

Manufacturing process and characterization of electrospun PVP/ZnO NPs nanofibers

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Abstract. Constantly developing nanotechnology provides the possibility of manufacturing nanostructured composites with a polymer matrix doped with ceramic nanoparticles, including ZnO. A specific feature of polymers, i.e. ceramic composite materials, is an amelioration in physical properties for polymer matrix and reinforcement. The aim of the paper was to produce thin fibrous composite mats, reinforced with ZnO nanoparticles and a polyvinylpyrrolidone (PVP) matrix obtained by means of the electrospinning process and then examining the influence of the strength of the reinforcement on the morphology and optical properties of the composite nanofibers. The morphology and structure of the fibrous mats was examined by a scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) and Fourier-transform infrared spectroscopy (FTIR). UV-Vis spectroscopy allowed to examine the impact of zinc oxide on the optical properties of PVP/ZnO nanofibers and to investigate the width of the energy gap.

Key words: electrospinning, PVP/ZnO, nanofibers, band gap, nanocomposites, optical properties.

1. Introduction

In recent years, nanocomposites with a polymer matrix, reinforced by semiconductor nanoparticles have gained a lot of interest due to the individual properties of the phases as well as the emergence of new, better properties by combining the organic and inorganic phases [1]. In particular, some improved optical and electrical properties are observed, as evidenced by the extensive range of potential functions of such nanocomposite materials in the type of polymer/semiconductor materials [2–8]. Resulting from a large surface-to-volume ratio, the most common structures, manifesting the ability to control pore size and having a very large contact surface area in comparison to solid, thin layers, are now nanofibers produced by the process called electrospinning. Spinning in an electrostatic field uses a strong, initiated electric field, where the droplets of spinning solutions are elongated, which results in micro- and nanometric nanofibers [9].

From among many inorganic compounds used in the production of composite nanofibers with a polymer matrix, zinc oxide nanostructures are becoming increasingly popular both in the scientific and industrial fields, due to their physical properties, with particular regard to electrical [10], optical [11] and piezoelectric properties [12]. ZnO owes its enormous popularity to the nanoelectronic field, mainly due to its properties, such as a 3.37 eV energy band gap or an excitation energy of 60 meV. Moreover, zinc oxide has a large group of nanostructures, which can be used as photonic and electronic components in nanodevices [13] as well as nanometric transducers and actuators [14].

The addition of a reinforcing phase in the form of ZnO nanostructures to the polymer nanofibers produced by the electrospinning process contributes to the production of composite nanofibers with significantly better thermal, mechanical and optical properties as compared with the fibers manufactured from a pure polymer solution [15–18]. Some studies on the optical properties of PVDF/ZnO nanostructure composites yield promising results concerning the applicability of this type of materials in screens protecting against harmful UV radiation [19, 20]. Great fluorescence properties of composite materials in the form of PVA/ZnO nanofibers can contribute to cheaper photovoltaic devices or UV sensors [21]. Furthermore, PVP/ZnO composite fibrous mats manufactured by Lee D. et al. show some potential applications in thermoelectric materials with much higher efficiency in comparison to the currently used materials [22]. It has been shown that addition of the zinc oxide nanoparticle reinforcing phase significantly lowers the diameter values of the resulting nanofibers, which contributes to the increase of sensitivity of the sensors constructed of this type of material [23]. In the case when polyvinylpyrrolidone is the organic phase, strong, hygroscopic properties of the polymer are observed, due to the presence of the hydrophilic pyrrolidone moiety, which results in the ability to form thin films. PVP, in view of the presence of C-N, C-H and C=O groups in the chemical structure, which are responsible for interaction with the nanoparticles of the reinforcement, is the ideal polymer for the formation of fine, fiber composite mats [24].

Based on the above information, the authors decided to focus on the manufacturing process of electrospun polymer nanofibers doped with zinc oxide nanoparticles, with the concentration of reinforcing phase much higher than the one reported previously [25]. That also contributes to novel industry application, for example, in UV shielding screens, which had not been manufactured to date.

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2. Materials and methodology

To prepare spinning solutions, polyvinylpyrrolidone (PVP, manufacturer: Sigma Aldrich, purity of 99%, $M_w = 1\,300\,000$ g/mole) and ethyl alcohol (EtOH, purity of 99.8%) were used. The reinforcing phase was zinc oxide nanopowder (ZnO). The first step was a polymer in an ethanol solution preparation (PVP/EtOH). To obtain a 10% (wt.) solution, 9 g (11.4 ml) of ethanol was mixed with 1 g of polymer. The solution was blended using a magnetic stirrer for 24 hours. ZnO/EtOH solutions were prepared in succeeding order steps: 9 g (11.4 ml) of ethanol with the following amounts of ZnO nanopowder were mixed: 0.15 g, 0.30 g and 0.45 g solutions and 15, 30 and 45% of the reinforcing phase mass concentration relative to the concentration of the polymer were made. The as-prepared ZnO/EtOH solutions were subjected to the ultrasonication process for 30 minutes. After the sonication process, the measured amounts of polymer – 0.85, 0.7 and 0.55 g – were added to ZnO/EtOH solutions and were subjected to blending using a magnetic stirrer for 24 hours. The obtained solutions of PVP/EtOH and PVP/EtOH/ZnO were placed in sequence in a device pump and were subjected to the electrospinning process, which was performed using the FLOW – Nanotechnology Solutions Electrospinner 2.2.0–500 device, using the following parameters: the distance between the collector and the pump was 15 cm, the electric voltage was 20 kV and the average flow rate stood at 4 ml/h.

The structure morphology of the obtained nanocomposites was analyzed using a scanning electron microscope (SEM, Zeiss Supra 35) and chemical content analysis was performed using the energy dispersive X-ray spectroscopy detector (EDS, Trident XM4, manufacturer: EDAX). In order to prepare the test specimen, a piece of aluminum foil, approx. 1 cm × 1 cm, covered with a fibrous mat, was cut. Then, a gold conductive layer was sprayed to improve sample conductivity during the PVP and PVP/ZnO mat surface morphology examination. For each sample, the fifty-fold measurement of fiber diameter values was performed, and the results were presented in the form of

histograms. The chemical bonds of the obtained nanofibers were studied with the use of Fourier-transform infrared spectroscopy (FTIR), with investigation of absorbance in the function of wavenumber spectra. Optical properties of the obtained composite materials were studied based on the absorbance in the function of wavelength graphs, which were received by the UV/VIS Evolution 220 spectrophotometer (manufacturer: Thermo Scientific). The width of the energy band gap analysis of the composite materials was evaluated on the basis of the obtained UV-Vis spectra and with the use of a method presented in works [26–28].

3. Results and discussion

3.1. Morphology, chemical composition and reinforcing phase formation analysis. The structure of the doped phase, i.e. the ZnO nanopowder, consisted of nanoparticles of shapes similar to cylindrical solids, which was confirmed by the examination applying a scanning electron microscope (SEM) (Fig. 1a). The average diagonal value of the tested zinc oxide nanostructures, which were designated on the basis of a fifty-fold measurement of randomly picked particles, was about 224 nm (Fig. 1c). Based on the ZnO nanoparticle EDS spectrum, the examination of which was applied to the whole area presented in Fig. 1a, the following chemical elements were confirmed: oxygen (O) and zinc (Zn), along with the presence of a gold (Au) peak, attributed to the conductive layer being sprayed onto the fibrous mats to improve conductivity during the SEM examination. Such results testify to the presence of pure ZnO nanopowder (Fig. 1b).

3.2. Morphology and chemical structure of produced nanofibers. The use of a constant parameter of the electrospinning process from a pure, polymer PVP/EtOH solution allows to obtain PVP nanofibers free of structural defects, characterized by constant diameter values along the entire length (Fig. 2a, b).

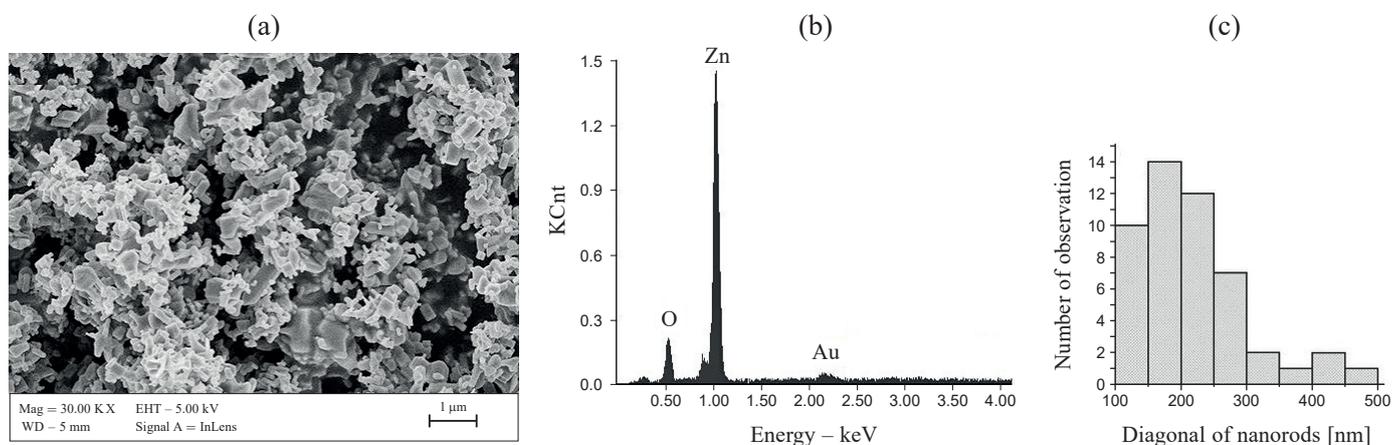


Fig. 1. a) SEM image of ZnO nanopowder, b) EDS analysis of the chemical composition of ZnO nanopowder (the presence of the gold peak is attributed to the conductive layer sprayed onto the fibrous mats to improve conductivity during the SEM examination), c) histogram showing the distribution of the diagonal values of the studied ZnO nanostructures

The average diameter values of the obtained PVP nanofibers ranged from 400 to 1200 nm and were confirmed on the basis of a fifty-fold measurement of randomly picked fibers. Moreover, the largest group of diameter values of fibers (28%) were those with diameters from 600 to 700 nm (Fig. 2d). EDS analysis of the obtained polymer PVP nanofibers affirmed the presence of carbon (C) and oxygen (O) in the chemical structure of organic materials, including the polymer used. The Al (aluminum) peak is caused by the conductive layer provided in order to collect fibers during the electrospinning process; besides, the Au (gold) peak is attributed to the gold layer sprayed on for better conductivity during the SEM examination (Fig. 2c).

The electrospinning process applied to the PVP/ZnO/EtOH solutions resulted in the production of PVP/ZnO composite fibrous mats, which were then analyzed for morphology and chemical composition. The presence of the reinforcing phase in the form of a ZnO nanopowder in spinning solutions resulted in obtaining nanofibers with distinctly smaller diameter values in comparison to the diameters of pure polymer nanofibers. In the case of composite fibrous mats with 15% (wt.) of the doped phase, the diameter values of the produced nanofibers ranged from 100 to 1000 nm. For 30% of the ZnO mass concentration they stood at 300–700 nm, while the largest mass concentration of zinc oxide in the polymer matrix – 45% – resulted in diam-

eter values of PVP/ZnO fibers from 100 to 500 nm (Fig. 3d, 4d, 5d). The noticeable decrease in the diameter values of composite nanofibers is due to the increased conductivity of the spinning solutions, which is caused by an increasing mass concentration of the semiconductor zinc oxide as compared with a polymer solution with a 0% concentration of ZnO [29, 30]. Moreover, dependence is observed between the decrease in the diameter values of PVP/ZnO nanofibers and the increase of the specific surface area of composite fibrous mats, which provides a massive opportunity in organic and inorganic ultra-sensitive gas sensor applications [31]. Topography analysis of the PVP/ZnO composite nanofibers (Fig. 3b, 4b, 5b) showed that the produced fibers are characterized by agglomerates of the reinforcing phase, which was also confirmed by the EDS examination. However, the number of agglomerates rise with the increase of the ZnO mass concentration in fibers. Such fact is caused by the trend of ZnO nanoparticle agglomeration, noticeable even when using small amounts (Fig. 3c, 4c, 5c). This is due to the high adhesion forces for a surface unit of the semiconductor nanostructures [32] used. The Al (aluminum) peak is due to the conductive layer provided in order to collect fibers during the electrospinning process; besides, the Au (gold) peak is attributed to the gold layer sprayed on for better conductivity during the SEM examination.

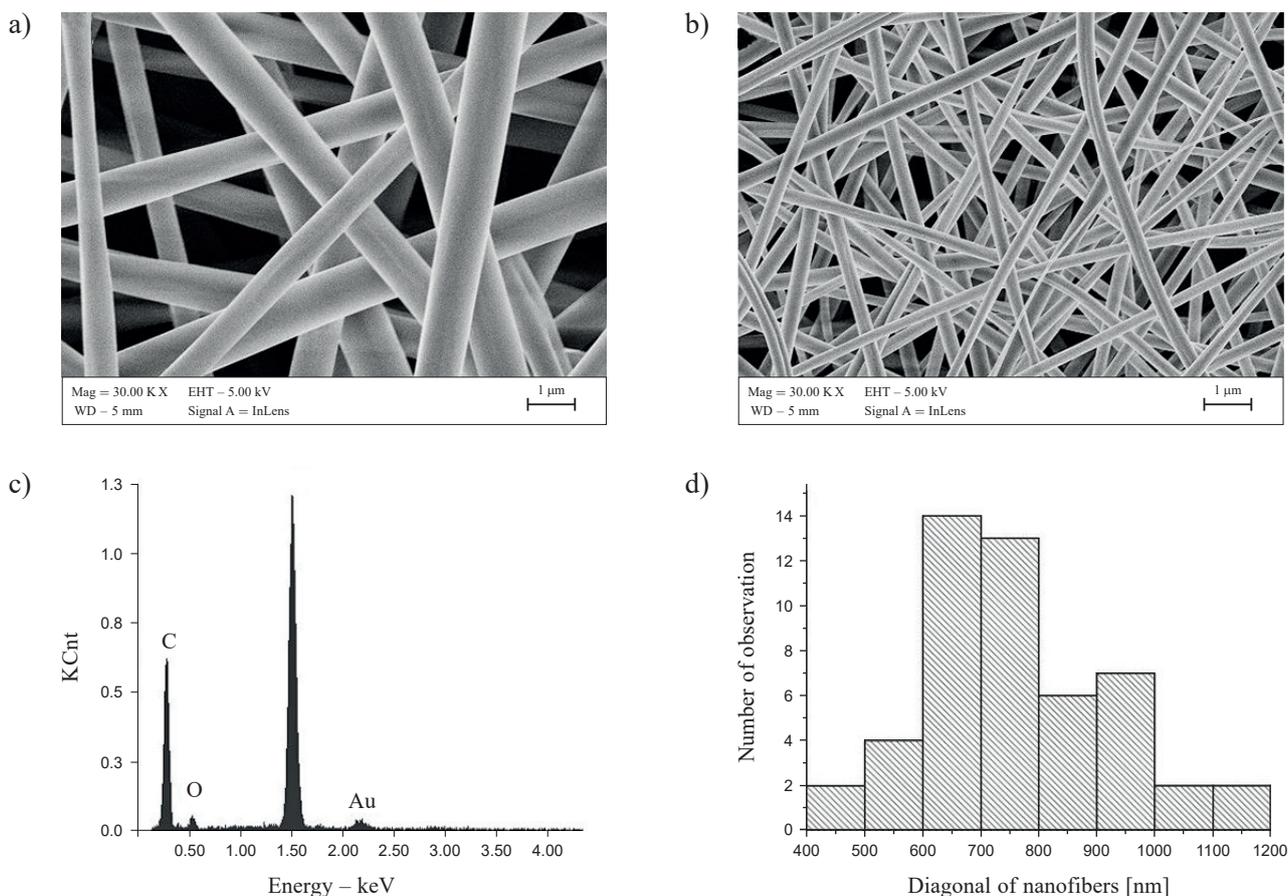


Fig. 2. SEM images of the obtained PVP nanofibers with magnification: a) of 30 K X, b) of 10 K X, c) EDS spectrum of chemical composition of PVP nanofibers, d) histogram showing distribution of diameter values of PVP nanofibers

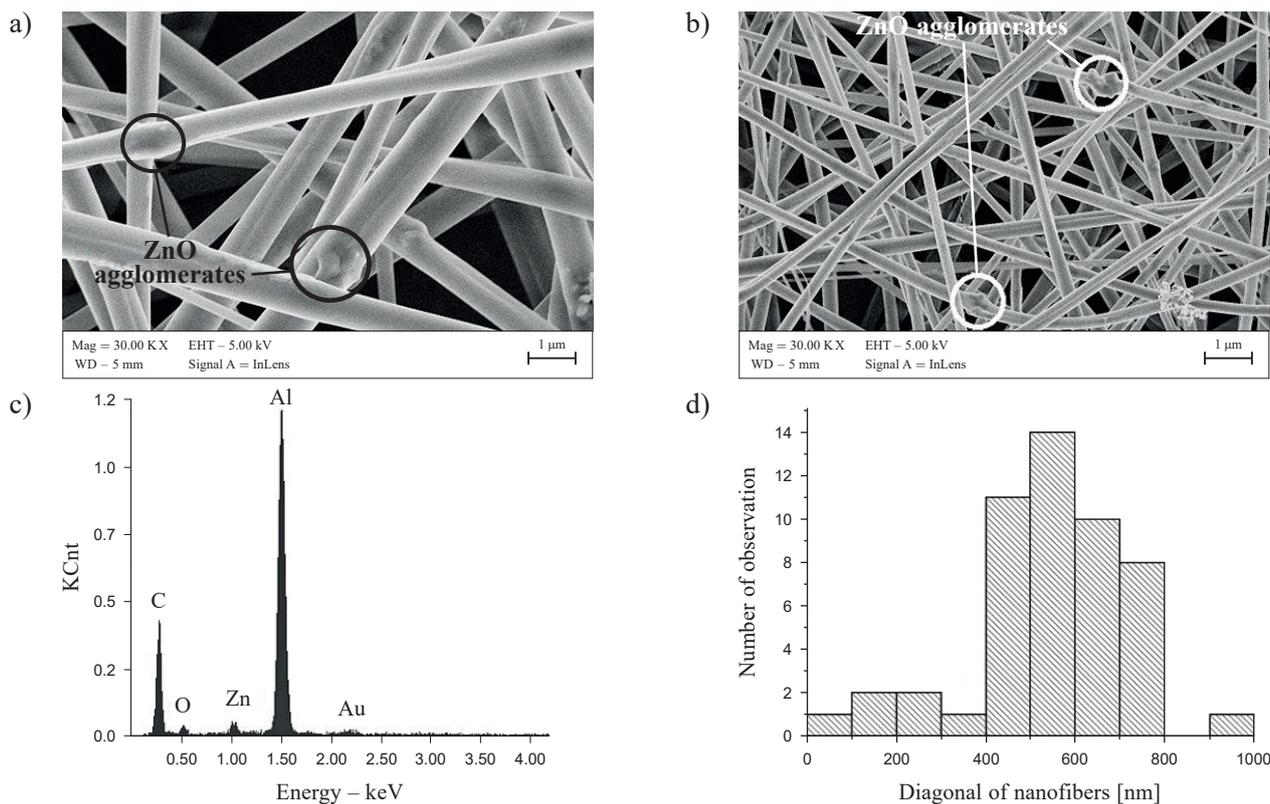


Fig. 3. SEM images of the obtained PVP/ZnO nanofibers with a 15% mass concentration of ZnO with magnification: a) of 30 K X, b) of 10 K X, c) EDS spectrum of the chemical composition of PVP/15% ZnO, d) histogram showing distribution of the diameter values of PVP/15% ZnO nanofibers

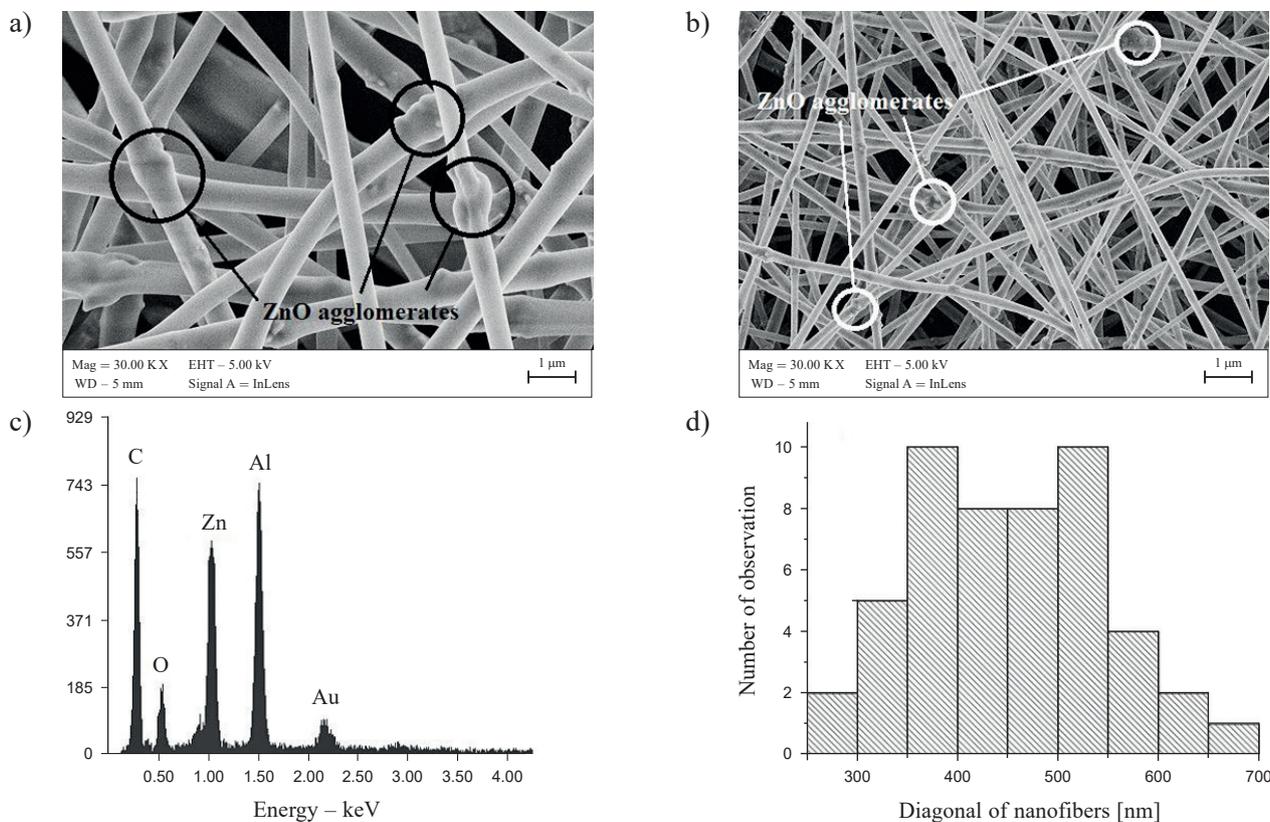


Fig. 4. SEM images of the obtained PVP/ZnO nanofibers with a 30% mass concentration of ZnO with magnification: a) of 30 K X, b) of 10 K X, c) EDS spectrum of the chemical composition of PVP/30% ZnO, d) histogram showing distribution of the diameter values of PVP/30% ZnO nanofibers

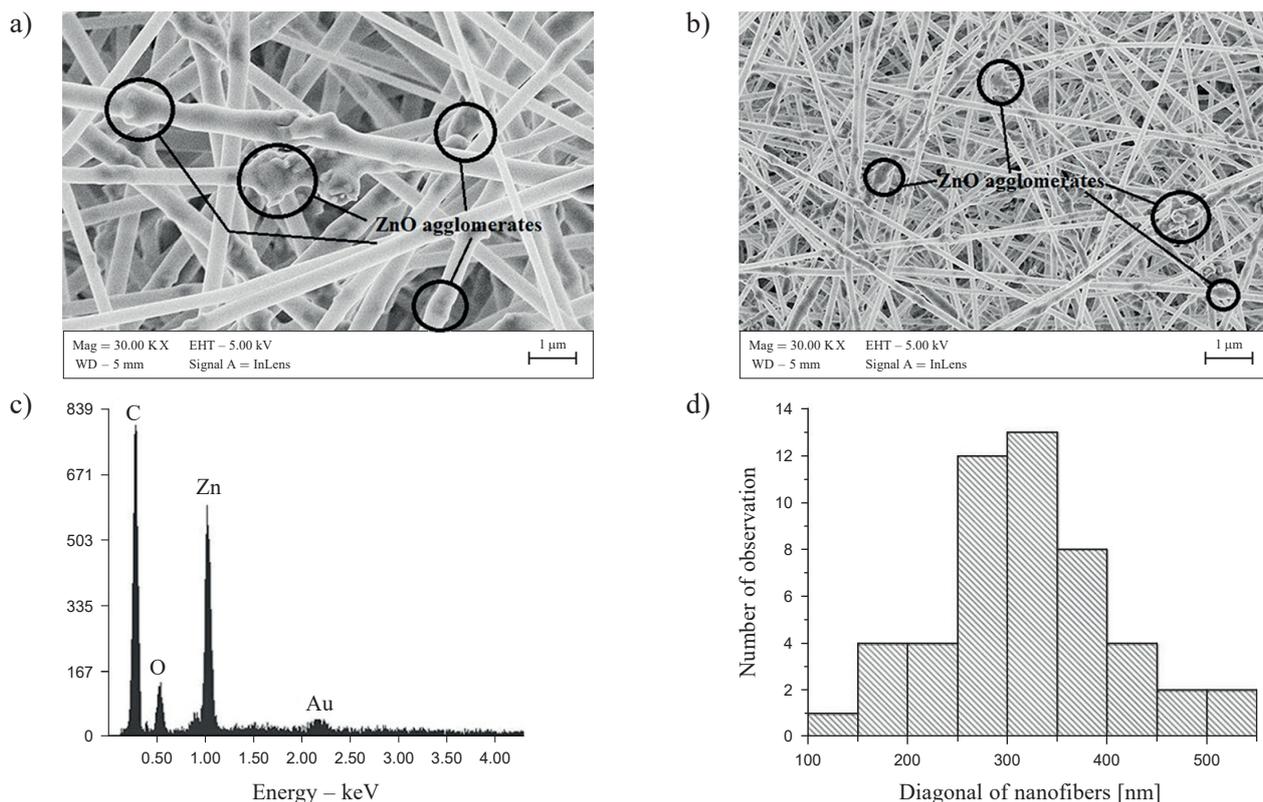


Fig. 5. SEM images of the obtained PVP/ZnO nanofibers with a 45% mass concentration of ZnO with magnification: a) of 30 K X, b) of 10 K X. c) EDS spectrum of the chemical composition of PVP/45% ZnO, d) histogram showing distribution of the diameter values of PVP/45% ZnO nanofibers

3.3. Thin fibrous mats FTIR analysis. Analyses of the intermolecular influences and bonds between ZnO nanoparticle atoms and the polymer matrix in the produced PVP/ZnO composite nanofibers were examined using Fourier-transform infrared spectroscopy (Fig. 6). The study of pure PVP fibrous mats showed the presence of characteristic peaks – 3400 cm^{-1}

– which is attributed to hydroxyl group O-H, probably caused in turn by water adsorption by a polymer molecule. The next few peaks: 1430 cm^{-1} and 1286 cm^{-1} , confirmed stretching bonds of C-N and the connection of the CH₂ group in pyrrole in PVP. The most intensive peak with the highest absorbance level referred to the C=O bond in the polymer molecule

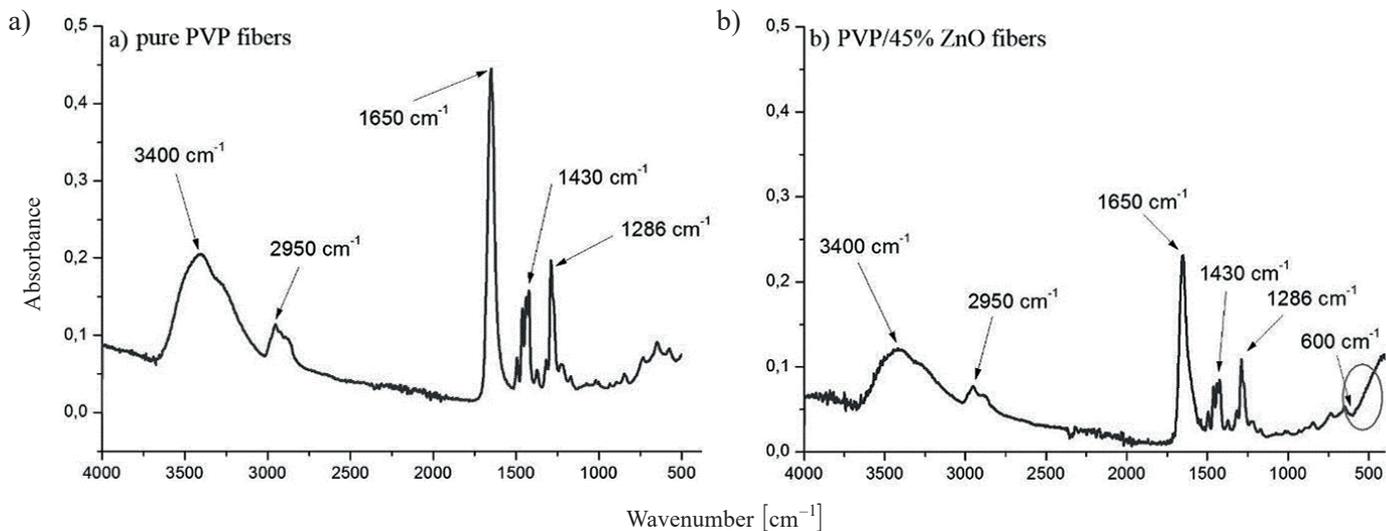


Fig. 6. FTIR spectra for: a) pure PVP nanofibers, b) PVP/45% ZnO composite nanofibers

at 1650 cm⁻¹ of the wavenumber value [33–36]. PVP/ZnO composite nanofiber FTIR examination with the highest ZnO mass concentration with respect to the polymer (45%) showed the presence of the characteristic peak in the wavenumber range from ~500 to 600 cm⁻¹, which is associated with the Zn-O bond and is confirmed by the same results obtained in work [37]. The comparison studies of FTIR spectra for PVP and PVP/ZnO nanofibers showed a significant increase in the absorbance level for composite fibrous mats as compared with polymer fibers, which was caused by the presence of ZnO in the composite material structure, of which the Zn-O bond is characterized by high electronegativity and the ZnO molecule stands out with its low molar mass. In summary, the FTIR examination confirmed the intermolecular influences and atomic bonds in the composite structure between PVP and ZnO molecules [38].

3.4. Analysis of optical properties using UV-Vis graphs.

Figure 7 shows absorbance in the function of the wavelength spectrum of the obtained pure PVP and PVP/ZnO composite nanofibers. The PVP nanofibers' sharp absorption edge is attributed to the wavelength of 300 nm, meanwhile the maximum absorption level is attributed to the wavelength of 290 nm. Those results confirm the results obtained in work [39] and testify to the proper methodology of the studies. With the increase of the doped phase in the form of the ZnO nanopowder, the absorption level decreases in comparison with pure polymer 10% nanofibers. However, in the case of the PVP/ZnO composite nanofibers, there can be observed some additional edge with the value of wavelength – 375 nm, which is attributed to the presence of ZnO nanoparticles [40–42]. The lack of widening in the absorption level to the near-ultraviolet range in the case of composite nanofibers with the 15% mass concentration of the reinforcing phase can be explained by the insufficient ZnO concentration relative to polymer, so that the greater importance in the mechanism of absorption of electromagnetic radiation is

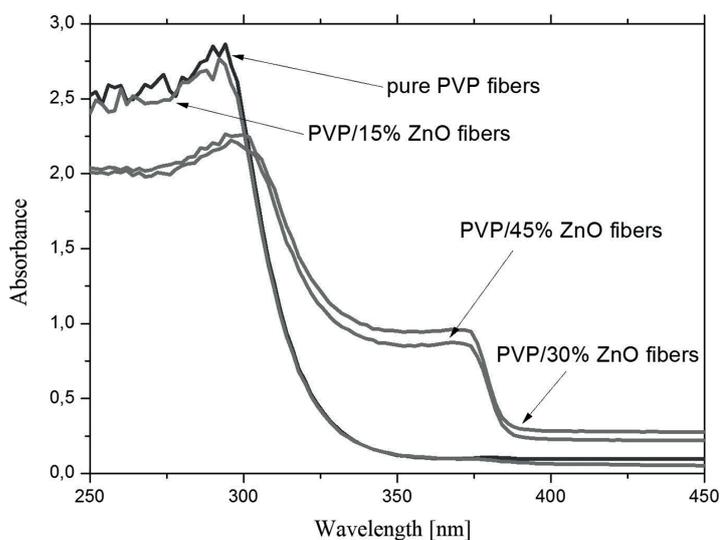


Fig. 7. UV-Vis spectrum for PVP and PVP/ZnO nanofibers

showed by the polymer matrix for quantum wavelengths below 325 nm. The noticeable increase of the absorption level and widening of absorbance spectra of electromagnetic radiation from 325 to 375 nm wavelengths, caused by an increase of zinc oxide mass concentration in the polymer matrix, opens up a wide range of potential applications of this type of materials, in particular in optical shields [41].

3.5. Energy band gap examination. Determination of the width of the energy band gaps of the obtained polymer and composite fibrous mats was based on investigating the dependence of the absorption coefficient of the material on the function of radiation energy (1) [26–28]:

$$\alpha h\nu = A(h\nu - E_g)^p \quad (1)$$

where α is the absorption coefficient, h is the Planck constant, ν is the frequency of electromagnetic radiation, E_g is the energy band gap and A is the constant dependent on the probabilities of electron transitions. In the case of the p coefficient, the value of 0.5 was used, which corresponds to every allowed optical transition [11]. The values of the absorption coefficient for each wavelength of electromagnetic radiation were determined on the basis of UV-Vis spectra. The obtained dependencies $(\alpha h\nu)^2$ in the function of quantum radiation energy with x-intercept, corresponding to the width of the energy gap of the studied composite fibers, are shown in Fig. 8. The energy gap for pure polymer PVP nanofibers was 3.99 eV, which is in accordance with the results obtained in works [43, 44]. Addition of the ZnO nanopowder to the spinning solutions, in the amount of 15% mass concentration relative to the polymer, resulted in a significant change in the width of the energy gap of PVP/ZnO nanofibers (3.98 eV) as compared with this value in PVP nanofibers. Such situation can be explained by the encapsulation of the reinforcing phase nanoparticles in the polymer fibers, which, in connection with the use of the smallest amount of ZnO, caused a lack of significant absorption of quantum electromagnetic radiation targeting the sample. The increase of the mass concentration of the reinforcement in the form of semiconductor ZnO nanostructures to 30 and 45% relative to the polymer concentration resulted in additional absorption curves, except for the peaks for pure polyvinylpyrrolidone, for which the determined zero of the function for the obtained functions $(\alpha h\nu)^2$ corresponds to the quantum radiation energy of, respectively, 3.23 eV (for PVP/30% ZnO) and 3.22 eV (for PVP/45% ZnO). Those values correspond to energy gaps of pure zinc oxide. The determined double values of band gaps for PVP/ZnO composite nanofibers containing ZnO nanoparticles with a 30 and 45% mass concentration, due to the significant amount of the semiconductor reinforcing phase particles, considering the decrease in fiber diameter values during the electrospinning process and an additional increase in the specific surface area, make such nanocomposite material particularly attractive in an extensive range of applications, such as sensors and in the new generation of piezoelectric nanogenerators.

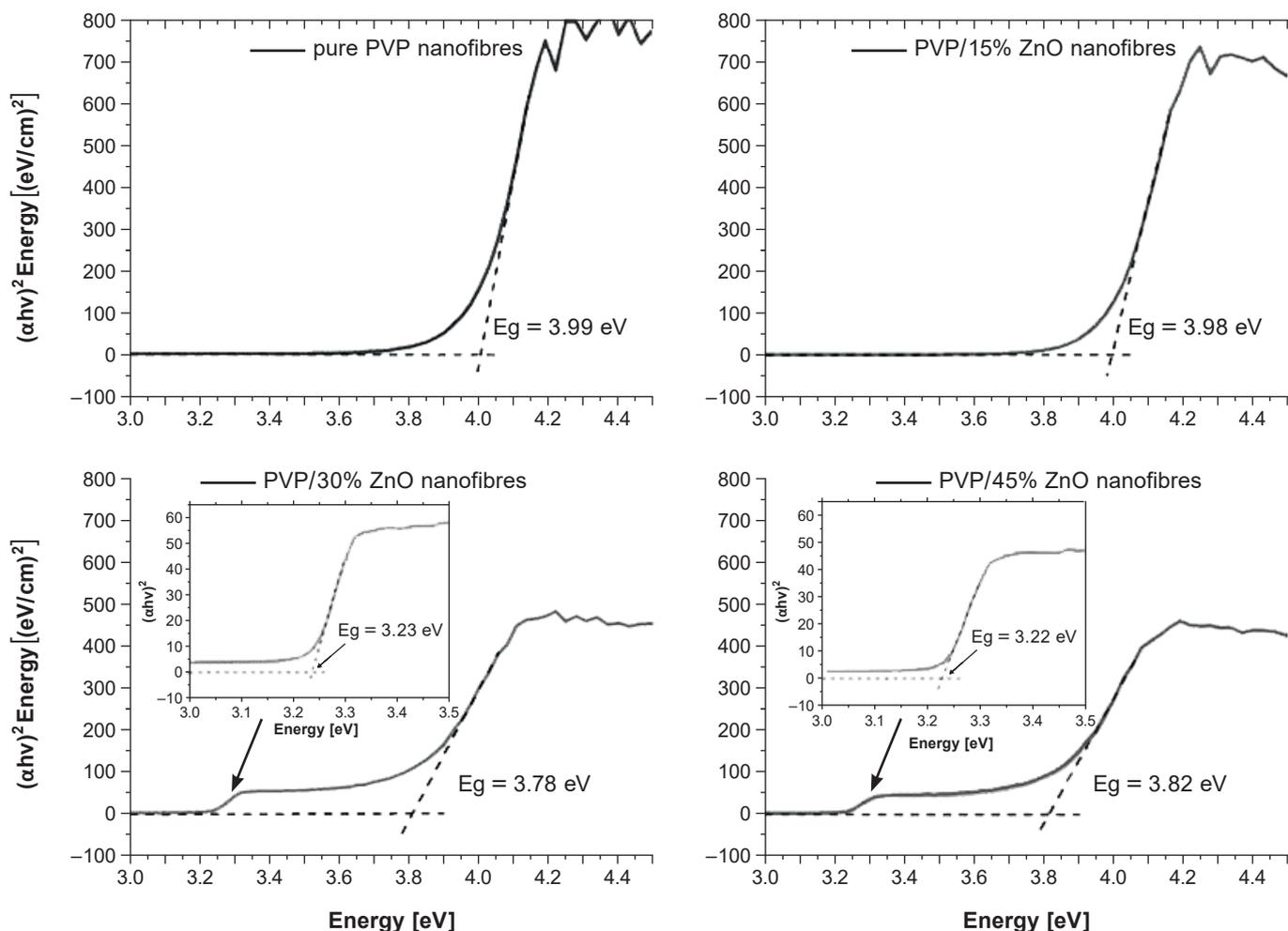


Fig. 8. Dependence $(\alpha h\nu)^2$ as function of quantum energy radiation determined based on UV-Vis spectra for the produced materials, and matching based on the smallest square method straight lines that define the zeros of linear functions corresponding to the band gap value

4. Conclusions

The PVP polymer and PVP/ZnO composite nanofibers with the following mass concentration of the reinforcing phase: 15, 30 and 45% relative to polymer concentration, were produced using the process of electrospinning from solutions. Examination of the morphology of the obtained materials showed a drop in fiber diameter values with an increase of zinc oxide nanoparticles, which is caused most probably by the increase in conductivity of spinning solutions. However, the decrease in diameter values resulted in an increase of the specific surface area of fibrous mats. This fact is attributed to the possibility of controlling the pore size in the process of making fibers, which is extremely attractive in view of the potential application range of this material. FTIR spectra revealed the presence of some characteristic peaks related to bonds in the PVP molecule and intermolecular interactions as well as bonds with zinc and oxygen ions in composite fibrous mats. The optical properties under investigation also revealed a decrease in the absorption level with an increase of the doped phase mass concentration in the form of semiconductor zinc oxide. The composite nano-

fibers with the 30 and 45% concentration of ZnO were characterized by double energy gaps. The first width of the band gap was approx. 3.2 eV, which corresponds to the reinforcing phase, and the second one was about 3.8 eV – for the matrix material.

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