NANOFIBERS WITH INCORPORATED MAGNETIC NANOPARTICLES

HAVLÍČEK Karel, GRÉGR Jan, KEJZLAR Pavel

Technical University of Liberec, Liberec, Czech Republic, EU

Abstract

The aim was to prepare magnetic nanofibers with a high content of magnetic nanoparticles in these fibres. Elements which can be used for prepare of magnetic nanoparticles and magnetic nanofibers are many, only some are satisfying. In terms of toxicity and subsequent treatment can be considered only those that can be used for safe work in the lab, and which possess properties that meet the end-use and processing. The most suitable nanoparticles were chosen Fe_3O_4, which are characterized superparamagnetic properties and their shape is suitable for incorporation into the polymer matrix. PVB, which is very good for creating the nanofibers, was used for matrix.

Nanofibers with magnetic properties are very specific materials that require special characterization. Important measurements such as - magnetic measurements, TGA, FTIR, etc. are performed by special methods that are described in this work. These measurements are very important for the further use in the biomedicine, industry etc.

Keywords: Magnetic nanofibers, characterizations, magnetic properties

1. INTRODUCTION

This work builds on primary research of magnetic nanofibers (article - "Nanofibers with magnetic properties).

Magnetic nanofibers which are sensitive to changes in external magnetic field is of great interest in the field of nanotechnology due to the wide range of potential applications, such as drug delivery systems, bone tissue engineering, local heating in body (cancer treatment) and microwave absorption. [1], [3]

Nanoparticles with superparamagnetic properties have advantages for building these nanocomposite including easy preparation and functionalization, low toxicity and price. Among those magnetic nanoparticles, iron oxide (Fe_2O_3 or Fe_3O_4) is superior to others because of its special magnetic properties and low toxicity. Magnetite was studied and used widely in biological applications, such as magnetic resonance imaging (MRI), biosensor, magnetic separation and medical diagnosis because of its superparamagnetism under sub-nanometers and innate biological compatibility. Most of these applications require that the Fe_3O_4 nanoparticles should be chemically stable, uniform in size and well-dispersed in liquid media, preferably in water. But significant agglomeration of magnetic nanoparticles is a major difficulty in the preparation of such nanocomposite, especially in electrospinning composite nanofibers. Nowadays are successfully produced magnetic nanofibers having a core / shell structure with individually dispersible magnetic NPs. Such nanostructures are promising for specific applications because each component may be functionalized without affecting the other. [4]

Recent trends in the preparation of the magnetic fibres is trying to use nanofibers from the "electrospinning" with using PVP and nitrate salt melt consisting ferrites nanofibers upon heating above 600 °C. These products find application in new applications such as ferromagnetic structures in nanocomposites, nanocomposites membranes in separation, also referred to as anodic material for Li-ion batteries, catalysts and possibly other electronic "nanodevices". There are many options for preparing such fibres by using various technologies and various matrixes. [5], [6], [7], [8], [9]

2. EXPERIMENTAL PART

2.1. Solution for spinning

Solution for spinning was prepared from PVB (polyvinyl butyral), ethanol and magnetite nanoparticles. Each solution after mixing of the components was mixed by ultrasound.

The solutions have a consistency similar to honey and degree of viscosity is dependent on the concentration of PVB (standardly 9%) and the concentration of magnetite nanoparticles (depending on dilution series). Conductivity measurement has been performed but due to the high content of nanoparticles does not representable results. The viscosity was determined at the outlet of the viscometer and the difference was determined for each solution.

Table 1 Overview of the viscosities for the individual solutions

Solution	Viscosity [mPa. s]
pure PVB in Et-OH 9%	158
1:1 Fe3O4:PVB	202
2.5:1 Fe3O4:PVB	259
5:1 Fe3O4:PVB	323

2.2. Nanofibers with incorporated magnetic nanoparticles

With the help of electrostatic spinning from rod were prepared nanofibers with the magnetic nanoparticles of three different concentrations (dilution series). Spinning conducted from prepared solutions (see above) at a constant voltage of 23 kV and the electrode distance was 11.5 cm. On the thus obtained materials were carried out individual analysis.

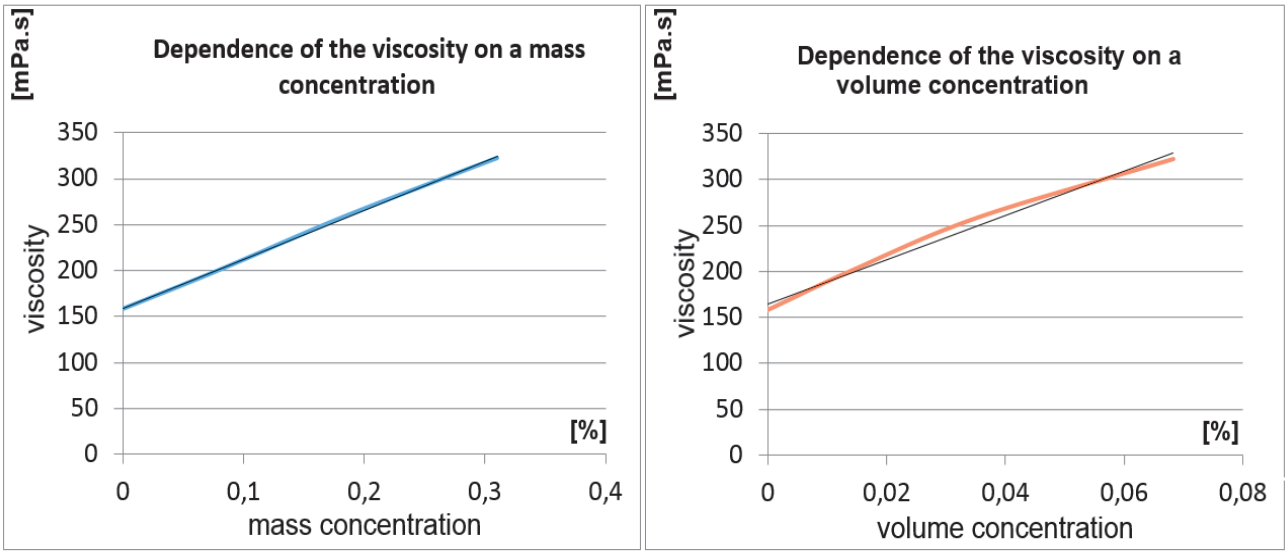

Figure 1 Graph of dependant of the viscosity on a mass and volume concentration

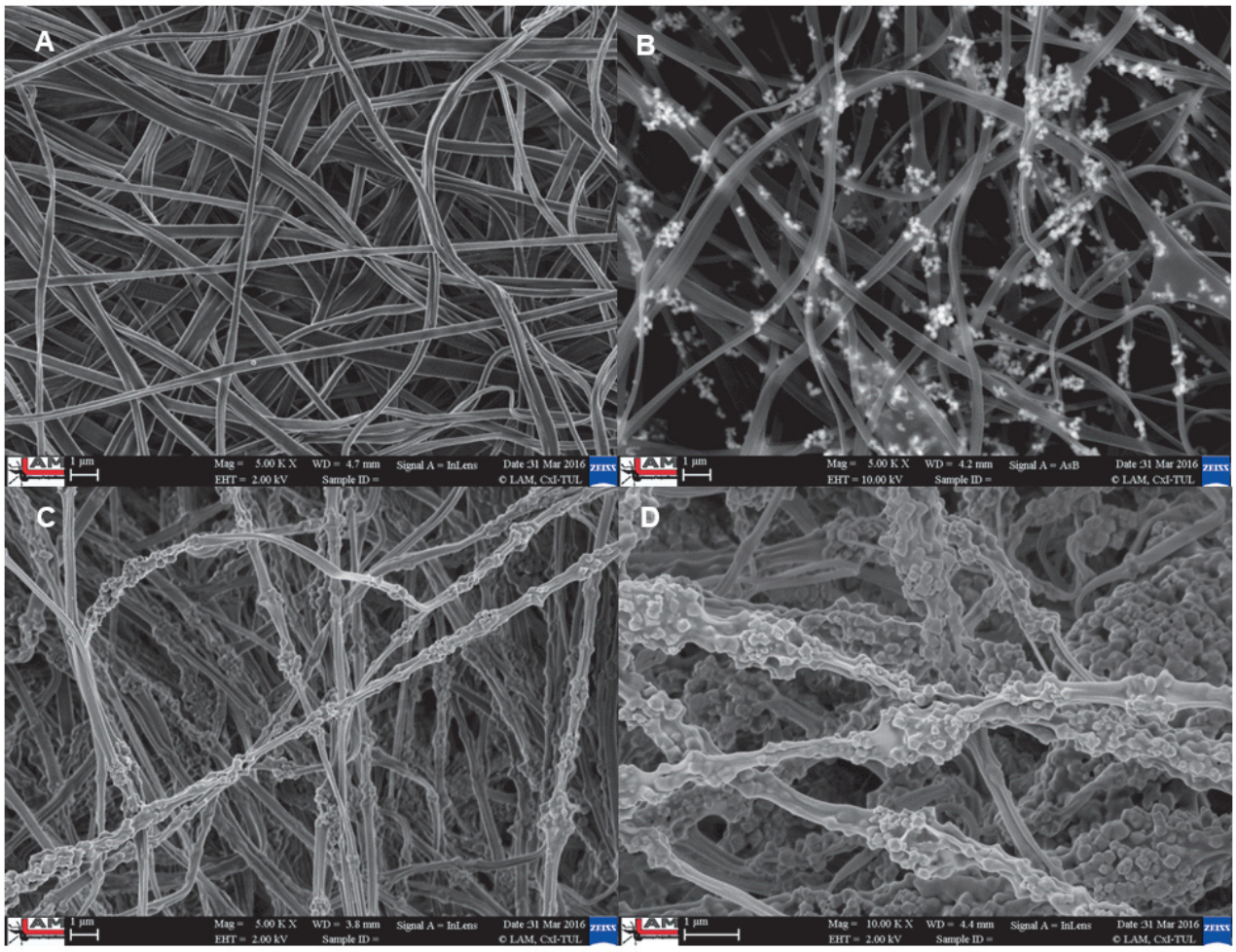

Figure 2 Images from the SEM - A) PVB in Et-OH 9%, B) 1:1 Fe3O4:PVB, C) 2.5:1 Fe3O4:PVB, D) 5:1 Fe3O4:PVB

2.3 Characterization of nanofibers

Nanofibers with magnetic properties were subjected to such analyses, which assess their main advantages and determine their basic chemical and physical parameters. Images from scanning electron microscopy (**Figure 2**) were created to study the structure of fibres and dispersion of nanoparticles in a matrix.

Magnetic measurements were performed on the device MPMS XL 7T - Magnetic Property Measurement System. It was measured magnetization and magnetic field intensity these substances. It was investigated the dependence of magnetization on the magnetic field strength and the results were interpreted as hysteresis loops.

To determine the exact content of almost nanoparticles of magnetite in the structures

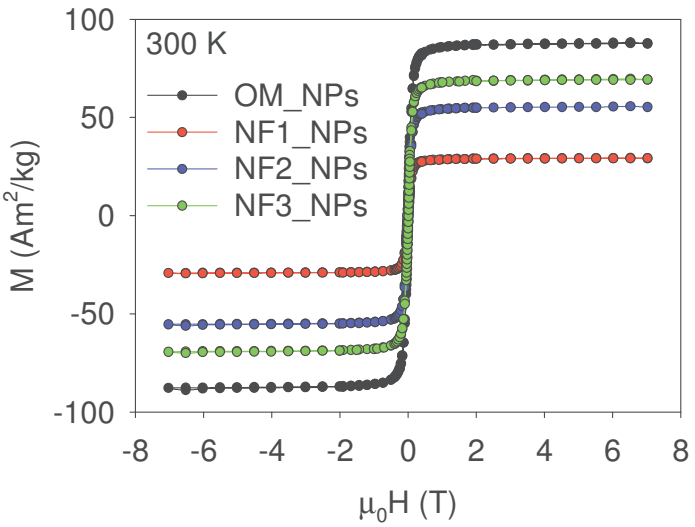

Figure 3 The dependence of the magnetization of the individual nanofibers from the dilution series for the magnetic field strength

of the fibre was used thermogravimetric method (TGA), which clearly shows the trend of growth of weight or volume percent of particles in the composite. Verification method was FTIR analysis, which confirms the results of casting nanoparticles.

Table 2 The results of thermogravimetric analysis

Sample	Weight percent w [%] Fe3O4 in the sample
pure PVB	0 %
1:1 Fe3O4:PVB	31.85 %
2.5:1 Fe3O4:PVB	66.18 %
5:1 Fe3O4:PVB	82.13 %

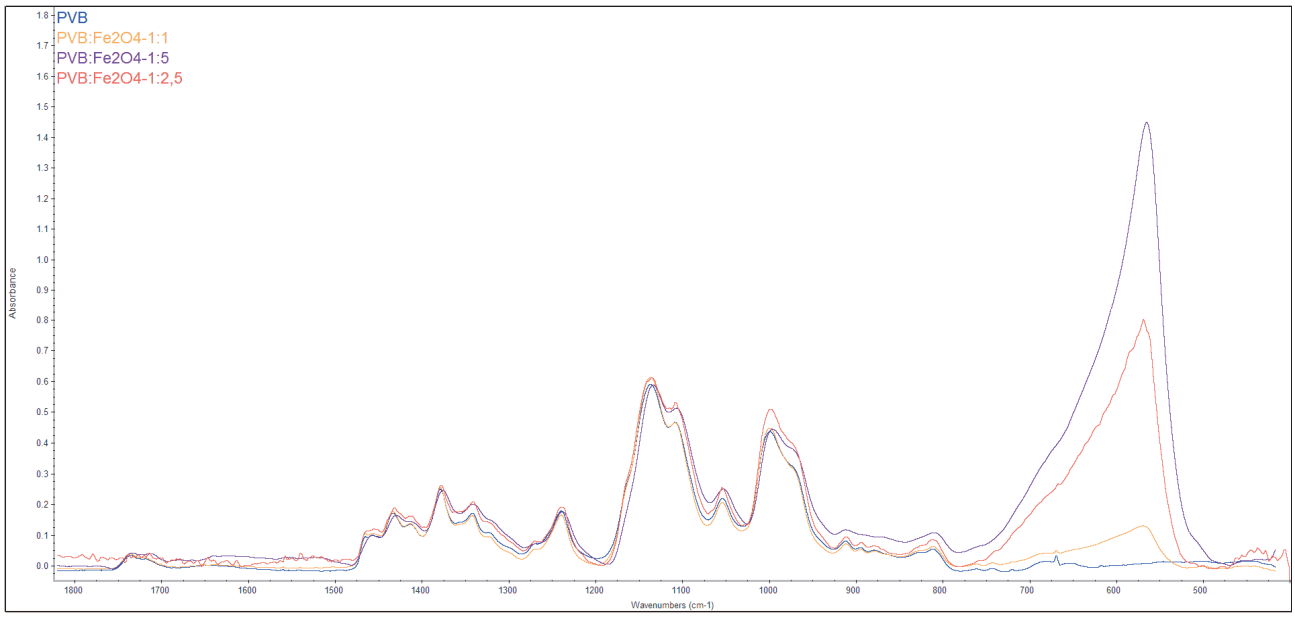

Figure 4 Graphical output of FTIR analysis

3. RESULTS AND DISCUSSION

Measurements and calculations show that the viscosity of the addition of the particles increases approximately according to the Einstein equation for viscosity. Deviation to higher values is due to the fact that Fe3O4 nanoparticles mainly occupy octahedral shape, which does not exactly match Einstein's definition (with perfectly smooth spherical particles). Since the viscosity of the spinning solutions significantly affects the process of creation of nanofibers, it is therefore important to select a suitable volume of solids in the solution, and the concentrations of PVB in ethanol. At very high or very low values of viscosity dopes no sufficient efficiency in transferring MNP into the polymer matrix. The high viscosity causes the formation of the drop-shaped defects in nanofibers and therefore bad distribution. When low viscosity is that the polymer component is not sufficiently strong to "hijacked" relatively heavy particles during the spinning process and these particles remain in a large number at the start. A similar process occurs even if the concentration of ferrite particles in the solution is too high, when to nanofibers, while receives a large amount of ferrite particles, but it happens that a large amount of the nanoparticles remain on the grid and the polymer is rapidly spun, so that they must be constantly regenerating the spinning solution on the electrode.

From magnetic measurements show that even these small particles embedded in a dense polymer matrix are able to exhibit strong magnetic properties and which increase with the amount of nanoparticles in the matrix. Such materials are useful for a lot of disciplines - medicine, transport, sensors, etc.

FTIR analysis, which confirms the results of TGA analysis, shows a clear trend of increase in the amount of magnetite nanoparticles concentration in a row. Band about 1400 cm-1 indicates the deformation vibration of C-H bonds of the hydrocarbon chain, between 1200 and 1100 cm -1 are reflected vibration of the C-CO and values near 600 cm-1 indicate vibration Fe3O4.

4. CONCLUSION

Generally, possibility characterization of magnetic nanofibers is numerous but a limitation occurs with the availability of such methods and sample preparation. As a basic analyzes were performed SEM and TGA. The most suitable method for the detection of the magnetic nanoparticles in the fibres is TGA that accurately determine the concentration of magnetic nanoparticles in a sample. For these particles does not occur due to high temperature for a significant change in their chemical structure other hand the fibres PVB evaporate already at considerably lower temperatures.

The images of SEM are best suited to assess the orientation and size of the fibres. At the same time this analysis was performed on some samples and EDS analysis, which because of its inaccuracies were not included in this work. Another possibility would be a display, transmission electron microscopy (TEM), which would perfectly show particle distribution on the fibres.

FTIR spectroscopy provides useful information about the occurrence of magnetic nanoparticles in polymer nanofibers on the basis of specific vibrations of particular chemical bonds. Using this method successfully characterize even very small amounts of sample (less than TGA).

Measurement of the magnetic properties of the products is very demanding and restricts the availability of measuring equipment. However, the measured values of magnetization of the material at various concentrations of particles in the sample show the great potential of these materials.

ACKNOWLEDGEMENTS

Thanks to all co-authors and other people who provide expert advice and also SGS TUL 21115 and project MLTL number LM2011025 and OP Research and Development for Innovation for 2014-2020, the Ministry of Education.

REFERENCES

[1] WANG, S. et al. Magnetic composite nanofibers fabricated by electrospinning of Fe3O4/gelatin aqueous solutions. Materials *Science and Engineering*: B 190, 126-132 (2014).

[2] HUANG, C. et al. Magnetic Electrospun Fibers for Cancer Therapy. *Advanced Functional Materials* 22, 2479-2486 (2012).

[3] SUNG Y. K., AHN W. B., KANG J. T. Magnetic nanofibers with core (Fe3O4 nanoparticle suspension)/sheath (poly ethylene terephthalate) structure fabricated by coaxial electrospinning. *Journal of Magnetism and Magnetic Materials* [online]. 2012-03, roč. 324, č. 6, s. 916-922. ISSN 03048853. DOI: 10.1016/j.jmmm.2011.03.004.

[4] ZHANG X., DAI Q., HUANG X., TANG X. Synthesis and characterization of novel magnetic Fe3O4/polyphosphazene nanofibers. *Solid State Sciences* [online]. 2009-11, roč. 11, č. 11, s. 1861-1865. ISSN 12932558. DOI: 10.1016/j.solidstatesciences.2009.08.003.

[5] MAENSIRI S., SANGMANEE M., WIENGMOON A. Magnesium Ferrite ($MgFe_2O_4$) Nanostructures Fabricated by Electrospinning. *Nanoscale Research Letters.* 2008, roč. 4, s. 221-228. DOI: 10.1007/s11671-008-9229-y.

[6] LI D., HERRICKS T., XIA Y. Magnetic nanofibers of nickel ferrite prepared by electrospinning. Appl. *Phys. Lett*. 2003, roč. 83, s. 4586. DOI: 10.1063/1.1630844.

[7] JU Y. W., PARK J. H., JUNG H. R., CHO S. J., LEE W. J. Fabrication and characterization of cobalt ferrite ($CoFe_2O_4$) nanofibers by electrospinning. *Mater. Sci. Eng. B*. 2008.

[8] SAENSUK O., MAENSIRI S., BOOTCHANONT A., SWATSITANG E. Fabrication and magnetic properties of electrospun $Ni_{1x}Cu_xFe_2O_4$ nanofibers. *Microelectronic Engineering. 2014* roč. 126, s. 158-164.

[9] XIANG J., CHU Y., SHEN X., ZHOU G., GUO Y. Electrospinning preparation, characterization and magnetic properties of cobalt-nickel ferrite ($Co_{1-x}Ni_xFe_2O_4$) nanofibers. *Journal of Colloid and Interface Science*. 2012, roč. 376, s. 57-61.