



CLSM and UV-VIS researches on polyoxadiazoles thin films

**J. Weszka^{a,b}, M.M. Szindler^{a,*}, M. Chwastek-Ogierman^b,
M. Bruma^c, P. Jarka^a**

^a Institute of Engineering Materials and Biomaterials, Silesian University of Technology,
ul. Konarskiego 18a, 44-100 Gliwice, Poland

^b Department of Physics, Center of Polymer and Carbon Materials,
Polish Academy of Sciences, ul. M. Curie-Sklodowska 34, 41-819 Zabrze, Poland

^c Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41a, Iasi, Romania

* Corresponding e-mail address: magdalena.szindler@polsl.pl

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ABSTRACT

Purpose: The purpose of this paper was to analyse the surface morphology and optical properties of polyoxadiazoles thin films.

Design/methodology/approach: A few different conducting polymers were dissolved in N-methyl-2-pyrrolid(in)one. Then the solutions were deposited on a glass substrate by spin coating method with a different spin rate. Changes in surface topography and optical properties were observed. A confocal laser scanning microscope CLSM Zeiss LSM 5 Exciter has been used. Photos have been taken from area of 120 x 120 microns.

Findings: The analysis of images and spectra 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 optical properties. The spin rate has got a strong impact on them.

Research limitations/implications: The morphology and optical properties of polyoxadiazoles thin films has been described. This paper include description how the spin rate influence on the polymer thin films. In order to use a polymer thin film in photovoltaics or optoelectronics it must have a high internal transmission density. Further research of polymer thin films are recommended.

Practical implications: The spin coating method allows to deposit a uniform thin films. It is important to know how the spin rate influence on the thin films properties. It is also important to find a new use for this group of material engineering in photovoltaic or optoelectronics devices.

Originality/value: The good properties of thin films make them suitable for various applications. The value of this paper is defining the optimal parameters of spin-coating technology for polyoxadiazoles thin films. 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 have the same thickness over the whole surface.

Keywords: Conducting polymer; CLSM microscopy; UV-VIS spectrometer; Spin coating method

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MATERIALS

1. Introduction

In last years, the most successful photovoltaic devices are made from semiconducting materials such as silicon. However, the production of these devices require no small financial resources. Engineers involved in photovoltaic and optoelectronics are still looking for solutions on how to reduce production costs. The key here may be the use of materials whose production is simpler and cheaper. For this purpose, looking for new organic materials that can conduct electricity [1-5].

One of the electrically conductive material is a group of polymers called polyoxadiazole. Electrical conduction in these polymers is carried out with located on alternating single and double bonds. They have high performance of electrical and optical properties, good hydrolytic stability, highly ordered systems, mechanical resistance and high thermal stability. These properties make that polyoxadiazoles can be used in photovoltaic and optoelectronic devices [6-13].

Progress in the manufacture of photovoltaic cells made mainly due to the increasing use of thin film deposition techniques. Here we can distinguish chemical vapour deposition (CVD), physical vapour deposition (PVD) and sol-gel methods. To these latter is a spin coating method, as shown in Fig. 1. The first step of the spin coating method is a drawing of a liquid solution (polymer and solvent) on the substrate. Then much of the solution is ejected from the surface of the centrifugal force. In result we obtain uniform thin film [11-17].

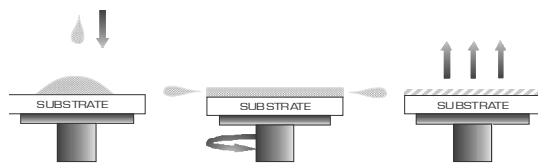


Fig. 1. Scheme of spin coating method

Through its research with the use of confocal laser scanning microscope, it is possible to imaging the surface morphology. The UV-VIS spectroscopy allows to pre-determine the suitability of materials for example as filters, or electrical conductors, and to examine some of the properties of their surfaces [18-20].

2. Materials and methods

The aim of this research was to analyze changes in surface morphology and optical properties of thin polymer films.

The scope of research included:

- preparing thin films by spin-coating method with a different spin rate,
- observation of surface morphology of polyoxadiazoles thin films with used confocal microscope Zeiss LSM 5 Laser Exciter,
- analysis of images and the roughness of the layers obtained on the microscope,
- researches of the absorption coefficient using a spectrometer UV/VIS.

The research of the surface morphology were performed by using the confocal microscope Zeiss LSM 5 Exciter at the

Institute of Engineering Materials and Biomaterials, Silesian University of Technology. The absorption coefficient was determined using a spectrometer UV/VIS in Center of Polymer and Carbon Materials in Zabrze.

The research were conducted for observation of surface topography and roughness for changes depending on the spin rate. To analyze the results of the morphology of thin polyoxadiazoles films were used Zeiss ZEN software. Determined the change of the absorption coefficient of the layers obtained depending on the length of the incident light wave.

In research was used six different polymers, whose molar ratio is shown in Table 1, and structure is shown in Table 2.

Table 1.
Molar ratio of investigated polymers

	Oxad	Molar ratio (x:y:z)
1	Oxm-Per-6F	(2:1:1)
2	Oxp-Per-6F	(2:1:1)
3	Ox-Per-6F	(2:1:1)
4	Oxp-Per-6F	(3:1:2)
5	Ox-Per-6F	(3:1:2)
6	Ox-Per-6F	(4:1:3)

In the experiment, as a substrate were used slides. The method of preparation of glass plates depends largely on the quality of the resulting layer. It is therefore important to follow the steps carefully and keeping clean. Each of the microscope slides were:

- cut to the desired size of 15x15 mm. For this purpose, was used diamond stylus;
- degreased with cut glass in hot water with detergent;
- slides placed in a bath of saturated solution of potassium dichromate (VI) solution $K_2Cr_2O_7$ in concentrated sulphuric acid (VI) H_2SO_4 , with strong oxidizing properties;
- purified in an ultrasonic washer (Fig. 2a) in acetone C_3H_6O and treated with ultrasound for 10 minutes;
- purified in an ultrasonic washer in methanol for 10 min;
- glass plates was placed in a centrifuge to evaporate the liquid.

Polymer samples were obtained in the solid state. In order to obtain the desired concentrations of each polymer was weighed. Using high-precision laboratory scale (Fig. 2b), the measurement accuracy is 0.0001 g.

The polymers were dissolved in NMP (1-methyl-2-pyrrolidone), a colorless, hygroscopic liquid. For each sample of material was added 1 ml of the substance and placed on a magnetic stirrer (Fig. 2c).

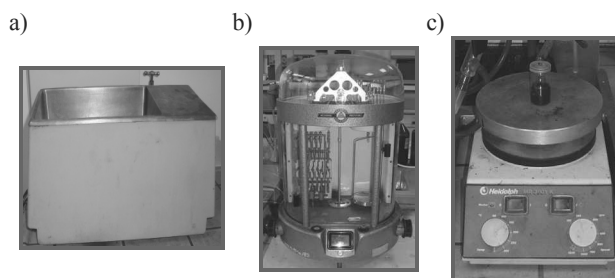


Fig. 2. a) Ultrasonic washer; b) high-precision laboratory scale; c) magnetic stirrer; in Center of Polymer and Carbon Materials in Zabrze

Table 2.
Schematic structure of investigated polymers

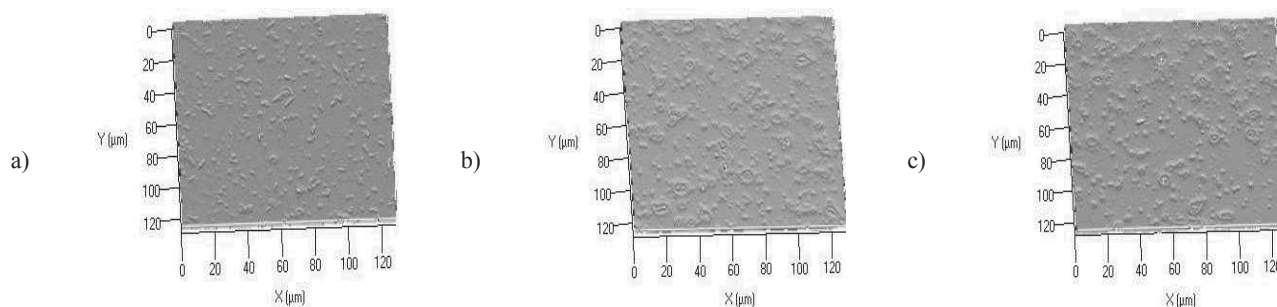
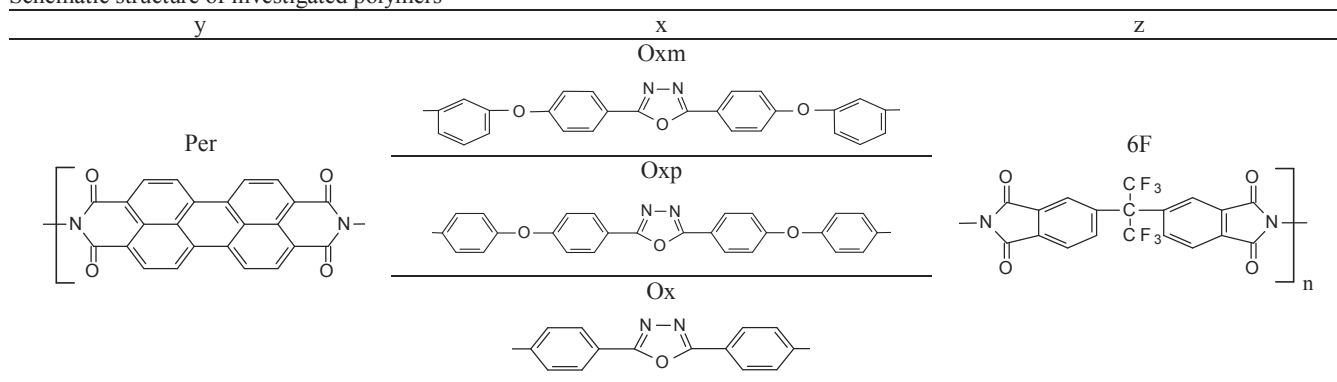


Fig. 3. Surface topography of polymer thin film, obtained by spin coating method with spin rate a) 1000 rpm; b) 2000 rpm; c) 3000 rpm; and seen with use CLSM

The process of dissolving these polymers was carried out during 10 h and elevated temperature on a magnetic stirrer. After this time the sample was removed from heat and allowed to cool to room temperature. In order to apply layers were asked time and spin speed. The solutions were applied sequentially the prepared glass substrate, then the sample was placed in an oven to evaporate the residual solvent. The stages were repeated for each polymer several times, changing the spin rate. The result is a layer used to the research, which is shown in Fig. 3.

3. Results

Studies using CLSM microscope were performed to assess the state of the quality of the layers. Images of thin films of polyoxadiazoles were observed at a magnification of 5000x (the area of 120x120 microns).

2D surface topography of polymer Oxm-Per-6F (2:1:1) rate at different speeds (1000, 2000 and 3000 rpm) are shown in Figure 4. Layers coated with at speeds of 1000 and 2000 rpm are characterized by the presence of large agglomerations of polymer exceeding 10 mm (Fig. 4a, Fig. 4b). Layer rate with a 3000 rpm is characterized by a uniform surface with small outcrops of the polymer, less than 10 microns (Fig. 4c).

Figure 5 shows a 2D surface topography of polymer Oxp-Per-6F (2:1:1) rate with at different speeds (1000, 2000 and 3000 rpm). In the case of polymer Oxp-Per-6F rate speed increase did not cause the reduction of agglomeration of the polymer formed. Even

at the speed of 3000 rpm can be seen in a layer of material accumulations in excess of 20 microns (Fig. 5c).

Figure 6 shows a view surface topography of polymer Ox-Per-6F (2:1:1) coated at different speeds (1000, 2000 and 3000 rpm). If the coated polymer is a polymer Ox-Per-6F, as in the case with Oxp-Per-6F, spin rate changes did not affect on the minimize agglomeration. However in 2000 rpm results in the appearance of areas where the solvent could not evaporate (Fig. 6b).

2D image surface topography of polymer Oxp-Per-6F (3:1:2) coated at speeds 1000, 2000 and 3000 rpm is shown in Figure 7. In Figure 7b, can observe that the speed of 2000 rpm is most suitable for the polymer Oxp-Per-6F. The layer coated with this rate is characterized by a uniform distribution on the surface, with small urban areas (Fig. 7b).

In Figure 8 is a view 2D surface topography of polymer Ox-Per-6F (3:1:2) coated with at different speeds (1000, 2000 and 3000 rpm). In Figure 8a it can be seen that for the polymer Ox-Per-6F (3:1:2) the best spin rate is 1000 rpm. However, little visible agglomerations not exceeding 10 mm (Fig. 8a-c). The topography of the surface layer coated with a speed of 1000 rpm is similar to the polymer layer Oxm-Per-6F (2:1:1) coated with at 3000 rpm (Fig. 4c).

Figure 9 shows a 2D surface topography of polymer Ox-Per-6F (4:1:3) coated with at speeds of 1000, 2000 and 3000 rpm. Regardless of the spin rate of the coated polymer layer Ox-Per-6F are characterized by a uniform surface topography (Fig. 9a-c). Emerging conurbations are infrequent and small.

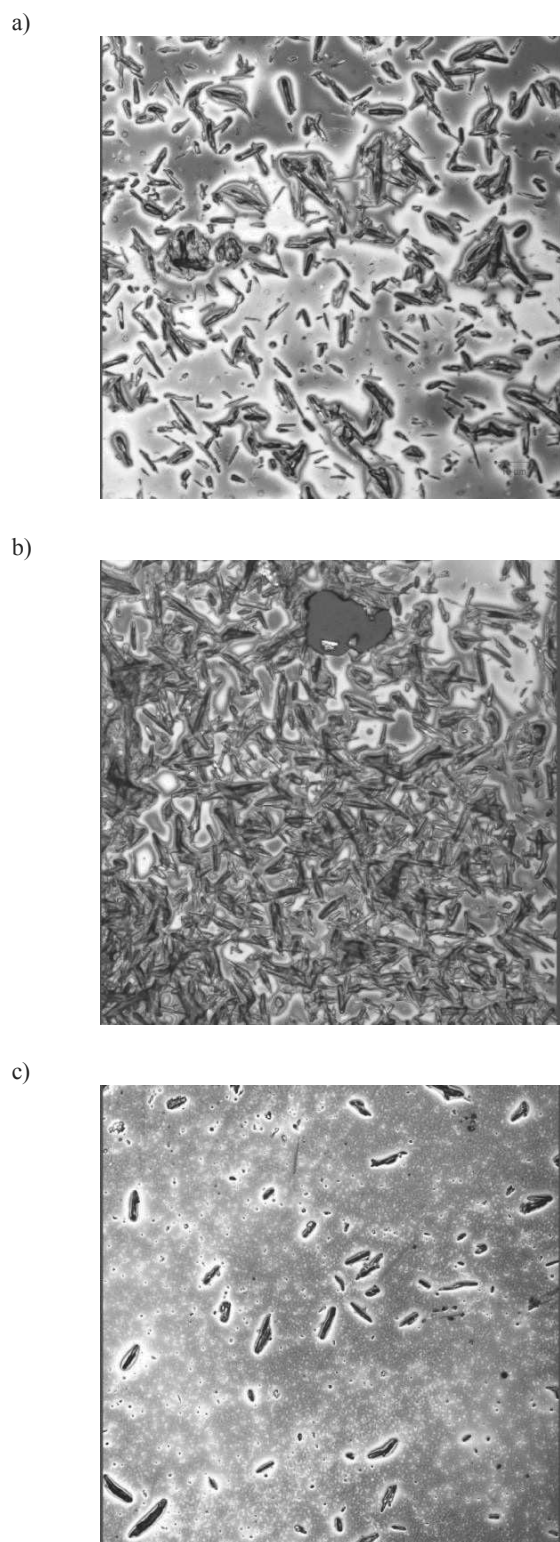


Fig. 4. The surface topography of polymer Oxm-Per-6F (2:1:1) rate with at different speeds: a) 1000 rpm; b) 2000 rpm; c) 3000 rpm

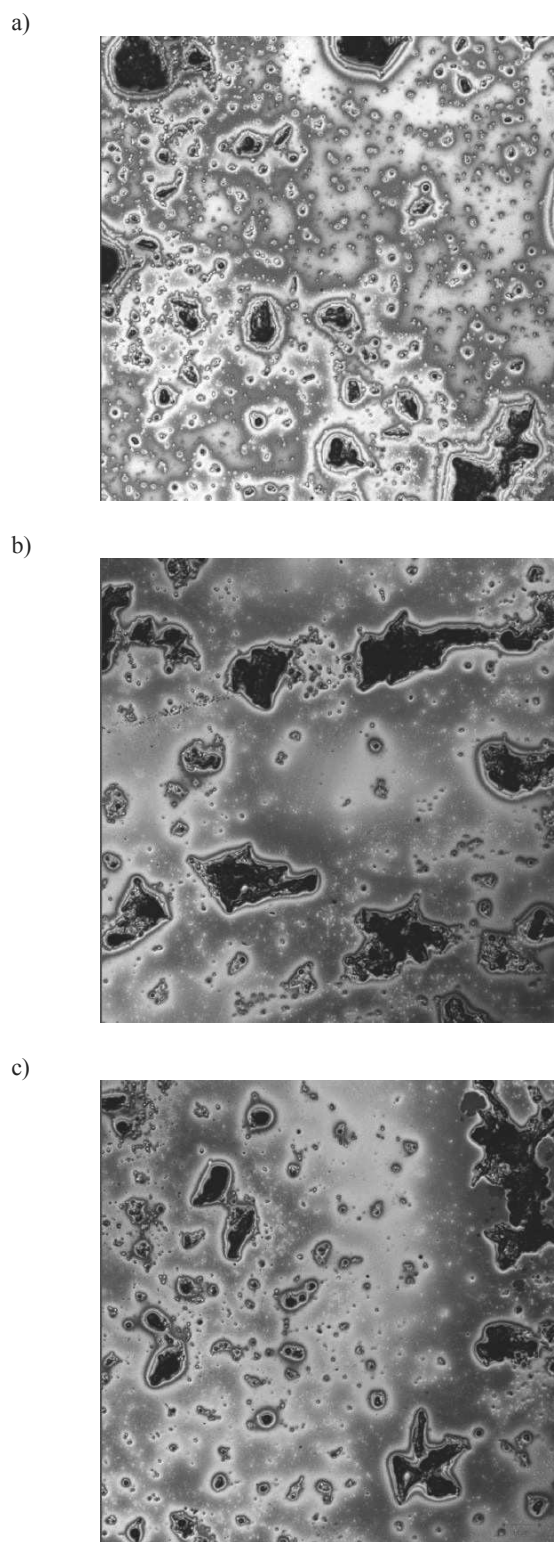


Fig. 5. The surface topography of polymer Oxp-Per-6F (2:1:1) rate with at different speeds: a) 1000 rpm; b) 2000 rpm; c) 3000 rpm

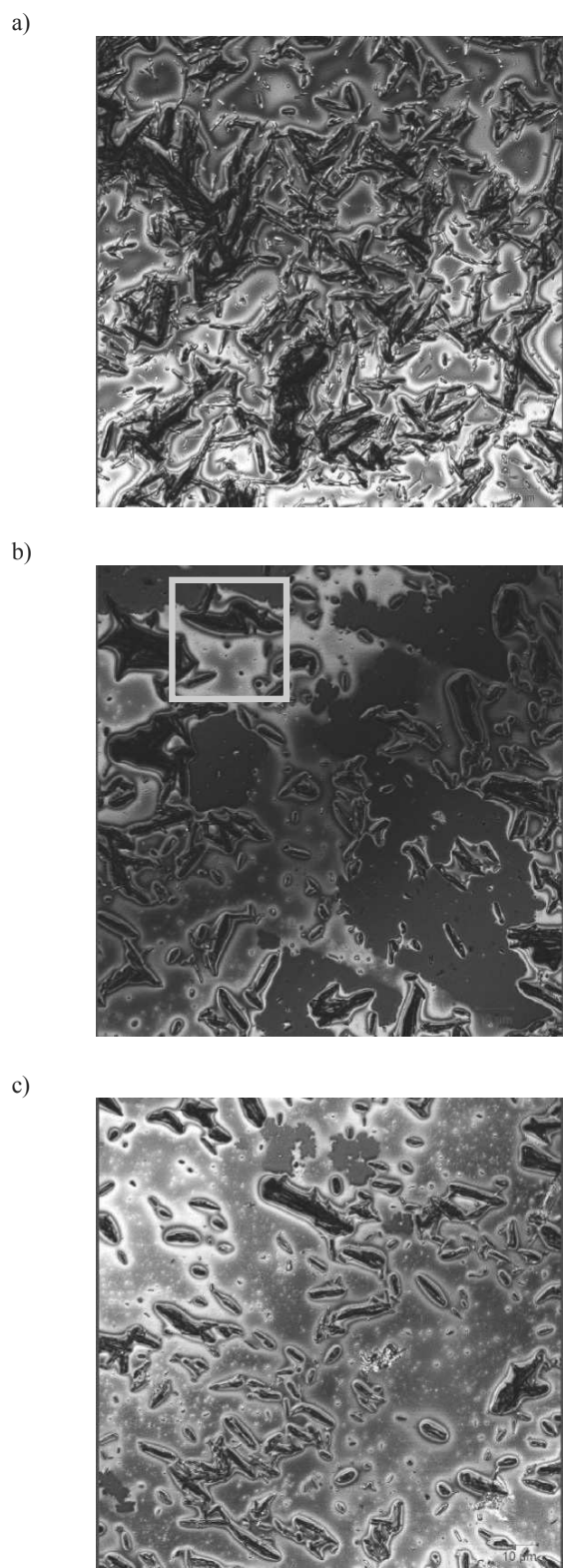


Fig. 6. The surface topography of polymer Ox-Per-6F (2:1:1) rate with at different speeds: a) 1000 rpm; b) 2000 rpm; c) 3000 rpm

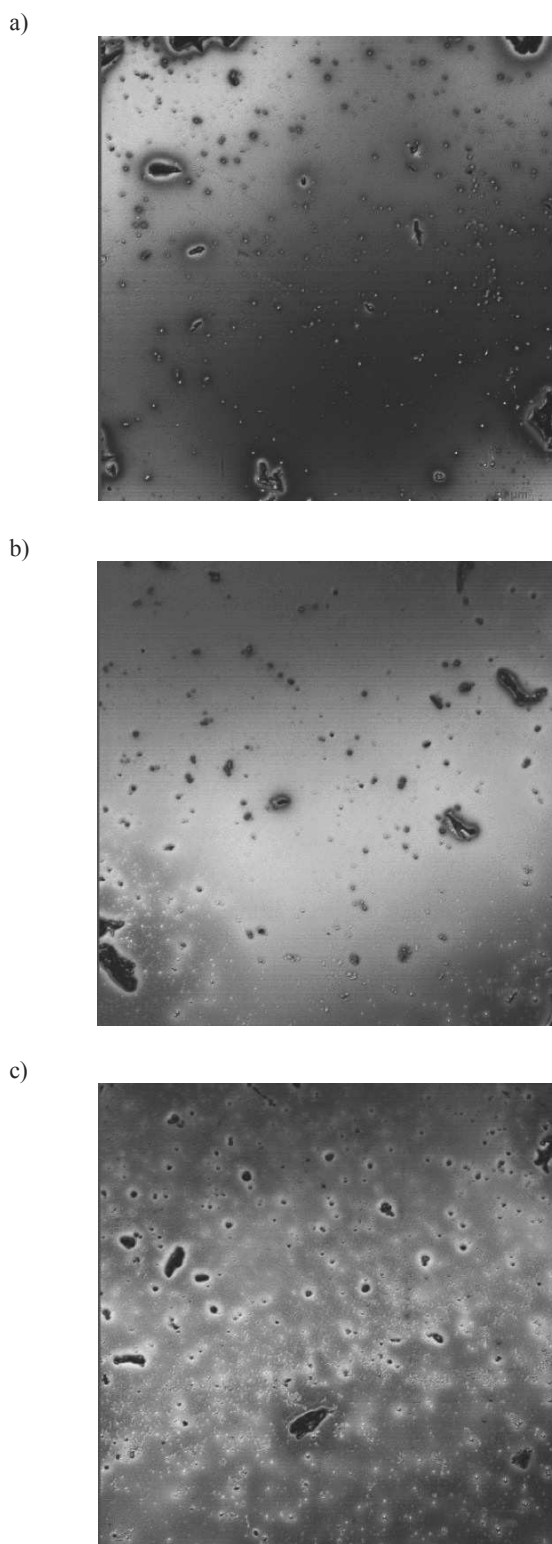


Fig. 7. The surface topography of polymer Oxp-Per-6F (3:1:2) rate with at different speeds: a) 1000 rpm; b) 2000 rpm; c) 3000 rpm

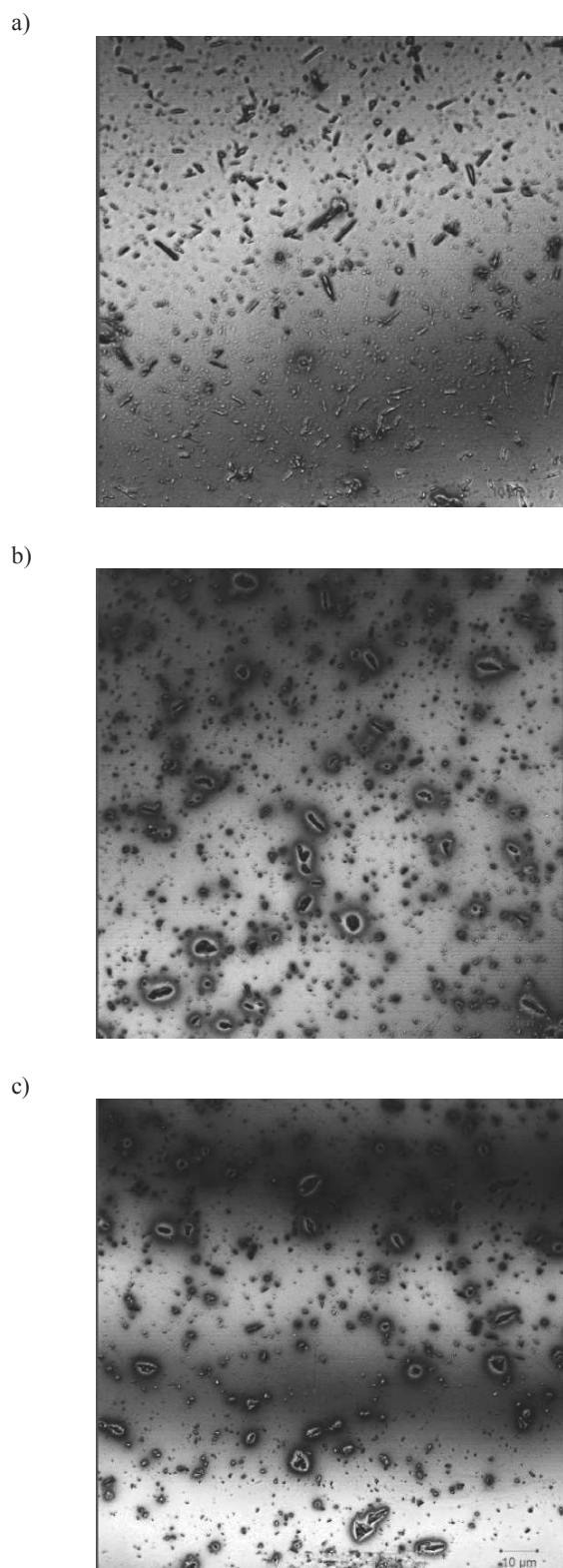


Fig. 8. The surface topography of polymer Ox-Per-6F (3:1:2) rate with at different speeds: a) 1000 rpm; b) 2000 rpm; c) 3000 rpm

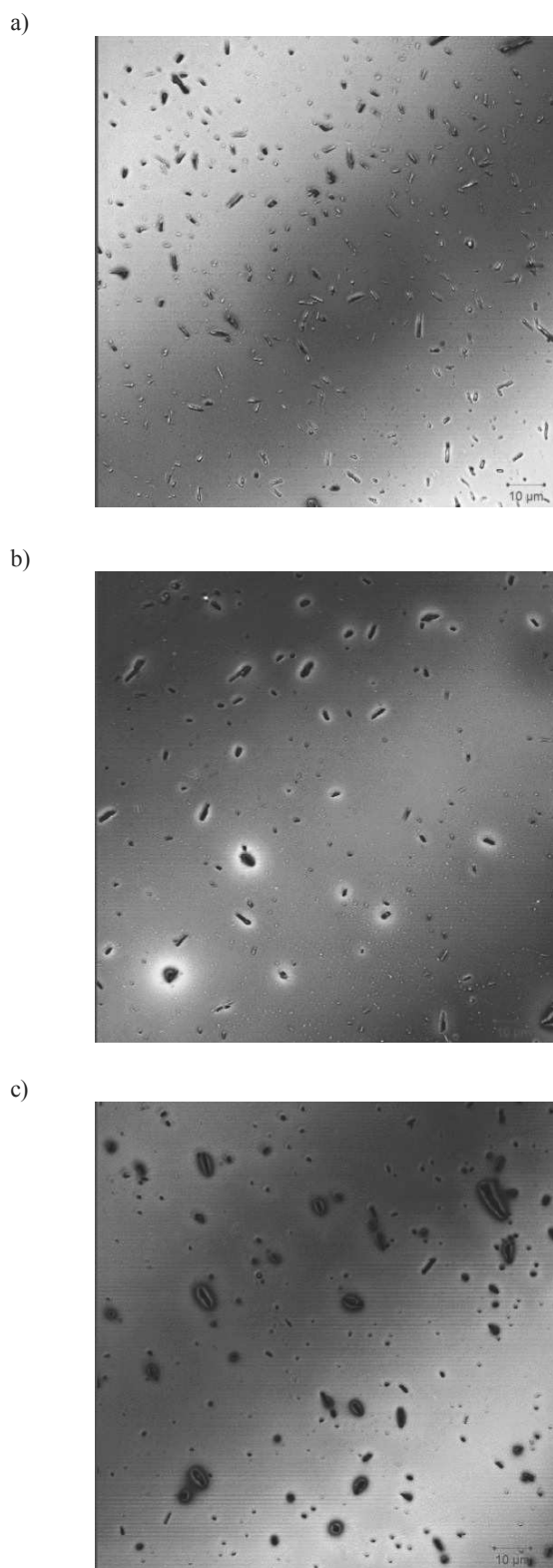


Fig. 9. The surface topography of polymer Ox-Per-6F (4:1:3) rate with at different speeds: a) 1000 rpm; b) 2000 rpm; c) 3000 rpm

Figure 10 shows the position of the measurement and analysis of the absorption of electromagnetic radiation of a wavelength.

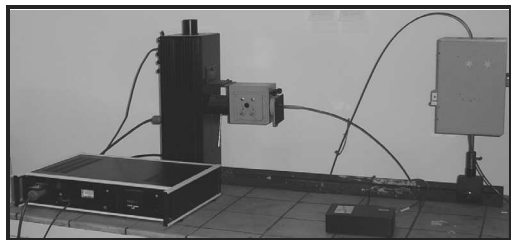


Fig. 10. The position of the measurement and analysis of the absorption spectra in Center of Polymer and Carbon Materials in Zabrze

The research using a spectrophotometer UV/VIS was performed to determine the absorption coefficient of the surface. Absorption curves for each of the polymeric material is shown in separate graphs.

In Figure 11 shows the measuring box spectrometer simultaneous detection.

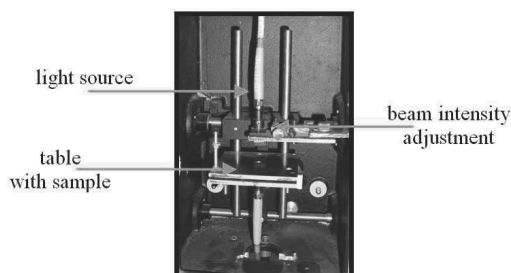


Fig. 11. The measuring box spectrometer simultaneous detection in Center of Polymer and Carbon Materials in Zabrze

There are shown in Figs. 12 and 13 UV-Vis absorption spectra taken on thin films of Oxm-Per-6F (2:1:1) and Oxp-Per-6F (2:1:1), respectively spin-coated with spinning rates 1000, 2000 and 3000 rpm. One can see that the absorption maxima are seen at the wavelength about 330 nm in the either figure. However, absorbance of the films shown in Fig. 12 is closely related to the spinning rate, being the highest for the film prepared with the rate 1000 rpm. Much lower absorption maxima of the films prepared with 2000 and 3000 rpm nearly coincide and seems to be slightly shifted towards shorter wavelengths.

In Figure 12 shows a plot of absorbance on the wavelength of the polymer Oxm-Per-6F (2:1:1) curves were determined for the layers deposited at different spin rate. The largest absorption coefficient of the polymer obtained at a spin rate 1000 rpm. Then the absorbance reached a value of 0.55 at a wavelength of about 330 nm. Subsequent absorption curves for layers coated with a 2000 and 3000 rpm are similar to each other. Both reached the absorbance of not greater than 0.15 at a wavelength around 330 nm.

The spectra for thin films of Oxp-Per-6F, shown in Fig. 13, are seen to reveal very similar behavior, while considering absorbance strength distribution and its dependence on the spinning rate. Though, the absorbance level of these spectra is higher than it was the case for Oxm-Per-6F thin films. In Fig. 13

shows a plot of absorbance on the wavelength of the polymer Oxp-Per-6F (2:1:1). The curves were determined for the layers deposited at different spin rate. The largest absorption coefficient of the polymer was obtained even at coated 1000 rpm. Then the absorbance reached a value of 0.95 at a wavelength of about 330 nm. At the same wavelength for maximum absorbance coated layer at 2000 rpm was 0.45, while for the layer coated at 3000 rpm was 0.35.

In Figs. 14-17 are shown absorbance spectra versus wavelength for Ox-Per-6F thin films prepared with various molar ratio. Figure 14 shows a plot of absorbance on the wavelength of the polymer Ox-Per-6F (2:1:1). The spectra were recorded for the layers deposited at different spin rate. The largest absorption level reveals thin films prepared with spinning rate of 1000 rpm. The absorbance reached a value slightly above 0.7 at a wavelength of about 340 nm. At the same wavelength for maximum absorbance layer coated at 2000 rpm was 0.45 while for layer coated at 3000 rpm was 0.35.

Figure 15 shows the plot of absorbance on the wavelength of the polymer Oxp-Per-6F (3:1:2). The curves were determined for the layers deposited at different spin rate. The absorbance did not exceed 0.3 at a spin rate 1000 rpm, the wavelength around 330 nm. The absorbance of the layers coated with at 2000 and 3000 rpm reached its maximum in the vicinity of 0.15 for the same wavelength.

In Figure 16 show a plot of absorbance on the wavelength of the polymer Ox-Per-6F (3:1:2). The curves were determined for the layers deposited at different spin rate. The largest absorption coefficient of the polymer obtained at a speed of coated 1000 rpm. The absorbance reached a value slightly above 1.2 at a wavelength of about 340 nm. Absorbance for layer coated with at 2000 rpm was 0.45, for layer coated at 3000 rpm was 0.25. The absorption maxima of these layers is shown at a wavelength of about 330 nm. Shift of maxima of these layers relative to the layer coated at 1000 rpm can be clearly seen in Fig. 16.

In Figure 17 shows a plot of absorbance on the wavelength of the polymer Ox-Per-6F (4:1:3). The curves were determined for the layers deposited at different spin rate. The largest absorption coefficient of the polymer obtained at a speed of coated with 1000 rpm. The absorbance reached a value slightly above 0.85 at a wavelength of about 340 nm. At a wavelength around 330 nm absorbance maximum coated layer at 2000 rpm was 0.45 while for layer coated at 3000 rpm was 0.2.

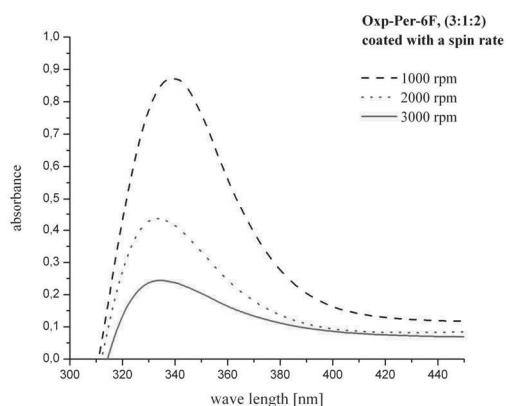


Fig. 12. Spectral absorbance curve for polymer Oxm-Per-6F (2:1:1)

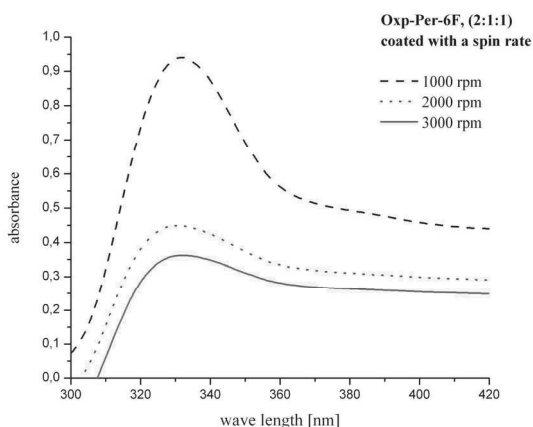


Fig. 13. Spectral absorbance curve for polymer Oxp-Per-6F (2:1:1)

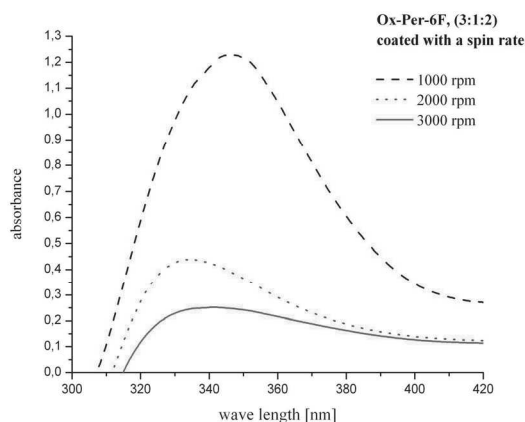


Fig. 16. Spectral absorbance curve for polymer Ox-Per-6F (3:1:2)

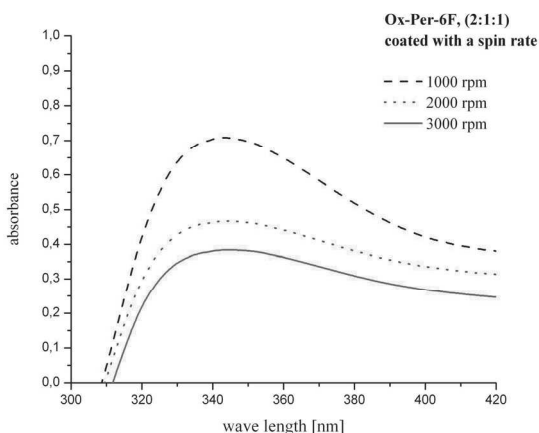


Fig. 14. Spectral absorbance curve for polymer Ox-Per-6F (2:1:1)

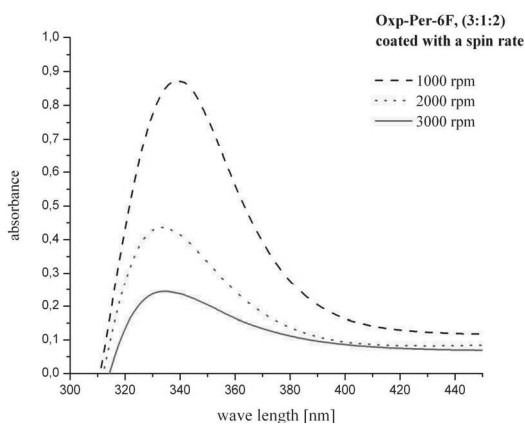


Fig. 17. Spectral absorbance curve for polymer Ox-Per-6F (4:1:3)

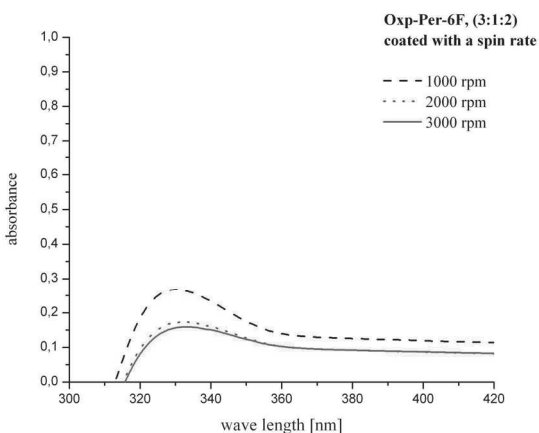


Fig. 15. Spectral absorbance curve for polymer Oxp-Per-6F (3:1:2)

4. Conclusions

Research of surface morphology by using confocal laser scanning microscopy has confirmed possibility to obtain uniform thin films. Research with using a spectrometer UV/VIS has confirmed favorable optical properties of polymers which belongs to the group of polyoxadiazoles. The results may lead to the conclusion that Oxp-Per-6F (2:1:1) and Ox-Per-6F (3:1:2) can be used in photovoltaic and optoelectronic devices.

5. Discussion

Absorption bands observed in all the spectra are attributed to optical transitions linking delocalized states on conjugated segments of oxad part, which are essentially similar. However, attaching to phenyl ring at meta position favors worse planarization of the oxad fragment than it is case for attaching at para position.

This affect is responsible for much higher absorbance of 330 nm band in the Oxp-Per-6F film than that from Oxm-Per-6F film. Intensity distribution observed in Figs. 12 and 13 is seen to follow

spinning rate, the lowest spinning rate the higher absorbance is. Once can see that spectra shown in Figs. 14-17 are real similar tendencies with respect to the spinning rate used to deposit thin film. However, the maximum of the absorption band in the spectrum of recorded on Ox-Per-6F films of various molar ratio but prepared with 1000 rpm spin rate is pushed to longer wavelength than absorption band shown in Figs. 12-13. This is a consequence that there are no oxygen atoms in the backbone of Ox-Per-6F films, which make the length of conjugated segments longer and HOMO-LUMO gap is narrower.

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