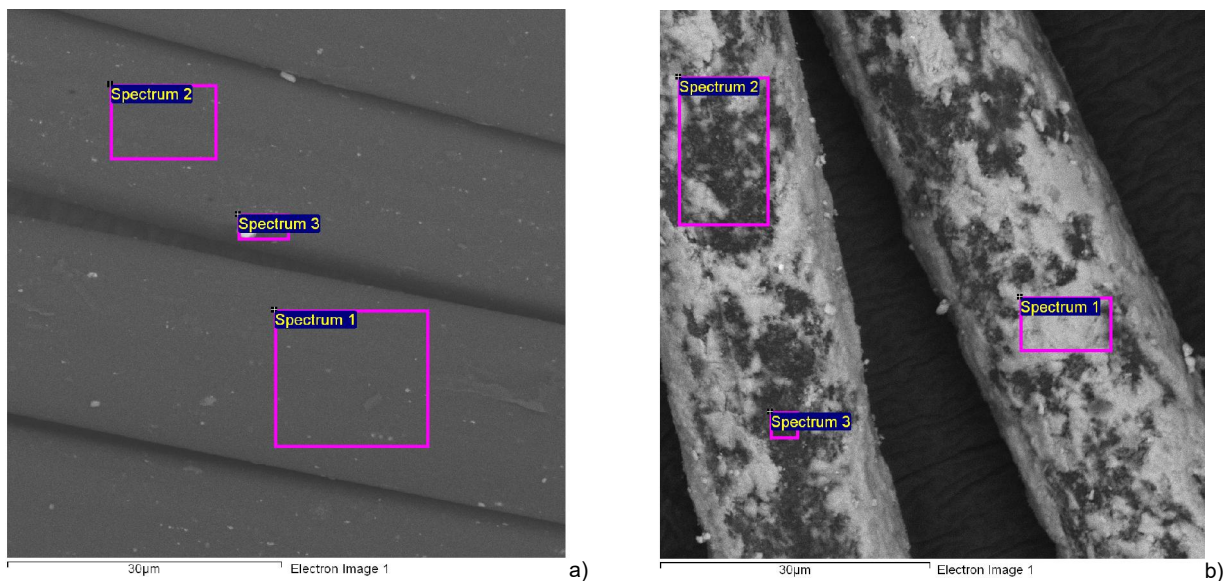


Figure 3 EDX spectra and mapping images of a) untreated and b) treated polyamide samples

The successful synthesis of the iron oxide nanoparticles on the treated samples was further confirmed by the chemical compositions analyzed by EDX. As shown in Figures 3a, 3b and in Table 1, iron and oxygen are two elements on the treated polyamide textile materials apart from the carbon that relates to the polyamide substrate.

Table 1 EDX results of untreated and modified polyamide textile material in selected areas

Elements / Areas of analysis	C	O	Fe
	Contents [%]		
Untreated sample 1	76.2	23.8	-
Untreated sample 2	77.5	22.5	-
Untreated sample 3	72.4	27.6	-
Treated sample, spectra 1	32.5	21.9	45.6
Treated sample, spectra 2	56.8	26.4	16.8
Treated sample, spectra 3	67.8	27.1	5.2

Moreover, the mapping images shown in Figure 3 further confirmed the presence of iron on the treated polyamide textile materials.

3.3 Magnetic properties

The magnetization curves of the synthesized magnetite nanoparticles and their corresponding treated polyamide textile materials were measured using a vibrating-sample magnetometer (VSM) at room temperature and the graphical representation of the relationship between the applied magnetic field (H) and the induced magnetization (M) is shown in Figure 4. A sharp increase in magnetization was observed by increasing the applied field from 0 to 8000 Oe, and the magnetization was saturated at about 7000, 3500, 5500 and 2500 Oe for synthesized magnetite nanoparticles, treated polyamide textile materials.

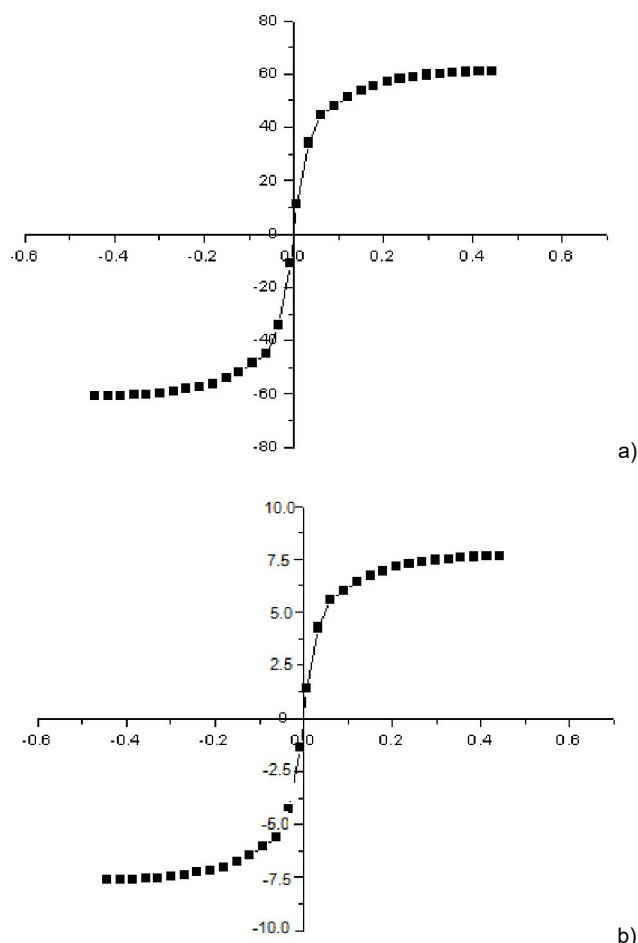


Figure 4 Magnetization curves of a) synthesized Fe_3O_4 nanoparticles, b) treated polyamide textile materials. X axis: magnetic field H [Oe], Y axis: magnetization M [$\text{emu}\cdot\text{g}^{-1}$]

A decrease in saturation magnetization of the treated samples (treated sample: 7.5 emu.g^{-1} , Fe_3O_4 sample: 65 emu.g^{-1}) was obtained compared to the corresponding nanoparticles. Also, it is apparent that the magnetic hysteresis loop was narrow for the treated sample and extremely small coercivity and remanence values were obtained for the iron oxide nanoparticles synthesized on the polyamide indicating the almost superparamagnetic nature of these particles. This transition from ferromagnetic to superparamagnetic behavior could be due to the smaller crystal size of the prepared nanoparticles on the treated polyamide textile materials.

The magnetic sensitivity of the treated polyamide textile materials was also confirmed by attraction towards a magnet. The hydrothermal synthesis of magnetite nanoparticles on polyamide textile materials has been reported to create a magnetic fabric with the saturation magnetization of 3.8 emu.g^{-1} . Therefore, *in situ* synthesis of Fe_3O_4 nanoparticles in polyamide fiber in this study was more effective in producing a magnetic fiber with saturation magnetization of 7.5 emu.g^{-1} .

4 CONCLUSIONS

The possibility of determination of the size of structural elements in a variety of nanocrystalline materials using SEM and XRD methods was analyzed. It is shown that the size of the nanoparticles depends on the methods of synthesis (in powder or with the use fiber matrix by mechanism *in situ*). Functional composites based on the polyamide textile material with stable magnetic properties were obtained. The practical potential of the treated samples in shielding electromagnetic waves was predicted and is under investigation.

There were obtained functional composites based on polyamide textile material with stable magnetic properties. Practical potential of treated textile materials is the ability to shielding of electromagnetic radiation and in the presence of antimicrobial effect and is in the process of research.

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