DOI: 10.24425/118930

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POLYVINYLPYRROLIDONE/SILICON DIOXIDE COMPOSITE THIN FILMS – PREPARATION AND ANALYSIS OF PROPERTIES

The purpose of this study was to produce composite thin films with polyvinylpyrrolidone (PVP) matrix with nanoparticles of silicon dioxide (SiO_2) as the reinforcing phase (5 and 10%) using spin coating method and to investigate the influence of mass concentration of silica particles and process parameters on the morphology and optical properties of the obtained PVP/SiO_2 nanocomposite coatings. The composite layer topography examination, made using atomic force microscope (AFM), showed the increase of roughness due to the increase of silica mass concentration in thin films. UV-Vis spectroscopy analysis showed that with the increase of SiO_2 nanoparticles in polymer matrix and use of higher rotation speed, the absorbance level decrease. Besides, composite layers with 10% mass concentration relative to polymer concentration were characterized by wider energy band gap, so it can be concluded that obtained nanocomposite thin films can be used as protective layers against UV radiation, with zero absorption in the range of visible light wavelengths.

Keywords: spin coating, PVP/SiO_2, thin films, composite coatings, optical properties

1. Introduction

Nanocomposites with organic polymer matrix and inorganic nanofiller attract much attention due to their unique chemical, physical and biological properties. When using nanoparticles of inorganic compounds, such as: titanium dioxide (TiO_2) [1], zinc oxide (ZnO) [2] or silicon dioxide (SiO_2) [3,4], better mechanical, thermal or optical properties of nanocomposites, relative to matrix material, can be obtained. In view of multitude of processes: sol-gel method [5], in-situ polymerization [6], electrospinning [7], chemical and physical vapor deposition (CVD and PVD) [8-11] and spin coating [12], which are repeatedly cheaper than commonly used production methods of conventional materials, it is possible to produce innovative nanocomposites, characterized by so far unattainable physical properties, on the industrial scale.

Spin coating method is one of the technique for producing thin films, which are characterized by nanometric scale thicknesses, while maintaining low costs and high performance. The thin layer production using spin coating method is carried out by four main steps including applying the solution on the device disc, imparting a rotation with specified rotation speed, uniform solution spin and final solvent evaporation. Important thing in using spin coating method is dependence between films thickness and process parameters. The layers thickness is inversely proportional to rotation speed of spin coating process and directly proportional to solution viscosity [13]. Moreover, studies have shown [14] that with the increase of rotation speed in composite thin films production technique, the size and amount of the agglomerates of reinforcing phase decrease, which positively affects the electrochemical properties of the obtaining thin layers.

SiO_2 nanoparticles find wide spectrum of application on chemical sensors [15], biosensors [16], catalysts [17] and in medicine in bioimagining [18]. Versatile usability of silica nanoparticles in so many fields is caused by exceptional electrical, magnetic and optical properties of pure silicon dioxide particles, which results in many attempts of making silica containing composites. Li et. al. in their paper examined the suitability of polymer-silica coatings in solar cells, which shown high transmittance level and strong adhesion of the composite layer to the substract surface [19]. Silicon dioxide and titanium dioxide fusion in composite materials with polyvinylpyrrolidone matrix is also used to produce high-performance lithium ion batteries [20]. Moreover, nanocomposites thin films reinforced SiO_2 are characterized by uniformity and smoothness of surface, which affects better electrical conductivity of the obtaining layers [21]. What is more, such nanocomposites find application in production of humidity sensors, which operate even in low temperatures and in fabrication of anticorrosive coatings [22].

In this paper we report the nanocomposite PVP/SiO_2 thin films production using spin coating method and investigation of influence of silicon dioxide mass concentration in composite

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material and spin coating parameters on surface morphology of composite layers. Moreover, spectroscopy UV-Vis have been made to examined the optical properties in form of spectres of absorbance level in function of wavelength and the width of energy band gaps.

2. Materials and methodology

In order to make spin solutions the following were used: polyvinylpyrrolidone (PVP, Mw = 1 300 000 g/mole, purity of 99%, Sigma Aldrich), ethanol (EtOH, purity of 99,8%, Sigma Aldrich) and silicon dioxide nanoparticles (SiO_2). In the first step of solutions preparation, the silica nanoparticles in amount of 0.01 g and 0.02 g were dispersed in 4 ml volume of ethanol. As obtained suspensions were applied to sonication process for 15 minutes, in order to break down the agglomerates of SiO_2. Afterwards the measured amount of polymer granulate were added to SiO_2/EtOH suspensions, respectively: 0.19 g and 0.18 g. The resulting solutions were subjected to spin coating process with application of constant process parameters, which included rotation acceleration, spinning time and variable rotation speed, respectively 3000 rpm (sample 1.1 and 2.1) and 4000 rpm (sample 1.2 and 2.2).

3. Results and discussion

3.1. Analysis of the surface topography of the composite thin films

The obtained thin composite PVP/SiO_2 films were examined using atomic force microscope (AFM) in non-contact mode. Analysis of the thin composite layers (sample 1.1) topography made by spin coating process with applied rotation speed of 3000 rpm showed presence of reinforcing phase agglomerates on the thin films surface. The SiO_2 agglomerates on the surface of nanocomposites were probably caused by strong specific surface free energy of the used ceramic powder, which are responsible for ability of silica nanoparticles to agglomerate (Fig. 1a) [23]. The increase of rotation speed to 4000 rpm resulted in partial breakdown of the silicon dioxide agglomerates on the surface of composite layer, besides some SiO_2 particles deposited on the films area (Fig. 1b). This fact can be explained by the occurring larger interial forces acting on solution molecules during spinning of composite coatings using higher rotation speed in spin coating method. The increase of surface roughness of composite PVP/SiO_2 thin layers were observed in case of using solution with twice the amount of reinforcing phase, in comparison to samples 1.1 and 1.2, which were respectively 10% (wt.) relative

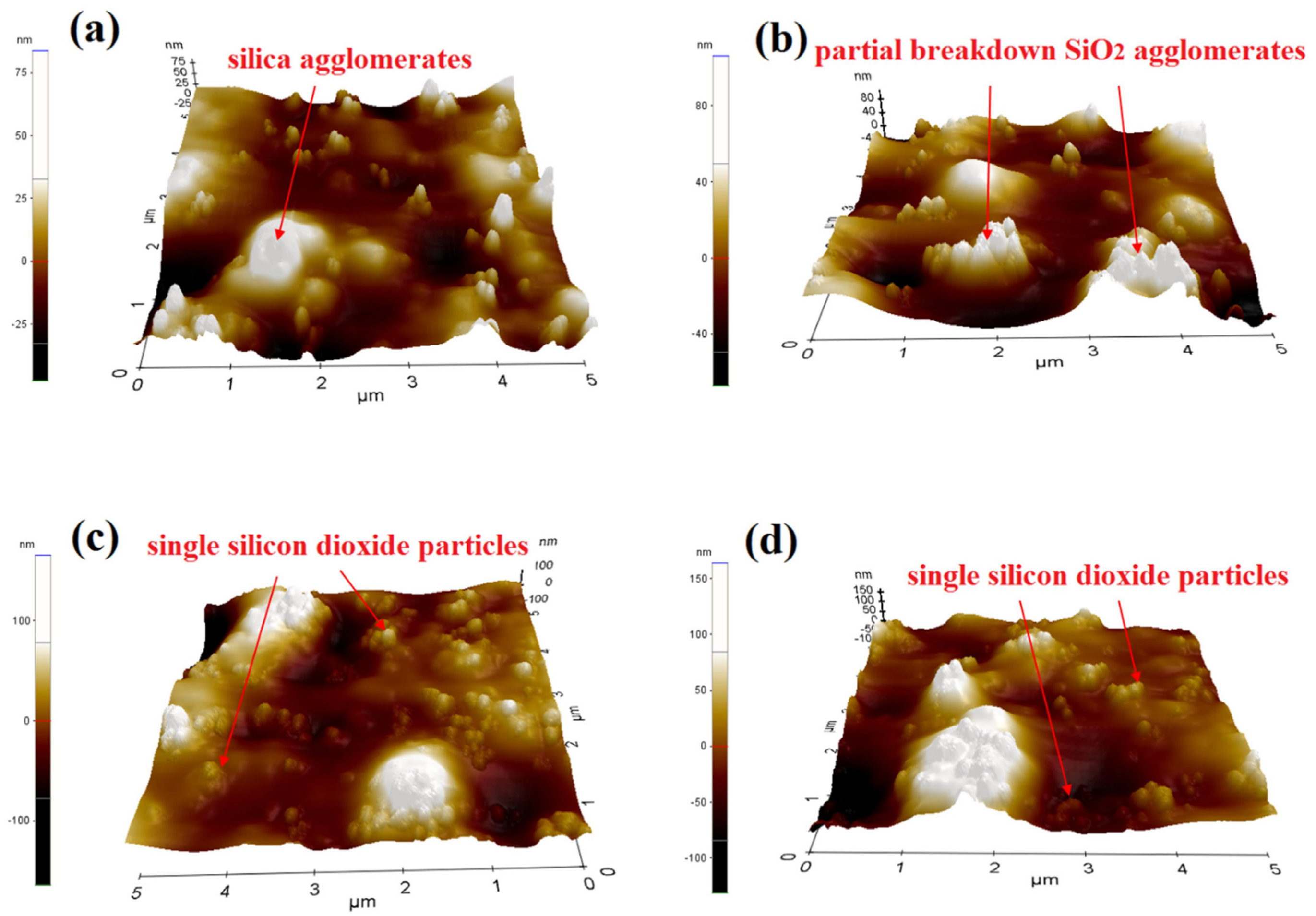


Fig. 1. The topography of the composite thin films surface images (AFM): (a) 1.1 Sample – rotation speed 3000 rpm, (b) 1.2 Sample – rotation speed 4000 rpm, (c) 2.1 Sample – rotation speed 3000 rpm, (d) 2.2 Sample – rotation speed – 4000 rpm

to final mass of the obtained composite material. The surface topography of sample 2.1 and 2.2 showed increased amount of agglomerates and single nanoparticles of silica, however increasing in rotation speed from 3000 rpm to 4000 rpm did not eliminated the agglomeration effect of silica on the surface of thin films, which affected the smoothness and uniformity of the obtained layers and finally it caused the increase of roughness of nanocomposite surfaces (Fig. 1c,d). To conclude the topography analysis of the composite thin films it can be said, that with the increase of SiO_2 mass concentration in nanocomposite materials, the amount of agglomerates and single silicon dioxide particles on the layer surface increased. Moreover, thin films samples with higher amount of mass concentration of the reinforcing phase are characterized by higher height amplitude, which proves that as obtained composite PVP/SiO_2 thin coatings have high level of surface roughness, which were intended and investigated thin films property and coincides with the data in [24,25].

3.2. UV-Vis analysis of thin films

The absorbance in function of electromagnetic radiation wavelength for the obtained thin composite PVP/SiO_2 films and for pure polymer granulate PVP plots are shown in Fig. 2. Analysis of the absorbance spectrum for pure PVP released that optical properties of polymer are characterized by sharp absorption edge on wavelength of 370 nm and the maximum absorption of radiation peak at 225 nm, which results in zero absorption in the range of visible light wavelengths [26].

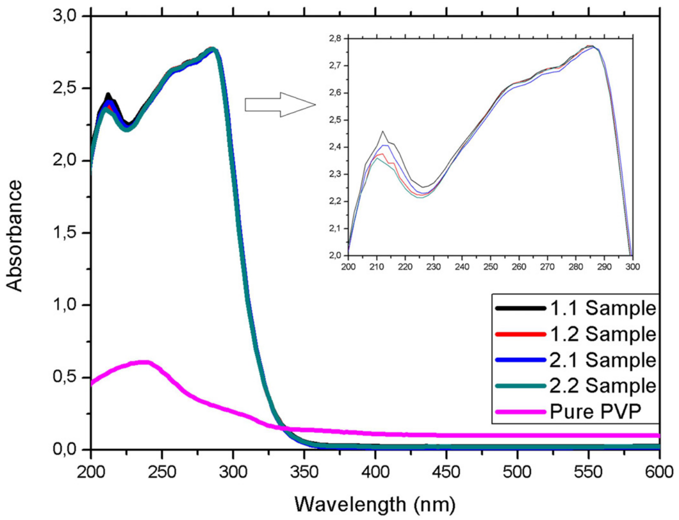


Fig. 2. UV-Vis spectrum for thin composite PVP/SiO_2 films and for pure PVP granulate

Spectres received for thin composite films are characterized by close to each other values of absorption peaks, which fall at 210 nm wavelength of the electromagnetic radiation in the range of visible light, hence the sharp absorption edge is for wavelength of 320 nm, which corresponds to the absorption spectrum of pure silica and is slightly blue shifted [27]. The level of absorption of the composite PVP/SiO_2 layers increase almost six fold in comparison to the absorption level, which were recorded for pure polymer. Nevertheless, volume ratios of silica nanoparticles and polymer granulate, which were 2.4% (v/v) for 1.1 and 1.2 Sample and 5% (v/v) for 2.1 and 2.2 Sample, showed slight differences in absorbance level. Although, the distinctions in absorbance level are shown to be affected by variable in this paper spin coating method parameter, rotation speed. The composite films, which were made by spin coating method with rotation speed of 3000 rpm are described by higher absorption level in comparison to composite coatings produced with 4000 rpm during spin coating, which were probably the result of higher amount of agglomerates on the composites surface formed with lower value of rotation speed. Based on the absorbance plots it can be established that with the increase of silica nanoparticles mass concentration in composite films, slight decrease in absorption level affected by the increasing amount of surface irregularity can be observed, which causes multiple reflection of radiation on sample surfaces decreasing the chance to absorb quanta of electromagnetic radiation by PVP/SiO_2 thin layer [27]. To conclude the optical properties investigation of the thin composite films with dioxide silicon as the reinforcing phase it can be stated that zero absorption in the range of visible light and high absorption level of the wavelengths of far ultraviolet allow for the production of protective layers against UV radiation using such nanocomposites [28].

3.3. The energy band gaps investigation

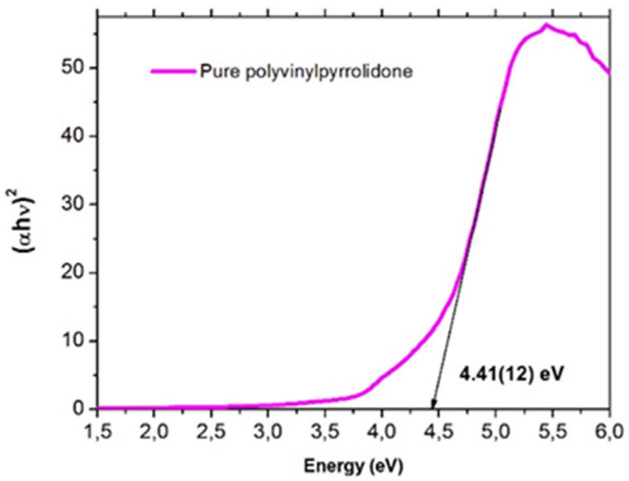
In order to determine the dependence between absorption coefficient (α) and the electromagnetic radiation waves energy, the UV-Vis spectroscopy analysis of the obtained thin composite PVP/SiO_2 films and pure PVP granulate were made. It was made measurement of absorbance in function of wavelength for all the obtained samples. Based on:

$$ABS = -\log(T) \tag{1}$$

where ABS is absorbance and T is transmittance, transmittance plot in function of wavelength of electromagnetic radiation were set. Afterwards, using the linear regression based on the plotted dependences $\left[h\nu \ln\left(\frac{1}{10^{-ABS}}\right)\right]^2$ in function of energy radiation, fit of linear function to straight sections of plot with the largest angular coefficient were made. The root-value of the function corresponded to width of the energy band gap. The dependence were determined using correlation of absorption coefficient of the examined samples:

$$\alpha h\nu = A(h\nu - E_g)^{\rho} \tag{2}$$

where α is absorption coefficient, h is Planck's constant, ν is electromagnetic radiation frequency, E_g is the width of energy band gap, A stands for constant quantity dependent on the prob-



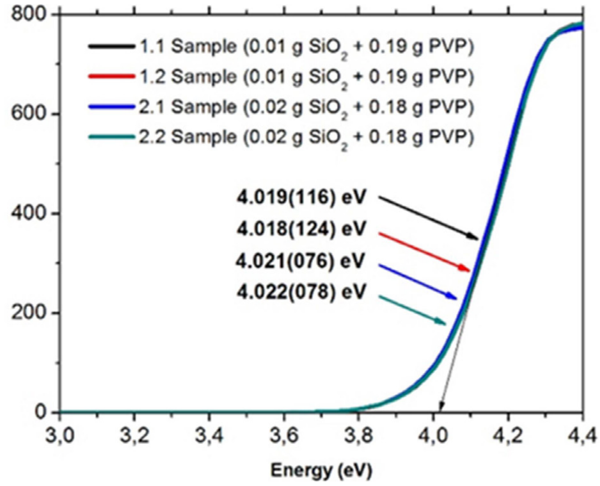


Fig. 3. The width of the energy band gaps as a function of electromagnetic radiation energy

ability of electron transitions and 1/2 was adopted value for ρ coefficient. After equation (1) transformation, it took the form:

$$\left[h\nu \ln\left(\frac{1}{10^{-ABS}}\right)\right]^2 = B\left(h\nu - E_g\right) \qquad (3)$$

where B is a constant quantity dependent on the thickness of layer.

The width of energy band gap obtained for the pure polymer PVP granulate was 4.41 eV, which is comparable with the value from [29] and confirm the fact that polyvinylpyrrolidone is an isolator. The energy band gap values of the nanocomposites are lower in comparison to the value of PVP band gap and are respectively 4.019, 4.018, 4.021 and 4.022 eV, which is the confirmation of uniform fusion and interatomic interactions in composite layer. Analysis of the obtained results of PVP/SiO_2 coating showed that with the increase of reinforcing phase mass concentration in form of silicon dioxide nanoparticles in composite material, there is slight increase in the width of energy band gap, which is affected by semiconductor nature of SiO_2. The value of energy band gaps width for composite thin films is associated with slight differences in sharp edges of absorbance for the obtained PVP/SiO_2 nanocomposites, which could be assigned to small volume ratio distinctions of silica nanoparticles and polymer in composite films.

4. Conclusion

This paper presents the technique of making thin composite PVP/SiO_2 films with 5 and 10% (wt.) of mass concentration of the reinforcing phase using spin coating method. Analysis of the surface topography of the obtained thin composite layers showed that with the increase of the SiO_2 in composites, increase the roughness of the sample surfaces, which is affected also by using higher value of rotation speed during spin coating process. Moreover, optical properties which were examined by making absorbance in the function of electromagnetic radiation wavelength plots, revealed that using rotation speed of 3000 rpm during spin coating resulted in making coating with higher absorbance level, than layers made by using rotation speed of 4000 rpm, which were also caused by much higher roughness of the coatings. The width of the energy band gaps of the composite thin films were characterized by lower values in comparison to the width of band gap of pure PVP, hence the energy band gap value increase slightly for composite layers with the SiO_2 mass concentration increase. The investigate optical properties and surface topography of the PVP/SiO_2 thin composite films allow for the application of such nanocomposites as protective coatings against UV radiation.

Acknowledgement

The research presented in this article was financed by the National Science Centre, Poland based on the decision number 2014/15/B/ST8/04767
This work was supported by the Ministry of Science and Higher Education of Poland as the statutory financial grant of the Faculty of Mechanical Engineering, Silesian University of Technology

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