SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
17 (2011)

EVALUATION OF PRINTED TRANSPARENT CONDUCTIVE LAYERS

Nikola PEŘINKA[1], Marie KAPLANOVÁ and Tomáš SYROVÝ
Department of Graphic Arts and Photophysics,
The University of Pardubice, CZ–532 10 Pardubice

Received September 30, 2011

Currently, the printing of functional materials is still becoming more significant. Very promising is the area of printed conducting polymers, which are nowadays already commercially available in a form of printing inks. To control the production process and to ensure a good functionality of resulting printed devices, the quality of printed layers must be further characterized and evaluated. In this work, different methods of a physical study were applied to assess the properties of screen-printed conductive layers on the base of PEDOT/PSS polymeric complex (e.g. electrical measurements, profilometry, UV-VIS spectroscopy, optical and scanning electron microscopy, photoacoustics and image analysis). The samples were prepared using the screen-printable dispersion Clevios S V3 from the producer Heraeus. The functional layers were deposited on several flexible polymer foils via screen-printing. In order to obtain a set of samples varying in thickness, the sieves with different mesh densities were used. In these prepared layers various properties were studied (e.g. thickness, surface morphology, resistance and specific resistivity, UV-VIS spectra and printing resolution).

[1] To whom correspondence should be addressed.

Finally, the influence of printing parameters on the resulting properties of the layers and the suitability of the used evaluation methods are discussed.

Introduction

Currently, the printing is also concerned with the application of the so-called functional materials. These materials are usually represented by new inks, being equipped with some additional properties (e.g., electrical conductivity). The application of these new materials results in a form of completely new printed products, such as printed flexible displays, photovoltaic cells, batteries, sensors etc. [1]. This area of printing is nowadays usually denoted as "printed electronics" or sometimes also as "organic electronics", while the organic conductive compounds are mainly used to prepare the functional layers. Significant role in the production of printed flexible functional devices has been fulfilled by the conducting polymers. The discovery of conducting polymers was awarded with the Nobel Prize in Chemistry in 2000 [2]. In the area of printing and application of conducting polymers, most of the work has been done on the polymeric complex 3,4-polyethylenedioxythiopene/polystyrenesulfonate (shortly PEDOT/PSS) [3]. The PEDOT/PSS polymeric complex is distinguished by its excellent film-forming properties and is commercially available in a form of conductive dispersion under the names Clevios and Orgacon from the companies Heraeus and Agfa Materials, respectively. These dispersions are ready-prepared and adjusted for the needs of each application and the printing techniques (e.g. screen printing, inkjet, gravure). This work deals with the characterization of the thin layers of conducting polymers prepared by the printing. The main accent is on the aqueous dispersions of PEDOT/PSS and its printable formulations.

Experimental

Samples

For the printing, five screen printing frames with different mesh densities were used (62 cm^{-1}, 77 cm^{-1}, 110 cm^{-1}, 140 cm^{-1} and 165 cm^{-1}). The material of the sieves was Saatilene HIBOND with enhanced durability (HD). For the contact copy of the testing image the emulsion Dirasol 914 from the producer Sericol was applied. The sieves were fastened on the frames with the bias angle of 22°. As substrates, the transparent polyester foil Melinex ST 504 (ISO A4 format) of the thickness 175 μm from the producer DuPont Teijin Films and two types of polycarbonate foil Makrofol from Bayer MaterialScience AG were used (white non-transparent foil Macrofol ID 6-4 white and partly transparent foil Makrofol DP

1234). Also a small number of samples on the optical glass were made. As the conductive material, a screen printable conductive dispersion of PEDOT/PSS was applied. The dispersion is available under commercial name Clevios S V3 from the company Heraeus.

For the printing, the semi-automatic screen printing machine Alraun AT 301 was employed. The temperature and the humidity during the printing were kept constant within the range from 19.0 to 19.5 °C and from 24 to 32 % RH. The printing speed of the squeegee was according to tests set to 400 mm s^{-1}, and the speed of the float bar was set to 150 mm s^{-1}. To obtain the best conductivity, the tested dispersion was printed in the undiluted form. Before the printing, the dispersion Clevios S V3 was stirred by means of the laboratory mechanical stirrer for 15 min at the constant speed of 250 min^{-1}. The distance between the screen frame and the printing table was kept constant on the value of approximately 3 mm. After the printing, the samples were dried in the hot-air oven for 30 to 45 min. The drying temperature was set to 100 °C. During the drying process the circulation of the air in the oven was enabled.

Study of Surface Morphology and Thickness of Prepared Layers

The thickness and the surface morphology of the prepared layers was studied by means of the mechanical profilometer Dektak 8 from the producer Veeco and also using 3D laser scanning microscope Keyence VK-9700 and optical microscope Bresser Erudit DLX 510200. The thickness was examined on the printed line of the width of about 800 μm and the average value of the thickness was then determined from the middle part of this line (of the width approximately 400 μm). The surface morphology was observed and subjectively evaluated by means of the images from CCD cameras of the mentioned microscopes.

Scanning Electron Microscopy of Prepared Samples

To compare the morphology, the layers prepared by each mesh density were also studied by means of the scanning electron microscopy (SEM) using the microscope JEOL JSM-5500LV with X-ray energy disperse (EDX) microanalyser IXRF Systems (detector GRESHAM Sirius 10).

Measurement of Electrical Properties

The measurement was implemented with the equipment Keithley 2612 System Source Meter in combination with electrode bridge Süss MicroTec PM5. For most

measurements the appliance Motech MT 4090 LCR Meter was employed. All the samples were measured using the DC voltage. For the first tests with Keithley 2612 System Source Meter, the voltage 20 V was applied. In the case of further measurements with Motech MT 4090 LCR Meter, the constant voltage of 1 V was always used.

For the electrical measurements, two methods were applied. Firstly, the comparative relative resistance measurements of the printed lines (varying in the width) using the 2 point probe were used. After these measurements, the 4 point probe (van der Pauw method) was utilized on the printed squares (of the area 1.5 ×1.5 cm) for the determination of the specific resistivity. For both methods, laboratory constructed contact bridges were implemented. The metal contact electrodes in both methods were placed directly on the printed layers. However, the samples with the highest conductivities were in the places of contact areas additionally coated with silver-based conductive ink to investigate its impact on decreasing of the transition resistance between the electrodes and the printed layer.

Measurement of Rheological Properties of PEDOT/PSS Based Dispersions

The rheology of the applied dispersion was studied by means of the rheoviscometer HAAKE RotoVisco 1. For the measurements of the dispersion Clevios S V3 the arrangement "cone-plate" was used. All the measurements were carried out at the temperature of 20 °C. The range of the used share rates was from 3 to maximally 2500 s^{-1}.

Measurement of UV-VIS Spectra of Printed Samples

Here, only the combination of the transparent substrate Melinex ST 504 and the Clevios S V3 were measured. The spectroscopic transmission measurements were carried out on the spectrophotometer SPECORD 210. The samples for the measurement were cut to squares of 2×2 cm and placed in the measuring chamber by means of the sample holders with circular holes of approx. 1.5 cm in diameter. All the samples, including the substrate, were then measured with air reference as the primary reference. Then the substrate was subtracted. The measured UV-VIS spectra range was from 320 to 1100 nm. The resulting absorbance, described by the Lambert–Beer law, was then plotted against the wave length. After these measurements, dependence between the conductive layer nominal thickness and the absorbance was examined (for the wave length of 655 nm, which corresponds to the wave length of the laser light used for photoacoustic measurements).

Photoacoustic Measurements of Printed Samples

The samples used in the UV-VIS spectroscopy were cut to the circular shape of 11 mm in diameter and fixed on backing. The measurement was implemented inside of the cylindrical photoacoustic cell, where the circular samples were placed and impinged by the laser beam (Flexpoint Minilaser FP 65/20ADF AV from Laser Components GmbH, wave length 655 nm, beam diameter approx. 1 mm). As the reference, a polypropylene foil with thin gold layer was applied, deposited *via* evaporation in high vacuum. Each sample was measured twice. The acoustic signal was detected by means of a 1/2" condenser microphone Brüel & Kjaer type 4137 and pre-amplified. The output signal was then led to a DSP lock-in amplifier Stanford Research Systems model SR380. The laser light was modulated using the internal oscillator of the lock-in amplifier. All the measurements were processed and controlled by computer.

Image Analysis

For the image analysis, the images acquired by means of the Bresser Erudit DLX 510200 optical microscope were utilised. All the samples were obtained at the same resolution of 2048×1536 pixels^2 using one type of the lens. Further, for the image analysis the programmes Adobe Photoshop, ImageJ and Matlab were used. During the image analysis, the smallest printed lines were firstly objectively selected. Then after the image selection some parts of the image were filled up with the black — and the other parts white colour. After conversion to black and white mode and cropping, the final analysis in Matlab was made. For the evaluation of the printing resolution the images of the finger structures from the used printed testing structure were applied. The lines were examined in the parallel direction to printing direction and in perpendicular direction as well. Also the difference of the line width in the middle and on the edge of the finger structures was observed. The last printable line was considered as the line, which was not "fused" with the neighbouring lines. It should be noted, that some of the examined lines may have had some small defects. The evaluation was then done statistically from arithmetical average and modus.

Results

Study of Surface Morphology and Thickness of Prepared Layers

Figure 1 shows the profile of the printed line of Clevios S V3. This figure indicates that the surface of the line has, in comparison to the substrate, higher roughness.

The three lines of different shade represent the profiles after the shift in *y*-axes direction. The three acquired lines also illustrate that the surface morphology changes along the y-axes (line length).

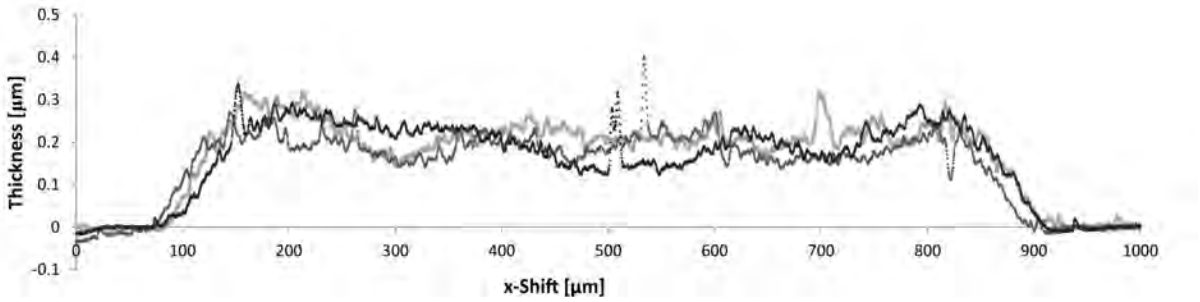

Fig. 1 Profile of printed line of Clevios S V3 on Melinex ST 504 (by mesh density 165 cm^{-1})

Table I Thickness of printed conductive layers (determined by profilimeter Veeco Dektak 8)

Substrate	Mesh density cm^{-1}	Thickness of dry layer Clevios S V3 (standard dev.) nm
Melinex® ST 504	62	956 (47)
	77	439 (20)
	110	382 (13)
	140	205 (8)
	165	195 (14)
Optical glass	62	501 (78)
	77	392 (54)
	110	265 (20)
	140	227 (29)
	165	144 (20)

Table I compares the values of the thickness for combinations of various used mesh densities and substrates. According to the data received after processing the profiles measured by the profilometer, the thickness of the prepared layers ranged from 150 nm to almost 1 µm. The thickness of the conductive layers prepared on the optical glass was lower than in case of the layers printed on Melinex foil. The lowest thickness was obtained by layers printed with the highest mesh densities. The thickness of the layers prepared on polycarbonate foils Macrofol ID 6-4 white and Makrofol DP 1234 could not be examined by means of

the profilometer, because the roughness of these substrates was approximately 2.5 μm, which is around 3 to 10 times more than the thickness of the printed layers.

Scanning Electron Microscopy of Prepared Samples

To be able to observe the surface morphology of the prepared layers, each one of them had to be coated with a thin gold layer via vacuum evaporation. No significant structures could be observed for the layers with different mesh densities by means of scanning electron microscope. However, the assumed higher roughness was confirmed for the layers prepared with lower mesh densities.

Measurement of Electrical Properties

For the 2 point probe, the resistance of the printed lines changed according to the line width, where the widest line showed the lowest resistance. The lowest resistance of the lines measured with 2 point probe was around 10 kΩ (for the printed line of nominal width 1 mm and the length 15 mm; at the mesh density 62 cm^{-1}), which after consideration of the layer thickness corresponds to the specific conductivity 15.7 S cm^{-1}. The measurement with the 2 point probe was very imprecise. The variation coefficient of the resistance estimation was up to 50 %; based on the standard deviation. By the 4 point probe, the value of the highest specific conductivity was estimated on 0.52 S cm^{-1} (also with variation coefficient up to 40 %). Since the transition resistance was supposedly very high by both methods (when putting the electrodes directly on the semiconductor PEDOT/PSS layer), the samples measured by 4 point probe were additionally obtained with silver-based ink contacts to improve the electrical contact with layer of conducting polymer. The resulting measurement was relatively precise (variation coefficient for two printed squares to 1.75 %). The measured conductivity was about 179.5 S cm^{-1} (at the mesh density 62 cm^{-1}) in this case.

Measurement of Rheological Properties of PEDOT/PSS Based Dispersions

The dispersion Clevios S V3 indicated a noticeable pseudoplastic behaviour. The viscosity of the dispersion was estimated on the value of approximately 3300 Pa s (by the shear rate of 100 s^{-1}). Furthermore, the values of yield point τ_c (32.5 Pa) and viscosity at the endless shear rate η_∞ (1.92 Pa s) were assessed according to Casson model. Additionally, the flow index p (0.271) and flow coefficient c (50.6) were estimated applying the Ostwald model.

Measurement of UV-VIS Spectra of Printed Samples

Since the fact of the absorbance of PEDOT/PSS layers in the field of the visible spectra was already reported, the absorbance of the printed layers of Clevios S V3 on Melinex ST 504 was also expected. This presumption was fulfilled. The interdependence between the absorbance of the conductive layers and their thickness was revealed. The mutual shift of the spectral curves, representing the various mesh densities (i.e. the different thickness of the printed layers) along the *y*-axes of the spectra can be observed in Fig. 2. This fact is obvious especially in the range of the longer wave lengths. The spectra were measured by two sets of samples, prepared at the same conditions, and the variation coefficient was less than 5 %. The correlation between the absorbance and the layer thickness for the wave length 656 nm was more than 90 %.

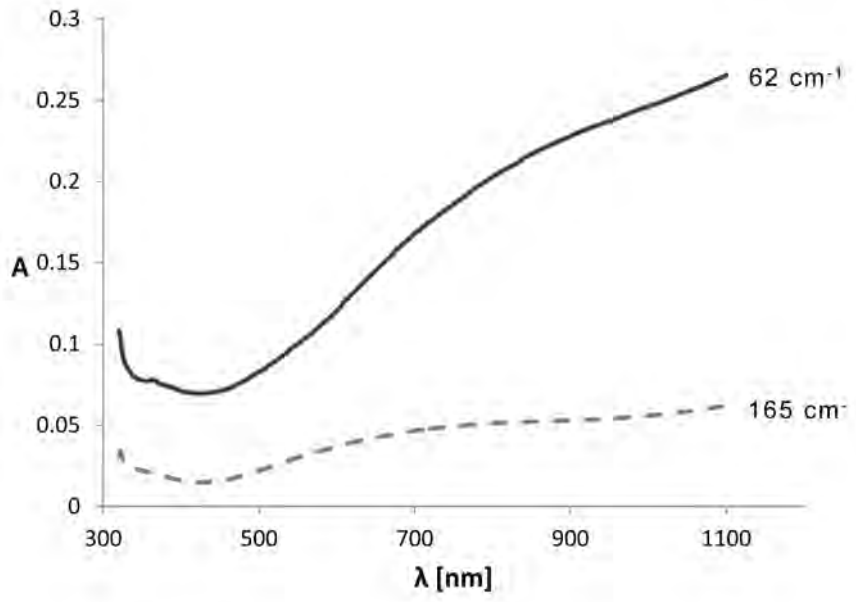

Fig. 2 Transmission UV-VIS spectra of Clevios S V3 on Melinex ST 504 at two different mesh densities (62 and 165 cm^{-1})

Photoacoustic Measurements of Printed Samples

By the photoacoustic measurements, the dependence between the normalized photoacoustic signal was searched for, represented by its amplitude and phase shift and the conductive layer thickness. It was revealed that the normalized amplitude of the photoacoustic signal also depends on the thickness of the measured layers of Clevios S V3 (represented by the various mesh densities). This was observed not only by the transparent Melinex ST 504 foil, but also by the non-transparent rough white polycarbonate foils Makrofol ID 6-4 white. The correlation between the photoacoustic signal and the thickness of the layers for the modulation frequency 278 Hz was about 95 %.

Image Analysis

After the evaluation of the lines of the printed testing structures using the image analysis, the best achieved print resolution was assessed by the mesh density of 165 cm^{-1}. The line width in this case was about 90 μm (55 cm^{-1}); orientated in the direction perpendicular to printing direction on the edge of the structure. However, in most cases the resolution was higher in the direction parallel to print than in perpendicular direction.

Conclusion

In this work, it was presented that by means of the screen printing, it is possible to produce the thin conductive layers based on conductive polymers. Further, it was shown that the properties of these printed layers can be influenced by modulating the initial parameters. The resulting layer thickness, surface morphology, achieved electrical parameters and the printing resolution can be varied by applying different mesh densities. The surface morphology of the prepared layer is feasible to examine by using the mechanical or optical microscopes and profilometers. The scanning electron microscopy can be applied to roughly estimate the surface morphology of the layers, prepared by screen printing. However, the structures of conducting polymers cannot be easily recognized using the SEM examination. This is caused due to the lack of absorbing atoms in the chains of the polymer. The evaluation of the electrical properties by the Van der Pauw method, with the contacts being additionally covered by the silver based paste, seems to be the best suited one. The results obtained by means of the 2 point probe and 4 point probe may differ significantly. The thickness of the prepared layers is possible to evaluate by both utilization of mechanical contact methods or by applying the spectroscopic methods (e.g. the UV-VIS in case of transparent layers and substrates or alternatively the photoacoustics, also for non-transparent layers and substrates; possibly rough substrates, as well). The image analysis may be a good tool for the controlling the resulting resolution of the printing of conductive polymers.

Acknowledgments

This work was supported by MŠMT ČR, grant No. MSMT 0021627501 and by MPO project FR-TI1/144.

References

[1] Aernouts T., Aleksandrov T., Girotto C. , Genoe J., Poortmans J.: App. Phys. Lett. **92**, 25 (2008).
[2] Menon R.: Curr. Sci.**79**, 25 (2000).
[3] Kirchmeyer S., Reuter K.: J. Mater. Chem. **15**, 2077 (2005).