NANOFIBERS WITH MAGNETIC PROPERTIES

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Abstract

The work aims to explain and demonstrate the possibility of preparing nanofibers with specific magnetic properties.

Described is the preparation of ferrite nanoparticles and magnetic nanofibers by using appropriate methods. Emphasis is placed on preparing quality spinning solution, the choice of effective methods of spinning and thorough characterization of the products obtained. They also described the preparation of magnetic nanofibers with a very high content of solid ferrite particles in a polymer matrix. Achieved results show interesting magnetic properties of nanomaterials that are applicable in various fields including medicine and industry.

Keywords: Magnetic nanoparticles, magnetic nanofibers, electrospinning

1. INTRODUCTION

Magnetic nanoparticles respectively nanofibers are not used only in industry but also in a much softer industry - biomedicine. Is important prepare such substances whose toxicity is not harmful to human health and the environment, but also needs to efficiently and effectively operate on the biological part of the body where they are to be used.

For correct function of nanosubstances is needed ensure a number of important aspects i.e. stabilization, the correct size and shape, magnetic characteristics and safety. What is important is the subsequent analysis, which shall be subject to ready products, so as to detect any deviations from the above mentioned features.

The aim was to prepare magnetic nanofibers various technological processes and also to explore the potential concentration of MNP (magnetic nanoparticles) in these fibers. Elements of which can be magnetic nanoparticles and magnetic nanofibers thus prepared are many, but only a few meet. In terms of toxicity and subsequent treatment can be considered only those that can be used for safe work in the laboratory and which possess properties that meet the end-use and processing.

Expert articles which focus on the preparation of magnetic nanofibres usually prepare these nanofibers only one way (usually by means of electrostatic spinning from the needle) and a small range of concentrations of MNP (e.g. articles [1], [2], [3], [4]).

2. MAGNETIC NANOPARTICLES AND NANOFIBERS

If the diameter of the magnetic nanoparticles reduce to a certain size, so true that can exhibit superparamagnetic properties, which are very interesting in terms of scientific and practical applications. [5]

The magnetic properties of ferrites are directly related to the distribution of cations over the tetrahedral and octahedral positions in the lattice. Because the magnetic moments of the ions are arranged in parallel in each of sublattices and anti-parallel between two sublattices, then the difference between the magnetic moments of sublattices gives the total magnetic moment on the ferrite crystal. [6]

In preparing magnetic nanofibres is needed to reach a sufficient dispersion of the magnetic nanoparticles in the polymer matrix and to select a suitable method of fabrication of nanofibers. Generally, the distribution of NP in the nanofibers is strongly dependent on many factors (dispersion of the particles in the polymer solution, applied voltage, ambient conditions etc.) and the method of spinning. Due to the high ratio surface / volume,

the magnetic NP tends to agglomerate (the reduction of the energy). This problem can be solved by using the stabilizers. [1], [2]

3. EXPERIMENTAL PART

3.1. Preparation of nanoparticles $CoFe_2O_4$

Preparation was performed by two processes - coprecipitation and sol-gel method. For comparison the properties was purchased ferric oxide Fe_3O_4 (size 50 nm) from Sigma-Aldrich.

With coprecipitation of ferric chloride hexahydrate $FeCl_3.6H_2O$ was dissolved in 25 ml water and mixed with 25 ml of cobalt chloride hexahydrate $CoCl_2.6H_2O$. The solution was dropped into 500 ml of NaOH of pH = 12.

$$2\ FeCl_3 + CoCl_2 + 8\ NaOH \rightarrow CoFe_2O_4 + 8\ NaCl + 4\ H_2O \quad (1)$$

After addition of isopropanol, the mixture was brought to a reaction temperature of 80 °C. The resulting precipitate was dried overnight at 100 °C and subsequently annealed at 600 °C for 10 hours in an electric furnace. [7]

In the sol-gel method was determined as follows. Cobalt nitrate hexahydrate $Co(NO_3)_2.6H_2O$ and ferric nitrate nonahydrate $Fe(NO_3)_3.9H_2O$ were first separately dispersed in deionized water and stirred for another half an hour. To each dispersion was added a chelating agent, citric acid and the mixture was reacted with vigorous stirring for about half an hour. Both solutions were mixed together and stirred for 15 hours on a magnetic stirrer. The pH was then adjusted to 8.5 by addition of dilute ammonium hydroxide. The mixture was then heated in a fume hood to a temperature, when the spontaneous reaction to start in phase gel.

$$Co(NO_3)_2.6H_2O + 2Fe(NO_3)_3.9H_2O + 8NH_4OH \rightarrow CoFe_2O_4 + 8N_2O + 44H_2O \quad (2)$$

The final heat treatment for the smallest particle size was carried out in a furnace at 250 °C for 10 hours. [8]

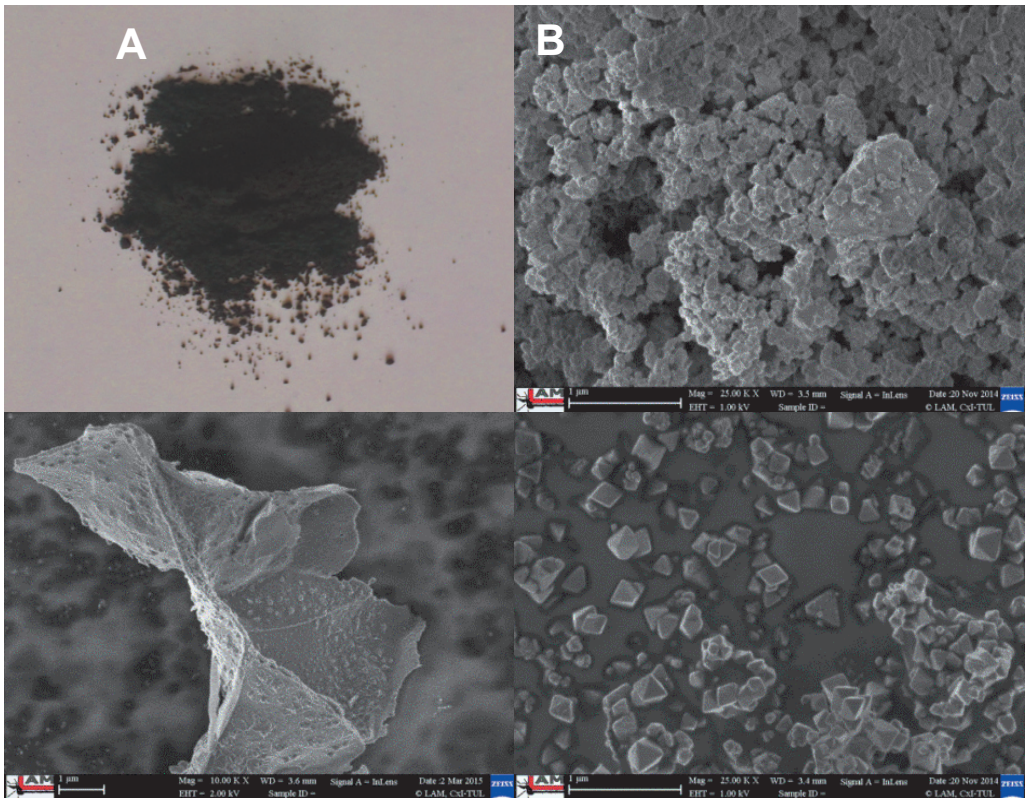

Fig. 1 A) Photo of nanopowder Fe_3O_4, B) SEM image of a nanopowder $CoFe_2O_4$ from coprecipitation C) SEM image of $CoFe_2O_4$ nanopowder from sol-gel method, D) SEM image of nanopowder Fe_3O_4

3.2. Preparation of nanofibers by electrospinning from the rod

Equipment for the spinning from the rod is consists of a metal rod, which is charged by the positive voltage source (in my case was chosen always 24 kV) and the collector on which are collect nanofibers. A drop of the polymer solution is inserted on top of the rod, where after the delivery voltage starts to run to the spinning process.

This technology was primarily used as a primary test whether the polymer solution suitable for spinning and to determine the highest possible concentrations, which should in nanofibres foothold and there were constant. To determine whether the magnetic nanofibers are toxic to organisms, it has been used as the polymer PCL (polycaprolactone) alone does not show toxicity - on these products cytotoxicity assays were performed as in the case of untied MNP.

Spinning solutions (all spinning methods) were prepared so, that the first was weighed precalculated amount of ethanol, respectively of chloroform to which was added the appropriate ferrite powder and to the resulting mixture was added polymer. PVB (polyvinylbutyral) in ethanol concentration was always 10%. Final mixture was allowed to ultrasound for 30 s.

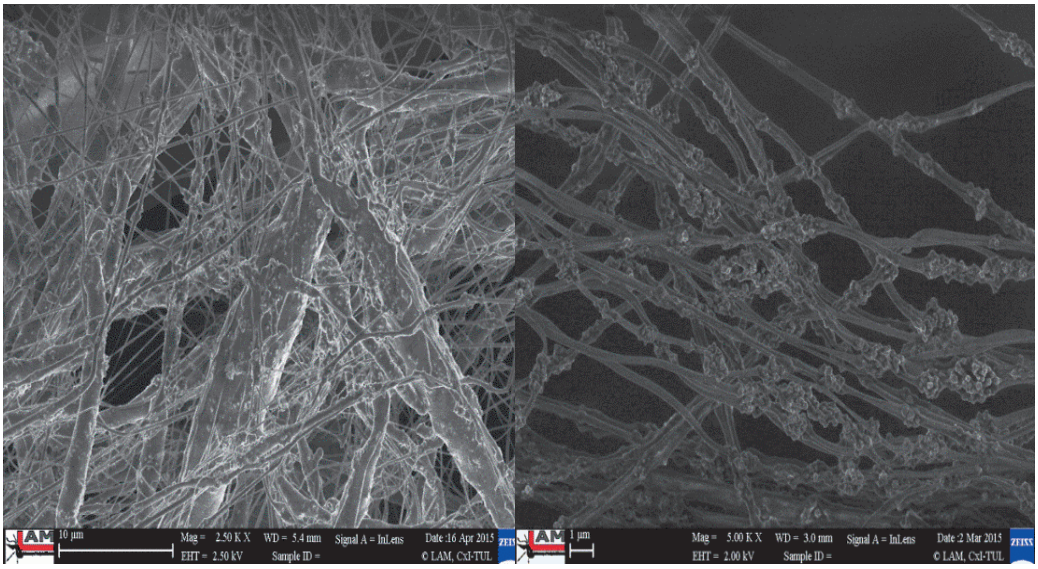

Fig. 2 A) SEM image of nanofibers 1:1 PCL(14%):Fe_3O_4, B) SEM image of 1:2 PVB:Fe_3O_4

Table 1 Overview TGA results for higher concentrations of ferrite nanofibres from rod

A sample of nanofibers	Weight of the residue / sample weight [mg]	Weight percent w [%] Fe_3O_4 in a sample
2:1 Fe_3O_4:PVB	4.5570 / 6.7680	67.33
3:1 Fe_3O_4:PVB	7.6720 / 10. 6510	72.03
9:1 Fe_3O_4:PVB	6.2210 / 7.2760	85.50

3.3. Preparation of nanofibers by AC electrospinning

The basic components of the device include: AC power supply, transformer and spinning electrode. This is a "brushless" fiberizing apparatus, where the emerging fibers are collected on a rotating drum respectively winding it on a longer non-conducting rod. At work, it is necessary to keep the distance from the device larger than the distance flashover - may cause an electric shock, which in this case is for a man to death.

The spinning process was carried out under normal laboratory conditions and parameters have been set by during spinning. Dispensing the solution into the electrode ranged from 15 to 20 ml / s, the voltage was set at 30 kV and frequency 50 Hz.

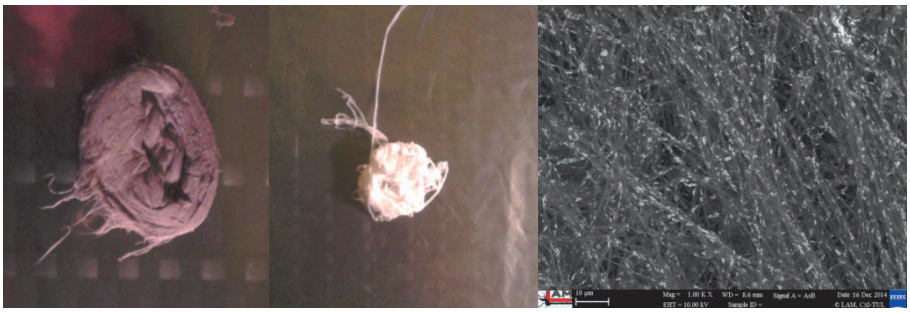

Fig. 3 A) Photo of nanofibers 1:1 $CoFe_2O_4$:PVB, B) clear PVB, C) SEM image of nanofibers 1:2 Fe_3O_4:PVB

Table 2 TGA overview of results for the magnetic nanofibers from AC electrospinning

A sample of nanofibers	Weight of the residue / sample weight [mg]	Weight percent w [%] Fe3O4 in a sample
1:2 Fe3O4:PVB	3.1880 / 9.3350	34.15
1:2 CoFe2O4:PVB	2.1750 / 9.0940	23.91
1:1 Fe3O4:PVB	4.3700 / 8.3720	52.20
1:1 CoFe2O4:PVB	2.7430 / 7.4190	36.97

3.4. Preparation of nanofibers on Nanospideru™

To prepare magnetic nanofibres on this device has been used stationary string electrode with a diameter of 0.5 mm stretched between two fixed points. The principle of the whole process is similar to other electrospinning methods, except that there is also charged collector. On the string is supplied positive voltage and the collector is charged negatively. Due to the high potential difference occurs in the formation of nanofibres from polymer solution. This solution is applied on the movable tray, where emerging fibers are captured on a spunbond sliding along the collector. [9]

The internal temperature in the process was constant 24.5 ° C and the ambient temperature was around 25 °C. Inside the device does not exceed humidity the value of 18% RH at an air flow 45.2 m^3 / hour. The distance of the electrodes was 176 mm, the speed of retraction spunbond nanofibers 27 mm / min was adjusted according to the coating thickness needed and the solution dispenser was moving at 180 mm / sec. Value of the positive voltage supplied to the string was 60.3 kV, electrical current 0.025 mA, and the overall electrical voltage between the electrodes was about 70 kV.

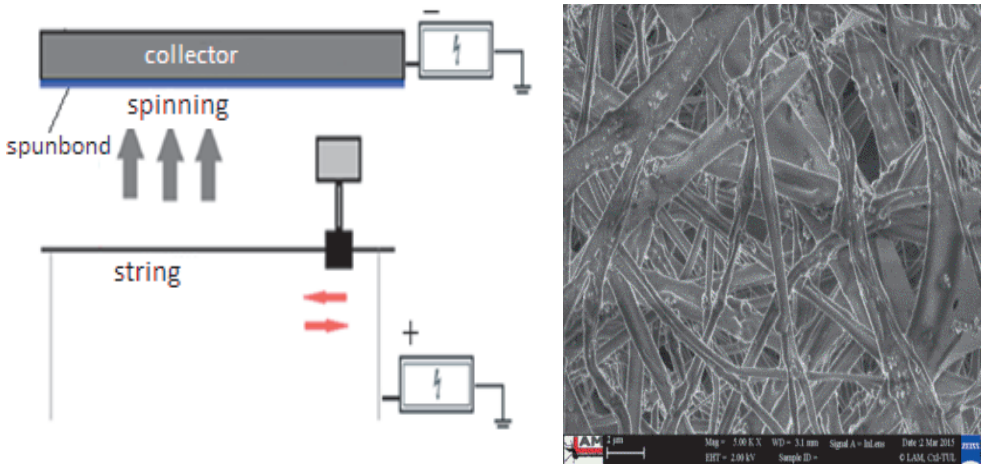

Fig. 4 (Left) the basic diagram of the device Nanospideru™ with the string spinning electrode, (Right) SEM image of nanofibres 1:1 Fe_3O_4: PVB

Table 3 TGA overview of results for the magnetic nanofibers from NanospiderTM

A sample of nanofibers	Weight of the residue / sample weight [mg]	Weight percent w [%] Fe3O4 in a sample
1:1 Fe3O4:PVB	1.8520 / 4.5210	40.96
1:1 CoFe2O4:PVB	0.6736 / 3.7150	18.13

3.5. FTIR spectroscopy

FTIR spectroscopy was carried out for a variety of concentrations of Fe_3O_4 in the PVB to determine whether it is possible using this method to determine the concentrations of ferrites in nanofibres.

The wave number band from 500-700 cm^{-1} is observed vibration Fe-O bonds, which of course increase with increasing concentrations of this component in the fibers. In the range 1050-1200 wave numbers cm^{-1} is located on deformation vibrations of the C-CO (in the plane). The range of 1200-1290 cm^{-1} shows the suppression of the passage of infrared radiation with increasing concentrations of Fe_3O_4. Neighbourhood around a wave number of 1400 cm^{-1} is characteristic of the deformation vibration of C-H bonds in the hydrocarbon chain.

On the basis of the individual spectra it is therefore possible to infer a rising trend Fe_3O_4 concentration in the PVB fibers according to how a given magnetic nanofibers was prepared (as the concentration of Fe_3O_4).

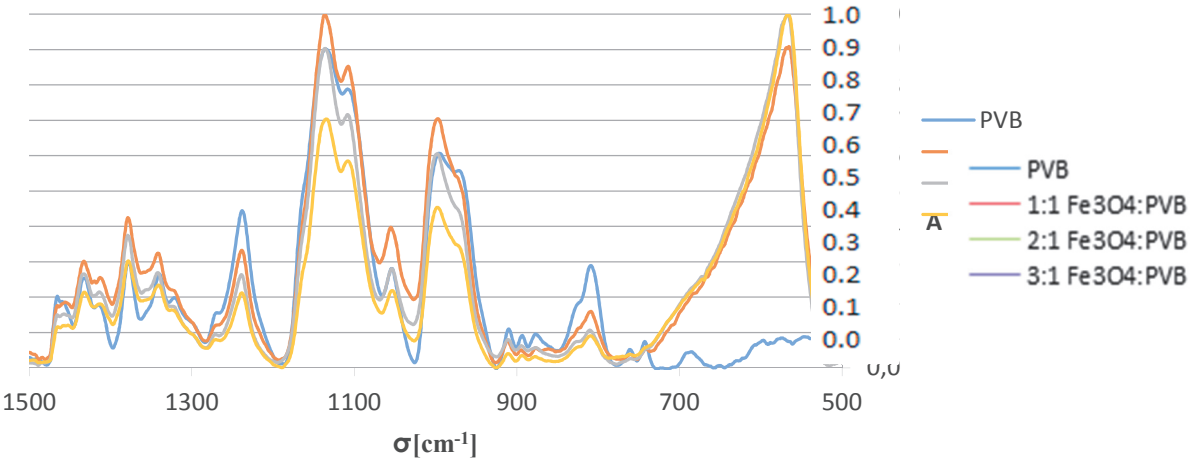

Fig. 5 The FTIR spectrum of magnetic nanofibres and pure PVB (*from dr. Müllerová, KCH, TUL*)

4. RESULTS AND DISCUSSION

Sample of magnetic nanofibres from individual spinning processes are significantly different, whether it is the structure and orientation of the fibers or the volume content of ferrite nanoparticles. For each method it was possible to observe a number of differences in the course of spinning and a different way of formation of the fiber itself. Basic overview of the structure of nanofibres was provided by SEM (from Ing. Kejzlar, KMT and Doc. Košťáková KNT, TUL) and an overview of the amount of all past MNP solution into nanofibers was provided by TGA (from Ing. Stuchlík, KCH, TUL).

The basic method for preparation of nanofibres was rod. Magnetic nanofibers exhibit a size of tens of nanometres and spreading ferrites (especially in the case of Fe_3O_4) in the whole volume of the fibers. For all methods for spinning seems better Fe_3O_4 than $CoFe_2O_4$, primarily due to the aforementioned particle agglomeration of the cobalt ferrite. When creating the nanofibres from the rod can be achieved a relatively large volume fraction of ferrite but only provided that the dope will suit its viscosity. In this method were prepared from PCL nanofibers.

Magnetic nanofibers prepared for AC electrospinning are organized into denser units and arise are a number of defects. During spinning was possible to observe a delayed response of fibers to the magnet after its attaching to these longer fibers. Most likely take some time before an arrangement of magnetic domains nanoparticles toward the magnet and thus this phenomenon can be observed.

If Nanospider be regarded as the greatest advantage of its high productivity (approximately 3 g / min). Significant difference was during the spinning of individual solutions with Fe_3O_4 as $CoFe_2O_4$, when in the second case, there was a significantly higher creation of nanofibres in the process. This is because the fibers formed don't carry so much MNP as in the case of Fe_3O_4, which also follows from the results of TGA.

5. CONCLUSION

The aim of this work was to develop a magnetic nanofibers different methods of spinning processes and appropriately be characterized using the available assays.

It was worked with a total of six different methods of spinning, with different concentrations of magnetic powders of Fe_3O_4 and $CoFe_2O_4$ and the resulting nanofibers were analysed primarily to determine the structure and volume fraction MNP.

Each method provides various kinds of magnetic nanofibres with different parameters, which depended on the incorporated magnetic nanoparticles, which were prepared in the laboratory or purchased for comparison.

The possibility of using such a nanofiber in everyday life is numerous. Cannot be excluded their application in medical areas, when not on the basis of simpler cytotoxicity tests demonstrated significant toxicity to living cells.

This theme offers in the future a number of additional questions and possible experiments and therefore will continue to be pursued in further research and development in this area.

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