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Morphological, chemical and structural characterization of silica-containing polyvinylpyrrolidone electrospun nanofibers prepared by sol-gel technique

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ABSTRACT

Purpose: The aim of this study was to produce poly(vinylpyrrolidone) (PVP) containing silica nanofibers using electrospinning method from 10% PVP/EtOH solutions with different mass concentration 0 and 30% of tetraethoxysilane. Sol-gel technique was used to obtain nanofiber membranes with high amount of inorganic phase. In the case when metal alkoxide, such as tetraethyl orthosilicate (TEOS) is mixed with an organic polymer, hydrolysis and condensation reaction of TEOS occur in-situ with polymer matrix, which allows to fabricate organic-inorganic hybrid structures with uniform dispersion.

Design/methodology/approach: The examination of the morphology of the obtained PVP/silicon dioxide nanofibers using scanning electron microscope (SEM) has been made. The chemical structure of produced nanostructures was investigated by Fourier - Transform Infrared spectroscopy (FTIR) and Energy Dispersive Spectrometry (EDX) to analyze the regular dispersion by examining types of bonds occurring between polymer matrix and SiO_2 phase.

Findings: Results obtained in this paper shows that the mass concentration of the reinforcing phase in form of TEOS have an influence on the average diameter of nanofibers and with the increase of tetraethyl orthosilicate in solution nanofibers diameters decrease. Moreover, structural examination shows uniform dispersion of the reinforcing phase in hybrid materials.

Research limitations/implications: Uniform dispersion of the reinforcing phase in silica-containing PVP nanofibers gives the opportunity to make nanowires in calcination process from such obtained fibrous mats and use in novel electrical devices.

Originality/value: This paper describes an easy and more effective way of making polymer nanofibers with the content of silicon dioxide with the perspective way of making silica nanowires in the future from obtained hybrid nanofibers, so that this method can replace commonly used nanowires growth processes.

Keywords: PVP; SiO_2; Nanofibers; Electrospinning method; Sol-gel technique; TEOS

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MATERIALS

1. Introduction

Nanofibers are structures with average diameters in the range of 50 to 500 nm and are characterized by large surface area to volume ratio. They may act as reinforcement of the matrix material composites or be the main component material. Electrospinning is a process which allows for the production of composite nanofibers with various and desired properties [1-3]. Spinning in electrostatic field is held with some important parameters, distance between the electrodes, potential difference between the electrodes and solution flow rate, which influence the morphology of the obtaining fibers. Moreover, the molecular weight of polymer used as matrix affects the nanofibers structure [4,5].

Sol-gel technique is widely used method for preparation of organic-inorganic nanocomposite structures, because of the ability of mixing polymer melts with metal oxides in form of metal alkoxides e.g. tetraethyl orthosilicate (TEOS). Due to the possibility of combining solvents for organic polymers and alkoxides, an easy way of producing reinforced metal oxides polymer composites is provided [6]. Lately, there are some described attends to make hybrid structures with organic polymer matrix reinforced silicon dioxide, such as poly(ethylene terephthalate) (PET) [7], poly(oxyethylene) (PEO) [8], poly(ether ketone) (PEEK) [9], poly(dimethylsiloxane) (PDMS) [10], polyamides (PA) [11] and polyacrylonitrile (PAN) [12]. Also, there are some papers describing preparation composite thin films with poly(vinylpyrrolidone).

Poly(vinylpyrrolidone) (PVP) is hydrophilic, biocompatible polymer with several desirable properties, such as very low toxicity, simplicity in processing, high complexing ability and good adhesion. Furthermore, PVP is soluble in water and many organic solvents e.g. ethanol, methanol and dimethylformamide (DMF). Also good environmental stability, non-conductivity, temperature resistance and transparency make PVP a good component using in pharmacy, cosmetics industry and medicine [13-20]. PVP fibrous mats produced in electrospinning process are widely used in any kind of gas sensors. In such applications the properties of specific surface area play a crucial role in responding to even low concentrations of gases [21]. PVP nanofibers reinforced with inorganic structures e.g. silver particles are finding applications in optoelectronic or fluorescent clothing because of its strong and stable photoluminescence conversion [22].

SiO_2 having high purity and some specific surface areas is used to produce fused quartz for telescopes and to produce silica gel with great adsorption ability. Silica nanoparticles, due to their mechanical, durability and electrochemical properties are widely used in many applications, such as sensors, catalysts, optical and magnetic devices [23,24]. Properties listed above allow for the production of PVP/SiO_2 composite nanofibers in use of temperature – regulating textiles and building more efficient solar panels [25,26]. However, physical and chemical properties of SiO_2 are closely connected with their particle size. Shang et.al. demonstrated in their paper, that with the reduction of particle size from 35 to 4 nm, the kinetic stability of cytochrome *c* increases [27]. On the other hand, in different work, Gu with co-authors described the influence of SiO_2 particle size on cavitation pressure with no measurable differences as the particle size increased. Although, increase in mass concentration of silica nanoparticles decrease the value of cavitation pressure [28].

The aim of this study was solutions preparation by sol-gel technique and nanofibers production using electrospinning process, which were the early steps to obtain polymer (PVP) and hybrid nanofibers (silicon dioxide-containing PVP). As obtained fibrous mats were investigated using scanning electron microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) to examine the morphology and chemical structure, including bond and vibration types occurring in molecules. Those study will give the opportunity to produce composite nanofibers, which can be used in novel electrical devices and gas sensors. Moreover, the investigated silica dispersion in polymer nanofibers would result in the possibility of producing pure silicon dioxide nanowires using this method in the future.

2. Materials and methodology

Silica poly(vinylpyrrolidone) hybrid nanofibers were prepared by the combination of sol-gel technique to obtain reinforcing phase in form of SiO_2 phase and electrospinning method. PVP solution 10% wt. was prepared by dissolving poly(vinylpyrrolidone) (PVP, purity of 99%, Mw= 1 300 000 g/mole, Sigma Aldrich) in ethanol (EtOH, purity of 99.8%, Sigma Aldrich). As prepared solution was subjected to magnetic stirrer for 30 minutes. In order to prepare TEOS/CH_3COOH solution the following were used: 4 ml of tetraethyl orthosilicate (TEOS, Sigma Aldrich) and 3 ml of acetic acid (CH_3COOH, Sigma Aldrich) to make homogeneous mixture. Such prepared solution was stirred on magnetic stirrer for 30 minutes. In-situ condensation and hydrolysis occurred when both prepared mixtures: PVP/EtOH and TEOS/CH_3COOH were mixed and stirred at magnetic stirrer for 24 hours. Directly after stirring, the solutions were placed in device pump, which was sterile syringe. Electrospinning process were held with following parameters: solution flow rate at 1.5 ml/h, potential difference between the electrodes of 20 kV and distance between the nozzle and the collector of 15 cm. The production of the nanofibers were made by using device FLOW – Nanotechnology Solutions Electrospinner 2.2.0-500.

In sol-gel technique the Stöber process is used to obtain uniform size of SiO_2 particles from tetraethyl orthosilicate (TEOS) alcoholic solution. The group of alkoxides is ideal chemical precursor, because they react readily with water, with the reaction, called hydrolysis as follows:

$$Si(OC_2H_5) + H_2O \rightarrow HO - Si(OC_2H_5)_3 + C_2H_5 - OH \quad (1)$$

When catalyst in form of acetic acid (CH_3COOH) is added to the solution, hydrolysis process may proceed to completion of silica:

$$Si(OC_2H_5) + H_2O \rightarrow SiO_2 + (C_2H_5 - OH)_4 \quad (2)$$

In the end, polycondensation process occurs by branching of the used polymer due to tetrafunctional nature of fully hydrolyzed monomer $Si(OH)_4$. Polymerization is linked with formation of siloxane network, by making bonds Si – O – Si (in addition H – O – H and C_2H_5 – O – H bonds are being made) [29].

Electrospinning process allows for the production of nanosized fibers from melted polymer solutions. The applied high voltage between electrodes, which are nozzle and collector, is applied to liquid solution droplet, so that the body of liquid is charged. Electrostatic field counteracts the surface tension and the droplet is being stretched until critical moment, called Taylor cone, where a stream of liquid erupts from the surface of droplet. The jet of solution is elongated in flight, which is caused by electrostatic repulsion until it is finally deposited on the grounded collector. Schematic outline of device is shown in Fig. 1.

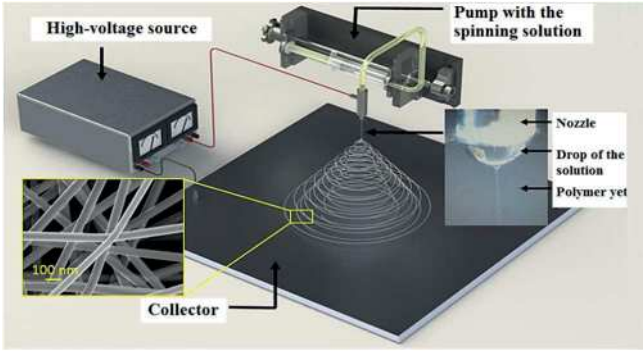

Fig. 1. Scheme of electrospinning process device

3. Result and discussion

3.1. Morphology and chemical structure investigation

In order to analyze the morphology of the obtained nanofibers the imagining of the fibrous surface using scanning electron microscope (SEM) has been applied. Fig. 2a,b shows SEM images obtained for the pure PVP nanofibers with different magnifications. As it can be seen fibers are characterized by smooth surface and constant diameter value along the entire length of fibers. Moreover, polymer fibers possess no structural defects on their surface. The mean diameter of the PVP structures is about 799 nm, whereas the most commonly occurring diameter values were from the range of 800 to 1000 nm (Fig. 2c). It can be deduced that such desirable polymer fibers properties would be a preferable material for gas sensors with much higher specific surface area [21]. The morphology investigation of the silicon dioxide-containing polymer nanofibers reveals the values of fibers diameter in range from 250 to 600 nm and the absence of any structural defects (Fig. 3a,b). Although, the average diameter value is 368 nm (Fig. 3c). It can therefore be concluded that with the addition of reinforcing phase in form of SiO_2,

conductivity of jet solution of producing fibers grows, so that the diameter of hybrid nanofibers increase. EDX spectra obtained for the pure PVP nanofibers shows some characteristic peaks corresponding to carbon (C) and oxygen (O), which are the main chemical elements of organic materials. Also, there can be seen peaks for aluminum (Al), due to aluminum foil, which was the collector for the obtaining fibrous mats and for gold (Au), because of sprayed gold layer for better conduction for SEM examination (Fig. 4). Moreover, EDX spectra for the silica PVP compound nanofibers have additional peak for silicon (Si), which was the reinforcing phase in obtained material (Fig. 5). Chemical structure investigation reveals uniform dispersion of SiO_2 in polymer matrix and confirm presence of TEOS in prepared solutions. With good inorganic phase dispersion in polymer comes improved properties from reinforcing phase, so it is crucial to obtain homogenous mixtures and fibers with good dispersal of SiO_2. From above, all possible applications result e.g. dielectric properties of hybrid films [30].

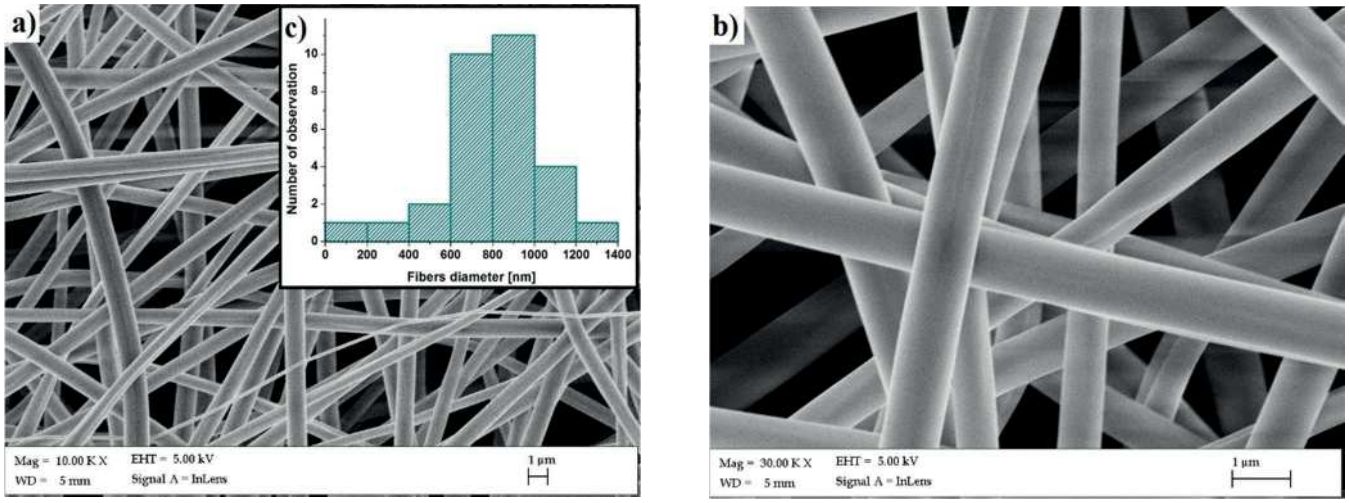

Fig. 2. SEM images obtained for pure PVP electrospun nanofibers with magnification: a) 10 k x, b) 30 k x, c) histogram showing nanofibers diameters distribution

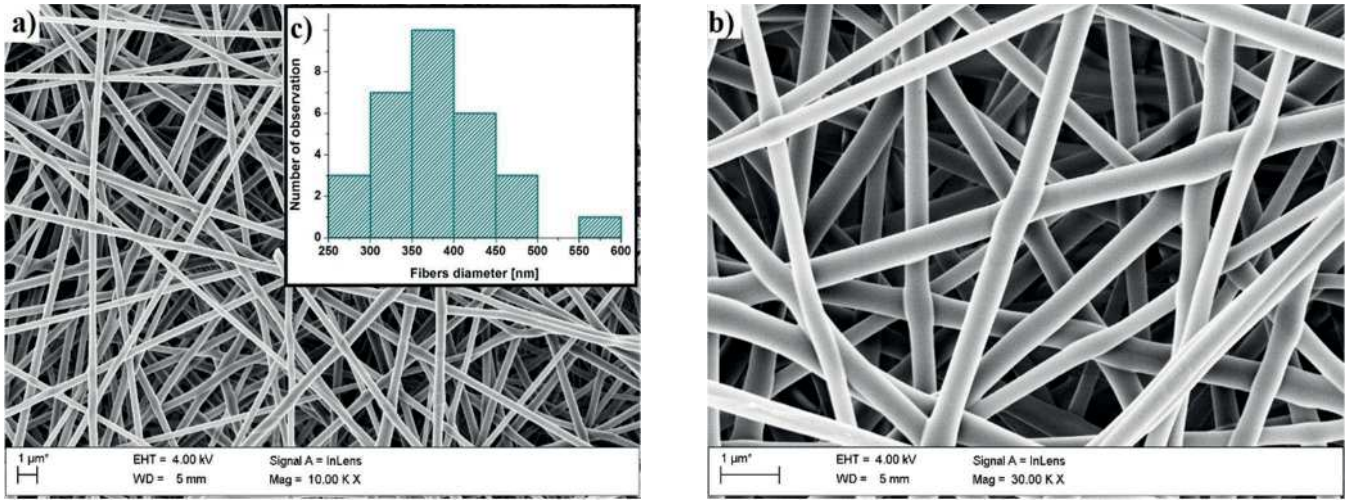

Fig. 3. SEM images obtained for PVP-silica hybrid electrospun nanofibers with magnification: a) 10 k x, b) 30 k x, c) histogram showing nanofibers diameters distribution

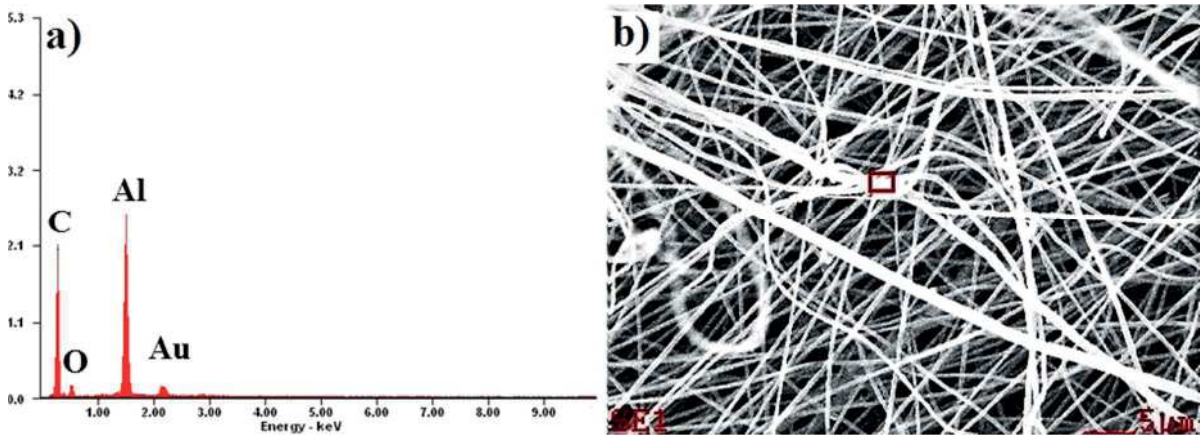

Fig. 4. a) EDX spectra for pure PVP nanofibers, b) the selected place site on SEM image

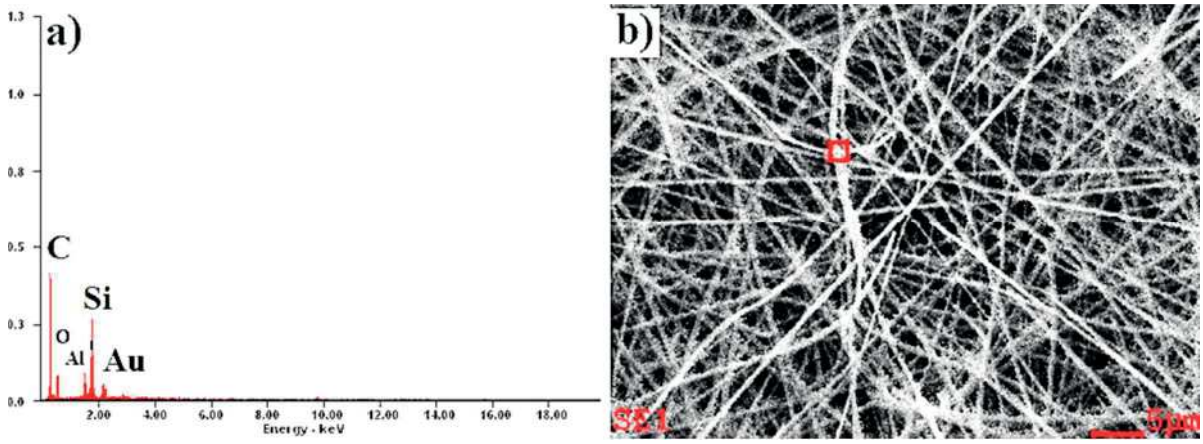

Fig. 5. a) EDX spectra for PVP-silica hybrid nanofibers, b) the selected place site on SEM image

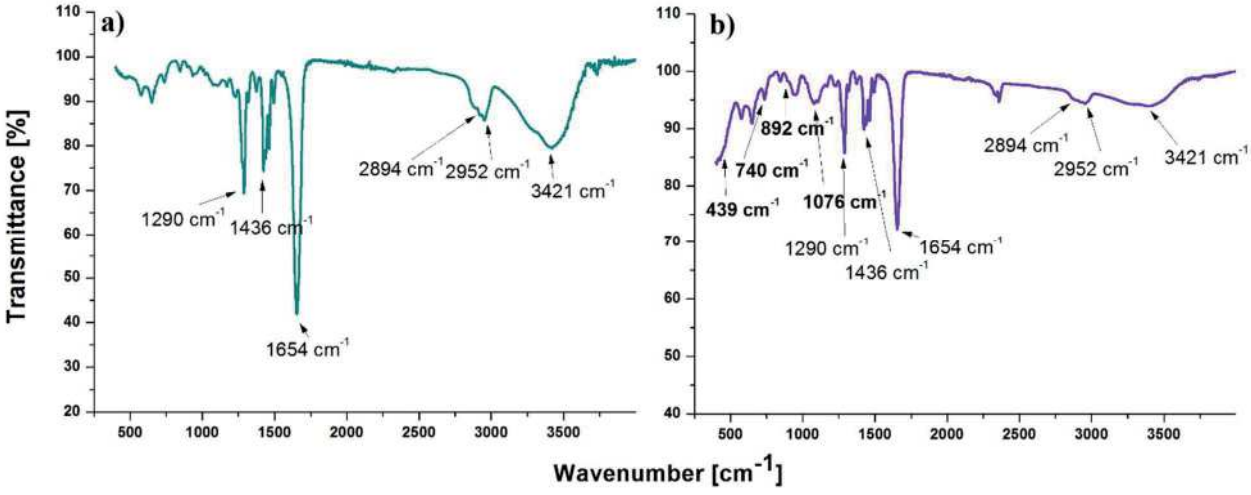

Fig. 6. FTIR spectra for: a) pure PVP nanofibers, b) hybrid nanofibers

3.2. FTIR examination

The transmittance in the function of wavenumber in the range of 0 to 4000 cm^{-1} graphs were plotted for the obtained PVP and silicon dioxide-containing poly(vinylpyrrolidone) nanofibers. Fig. 6a shows FTIR spectra for pure PVP fibrous mats with some characteristic peaks for individual vibration molecules or functional groups. Bond and vibration types and corresponding wavenumbers are shown in Table 1.

Table 1.
Bond and vibration types corresponding to wavenumbers for pure PVP nanofibers

Wavenumber, cm^{-1}	Bond type	Vibration type
1288	C-N or C-O	stretching
1436	CH_2	scissor
1654	C=O	stretching
2952	CH_2	stretching (asymmetric)
2894	CH_2	stretching (asymmetric)
3421	O-H	stretching

FTIR examination of pure PVP structures reveals four bond types occurring in chemical structure of poly(vinylpyrrolidone) fibers: C-N (or C-O), CH_2, C=O, O-H to which corresponds values of wavenumber: 1288, 1436 (2952, 2894), 1654 and 3421 cm^{-1} respectively [31-34]. Furthermore, FTIR investigation of silicon dioxide PVP hybrid nanofibers show some additional peaks corresponding to present bonds in chemical structure of reinforcing phase: 439 cm^{-1}, corresponds to Si-O-Si rocking vibration type, 740 cm^{-1} is Si-O-Si bending bond type, 892 cm^{-1} responds to SiO-H bending bond and 1076 cm^{-1} is stretching Si-O-Si bond type (Fig. 6b) [35]. Moreover, Si-O-Si bonds are responsible for making SiO_2 molecules, whereas SiO-H bonds corresponds to condensation reaction and connection bond with polymer. What is more, there can be seen one drastic decrease (40 percentage points) in transmittance level at wavenumber value of 1654 cm^{-1}, which is probably linked to hybrid connection between PVP and silica. Results obtained in FTIR investigation overlap chemical composition examination from EDX, which means that all reinforcing phase molecules are uniform distributed in polymer matrix. This proves that the reinforcing phase in evenly distributed in polymer matrix in polymer nanofibers with silicon addition, so that in the future in calcination process we can obtain pure SiO_2 nanowires and apply them in novel electrical devices.

4. Conclusions

To conclude, this paper describes successful solutions preparation and production of polymer (PVP) and silica-containing poly(vinylpyrrolidone) using sol-gel and electrospinning technique. Pure PVP fibrous mats received in this work are good material for gas sensing applications, with very large surface area to volume ratio. With the addition of reinforcing phase in form of tetraethyl orthosilicate, nanofibers diameter decreases from 799 to even 250 nm. Moreover, on the surface of PVP fibers as well as hybrid fibers no defects occur. It can therefore be concluded that electrospinning process parameters values were chosen properly. FTIR examination confirmed uniform dispersion of SiO_2 in polymer matrix by some characteristic peaks and corresponding bonds and vibration types in compound material molecules. Good dispersion gives the opportunity to application such nanostructures in devices with much lower energy consumption, so that in the future we can save more energy.

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