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Comparison of optical properties of PAN/TiO_2, PAN/Bi_2O_3, and PAN/SbSI nanofibers

Wiktor Matysiak[a,*], Tomasz Tański[a], Paweł Jarka[a], Marian Nowak[b], Mirosława Kępińska[b], Piotr Szperlich[b]

[a] Institute of Engineering Materials and Biomaterials, Silesian University of Technology, Konarskiego 18a Str., 44-100, Gliwice, Poland
[b] Institute of Physics – Center for Science and Education, Silesian University of Technology, Krasińskiego 8, 40-019, Katowice, Poland

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ABSTRACT

The aim of the study was to prepare PAN nanofibers reinforced by TiO_2/Bi_2O3 nanoparticles and SbSI nanowires as well as to investigate their morphology and optical properties. The polymer and composite nanofibers were obtained using the electrospinning method from PAN/DMF solutions doped by nanofillers. The investigations of the influence of process parameters on the morphology of the obtained fibrous mats were carried out on the basis of their images of surface topography obtained using scanning electron microscopy (SEM). The incorporation of semiconductor nanofillers on the surfaces and in the volume of PAN nanofibers was confirmed by energy dispersive X-ray (EDX). Spectral investigations of diffusive reflectance and transmittance have been used to determine the absorption as well as the scattering coefficients of the PAN, PAN/TiO_2, PAN/Bi_2O_3, and PAN/SbSI nanofibers. Mechanisms of absorption and energy gaps of the investigated materials have been determined.

1. Introduction

A characteristic feature of composites materials with polymer matrix reinforced with semiconducting nanoparticles is a significant improvement of physical properties, with particular emphasis on electrical [1], magnetic [2], mechanical [3], optical [4] and photocatalytic [5–8] properties, both in relation to the used matrix and the reinforcing phase. This combination of materials makes possibility to obtaining materials with a low mass and flexibility characteristic for organic material, while maintaining properties such as a low energy gap, high refractive index, resistance to sunlight characteristic of an inorganic material. Especially the optical properties modification of nanocomposites is a frequent object of research. Combination of materials, such as poly(methyl methacrylate) (PMMA), poly(lactic acid) (PLA), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) with particles such as (titanium oxides) TiO_2 or (bismuth oxides) Bi_2O_3, enabled a significant improvement of their optical and electrical properties in comparison to pure polymer [9–12]. It was also shown the effect of TiO_2 share in polymeric matric composites on the photocatalytic efficiency in degrading organic dyes (fluorescein, rhodamine B, and methylene blue) [13]. Due to its advantages (photocorrosion resistance, chemical inertness, non-toxicity, high redox ability, low cost), TiO_2 is currently one of the most promising nanofillers in the polymer matrix composites technology; however, in recent times, there has been a significant increase in the interest of using bismuth oxide [14–17]. The wide application of Bi_2O_3 is associated with its optical properties, such as a band gap of 2–3.96 eV, significant photoluminescence, high refractive index of 2.3, high photoconductivity, dielectric permittivity, chemical thermal stability, low resistivity as well as high transparency in the visible region, [18–24]. The use of the connection of Bi_2O_3 with nickel oxide in form of thin films, which due to special chemical and physical properties can find applications in electrochromic devices, transparent electronic devices, gas sensing, fuel cells, metal-insulator, heat mirror, is described [24–28]. Similarly to Bi_2O_3 and promising in terms of application possibilities e.g. in the next generation of photovoltaic cells, γ-ray detection, and in optoelectronic devices, semiconductor materials incldue antimony selenoiodide (SbSI). Especially promising properties have been noticed in the case of the use of nanowires of SbSI with needle-like shape nanocrystals in the direction of the [001] axis, sparking interest in due to its optical properties, in particular, in uses as a nanocomposite filler [29–34]. The special properties of SbSI nanofibres are due to their structure, which creates chains in the form of binary screw axis, connected by strong Sb–S covalent bonds [35,36].

Achieving high properties of the composite material is dependent on the materials used and also on the geometric form of the obtained composite. Promising properties have been archived for composites in the form of nanostructures and especially for nanocomposites in the

* Corresponding author.
E-mail address: wiktor.matysiak@polsl.pl (W. Matysiak).

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form of mats made of polymeric nanofibers filled with nanoparticles [9]. For this type of materials extremely important is control of the geometry of the produced nanofibres with high repeatability and dimensional uniformity as well as the correct distribution of filler nanoparticles in the matrix fiber [37]. One of the most efficient and most developments production methods of allowing to obtain high-quality nanofibers is electrospinning [38–41]. The geometrical form of electrospinned composites guaranteeing a large specific surface area and the possibility of homogeneous distribution of the filler particles. Work with the use of composite nanofibers produced using the electospinning method has been showing significant progress over the last years. Researches have been conducted on polyacrylonitrile with SiO_2, TiO_2, Bi_2O_3 nanoparticles. That composite nanofibres find application as membranes, batteries gas absorbents and solar cells. Nanofibrous structures with PAN matrix reinforced by TiO_2 have presented the high efficiency of photocatalytic effect under ultraviolet which allows them to be used in catalytic decomposition of compounds of aromatic airborne, phenol, methylene blue [9].

Especially promising properties have been noticed in the case of the use of nanofibrous composites reinforced with SbSI nanowires. In the case of application PAN/SbSI nanofibers composite completed tests showed that this material has an energy gap of Eg = 1,94 eV, which in combination with the strongly coupled ferroelectric and semiconductor properties of SbSI crystals testifies to the wide application capabilities of newly developed composite, with particular emphasis on the use this type of materials for the production of new generation of nanogenerators [42–47].

Considering the above studies, the authors focus on producing nanofibers with a polyacrylonitrile (PAN) matrix, reinforced with nanoparticles of TiO_2, Bi_2O_3 and SbSI nanofibers by using the electrospinning method.

The aim of this paper is to determine the influence of the process parameters on the structure, surface morphology and optical parameters, such as mechanisms of absorption and energy gaps width, diffusive reflectance and transmittance, determining the absorption of the obtained fibrous structure represented by the incorporation of various forms of semiconductor nanofillers of TiO_2, Bi_2O_3 and SbSI on the surfaces and in volume of PAN nanofibers.

It was expected that the application of nanostructural semiconducting materials like the reinforcement of polymer matrix composite would provide optical properties of the nanocomposite, such as absorption range and energy gap width. Additionally, the content of nanoparticle results in the changes of the surface morphology and structure of nanofibers, which is a very important parameter in the potential applications. The novelty of the work is the utilization of the most modern material and electrospinning technique. Obtaining the nanocomposite in the form of nanofibrous mates is a new solution, especially due to the high proportion of nanoparticles in the composite. In addition, the use of the Bi_2O_3 material, and in particular SbSI, is especially innovative and undisclosed.

2. Methodology

In order to prepare the spinning solution, a polymer, polyacrylonitrile (PAN) (manufacturer Sigma Aldrich, with purity of 99%, Mw = 150 000), were used. The reinforcement phase was successively titanium dioxide (TiO_2) nanoparticles, bismuth (III) oxide (Bi_2O_3) nanoparticles and SbSI nanowires. As a solvent, N, N-dimethylformamide was used (Sigma Aldrich, 99,8% purity). The final products were the solutions of PAN/DMF/nanofillers at a concentration of polymer of 15% by weight and 50% concentration by weight of the used nanofillers. Polymer and composite nanofibers were obtained using the electrospinning method from the solution, using the device: FLOW - Nanotechnology Solutions Electrospinner 2.2.0–500. The used process parameters are presented in Table 1. During the electrospinning process, the obtained nanofibers were deposited on glass substrates.

Table 1
The electrospinning process parameters.

Parameters of electrospinning process	
Parameter	Value
The flow rate of the solution, [ml/h]	35
Potential difference between the electrodes, [kV]	12.5
Duration of the process, [min]	20
Distance between the electrodes, [cm]	20

The obtained polymer and composite nanofibers as well as microparticles were analyzed in terms of quantity and quality using X-ray EDS micro-analysis and topography imaging of the surface with the use of scanning electron microscope Zeiss Supra 35 with x-ray spectrometer Trident XM4 series provided by EDAX. Simultaneous measurements of the optical diffuse reflection and transmission of thin films of PAN, PAN/SbSI, PAN/Bi_2O_3 and PAN/TiO_2 deposited on glass substrates were carried out by two integrating spheres (Ocean Optics Inc.). One of them measured the light diffusely transmitted through the sample. The second one, equipped with a light source, measured the diffuse reflection. The optical signals were measured at room temperature using the PC2000 spectrophotometer (Ocean Optics Inc.). The multiple averaged optical characteristics were registered using the OOI-Base program (Ocean Optics Inc.) from 300 nm to 1000 nm. The standard WS-1 (Ocean Optics Inc.) was used as a reference for diffuse reflectance measurements. The standard WS-1 (Ocean Optics Inc.) was used as a reference for diffuse reflectance measurements. Examples of the measured spectra of diffuse reflectance (Rd) and transmittance (Td) are shown in Fig. 1. In addition, in the case of PAN and PAN/TiO_2, absorbance measurements have been conducted using the spectrophotometer UV-VIS Evolution 220 by Thermo-Scientific Company. During the studies, the light beam with a wavelength in the range 190–1100 nm fell perpendicularly on the sample.

3. Results and discussion

3.1. Morphology analysis

Using stable parameters of the electrospinning process presented in Table 1, for all configurations of spinning solutions, polymer or composite nanofibers with 50% concentration of the reinforcing phase have been obtained. In the case of a clean polymer solution, the morphology of PAN nanofibers showed that these measured fibers are deprived of structural defects and are characterized by a homogeneous thickness along the entire length (Fig. 1a). The tests of the PAN fiber diameters indicate that the measured diameters ranged from 100 to 450 nm, with the most frequent diameter values being included in the range of 250–300 nm, representing about 40% of all fiber diameter values of the sample (Fig. 1a histogram). The determined average layer thickness of the fiber is 243 nm.

The SEM images obtained for the nanofibres of PAN reinforced with TiO_2 nanoparticles indicate numerous structural defects of the surface of the obtained nanocomposite fibers (Fig. 1b). One can see that X-ray microanalysis points to visible defects of the nanofibres' structure in the form of local TiO_2 nanoparticle agglomerations. This is a consequence of strong interactions between nanoparticles. The analysis of fiber diameter values of nanocomposites reinforced with TiO_2 indicates that the obtained diameters of fibers have been in the range from 150 to 700 nm and the largest group of 28% had a diameter in range of 300–350 nm (Fig. 1b, histogram).

The morphology of the fibrous mats reinforced with Bi_2O_3 was characterized by a uniform diameter along the entire length. The PAN/Bi_2O_3 morphology analysis showed no occurrence of defects caused by Bi_2O_3 agglomerates (Fig. 1c). The observed spindled beads and spherical shapes are typical for nanofibers obtained by the electrospinning