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Surface morphology of thin films polyoxadiazoles

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Properties

ABSTRACT

Purpose: The purpose of this paper was to analyse the surface morphology of thin films polyoxadiazoles. **Design/methodology/approach:** SSix different polymers which belong to the group of polyoxadiazoles were dissolved in the solvent NMP. Each of these polymer was deposited on a glass substrate and a spin coating method was applied with a spin speed of 1000, 2000 and 3000 rev/min. Changes in surface topography and roughness were observed. An atomic force microscope AFM Park System has been used. Photos have been taken in noncontact mode while observing an area of 10 x 10 microns.

Findings: The analysis of images has confirmed that the quality of thin films depends upon the used polymers. It was also observed that the parameters of the spin coating method have significant effect on the morphology and the surface roughness. The speed of the spin has got a strong impact on the topography of the thin films obtained.

Research limitations/implications: The morphology of polyoxadiazoles thin films has been described. This paper include description how the spin speed influences the morphology of polymer thin films. In order to use a polymer thin film in photovoltaics or optoelectronics it must have a uniform thickness and a low surface roughness. Further research, in which the optical properties of thin films are investigated, is strongly recommended.

Practical implications: Conductive polymers may find applications in photovoltaics or optoelectronics. It is important to study this group of material engineering and to find a new use for them. Materials from which thin films are made of will have an impact on the properties and characteristics of electronics devices in which they are be applied.

Originality/value: The value of this paper is defining the optimal parameters of spin-coating technology for six polyoxadiazoles. The results allow the choosing optimal parameters of the deposition process. Spin coating is a very good method to obtain thin films which are obligated to heve the same thickness over the whole surface. **Keywords:** Organic polymer; AFM microscopy; Spin-coating method

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1. Introduction

The rapid development of electronics and materials science, and especially for semiconductor and chemistry of polymeric materials is related to the introduction of modern engineering materials. Organic materials can let create innovative sources of light (electroluminescent properties), and their optoelectronic opposites - photovoltaic cells. Solar cells are the devices to the transform solar energy into electrical energy [1-4].

An important group are polymers whose main chains are composed of carbon atoms connected by alternating single and double bonds. The most famous of conductive polymer materials include polyacethylene, polyaniline, polypyrrole, polythiophene, poly (3,4-etylenodioksytiofen) polyphenylene [5-7].

Fig. 1. Schematic structure of one of the investigated polymers [6]

Table 1. Schematic structure of polymers

Oxm- Per-6F (2:1:1)

Oxp- Per-6F (2:1:1)

Ox- Per-6F (2:1:1)

Oxp- Per-6F (3:1:2)

Ox- Per-6F (3:1:2)

Ox- Per-6F (4:1:3)

Polyoxadiazoles belong to a group of conductive polymers that can be used in photovoltaic and optoelectronics. Responsible for the transport of electrons is a system of conjugated double bonds of the polymer chain. Representative of this group is shown on Figure 1. Polyoxadiazoles characterized by their high performance of electrical and optical properties, good hydrolytic stability, highly ordered systems, mechanical resistance and high thermal stability [8,9].

Technological advances led to the development of many methods for obtaining thin films of organic compounds, small molecule and polymer ones. These films can be deposited on various substrates by chemical vapor deposition (CVD) and physical vapor deposition (PVD). In CVD methods, thin film is formed during a chemical reaction between the reactants. PVD methods relays on direct evaporating material onto substrate, so that the substrate surface parity strongly affects film adhesion to it [10-12].

In spin coating method centripetal acceleration leads to the spread of the gel on the surface and a thin film of gel is formed on it. The final film thickness and other properties depend on the type of gel (viscosity, drying rate, surface tension, etc.) and the parameters selected in the process of spinning. Impact on the properties of the thin films have such factors as speed, acceleration, pollution. Small differences in the parameters which define the spin coating process can be cause of drastic changes in the deposited thin films [13,14].

Atomic force microscopy (AFM) is the primary research method that allows to characterize the surface morphology of polymer thin films. AFM belongs to a group of scanning probe microscopes (SPM) it allows for magnification up to tens of millions of which is sufficient to observe individual atoms. It is characterized by high vertical resolution (0.01 nm) which allows 3D imaging of good quality [15,16].

2. Materials and methods

Research was conducted on six different polymers, whose structure is shown in Table 1. They have differed in their construction and the molar ratio of the particles. These polymers belonging to the group of polyoxadiazoles were dissolved in the solvent NMP (1-methyl-2-pyrrolidinone). Then their thin films were deposited on glass substrate spin coating method with a spin speed of 1000, 2000 and 3000 rev / min.

Research using atomic force microscopy AFM XE 100 was conducted to characterize the surface morphology and surface roughness analysis. Photos taken in the mode without contact, the area of 10×10 microns.

The measuring microscope AFM consists of three main elements: the unit of measurement, control unit and a computer with monitor (Figure 2).

3. Results

Figure 3 show 3D views surface topography of polymer Oxm-Per-6F (2:1:1) coated with a different spin speeds. Spin coated thin film at 1000 rev / min is characterized by

a succession precipitation 2.5 x 1 micron. With the increasing speed large precipitates disappear and the test area resembles a regular structure, without the occurrence of larger precipitates.

A view 3D surface topography of polymer Oxp-Per-6F (2:1:1) spin coated at different speeds are shown in Figure 4. Increase speed spin coated in a slight way impact on the morphology of the polymer surface Oxp-Per-6F (2:1:1).

Figure 5 are shown 3D images of surface topography of polymer Ox-Per-6F (2:01:01) with different spin speeds. Irrespective of spin speed changes on the surface thin film appeared numerous precipitates occupying a significant part of the study area.

The view 3D surface topography of polymer Oxp-Per-6F (3:1:2) coated with a different spin speeds are shown in Figure 6. Embedded polymer thin films are characterized by a uniform structure without significant precipitation. There are only minor irregularities in the surface.

In Figure 7 is a view 3D surface topography of polymer Ox-Per-6F (3:1:2), spin coated with a different speeds. In the case of polymer Ox-Per-6F can be seen that with increasing spin speed large precipitates disappear, and there are numerous smaller surface irregularities.

In Figure 8 is a view 3D surface topography of polymer Ox-Per-6F (4:1:3) spin coated with a different speeds. Deposited thin films are characterized by a uniform surface topography without major precipitation.

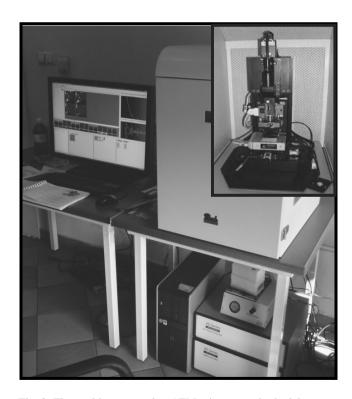


Fig. 2. The position measuring AFM microscope in the laboratory of the Institute of Engineering Materials and Biomaterials, Silesian University of Technology

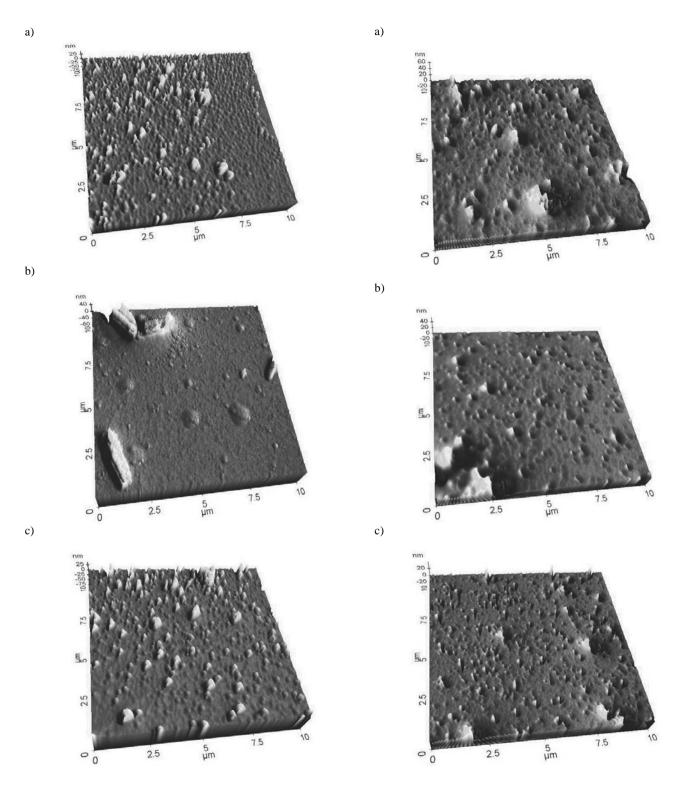


Fig. 3. The AFM topography image of the surface thin film of polymer Oxm-Per-6F (2:1:1) coated with a spin speed: a) $1000~\text{rev}\,/\,\text{min},$ b) $2000~\text{rev}\,/\,\text{min},$ c) $3000~\text{rev}\,/\,\text{min}$

Fig. 4. The AFM topography image of the surface thin film of polymer Oxp-Per-6F (2:1:1) coated with a spin speed: a) 1000~rev~/min, b) 2000~rev~/min, c) 3000~rev~/min

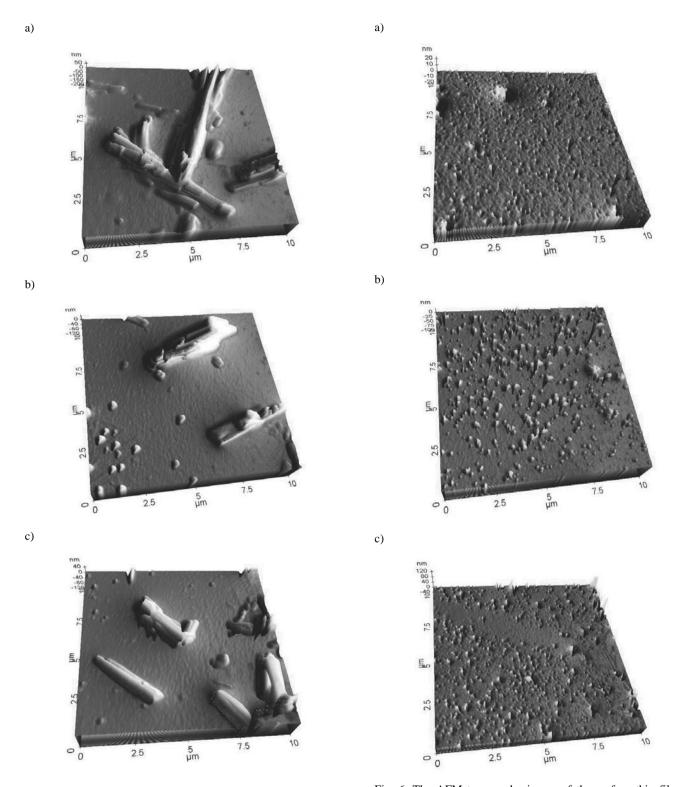


Fig. 5. The AFM topography image of the surface thin film of polymer Ox-Per-6F (2:1:1) coated with a spin speed: a) 1000 rev / min, b) 2000 rev / min, c) 3000 rev / min

Fig. 6. The AFM topography image of the surface thin film of polymer Oxp-Per-6F (3:1:2) coated with a spin speed: a) $1000~\rm{rev}~/$ min, b) $2000~\rm{rev}~/$ min, c) $3000~\rm{rev}~/$ min

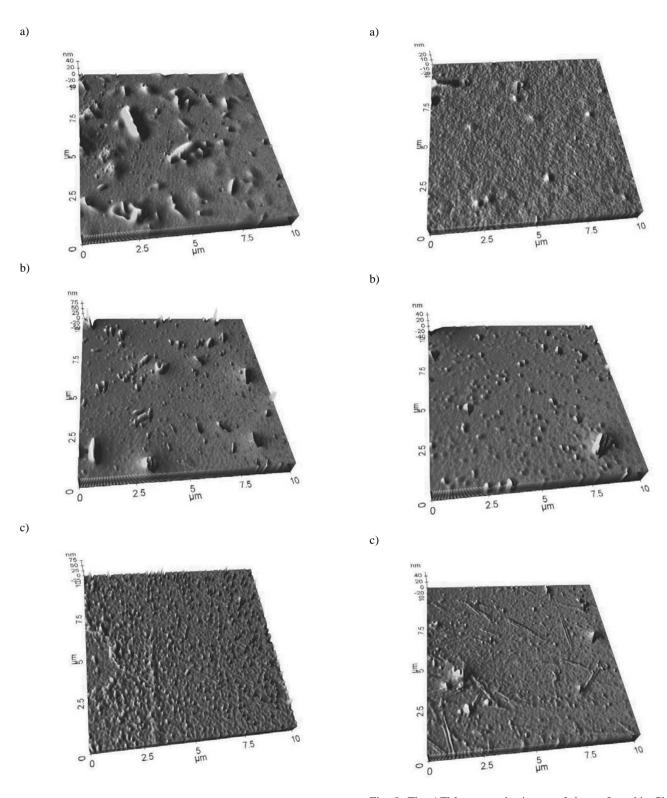


Fig. 7. The AFM topography image of the surface thin film of polymer Ox-Per-6F (3:1:2) coated with a spin speed: a) 1000 rev / min, b) 2000 rev / min, c) 3000 rev / min

Fig. 8. The AFM topography image of the surface thin film of polymer Ox-Per-6F (4:1:3) coated with a spin speed: a) 1000 rev / min, b) 2000 rev / min, c) 3000 rev / min

Figure 9 -14 presents an analysis of the roughness of each thin film in the program carried out XEI's Park System. Surface roughness was characterized by calculating the roughness parameters Rq, Ra, maximum elevation and presenting histograms.

Histograms of the polymer thin films Oxm-Per-6F (2:1:1) are shown in Figure 9 the shape of the histogram indicates that the thin film spin coated with a spin speed 1000 and 3000 rev / min are characterized by lower roughness than the thin film coated at 2000 rev / min.

Figure 10 shows histograms of the polymer thin films Oxp-Per-6F (2:1:1) - the distribution of surface irregularities. The distributions of inequality can observe that the thin films coated with a spin speed at 2000 and 3000 rev / min should have a lower roughness than thin film at 1000 rev / min.

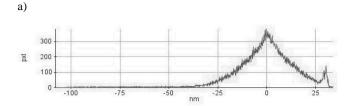
In Figure 11 shows histograms of the polymer thin film Ox-Per-6F (2:1:1) - the distribution of surface irregularities. According to the result of decomposition of inequality, spin coated thin film at 3000 rev / min should be characterized by the lowest surface roughness.

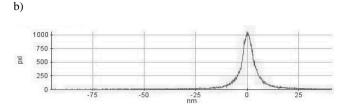
In Figure 12 shows histograms of the polymer thin films Oxp-Per-6F (3:1:2) - the distribution of surface irregularities. According to the schedule shown in Figure 5 a) thin film coated with a spin speed at 1000 rev / min should have a minimum surface roughness.

In Figure 13 shows histograms of the polymer thin film Ox-Per-6F (3:1:2) - the distribution of surface irregularities. Illustrated the distribution of the surface (Figure 13 a) shows that the thin film with a spin speed at 1000 rev / min should have a minimum surface roughness.

Table 2. Roughness parameters of the polyoxadiazoles thin films

Polymer	Max hight [nm]	R _a [nm]	R _q [nm]
Oxm-Per-6F (2:1:1)	48.155	2.677	6.661
	40.958	4.830	8.136
	35.813	3.700	7.385
Oxp-Per-6F (2:1:1)	61.875	3.065	5.339
	54.376	1.640	3.866
	38.335	1.738	3.363
Ox-Per-6F (2:1:1)	73.275	10.205	18.042
	76.873	11.596	23.436
	48.558	5.917	12.299
Oxp-Per-6F (3:1:2)	23.842	0.745	1.475
	21.589	2.440	5.635
	130.172	3.082	6.561
Ox-Per-6F (3:1:2)	40.521	1.606	3.592
	88.743	1.787	5.095
	75.696	3.370	5.589
Ox-Per-6F (4:1:3)	28.214	0.264	0.646
	48.592	0.895	3.016
	53.064	0.638	1.686





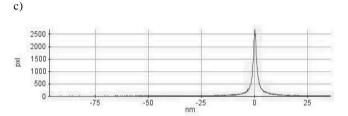
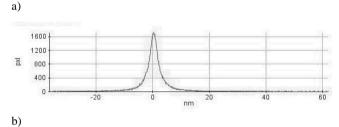
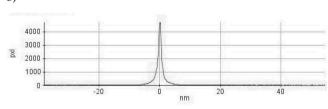


Fig. 9. The histogram of frequency of the occur height for a thin film of polymer Oxm-Per-6F (2:1:1) coated with a spin speed at: a) 1000 rev / min, b) 2000 rev / min, c) 3000 rev / min





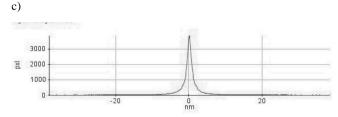


Fig. 10. The histogram of frequency of the occur height for a thin film of polymer Oxp-Per-6F (2:1:1) coated with a spin speed at: a) 1000 rev / min, b) 2000 rev / min, c) 3000 rev / min

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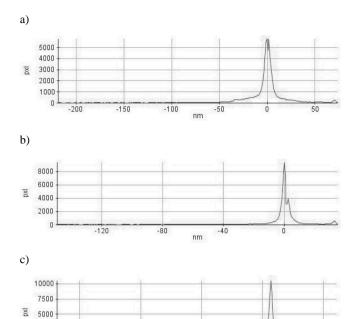


Fig. 11. The histogram of frequency of the occur height for a thin film of polymer Ox-Per-6F (2:1:1) coated with a spin speed at: a) 1000 rev / min, b) 2000 rev / min, c) 3000 rev / min

2500

0

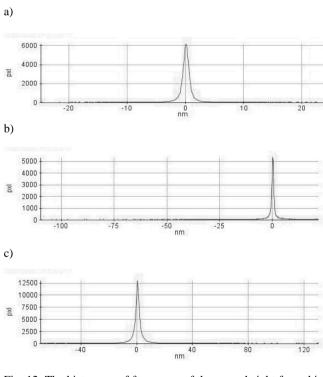
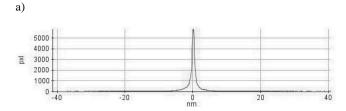
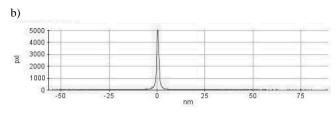


Fig. 12. The histogram of frequency of the occur height for a thin film of polymer Oxp-Per-6F (2:1:1) coated with a spin speed at: a) 1000 rev / min, b) 2000 rev / min, c) 3000 rev / min





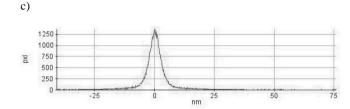
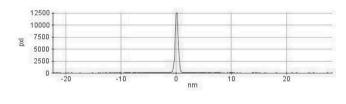
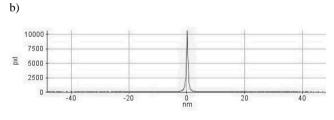


Fig. 13. The histogram of frequency of the occur height for a thin film of polymer Ox-Per-6F (3:1:2) coated with a spin speed at: 1000 rev / min

a)





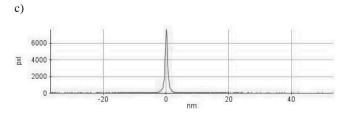


Fig. 14. The histogram of frequency of the occur height for a thin film of polymer Ox-Per-6F (4:1:3) coated with a spin speed at: a) 1000 rev / min, b) 2000 rev / min, c) 3000 rev / min

In Figure 14 shows histograms of the polymer thin film Ox-Per-6F (4:1:3) - the distribution of surface irregularities. All thin films should have a similar surface roughness, indicating the thin film coated with a spin speed at 1000 rev / min (Figure 14 a).

According to the compiled in Table 2, the basic parameters of surface roughness and presented in Figures 9 - 14 distributions of inequality in the form of histograms preferably deposited polymer thin film:

- Oxp- Per-6F (2:1:1),
- Oxp-Per-6F (3:1:2),
- Ox-Per-6F (3:1:2),
- Ox-Per-6F (4:1:3).

4. Conclusions

The analysis of images has revealed the relationship quality of the thin films of the polymer used. We also observed that a significant effect on the morphology and surface roughness are parameters spin coating method. Spin speed a strong impact on topography of the thin films obtained, and their surface roughness. To use a thin layer in photovoltaics and optoelectronics it must have a uniform thickness and low surface roughness.

Conductive polymers may find applications in photovoltaics and optoelectronics. It is important to study this group of material engineering and find a use for it. Materials from which thin films are made is decided about the characteristics.

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