TEHNOLOGII INOVAȚIONALE PENTRU DEZVOLTAREA DURABILĂ ÎN TEXTILE

PROTECTIVE TEXTILE MATERIALS: OBTAINING AND PROPERTIES

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Abstract: *Protective textile materials with magnetic properties were obtained by* in situ *synthesis of magnetite nanoparticles using ferric chloride, ferrous sulfate and sodium hydroxide. The work is presented of the method of creating of the magnetic textile materials in the process of his modification by the synthesis of the nanoparticles in situ, taking into account the structure of textile material and nanotechnological processes. The morphology, crystal phase, magnetization properties of the treated textile materials were characterize by scanning electron microscopy (SEM), X-ray diffraction (XRD), vibrating sample magnetometry (VSM). It was found that magnetite nanoparticles with average crystal sizes of about 12.5 nm. The magnetite treated samples showed reasonable saturation magnetization values of about 7.5 emu* g^{-1}*. The uniform distribution of the iron oxide nanoparticles on the surface of textile material was confirmed by SEM. Practical potential of treated materials is the ability to protective from shielding of electromagnetic radiation and in the presence of antimicrobial efficacy and is in the process of research.*

Key words: *Nanotechnology, Nanoparticles, Structure, Morphology*, *Treatment.*

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 including magnetism and shielding for protection against electromagnetic radiation. The search for new approaches and methods for the creation of textile materials that contain nanoparticles of iron-oxide compounds linked with the possible creation of textile materials with a set of specified properties (magnetic and protective). Obtaining and properties of iron-oxide nanoparticles compounds are the subject of many studies [1, 2]. But to the questions of obtaining of the magnetic materials are devoted only a few works and the creation of the textile materials with magnetic properties by the treatment for the mechanism of heterocoagulation with using of the surface active substances is presented in [3].

The purpose of the study. Development of the method of creating of textile materials with magnetic properties in the process of his modification by the synthesis of the nanoparticles *in situ*. The investigation of morphological and structural characteristics the starting materials and of the magnetic nanocomposites based on them using XRD and SEM, determination of a particle size of the iron oxide inside and on the surface of the protective textile materials.

2. EXPERIMENTAL

2.1. Materials

For studies used polyamide comprehensive thread with a linear density of 15.6 Tex and polyamide knitted fabric with satin weave, which is obtained from this polyamide thread.

Polyamide textile material containing particles of synthetic magnetite, obtained of using the mechanism *in situ*. As reagents used chemical substances without further purification: iron chloride ($FeCl_3$ * $6H_2O$), ferrous sulfate ($FeSO_4$ * $7H_2O$) and ammonium hydroxide (NH_4OH).

Prior to the treatment polyamide textile material washed with 1 g/l nonionic detergent at 60 °C for 20 minutes, 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 $FeCl_3$ * $6H_2O$, $FeSO_4$ * $7H_2O$ in amounts previously calculated (Fe^{2+}/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.

2.2. Test methods

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

The surface morphology of the treated polyamide materials were characterized by scanning electron microscopy MIRA 3 LMU, Tescan with a resolution of ± 1 nm, and energy-dispersive spectroscopy (EDX) with chemical analysis Oxford X – MAX 80 mm^2 with appliance uncertainty ± 1%.

3. RESULTS

In the proposed method of obtaining of iron oxide particles formed after mixing of the iron salts with a solution of NH_4OH. The final product is a black precipitate of the Fe_3O_4. In this research the molar ratio of Fe^{2+}/Fe^{3+} was more than the stoichio-

metric ratio, which guarantees enough of Fe^{2+}, full consumption of FeOOH and forming particles of pure magnetite. Under the action of the necessary conditions, the reaction mixture containe d an excess of OH^- ions and a sufficient amount of iron ions, which caused to instantaneous formation of a large number of nucleate nanoparticles.

Fig. 1 shows the XRD spectra of the synthesized iron oxide nanoparticles and the treated polyamide textile materials (Fig. 2). By comparison of the XRD pattern of the synthesized magnetite nanoparticles with diffraction peaks at 2*θ* angles 30°, 35° (major), 43° the successful synthesis of Fe_3O_4 nanoparticles in the treated polyamide sample can be confirmed by the characteristic peak at 2*θ* angle 35° in addition to the main peak of the original polyamide textile material at 2θ = 17° – 25°.

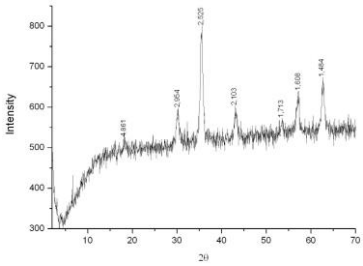


Figure 1: XRD spectra of the synthesized iron oxide nanoparticles

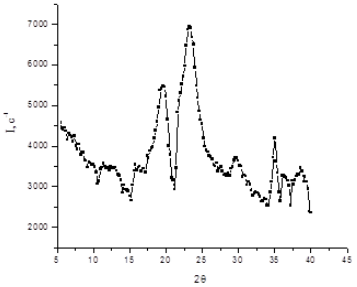


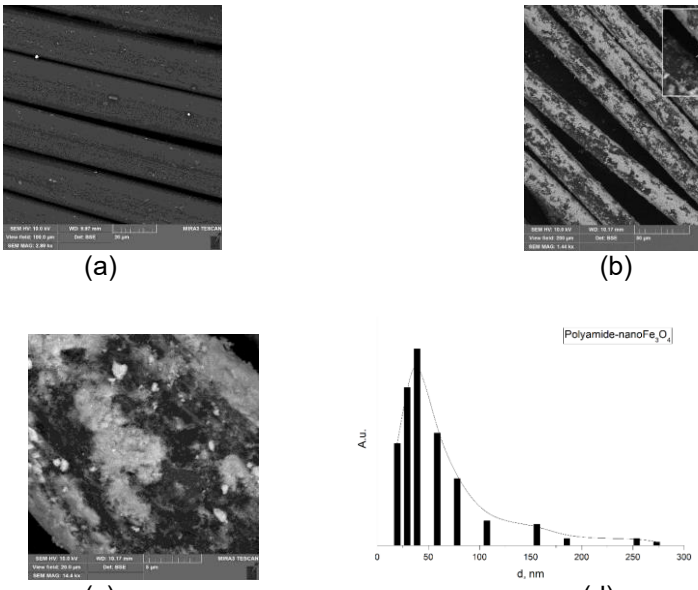
Figure 2: XRD spectra of the treated polyamide textile material

Using Scherer's equation [11] and from the widths of the peaks at *30*°, 35° and 43° the crystallite sizes of the Fe_3O_4 nanopowders and the synthesized nanoparticles in the treated samples 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 magnetite is typical formation of the nanocrystallites with size about 12.5 nm with a relatively low polydispersity (standard deviation of size does not exceed 5%).

The applied mechanism *in situ* for the synthesis of magnetite nanoparticles within the textile material provides for co-precipitation of the particles in the volume of the fiber because determination of the phase composition and the size of synthesized particles investigated by XRD. However, it is appropriate to consider and study the surface of the fibers after treatment with using SEM.

The SEM images of the untreated polyamide material and polyamide material with nanoparticles of the Fe_3O_4 and a histogram of the distribution of the particles at the surface of the studied materials are demonstrated in Fig. 3. It is shown that the

light particles located at the surface the polyamide are the particles of magnetite. Is also seen that there are areas with a continuous a layer of nanomagnetite and areas where the nanomagnetite is located in the form of individual small particles of Fe_3O_4, and in the form of clusters or agglomerates.



(a) (b) (c) (d)

Figure 3: The SEM images of the (a) untreated and treated polyamide materials (b, c), the histogram of distribution of particles in size (d)

That is the particle sizes covered a range from the nanometer to micrometer. The distribution of particles in the surface is evenly, resulting polymodal dependence (Fig. 3, d). The successful synthesis of iron oxide nanoparticles in the treated samples with determining their composition additionally confirmed by energy dispersive analysis (EDX) (Fig. 4 a, b).

(a) (b)

Figure 4: EDX images of (a) untreated and (b) treated polyamide samples

The magnetization curves of magnetite nanoparticles synthesized and treated polyamide textile material was measured using a vibrating magnetometer (VSM) at room temperature. The graphical representation of the relationship between the applied magnetic field (H) and induced magnetization (M) is shown in Fig. 5. The

sharp increase of magnetization observed due to the increase of the applied field from 0 to 4500 Oe. The values of saturation magnetization, in such a case was about 3500 Oe, 3000 Oe, 2500 Oe, 2000 Oe, 1500 Oe and 1000 Oe for of synthesized magnetite nanoparticles and for the treated polyamide textile materials.

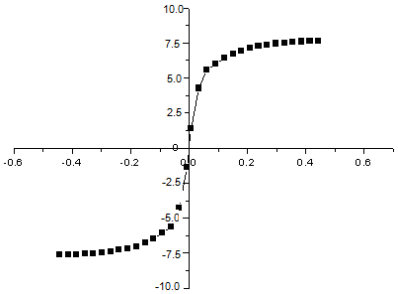


Figure 5: Magnetization curves of treated polyamide textile material.
X axis: magnetic field (H/Oe), *Y* axis: magnetization (M/emu g^{-1})

A decrease of the value of saturation magnetization of the treated samples (for treated sample – 7.5 emu g^{-1}, for Fe_3O_4 – 65 emu g^{-1} [1, 2]) was obtained compared to the corresponding nanoparticles. Moreover, narrow curve of the magnetic hysteresis for treated samples and are extremely small coercivity and remanence values which obtained for iron oxide nanoparticles in polyamide indicates about the almost superparamagnetic nature of these particles.

4. DISCUSSION

For composite polyamide textile material/nanomagnetite average size of the crystallites of inorganic phase is 10.0 ± 1.42 nm. For this composite system, also decrease of the average size of magnetite crystallites during their formation in the volume of polyamide matrix is fixed. It can conclude that the synthesis of nanoparticles in the textile material inhibited the further growth of the prepared iron oxide crystallites contributes to smaller crystallites because textile material, in this case acts as a nanoreactor. The crystal structure of the textile material in the processing did not change, which indicate at the placing nanomagnetite on the surface of microfibrils or in amorphous areas of polyamide structure

For this composite system characterized the coverage of the surface of polyamide textile material, is slightly higher than 60 %, which is possibly due to the relative chemical inertness of polyamide as substrate. During the deposition of the nanomagnetite on the surface of polyamide is formed the layer of Fe_3O_4 nanoparticles with an average thickness of 360 ± 56 nm. On other parts of the polyamide surface covered with a layer of polyamide can see individual particles of Fe_3O_4 of about 25 nm, the size of their aggregates 100 − 300 nm and micron size particles. Analysis of the surface of obtained nanocomposites shows that the average size of individual particles of nanomagnetite is 54 ± 30 nm.

With all things being equal we can assume that the low reactivity of polyamide surface slightly affects the stability of the dispersion of magnetite nanoparticles

and, as a result of the aggregation processes are weakly expressed. Formation of large-sized aggregates though it is, but is atypical for this composite system – polyamide textile materials – nanoparticles of Fe_3O_4. In the structure of the surface layer identified of large quantity of nanomagnetite particles of small by size (about 20 nm). Polyamide-nanomagnetite nanocomposites are characterized by sufficient content of the iron in the surface layer, which reaches 22 wt. %.

The transition from the ferromagnetic to the super paramagnetic behavior can be caused by smaller size crystallites of synthesized nanoparticles in the treated polymer matrix. Therefore, *in situ* synthesis of Fe_3O_4 nanoparticles in polyamide textile materials in this study was more effective in producing a magnetic textile with saturation magnetization of 7.5 emu g^{-1}.

5. CONCLUSIONS

Thus, analyzed the possibility of determining the size of the structural elements in a variety of nanocrystalline materials by XRD and SEM. It is shown that the size of the nanoparticles depends on the methods of synthesis (in powder or with the use textile matrix by mechanism *in situ*). Protective composites based on the base of the polyamide textile materials with stable magnetic properties were obtained. Practical potential of treated materials is the ability to protective from shielding of electromagnetic radiation and in the presence of antimicrobial efficacy and is in the process of research.

6. REFERENCES

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