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The analysis of surface morphology, band gaps and optical properties of PAN/GO thin films

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ABSTRACT

Purpose: PAN/GO nanocomposites are gaining more and more interest from research and industrial environments. According to theoretical studies and experimental tests, PAN/GO exhibits excellent properties such as tensile strength, good thermal and electrical conductivity, excellent thermal and tribological properties. Thanks to this property, the composite is considered the ideal successor to the nanocomposites used so far. The PAN/GO nanocomposite has great potential in the filtration, automotive, electrical and photovoltaic industry.

Design/methodology/approach: The spin-coating process is used to produce thin layers by centrifuging a liquid substance on flat surfaces. The advantages of the spin-coating process are simplicity and ease with which the process can be carried out. Due to the ability to high spin speeds, high airflow leads to fast drying time, which in turn results in high consistency in both macroscopic and nanometre scales. The spin-coting method is usually the starting point and reference point for most academic and industrial processes that require a thin and uniform coating. The use of spin coating has a wide spectrum. This technique can be used to coat small substrates (from a few square mm) up to the coating of flat displays, e.g. TV sets, which may have a meter or more in diameter.

Findings: Among the existing methods for producing thin layers, including physical and chemical methods for gas phase deposition or the self-assembly process, the spin-coating process makes it possible to produce uniform thin nanocomposite layers in an easy and cheap way. Spin coating is usually the starting point and reference point for most academic and industrial processes that require a thin and uniform coating. The advantage of the method is the wide spectrum of use. It is used for coating substrates with everything from photoresists, insulators, organic semiconductors, synthetic metals, nanomaterials, metal precursors and metal oxides, transparent conductive oxides and many other materials. Often, spin coating is used to unravel polymer layers or photoresist on semiconductor substrates.

Research limitations/implications: Due to the ongoing research on the potential applications of PAN/GO thin layers, including electronics, automotive and photovoltaics, it is worth trying to optimize the parameters of the spin-coiling process such as rotational speed or duration of the process. It is also worth trying to optimize the concentration of GO in the nanocomposite.

Practical implications: Despite mixing the solution with an ultrasonic homogenizer to disperse the nanoparticles, the particles dispersed to form a rough surface.

Originality/value: Low-cost, easy to carry out method of producing thin nanocomposite layers, having significant application in laboratory environments.

Keywords: Nanomaterials, Spin coating, Nanocomposite, Polyacrylonitrile, Graphene oxide, Band gaps

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MATERIALS

1. Introduction

At the beginning of the 21st century, a dynamic increase in interest in nanotechnology and nanomaterials is observed. Such materials, due to their size, have properties that cannot be obtained with conventional materials. Due to this, they become an opportunity to obtain materials with much better properties than those used so far. Based on the literature review, it is possible to obtain particularly satisfactory optical, strength, and physicochemical properties by producing nanocomposites. Thanks to various and continuously improved production methods, it is possible to keep production costs low, which, combined with the obtained properties, gives wide possibilities of using nanocomposites [1-4].

The key to producing material with special properties is the right selection and proportion of materials, and the use of the right manufacturing method. Satisfactory properties of nanocomposites are noted using a polymer matrix reinforced with nanoparticles. The features of this type of materials are good electrical, magnetic, optical and mechanical properties. In addition, the obtained materials have a low mass and flexible, typical for organic materials [5].

In the presented work, nanocomposite thin layers were produced, in which polyacrylonitrile (PAN) was used as the matrix, and graphene oxide (GO) as the nanofiller. A review of the literature on the materials used was carried out, focusing on their properties, disadvantages and advantages as well as general characteristics.

Polyacrylonitrile is an important and frequently used polymer in the field of nanotechnology. It is a copolymer made from a mixture of monomer and acrylonitrile. It has a number of features that make it attractive. PAN provides high thermal and chemical stability, resistance to oxidative degradation, good mechanical strength, good conductive properties and improves retention. An additional advantage is the relatively low price and general availability of the material. Thanks to its properties, a large share of polymer can be noticed in the electrochemical, filtration, textile, space and energy storage industries [6-10].

Graphene oxide used in the study is a two-dimensional hydrophilic nanomaterial exhibiting extremely attractive properties, which it owes to its dimensions, geometry of particle arrangement and oxygen function group. As a nanofiller, it improves the mechanical properties, rigidity of nanocomposites, has excellent electrochemical, physicochemical, optical and electrical properties. Graphene oxide exhibits variable resistance, and retains saved data in data storage devices after a power interruption. An additional advantage is the relatively low cost of the material and its good availability. Due to a number of attractive properties, this material is used in the automotive, space, aviation, pharmacy, cosmetology, military, construction, electronics, chemical, photovoltaic, clothing and many other industries [11-16].

The combination of PAN/GO materials into a composite material according to theoretical studies and experimental tests gives excellent properties such as tensile strength, good thermal and electrical conductivity. Thanks to this property, such a composite is considered the ideal successor to the previously used composites and nanocomposites. Tribologically, PAN/GO has great industrial potential as a lubricant because it has excellent thermal and tribological properties. There is a large potential of nanocomposite in the production of water filtering membranes or flexible electrolyte, which can replace the liquid electrolyte used in lithium-ion batteries [17-21].

2. Materials and methodology

Two 10% solutions were prepared for accurate analysis. The first was a pure solution of polyacrylonitrile polymer (PAN, manufacturer Sigma Aldrich, purity 99%, Mw = 150,000) with a solvent N,N-dimethylformamide (DMF, manufacturer Sigma Aldrich, purity 99.8%). The second solution is polyacrylonitrile/N,N-dimethylformamide/graphene oxide (manufacturer ATH Bielsko-Biała). The ratio used is shown in Table 1.

Table 1.
The table shows the proportion and concentration of substrates used to obtain two solutions

<table>
<tr><td colspan="6">10% PAN/DMF solution</td></tr>
<tr><td colspan="3">PAN</td><td colspan="3">DMF</td></tr>
<tr><td colspan="3">2.1 g</td><td colspan="3">20 ml</td></tr>
<tr><td colspan="6">10% PAN/DMF solution with 5% GO (graphene oxide)</td></tr>
<tr><td colspan="2">PAN</td><td colspan="2">DMF</td><td colspan="2">GO</td></tr>
<tr><td colspan="2">1.995 g</td><td colspan="2">20 ml</td><td colspan="2">0.105 g</td></tr>
</table>

The first stage of preparing the solution involved mixing the polymer with a solvent to disperse the particles. Mixing was carried out using a Bandelin Sonoplus ultrasonic homogenizer in a sonication process that lasted 20 minutes.

The second stage involved mixing the PAN/DMF/GO solution on a magnetic stirrer. The process lasted over 3 days, which allowed for good dispersion and prevented the formation of agglomerates.

The third stage involved the formation of thin layers from the resulting solutions. The spin-coating method was used to make thin layers using the Laurell Modular 23 device. The rotational speed was a variable parameter during production, which largely determines the thickness of the obtained coating. Two samples were prepared from each solution. Process parameters are presented in the table below (Tab. 2). Then the produced material was allowed to dry for 15 minutes.

Table 2.
The table presents the parameters of the spin-coating process

Solution	Rotational speed, rpm	time, s
PAN/DMF	2000	60
PAN/DMF	4000	60
PAN/DMF/GO	2000	60
PAN/DMF/GO	4000	60

Then, an analysis of the surface morphology, band gaps and optical properties of thin PAN/GO layers was performed. Morphological analysis was performed on an atomic force microscope (AFM) Park System XE-100, working in non-contact mode. Another study of the analysis of the optical properties of the material was carried out on a UV-vis Thermo Scientific Evolution 220 spectrophotometer.

3. Results and discussion

This part of the work presents and discusses the results of conducted research. Below are photos presenting the surface topographies of PAN and PAN/GO materials at various rotational speeds of the manufacturing process (Fig. 1).

The surface roughness of thin layers represented by the RMS mean square value was also examined. The results obtained are shown in the table below (Tab. 3).

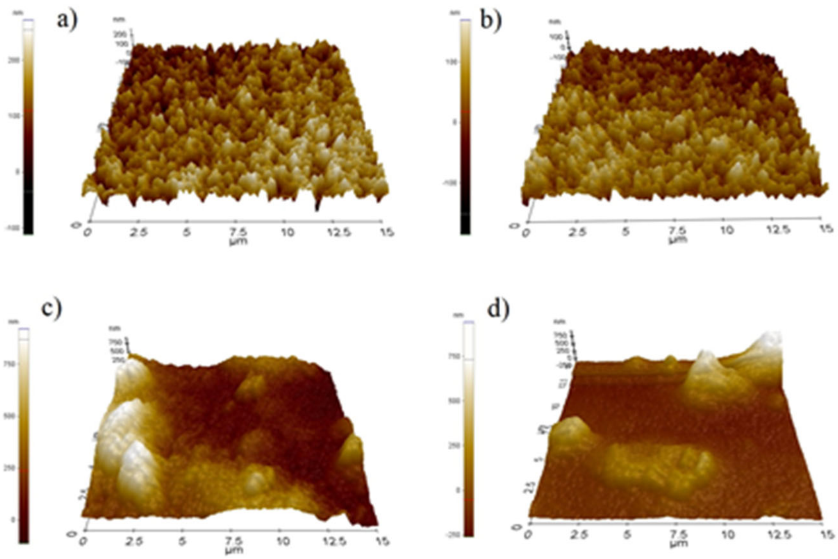

Fig. 1. Surface topography: a) PAN; rotational speed – 2000 rpm, b) PAN; rotational speed – 4000 rpm, c) PAN/GO; rotational speed – 2000 rpm, d) PAN/GO; rotational speed – 4000 rpm

Table 3.
Coefficient of surface roughness (RMS) of created layers

Material	Rotational speed, rpm	RMS value, nm
PAN	2000	48.80
PAN	4000	48.78
PAN/GO	2000	209.25
PAN/GO	4000	189.35

Table 4.
Thickness measurement of thin films

Material	Rotation speed, rpm	Thickness, µm
PAN	2000	8.7
PAN	4000	7.2
PAN/GO	2000	7.1
PAN/GO	4000	6.4

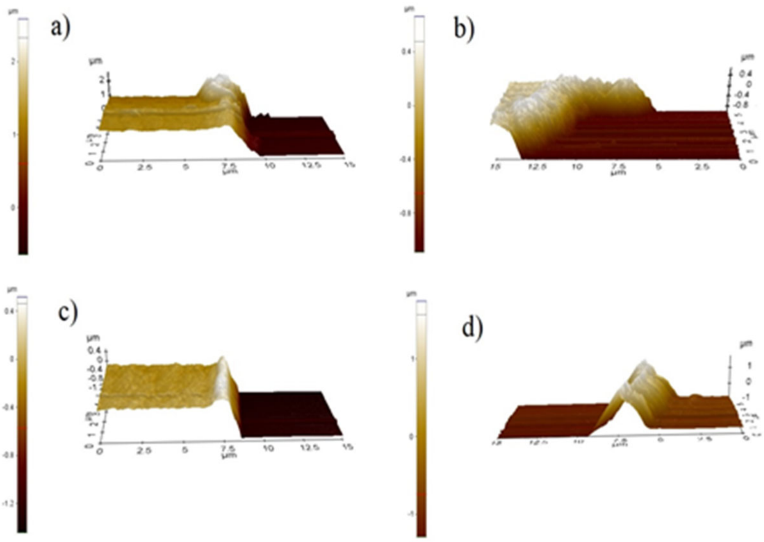

Fig. 2. Thickness measurement test: a) PAN; rotational speed – 2000 rpm, b) PAN; rotational speed – 4000 rpm, c) PAN/GO; rotational speed – 2000 rpm, d) PAN/GO; rotational speed – 4000 rpm

Another atomic force microscope study included measuring the thickness of the layers obtained (Fig. 2). The results of the study are presented in the table below (Tab. 4).

Topographic images of thin layers do not indicate a change in surface roughness due to the rotational speed of the spin-coating process. The values of the mean square factor (RMS) are almost identical for the PAN material – rotational speed 2000 rpm and PAN – rotational speed 4000 rpm and similar for thin layers PAN/GO – rotational speed 2000 rpm. and PAN/GO – rotational speed 4000 rpm PAN/GO surface topography images – rotational speed 2000 rpm and PAN/GO – rotational speed 4000 rpm. indicate a much greater surface roughness compared to materials without the addition of graphene oxide, which suggests that the addition of graphene oxide affects the increase in surface roughness. The pictures are porous. It is stated that the most likely cause of pore formation is the solvent used, which evaporated during the processes of making and drying thin layers. Examination of the thickness of the layers produced indicates the influence of the rotational speed of the material manufacturing process on its thickness. It can be concluded that as the rotational speed parameter increases, the thickness of the obtained layer decreases. Material with the addition of graphene oxide exhibits smaller thicknesses compared to PAN materials, and it can be assumed that graphene oxide affects the change in material viscosity.

Studies on the UV-vis spectrophotometer were used to analyse optical properties. Absorption of electromagnetic radiation as a function of wavelength was examined in all thin layers produced (Fig. 3). The study took into account the wavelength in the 200-800 nm range.

Absorption spectra for PAN materials swirled at 2000 rpm and 4000 rpm they are almost identical. They are characterized by a sharp absorption edge in the ultraviolet region and a peak width in the range of 200-310 nm. The absorption maximum for both materials falls for a wavelength of 300 nm and assumes a value of 2.1. Absorption spectra for PAN/GO materials, which were centrifuged at 2000 rpm. and 4000 rpm show similar relationships as in the case of materials from a pure PAN. Both spectra have a sharp absorption edge at a wavelength of 330 nm and a peak width in the range of 200-330 nm. The absorption maximum for both materials falls on a wavelength of 290 nm and assumes a value of 2.4. It is assumed that with higher rotational speed of the produced layers, their thickness decreases, and this causes a decrease in the value of absorption. The analysis of the obtained absorption spectra shows that the rotational speed with which the thickness value of the thin layers obtained is identified does not affect the absorption. It is believed that this is due to the relatively small difference in thickness of swirled materials at 2000 and 4000 rpm. The analysis shows that graphene oxide increases the maximum absorption value and increases the absorption range as a function of wavelength that falls on the ultraviolet region. The increase in absorption achieved by the addition of graphene oxide is associated with the possibility of using this material as transparent coatings providing protection against ultraviolet radiation, or using it in the photovoltaic cell industry.

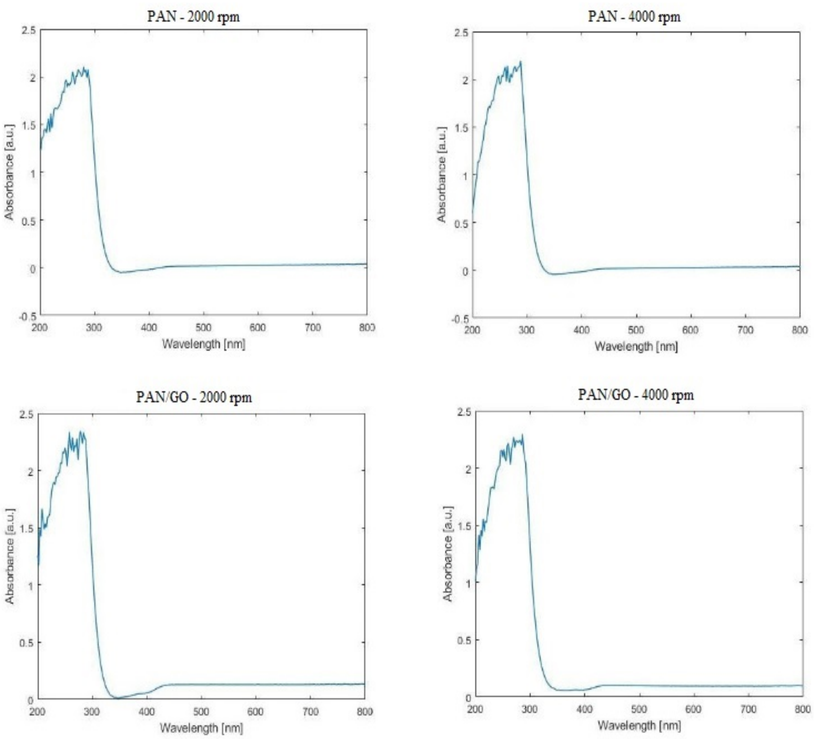

Fig. 3. Absorbent spectra: a) PAN; rotational speed – 2000 rpm, b) PAN; rotational speed – 4000 rpm, c) PAN/GO; rotational speed – 2000 rpm, d) PAN/GO; rotational speed – 4000 rpm

The next study involved determining the energy gap. The energy gap was determined based on the recorded absorbance spectra as a function of the wavelength recorded for the produced thin layers PAN and PAN/GO, and on the equation:

$$\left[h\nu \ln\left(\frac{1}{10^{-ABS}}\right)\right]^2 = B(h\nu - E_g) \qquad (1)$$

where B is a constant depending on the probability of electron transitions divided by the thickness of the tested layer. Then, the relationships $\left[h\nu \ln\left(\frac{1}{10^{-ABS}}\right)\right]^2$ are plotted as a function of radiation quantum energy for all produced nanomaterials (Fig. 4).

The conducted research in the scope of band structure analysis of thin films produced showed a negligible effect of the presence of graphene in the polyacrylonitrile matrix on the width of the energy gap of the thin films analyzed. The influence of the spinning speed of thin layers on the value of the energy gap is noticed. A relationship is observed – the higher the spinning speed of nanomaterials, the lower the value of the energy gap (Tab. 5). The decrease in the value of energy gaps is probably caused by a decrease in the thickness of the layer with an increase in the spinning speed of nanomaterials.

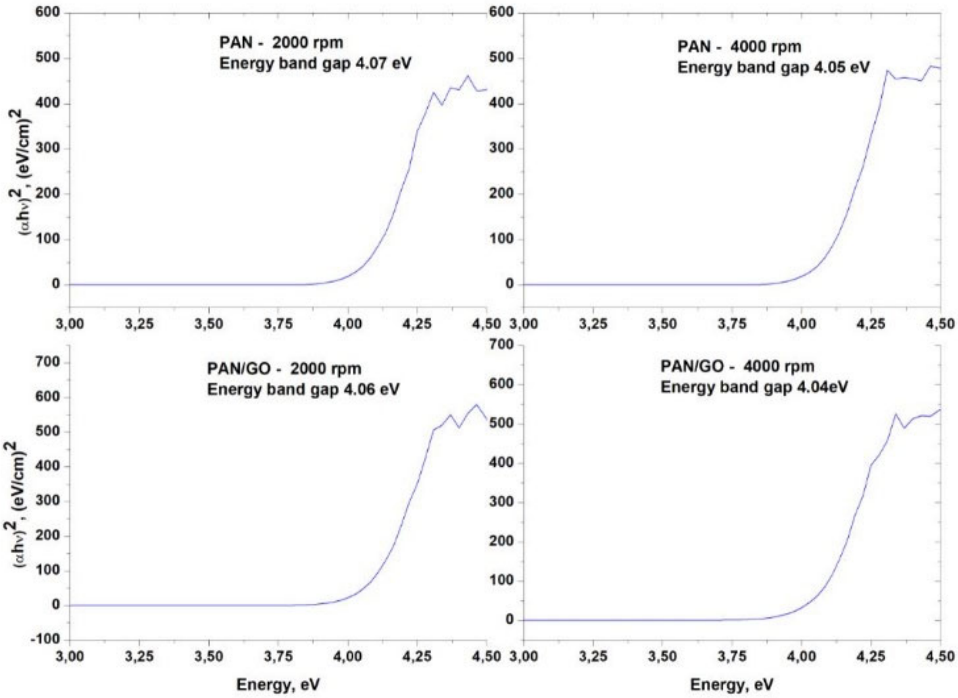

Fig. 5. Graphs of the quantum radiation energy function obtained for the thin films produced

Table 5.
Energy gap values for the nanomaterials tested

Material	Rotational speed, rpm	Energy band gap, eV
PAN	2000	4.07
PAN	4000	4.05
PAN/GO	2000	4.06
PAN/GO	4000	4.04

4. Conclusions

The aim of the study was to analyse surface morphology band gaps and optical properties of thin PAN/GO layers. To obtain thin layers, two solutions were made, one of which was a 10% PAN/DMF solution and the other was a 10% PAN/DMF/GO solution. Then using the spin-coating method, these solutions were centrifuged. Two samples were prepared from each solution, one of which was centrifuged at 2000 rpm and the next 4000 rpm. The produced materials were subjected to surface morphology tests, for which an atomic force microscope (AFM) was used. Optical properties analysis tests were also carried out, for which a UV-vis spectrophotometer was used.

Based on the analysis of surface morphology, it is found that the materials produced have a porous structure. It is presumed that it was formed as a result of solvent evaporation during manufacturing and drying processes. From surface topography studies, it is concluded that the production speed does not affect to the surface roughness of the materials obtained and the effect of the addition of graphene oxide for increased surface roughness. The reason for the greater surface roughness in materials with the addition of graphene oxide is the agglomeration of nanoparticles. Examination of thin layer thickness indicates the influence of the rotational speed of the manufacturing process on their thickness. It is concluded that as the rotational speed parameter increases, the thickness of the obtained layer decreases. Materials with the addition of graphene oxide exhibit smaller thicknesses compared to pure PAN materials, and it can be assumed that graphene oxide affects the change in material viscosity. Based on the analysis of optical properties tests that were carried out on a UV-vis spectrophotometer, it is concluded that the rotational speed of the manufacturing process has no effect on absorption. It is concluded that graphene oxide increases the maximum absorption value and increases the absorption range as a function of wavelength that falls on the ultraviolet region.

Analysis of the value of energy breaks showed no effect of graphene content on the value of energy breaks. The influence of the spinning speed of thin layers on the value of the energy gap is noticed. A relationship is observed – the higher the spinning speed of nanomaterials, the lower the value of the energy gap. The decrease in the value of energy gaps is probably caused by a decrease in the thickness of the layer with an increase in the spinning speed of nanomaterials.

Morphological analysis, band gaps and optical properties show that thin PAN/GO layers are an interesting material with great potential for many applications, for example transparent coatings protecting against ultraviolet radiation or the use of material in the solar cell industry.

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