

# PHYSICO-CHEMICAL PROPERTIES OF MAGNETITES IN NANOCOMPOSITES ON THE TEXTILE BASES

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## ABSTRACT

The article is devoted to investigation of the physico-chemical properties of magnetites in nanocomposites on the textile bases. It studies of the structure and phase composition of nanocomposite materials on the polyamide and viscose textile bases. It is shown that magnetite particles synthesized in textile material with average sizes of 9.4 nm in viscose textile material and 9.7 nm in polyamide textile material. The influence of synthesis conditions on the size of magnetite nanocrystallites in textile material is established.

## KEYWORDS

Textile materials; Magnetite; Structure; Nanotechnology; X-ray phase analysis.

## INTRODUCTION

Today's challenges encourage the search for new approaches and methods of creating textile materials (TM) containing iron oxide compounds of nano sizes, due to the unique properties of magnetic nanoparticles [1–4], for example, their ability to absorb microwaves and have a bactericidal effect [5]. Currently, for the practical implementation of products that are nanostructured materials, it is necessary to develop new technologies for their production for the successful implementation of the potential of nanotechnology in the consumer properties of the product.

In this regard, the developer must solve the following tasks: to determine the limit of the nanoscale range of dispersed particles of matter; to work out the technology of obtaining the substance in the form of dispersed particles of the substance; to work out the technology of introducing nanoparticles into the appropriate matrix, which protects nanoparticles and preserves the properties of nanoparticles from oxidation. When choosing a method for the synthesis of nanoparticles of magnetic materials, it is necessary to implement the production of nanoparticles of magnetic materials of a given size and shape; to provide nanoparticles of a certain phase composition with reproducible and time-stable properties; to ensure technological simplicity of nanoparticle synthesis.

Many chemical methods can be used to synthesize magnetic nanoparticles [5–11]: synthesis in microemulsions, sol-gel synthesis, chemical reactions using ultrasound, hydrothermal reactions, hydrolysis and thermolysis of precursors, flow-injection synthesis, electrochemical synthesis. These methods are used for the production of nanoparticles of homogeneous composition and with a narrow size distribution. However, the most common method of obtaining magnetic nanoparticles was and remains the method of chemical coprecipitation of iron salts [12–15]. Solving similar problems is of great importance for the development of nanotechnologies for the creation of materials, in order to control the synthesis of nanoscale magnetite by in situ mechanism in nanocomposites based on textiles of different nature. Despite the large number of works performed, in general, this area of research is only at the initial stage of its development. Issues related to the synthesis of magnetite [5–15] and the study of its magnetic properties and structural characteristics in textile materials of various natures have not been studied.

The purpose of this work: study of physico-chemical properties of nanomagnetite by X-ray phase analysis, as well as establishing the influence of synthesis and nanoprocessing conditions on the structure, size of particles of the magnetite and magnetic properties of textile-based nanocomposites.

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## OBJECTS OF INVESTIGATION

For studies as textile materials (TM) was used polyamide (PA) and viscose (Vis) comprehensive threads with a linear density of 15.6 tex and PA and viscose knitted fabrics. These were obtained from polyamide and viscose threads.

## EXPERIMENTAL

Textile materials with nanomagnetic particles are nanocomposites based on textiles (TM/NM). Textile materials with magnetic nanoparticles are prepared as follows. Magnetic textile materials obtained by a two-stage method. Stage 1: iron salts ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) of various concentrations from 40 g / l to 80 g / l are added to the treatment solution at a certain bath module. The resulting solution is stirred for 5 - 10 minutes until complete dissolution of salts. A sample of textile material soaked in distilled water is immersed in the prepared solution. The process of sorption of iron salts continues at a temperature of 95 - 98 °C for 60 - 80 minutes with periodic stirring. Stage 2: the process of co-precipitation of iron salts in the textile material with an aqueous solution of ammonia at pH 10-11 for 60 - 80 minutes. The final stage of processing is washing the obtained sample of textile material with distilled water.

Thus, the formation of nanosized magnetite in textile material of different nature by the in situ mechanism [2]. Textile material acts as a nanoreactor in which magnetite nanoparticles are formed. Next, the obtained magnetic textile material is washed with distilled water and dried.

X-ray phase analysis (XRD) was performed with a DRON-UM1 X-ray diffractometer using a  $\text{Co K}\alpha$  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 of 10 - 80 degrees, in increments of 0.05 degrees. Diffraction patterns are recorded digitally in a file format  $2\theta$  (degrees) - I (Intensity, s-1) and shown in Fig. 1.

The study of the magnetic characteristics of the samples was performed using a magnetometer with a Hall sensor, which is designed to measure the parameters of the hysteresis loop of powder materials. Measurements of the parameters of the magnetization curves and hysteresis loops take place in an open magnetic circuit.

## RESULTS AND DISCUSSION

On the diffractograms of the synthesized nanomagnetite (NM) particles in the absence of textile material, differing in the initial concentration of iron salt in the treatment bath: a) 10 (C10), b) 40 (C40), c) 60 (C60) g/l (Fig. 1), the presence of a number of reflexes with angular position  $2\theta$  18.3°, 30.1°, 35.5°, 37.0°, 43.1°, 53.6°, 57.1° and 62.3° was identified, corresponding to the scattering maxima of the planes (111), (220), (311), (222), (400), (422), (511) and (440) nanocrystals, respectively, according to the PDF-2 database, ICDD n. 880866).

Reflexes of the (220), (311) and (400) planes of magnetite nanocrystals are usually used to calculate the crystal size with the required accuracy. Using the Bragg equation (1), the indices of the interplanar distance  $d_{hkl}$  were calculated:

$$d_{hkl} = \frac{\lambda}{2 \sin \Theta}, \quad (1),$$

where  $d_{hkl}$  – interplanar distance [Å],  $\lambda$  - wavelength used  $\lambda$  ( $\text{CuK}\alpha$ ) = 1.54051[Å],  $\theta$  - diffraction angle [°],  $k = 0.89$ .

According to the obtained results, the values of  $d_{hkl}$  do not depend on the conditions of nanomagnetite synthesis, which indicates the same mechanism of formation of the crystalline phase of the particles. The results of the calculation of the size of nanomagnetite crystals are given in Table 1.

Using the Debye-Scherrer formula (2), the average size of magnetite crystallites was determined [10]:

$$d = \frac{k\lambda}{\beta \cos \theta}, \quad (2),$$

where  $d$  - the average size of the crystallites [nm],  $\lambda$  - wavelength used  $\lambda$  ( $\text{CuK}\alpha$ ) = 1.54051[Å],  $\beta$  - width of the peak at half height,  $\theta$  - diffraction angle [°],  $k = 0.89$ .

Samples C10 and C60 are characterized by the formation of larger magnetite nanocrystals (16.4 nm and 12.5 nm, respectively) with relatively low polydispersity (standard deviation of size does not exceed 5 %). Sample C40 has a smaller average size of magnetite nanocrystals (about 11 nm), but the standard deviation is much larger (~ 15 %). The most probable reason for this behavior is the synthesis conditions, such as the concentration of iron salt in the treatment bath. The lower concentration of iron salt provides fewer crystallization centers and the possibility of their growth. The high concentration of reagents (60 g/l of iron salt in the original bath), on the contrary, promotes the formation of a large number of nucleation centers and ensures uniform growth of particles and the formation of nanocrystals similar in size.

**Table 1.** The results of X-ray phase analysis of nanomagnetite (NM) samples

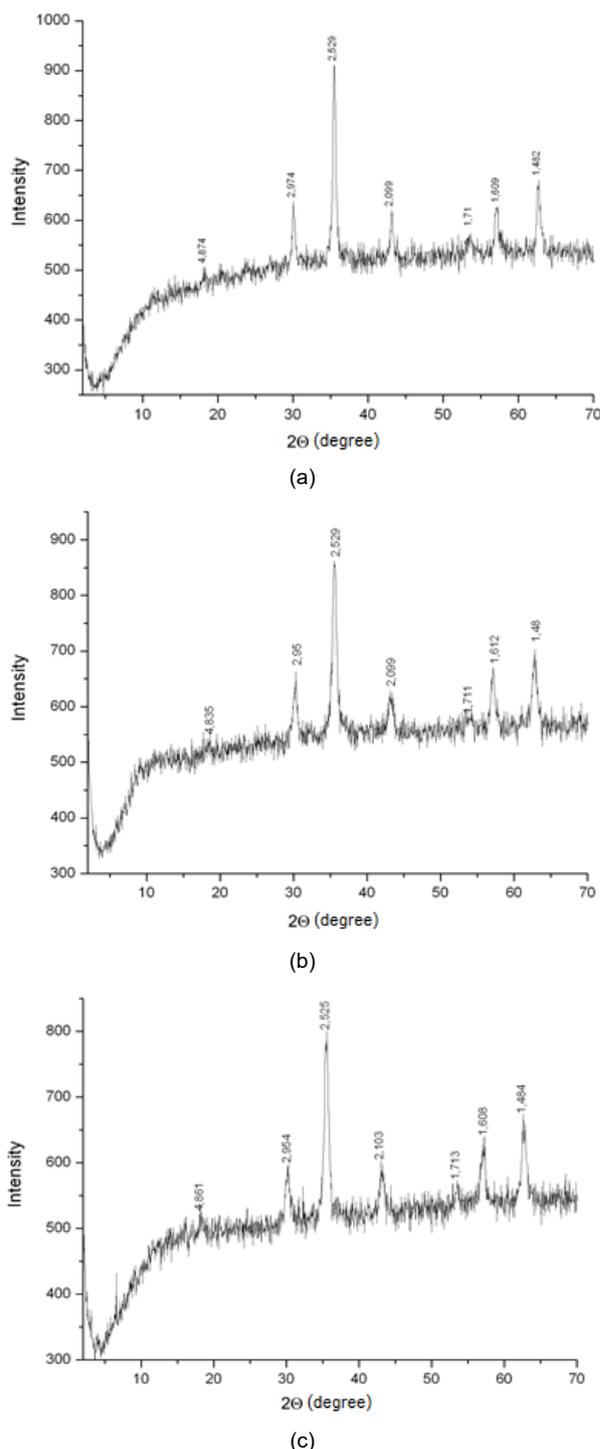
NM	2 $\theta$ [°]	Crystal lattice	d <sub>hkl</sub> [Å]	D <sub>hkl</sub> [nm]	d [nm]
c10	30.1	(220)	2.97	15.2	16.4±0.8
	35.5	(311)	2.53	16.7	
	43.1	(400)	2.10	17.4	
c40	30.1	(220)	2.95	13.3	10.9±1.6
	35.5	(311)	2.53	10.8	
	43.1	(400)	2.10	8.6	
c60	30.1	(220)	2.95	11.8	12.5±0.5
	35.5	(311)	2.53	12.8	
	43.1	(400)	2.10	12.9	

Diffraction patterns of X-ray phase analysis of samples of TM/NM composites are shown in Fig. 2. Analysis of the inorganic phase (nanomagnetite) of the viscose TM/NM composite shows that the size of nanomagnetite crystals is  $9.4 \pm 1.1$  nm when passing an X-ray beam through the central part of the TM/NM system (designation "equator" (E) in table 2) containing NM. When transmitting a beam of radiation near the surface of the composite (through the surface layer of nanoparticles immobilized on the surface of the fibers; denoted as "meridian" (M) the size of nanomagnetite crystals is  $14.7 \pm 5.3$  nm (Table 2).

For nanocomposite polyamide TM/NM, the average crystal size of the inorganic phase is  $10.0 \pm 1.42$  nm (measurement in the "meridian" mode) and  $9.7 \pm 1.2$  nm when measured in the "equator" mode. For this composite system, there is also a decrease in the average size of magnetite crystals during their formation in the volume of the fiber-forming polymer - polyamide TM. Assuming that the content of magnetite nanoparticles in the volume of different types of polymer fibers is the same, there is no doubt that cellulose macro chains are more active and affect the formation of nucleation centers of the crystalline inorganic phase and their growth. It should be noted that for both composites the values of the interplanar distance are very close, which indicates a similar mechanism of in situ formation of the inorganic phase Fe<sub>3</sub>O<sub>4</sub>.

The crystal structure of TM in the process of modification did not change (Fig. 3), which indicated the location of NM on the surface of cellulosic microfibrils (viscous TM) or in amorphous zones of cellulosic and polyamide structure. The saturation magnetization of nanocomposites based on textiles are from 2 A\*m<sup>2</sup>/kg to 10 A\*m<sup>2</sup>/kg.

It is important that the coprecipitation of iron salts in a strongly alkaline medium with the formation of nanomagnetite in TM occurred to a greater extent in viscous TM, given its crystalline-amorphous structure. And less in polyamide TM, which was confirmed experimentally and reflected by the lower profile intensity of the most important reflex at 2 $\theta$  = 35° on the presented diffraction patterns (Fig. 2).

**Figure 1.** Diffraction patterns of magnetite nanoparticle samples obtained under different synthesis conditions.

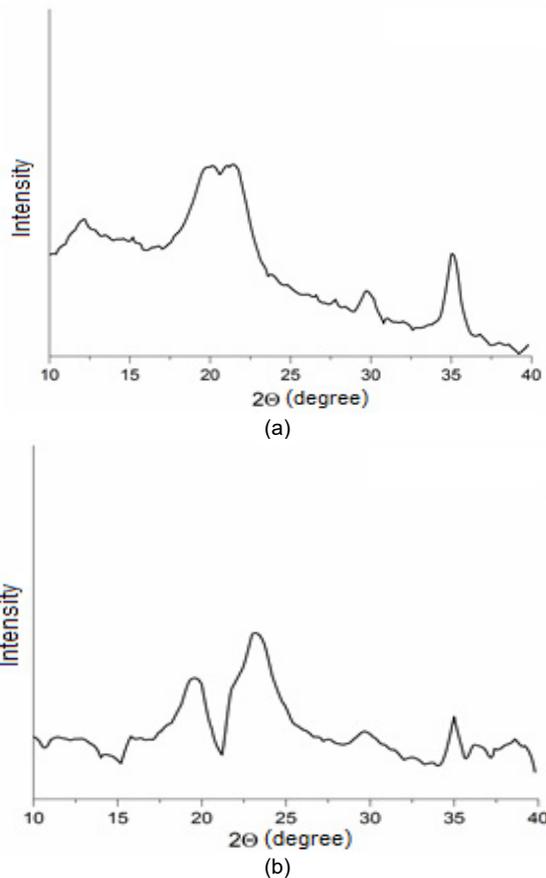
Diagrams of changes in the intensity of X-ray scattering during the rotation of TM with nanomagnetite around its own axis relative to the radiation source are shown in Fig. 4. Analysis of the scattering intensity shows the close nature of the distribution of phase inhomogeneity in both textile composites.

**Table 2.** The results of X-ray phase analysis of textile materials with nanomagnetite (TM/NM)

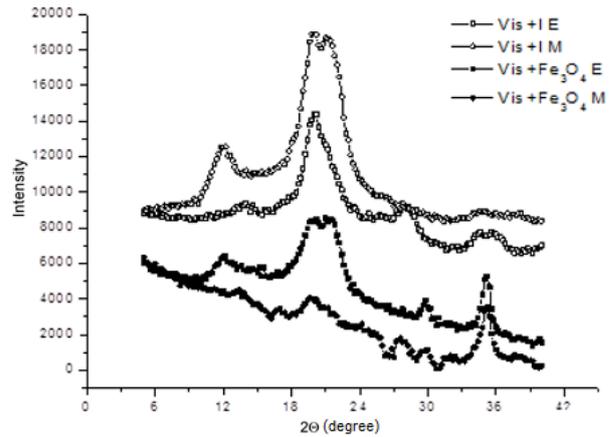
TM/NM	Mode	2θ [°]	d <sub>hkl</sub> [Å]	D <sub>hkl</sub> [nm]	d, [nm]
Viscose TM/NM	M	29.9	2.98	20.0	14.7±5.3
		35.1	2.55	9.4	
	E	29.8	2.99	9.3	9.4±1.1
		35.2	2.55	9.5	
Poly-amide TM/NM	M	30.0	2.98	10.2	10.0±1.4
		35.3	2.54	9.8	
	E	29.8	2.99	8.5	9.7±1.2
		35.0	2.56	10.9	

Since the intensity distribution is obtained by comparing the X-ray diffraction of the original TM and composites based on them, the angular regions marked on the diagram with increased scattering intensity are due to the presence of a certain structured inorganic component. For the obtained composites, the angular position of the wide scattering region practically coincides and lies in the range of 70 - 170° (polyamide TM / HM) and 80 - 160° (viscose TM / HM).

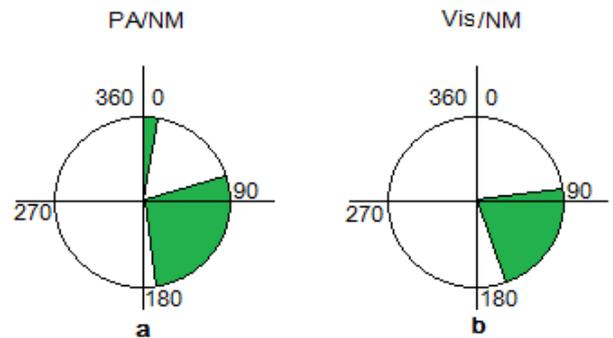
The reasons for the manifestation of such structural activity of the polymer fiber-forming matrix can most likely be related either to the activity of functional groups of polymer macro chains relative to the surface of magnetite nanocrystals or to the influence of polyamide TM macro chain ordering on nanomagnetite particle growth processes.



**Figure 2.** X-ray diffraction patterns of polyamide (a) and viscose (b) TM containing nanomagnetite.



**Figure 3.** X-ray diffraction patterns of untreated viscose TM (Vis) and viscose TM containing nanomagnetite (Vis+Fe<sub>3</sub>O<sub>4</sub>).



**Figure 4.** Distribution of X-ray scattering intensity with different orientation of the radiation source. Areas with increased, relative to the general background, scattering intensity are marked by color.

From obtained experimental data it can be stated that the structuring effect of viscose TM macro chains is more significant. This system is characterized by a more significant reduction in the size of nanocrystallites of the inorganic phase - nanomagnetite (from 14.7 to 9.4 nm). As well as a narrower range of X-ray scattering angles in determining the orientation of magnetite nanocrystals in the volume of the viscose fiber-forming matrix (Fig. 4).

Thus, it can be argued that using cellulosic (viscose) and PA textile materials is more promising because it allows more precise control of the phase and chemical composition of magnetic nanocomposites on a textile basis. The dependence of the structure, phase composition and particle size on the raw material composition and conditions of synthesis of nanomagnetite formed in the stabilizing fiber-forming matrix was established, which allowed obtaining magnetic textile materials containing magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) with controlled magnetic properties.

## CONCLUSIONS

Determination of the structure and dimensional characteristics by X-ray diffraction of textile nanocomposites revealed a number of patterns necessary for the development of scientific bases of nanotechnologies for the creation of textile materials with magnetic properties. The influence of synthesis conditions on the size of magnetite nanocrystallites in textile material is established. A significant reduction in the size of nanocrystallites of the inorganic phase (from 14.7 to 9.4 nm) and a narrower range of X-ray scattering angles in determining the orientation of magnetite nanocrystals in viscose textile material indicates that the structuring effect of macro chains of cellulose in situ mechanism in a textile-based nanocomposite.

According to the results of X-ray diffraction, it is established that nanoparticles are evenly distributed in the volume of magnetic nanocomposites on a textile basis. The average size of nanoparticles is determined by the synthesis conditions, the concentration of precursors and the nature of the textile material. With increasing precursor concentration in the synthesis of nanomagnetite, the average size of nanoparticles of magnetite  $\text{Fe}_3\text{O}_4$  increases, while for nanocomposites based on viscose TM there is less growth than for nanocomposites based on polyamide TM in the concentration range of 40 - 60 g / l. As the concentration increases, the average size of nanoparticles increases regardless of the raw material composition of the textile material.

The influence of conditions for obtaining textile materials with magnetic properties on their structure and characteristics is determined, which allows to change: particle size from 9.4 nm to 14.7 nm and saturation magnetization from 2  $\text{A}^*\text{m}^2/\text{kg}$  to 10  $\text{A}^*\text{m}^2/\text{kg}$ . Thus, the study of the structure and phase composition of nanocomposite materials revealed the presence of magnetite particles synthesized in textile material with average sizes of 9.4 nm in viscose textile material and 9.7 nm in polyamide textile material. At the current level of methodological development for the quantitative determination of the dimensional characteristics of nanostructured materials, it is advisable to conduct a comprehensive study using various methods, such as scanning electron microscopy.

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