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UV-VIS ANALYSIS OF COMPOSITE POLYACRYLONITRILE/IRON OXIDE NANOPARTICLES THIN FIBROUS MATS

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Abstract:
Iron oxide nanoparticles have a wide range of properties and a lot of applications in today nano-world. They can be used as: catalyst system [1], biomaterials for the tissue engineering [2], good base for magnetic nanoparticles – to locate hyperthermia, membranes for water purification or thermal energy storage. Poliacrylonitrile, although thermoplastic, is also rigid and brittle and used in manufacturing of synthetic fibers.
The most useful applications of nanofibers reinforced by the Fe_2O_3 nanoparticles are in catalyst systems. Space between nanofibers is so small that all impurities are stopped and removed. In water treatment plants, chrome is the main element to be removed, because of its noxiousness to humans.
The aim of this study was to fabricate composite nanofibers reinforced by the Fe_2O_3 nanoparticles with a polymer matrix of polyacrylonitrile (PAN) by the method of the solution electrospinning. After the production, morphology and structure were analyzed on scanning electron microscope; optical properties were analyzed by UV-VIS spectroscopy.

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1. INTRODUCTION

Iron (III) oxide due to its physical properties such as energy gap containing in the range 2.1 - 2.94 eV [1-4], or slightly alkaline properties, is used in the steel industry as the raw ceramic and glass material [5,6]. In addition, iron (III) oxide is used as a pigment in [7-10] or as an electric semiconductor [2,11-13]. However, due to the oxidation rate of pure iron (III) oxide, it is subjected to encapsulation [14] - a polymer coating covering the particles, which provides a simple method of protecting against loss of catalytic activity. The nanofibers of polymer matrix composites that are reinforced with nanoparticles of iron (III) oxide also have flexible magnetic properties [15,16], which may be subject to modification [17] and enable the composite to gain new electrochemical properties [18].

The reinforced nanofibrous composites are used for a wide range of nanofillers with nanoparticles such as oxides of iron [14-22], graphene [23-26], zinc [27-30], bismuth [31-34], aluminum [35-38], cobalt [39,40] and titanium [41-44], in order to improve the physical properties of the resulting composite materials, impossible to achieve using pure polymers. Membranes formed from nanofibrous polymer composites doped with Fe_xO_y particles, due to their catalytic properties [14] and the ability to remove harmful hexavalent chromium and other harmful compounds [22], are used in filters and components of catalysts [45,46], and also in water treatment [21]. Nanofibrous PVA/Fe_2O_3 composites are also used in tissue engineering – as a biocompatible material constituting the scaffold for tissue [20], as well as in the field of medicine during the treatment of hyperthermia - ferromagnetic or superparamag-

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netic particles PVA/Fe_2O_3 are introduced into the human body, as close to the tumor tissue as possible, whereupon they are heated by an external magnetic field, which results in destruction of tumor cells [47]. Furthermore, the nanofibers based composite polymers, reinforced by nanoparticles of iron oxide, which has undergone calcination at a temperature of approximately 600° C for 5 hours, in order to cause physical or chemical changes, showed a very good thermal stability and were examined by DSC-TG. Furthermore, the calcination process is also used to obtain the hollow Fe_2O_3 nanofibers which are used to produce gas sensors [48-50].

The goal of this article was to optimize the process of electrospinning with the aim to obtain the PAN composite fiber, reinforced by the Fe_2O_3 nanoparticles, used then to determine the effect of the process parameters on the morphology of the filaments and the analysis of their optical properties in a wide spectrum of radiation. Analysis of the morphology of produced nanofibers was performed using a scanning electron microscope (SEM). In addition, they were micro analyzed by the EDS (Energy Dispersive X-Ray Spectroscopy), which helped to identify the chemical elements included in the composite nanofibers. The optical test was carried out based on the absorbance spectra as a function of wavelength obtained for all of the materials produced using the UV-Vis spectroscope.

In order to analyze the morphology and chemical composition of the obtained samples, a scanning electron microscope (SEM) Zeiss Supra 35 was applied and integrated with TRIDENT XM4 manual EDAX consisting of: spectrometer with energy dispersive X-ray EDS and a comprehensive software. Analysis of the optical properties of the manufactured fiber mats and polymeric composite was based on the absorbance spectra versus wavelength obtained using a computer-controlled Thermo Scientific Evolution 220 UV-Vis spectrophotometer. During the test, the light beam with wavelength range of 250 - 1100 nm fell at an angle of 8 ° to the sample.

2. METHODOLOGY

In order to prepare polymer solutions for electrospinning, the following were used: polyacrylonitrile (PAN) (manufacturer Sigma Aldrich, purity of 99%, Mw = 150 000 g/mol); the reinforcing phase were Fe_2O_3 nanoparticles; dimethylformamide (DMF) (purity of 99.8%) was used as a solvent. Final products were the solutions of 15% PAN in DMF, 15% PAN in DMF with 5% Fe_2O_3 nanoparticles with respect to the polymer, and 15% PAN in DMF with 10% content of Fe_2O_3 nanoparticles with respect to the polymer. In order to break the agglomerates of the reinforcing phase, a measured amount of nanoparticles was added to dimethylformamide, and so prepared solutions were sonificated for a process time of 15 minutes. Immediately after the process of sonification, the solution was added with measured amount of the polymer and subjected to stirring using a magnetic mixing over a period of 24 h at room temperature. Straight away after mixing, the solution was placed in the pump device, which was the sterile syringe. Nanofibrous composites were obtained by using the electrospinning method from the solution using the FLOW - Nanotechnology Solutions Electrospinner 2.2.0-500 device. The parameters used in this process were: the distance between the electrodes – 15 cm, the difference in potential between electrodes - 20 kV and the spinning solution flow rate - 3 ml/h.

3. RESULTS AND DISCUSSION

The applied electrospinning process parameters resulted in obtaining polymer and composite fibers without structure and surface defects (Fig. 1). The conducted investigations have shown that the obtained nanofibers from 15% polymer solution in dimethylformamide (DMF) nanofibers were characterized by an average fiber diameter of 310 nm, while the composite nanofibers with 5% mass fraction of Fe_2O_3 nanoparticles have an average fibers diameter of 340 nm, which allows to conclude that the mass fraction of used reinforcing phase has an influence on the diameter of fibers.

In the case of PAN/Fe_2O_3 composite nanofibers with 10% concentration of Fe_2O_3 nanoparticles, an average dimension of fiber diameter is 640 nm. Based on the conducted surface topography analysis of manufactured fibrous polymer and composite mats, it can be concluded that with an increase of concentration of reinforcing phase, in the form of Fe_2O_3 nanoparticles, the diameter of obtained fibers increases.

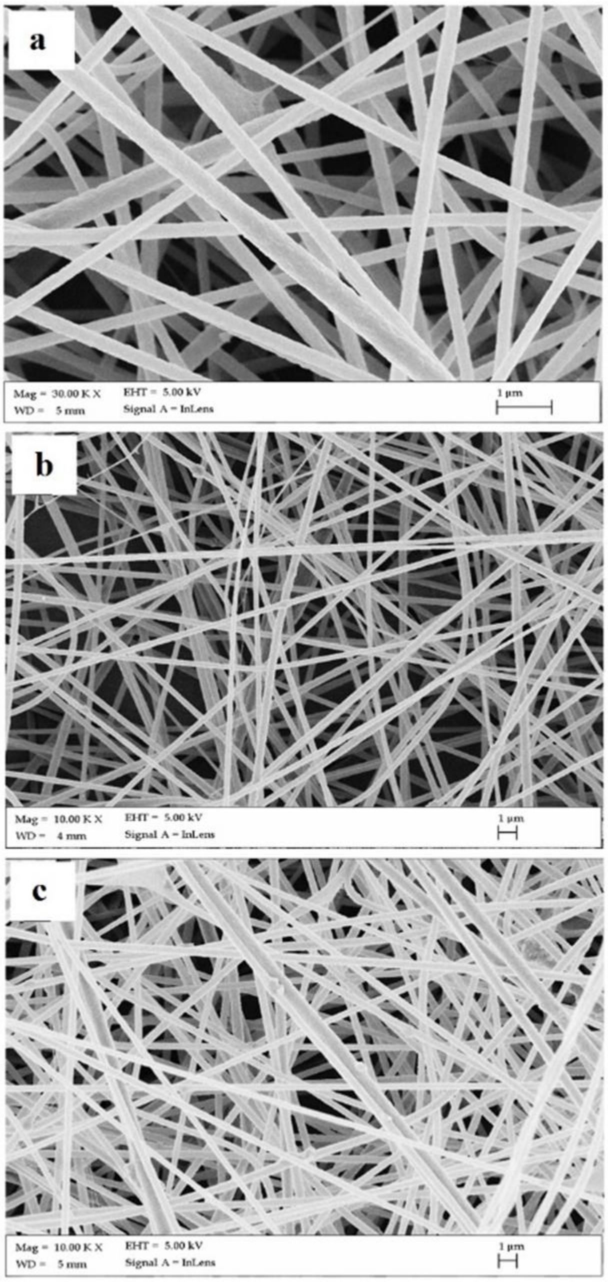

Fig. 1. The SEM images of nanofibrous surface topography
a) PAN polymer, b) PAN/5%Fe_2O_3 composite,
c) PAN/10%Fe_2O_3 composite.

The investigations of optical properties of the obtained polymer and composite nanofibers were prepared based on the absorbance spectrum in the function of wavelength obtained using UV–Vis spectroscopy (Fig. 2). An analysis of the absorbance spectrum in terms of wavelength obtained for pure polymer nanofibers, have shown a sharp edge of absorption for the wavelength of 340 nm, while the maximum absorption was observed for the wavelength of 310 nm. The obtained results of an absorption spectrum of PAN nanofibers are similar with those reported in [51, 52]. With a 5% addition of Fe_2O_3 nanoparticles to the polymer, there is a second, gentle absorption edge on the wavelength of 600 nm. The second absorption edge is a result of an addition of Fe_2O_3 nanoparticles to a polymer solution, which confirms the absorption edge of pure Fe_2O_3 in work [53].

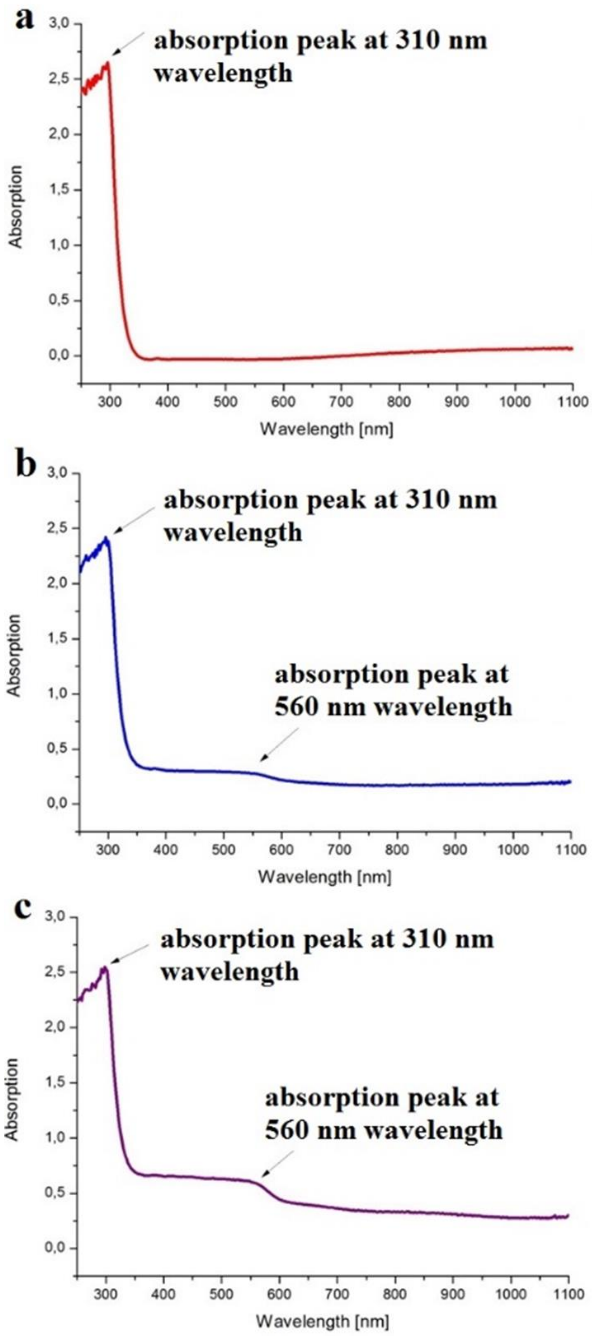

Fig. 2 UV-Vis spectrum obtained for nanofibers
a) PAN polymer, b) PAN5%/Fe_2O_3 composite
c) PAN/10%Fe_2O_3 composite.

With 10% content of Fe_2O_3 nanoparticles in polymer solution, the degree of absorption changes and is respectively: 2.4 for pure polymer, 2.7 for 5% Fe_2O_3 concentration in polymer solution and 2.6 for 10% Fe_2O_3 concentration in the polymer solution, whereas a gentle absorption edge has increased from 0 in the pure polymer to 0.3 for 5% Fe_2O_3 concentration in polymer and to 0.6 for 10% Fe_2O_3 concentration in the polymer. The obtained results indicate that with an increase of nanoparticles content in PAN/Fe_2O_3 composite the degree of absorption in the function of wavelength increases, which probably is caused by an increase in nanofibers diameter resulting from an increase in the concentration of nanoparticles in the polymer.

4. CONCLUSIONS

The article describes the method of manufacturing of PAN/Fe_2O_3 composite nanofibers, with 5 and 10% Fe_2O_3 nanoparticles mass content. The nanofibrous composites were manufactured using the electrospinning method from a solution, which allows obtaining the nanofibers with an average diameter in the range of about 250 to 700 nm. An addition of Fe_2O_3 nanoparticles to polymer solution resulted in obtaining fibers with a greater diameter in comparison to nanofibers obtained from pure polymer solution. An UV-Vis absorption spectrum analysis in terms of wavelength obtained for manufactured polymer fibrous mats and composite mats have shown an increase of the degree of absorption of the obtained nanofibers over the entire range of radiation spectrum accompanied by an increase in the mass concentration of Fe_2O_3 nanoparticles in the polymer solution. The obtained results testify that there is a possibility for application of this type of fibrous composite mats as electromagnetic radiation absorption layers with particular consideration of UV radiation.

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