

Properties of Conductive Features Printed on Papers and Foils

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Abstract

Two types of coated paper sheets and plastic foil, treated by corona discharge (in nitrogen at atmospheric pressure), were used as substrates for printing by conductive inks using inkjet technique and pen plotter. Printed inks were formulated on commercial water-based PEDOT:PSS and different concentrations of additives, as water, dimethylsulfoxide (DMSO), isopropanol (IPA), and others. The ink formulations were characterized by viscosity and surface energy, substrates and prints by AFM, STM microscopy and by FTIR, UV-Vis and NIR spectroscopy. Printed structures, lines with different thickness and full areas were characterized namely by electric conductivity and topography. The influence of substrate quality, plasma treatment and ink formulation onto conductivities are discussed. Addition of 5 % of DMSO increased conductivity of features considerably. Surface roughness, wetting and imbibition were key factors of features quality. Plasma treatment as well as IPA enhanced the printability and structure conductivities of foils particularly printed by plotter. Sufficient conductivities of ink-jet prints were achieved just by repeated printing (up to 10 times), so the misregistration is the limiting factor of print quality.

Keywords: conductivity, PEDOT, printed foil, paper

Introduction

Printed electronics based on solution-processable organic inks has big potential to decrease the cost of electric circuit fabrication (Kallberg 2006, Mäkelä 2005). Principal advantages are mass or large area production, low cost, flexibility of substrates and production variability, as

Radio frequency identification chips RFID, flat Organic light-emitting diodes (OLEDs) lightings, flexible displays and solar cells, intelligent packaging and papers etc.

Inkjet printing is applicable to all required materials (conductors, semiconductors and dielectrics) including OLEDs and TFTs (Yoshioka 2006, Svanholm 2007). Inkjet was used to print conducting links based on nanosilver colloid (Lee, Chou and Huang 2005) and conductive/semiconductive structures based especially on conjugated polymer chain poly(3,4 ethylenedioxythiophene) in complex with poly-(styrene sulfonate), PEDOT:PSS, to create conductive links or OLED (Soltman 2008). Conductivity of the complex was increased adding specific organic solvents like dimethylsulfoxide (DMSO) (Kim, Jung, Lee and Joo 2002). The clustering of the PEDOT particles into larger domains (Timpanaro et al. 2004) after addition of these solvents was investigated with help of AFM and STM measurements. The substrate wettability, roughness and dielectric properties are also key parameters of quality.

In this work, two coated papers and plasma treated plastic foil were printed by water-based PEDOT:PSS ink with different solvent additives to get high conductivity structures. The influence of substrate roughness, plasma treatment and ink formulation are discussed.

Experimental

The plastic foil, polyethyleneterephthalate for laser printers (120 g m^{-2} , "PET") and two coated paper sheets: Novatech gloss (150 g m^{-2} , disperse lacquer, "DLG"), Novatech satin (1150 g m^{-2} , UV lacquer, "UVL") were used as the substrates for printing. PET foils for inkjet printers were shown as unsuitable due to receiving layer, where the ink is absorbed and does not create the conductive line.

Standard dielectric barrier discharge (DBD, 15 kV, 5 kHz, 10 J cm^{-2}) in N_2 at atmospheric pressure (at flow rate of 10 l min^{-1}) was used for plasma treatment of the substrates. The commercial conductive polymer PEDOT:PSS, 1.3 wt. % in water from Aldrich was first diluted by water (2:1) and small amount of chosen solvents, dimethylsulfoxide (DMSO), dimethylformamide (DMFA), ethyleneglycol (EG) and used as the ink in inkjet printer EPSON Stylus Photo R360 to print different lines, points and full areas in slow mode (Fig. 1). Inkjet printing ought to be repeated several times onto the same substrate (overprinted) to get sufficient features and conductivities. PEDOT:PSS was printed onto the substrates also by the line plotter HP 7475A. In this case it was not diluted by water

and just 5 wt. % of DMSO was added. Some amount of isopropanol (IPA) was added just when extra glossy substrates (PET and UVL) were printed by the plotter. Moreover, the inks were applied by spin coating onto glass substrates cleaned in chromosulfuric acid to measure the properties of compact layers.

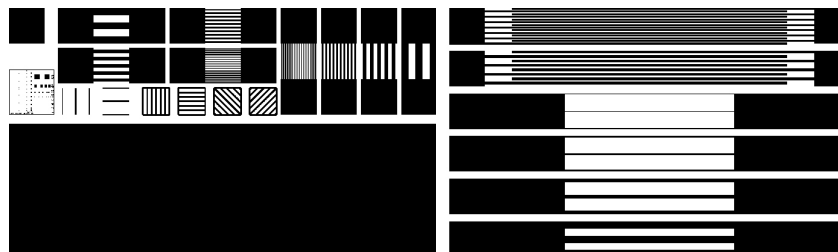


Figure 1: Inkjet printed features.

Ink formulations were characterized by viscosity and surface energy, the substrates by AFM topography including RMS roughness and printed structures by electric conductivity (DC by 4-point method and AC by digital bridge) and topography, using the equipments: capillary viscometer UNITEX, contact angle goniometer (SEE, MU Brno), optical and atomic force microscopy CP II, Veeco, multimeters Keithley 2000 and Metex M-3650D, and LCR Digibridge Quadtech 1715.

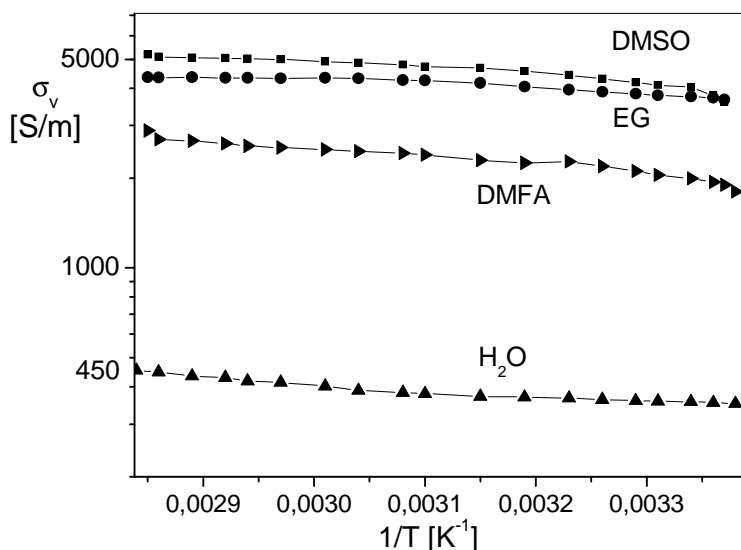


Figure 2: Specific volume conductivity (AC, 100 Hz) of PEDOT:PSS layers with different solvent additives on glass substrates depending on inverse temperature.

Results and Discussion

Viscosity and surface energy were determined for various ink formulations and as the most appropriate formulation PEDOT:PSS : water (2:1, with 5 % DMSO) was chosen, with the viscosity of 21.1 mPa s and the surface energy of 67.6 mN m⁻¹.

Addition of 5 % of DMSO, DMFA or EG to PEDOT/PSS : water solution (2:1) increased considerably (100 times) the conductivity of layers (Fig. 2). Reverse temperature dependences indicate semiconductor (or quasi-metal) character of the layers, with the similar and low activation energy (about 0.1 eV). It confirms that solvent additives change just supramolecular structure (ordering of macromolecules). The highest conductivity was achieved by DMSO, where addition of 5 wt. % was found as the optimal. However, specific volume conductivities of the PEDOT:PSS systems are still 3 order lower under metal systems based on silver ink and evaporated aluminum. Surface conductivities of PEDOT:PSS are just 2 (or 1) order lower under metal layers, considering lower thickness used of nano-silver or evaporated Al layers.

AFM measurements, contact mode as well as intermittent-contact (tapping) mode, have shown a very slight increase of surface roughness of PEDOT:PSS layers for samples with 5 wt. % DMSO addition caused by more visible grain domains with the average size of 25 nm (Fig. 3, root mean square roughness was 0.6 nm and 1.0 nm for a and b samples, respectively) that is in correlation with findings of others (Pingree et al. 2008).

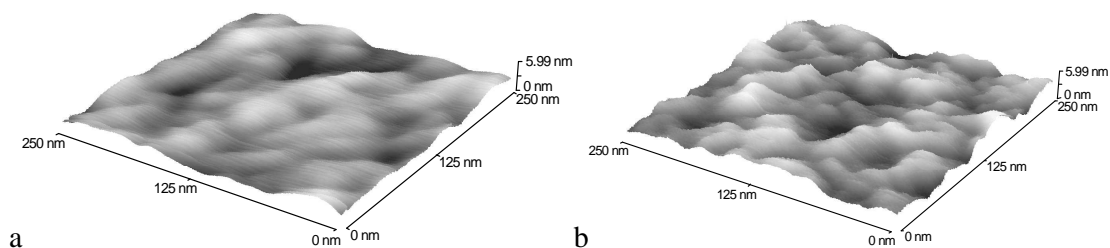


Figure 3: AFM images of PEDOT:PSS layers (tapping mode) without (a) and with (b) 5 wt.% DMSO addition.

The similar results was obtained by STM measurements, however, characteristic 10 nm wide and 25-50 nm long cigar shaped particles (Timpanaro et al. 2004) were not positively detected.

Reflectance spectra in a wide range of wavelengths (Fig. 4) correlate with the theory and expectations (Chang, Lee, Kiebooms and Aleshin 1999), including sharp increase below plasma frequency of free charge carriers (electrons and holes) situated in NIR, corresponding to 1 eV. The spectra of both layers (with and without DMSO) are practically identical, it means that the concentrations and the mobilities of the carriers did not change with the addition of DMSO, and the considerable increase of conductivity (with DMSO) is caused just by better charge transfer among distinct macromolecules of PEDOT. So, the addition of the solvent changes just the supramolecular structure and does not change the electronic properties of macromolecule itself.

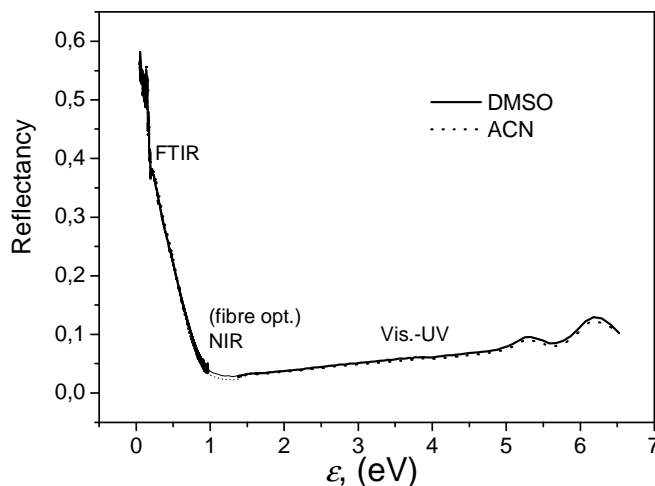


Figure 4: Reflectance spectra of PEDOT:PSS layers on glass substrates in photon energy scale.

Original high viscosity PEDOT:PSS could not be inkjet printed. It had to be diluted (2:1 with water). Because of high dilution the coatings were very thin, so to get stable results, features had to be overprinted several times on each other (more than 4, up to 10 times) that could cause misregistration problems. Eight substrates were 10 times inkjet printed with the ink formulation with the addition of 5 wt. % of DMSO that was found as the most effective considering overall topography and conductivities (Fig. 5). Surface conductivity of printed lines depends on roughness, ink wettability and imbibition. Conductivities on smooth foil PET and UVL are much higher than on DLG substrate. Specific conductivity ought to be independent on line width, however the lines are partially discontinuous. The increase of

conductivity depending on the number of repeated inkjet printing onto three gloss substrates is illustrated in Fig. 6.

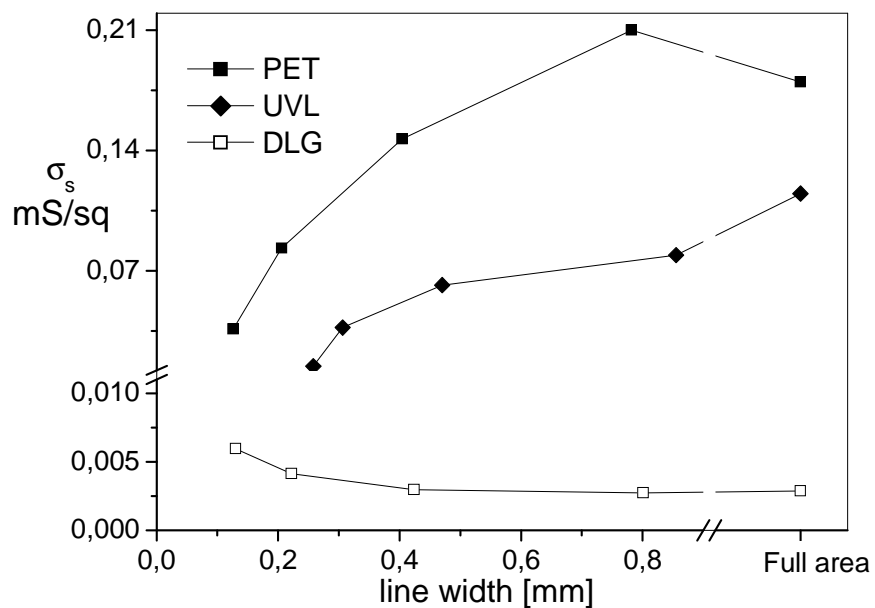


Figure 5: Specific surface DC conductivities of different lines and of full areas of 10 times inkjet printed PEDOT:PSS/DMSO onto different substrates

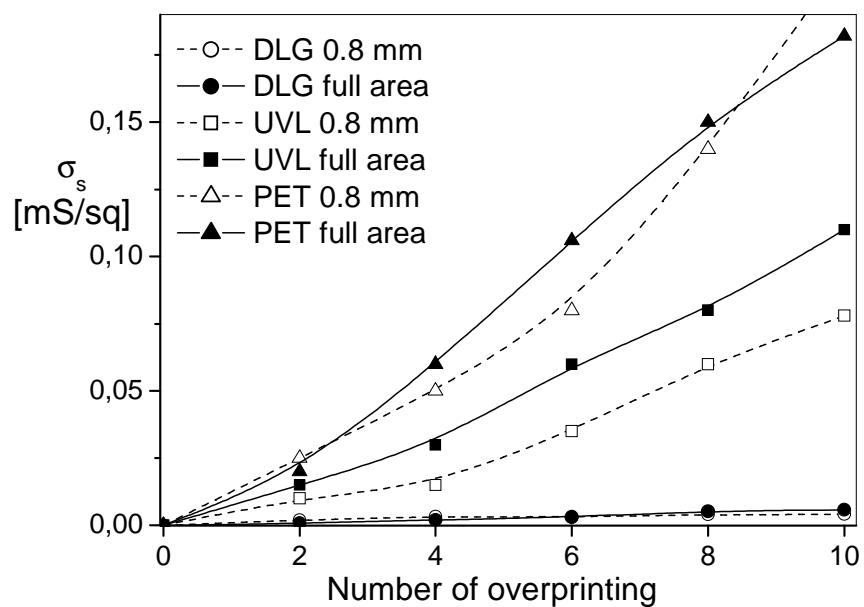


Figure 6: Specific surface DC conductivities of 0.8 mm line and full area of inkjet printed PEDOT:PSS/DMSO onto 3 chosen substrates depending on the number of overprinting

In the case of printing by plotter, PEDOT:PSS was not diluted by water, just 5 % of DMSO was added again. The lines were drawn by the pen with diameter of 0.7 mm. PET foil could not be plotted without of plasma treatment that enhanced the printability and also the stability of the results. Better wetting was achieved also by addition of IPA. After all the conductivities achieved by single drawn by plotter were similar to those obtained by 10 times inkjet printed (Fig. 7).

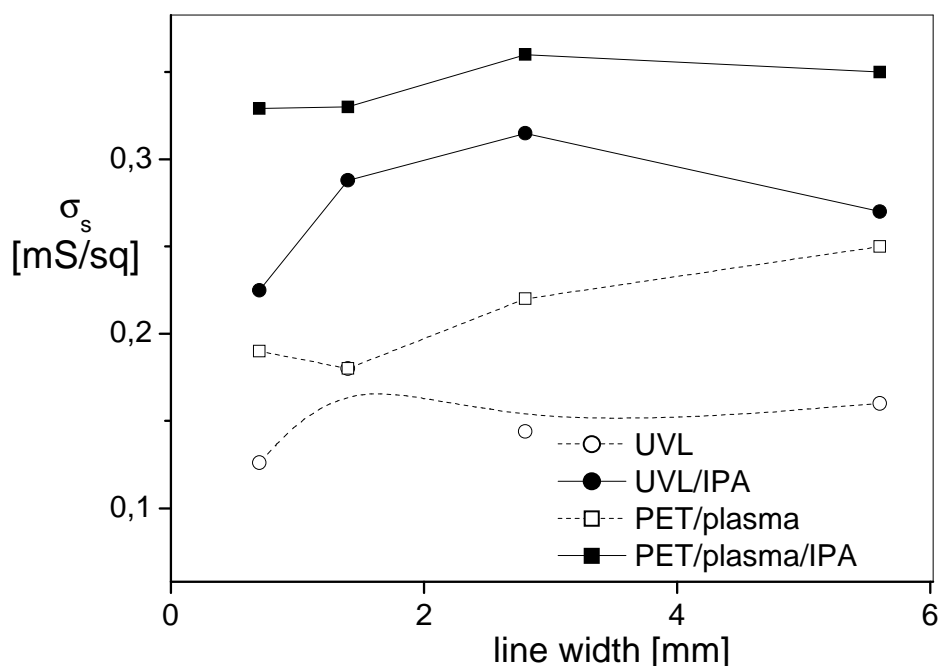


Figure 7: Specific surface DC conductivities of PEDOT:PSS/DMSO lines (including IPA addition) printed by plotter onto glossy UVL paper and plasma treated PET substrates

Mechanical, UV and thermal fastness of PEDOT inkjet printed lines were tested at the best substrates, considering conductivity (PET and UVL, Fig. 8). Mechanical treatment (25 crossings by abrasive tester UGRA) was relatively more effective at the PET substrate, while the UV treatment (1 hour of UV-A exposition by 400 W HPA Philips lamp) decreased more the conductivity of lines at UVL. Thermal treatment (5 days at 100 °C and relative humidity 50 %) was the most destructive for the conductive lines on both substrates.

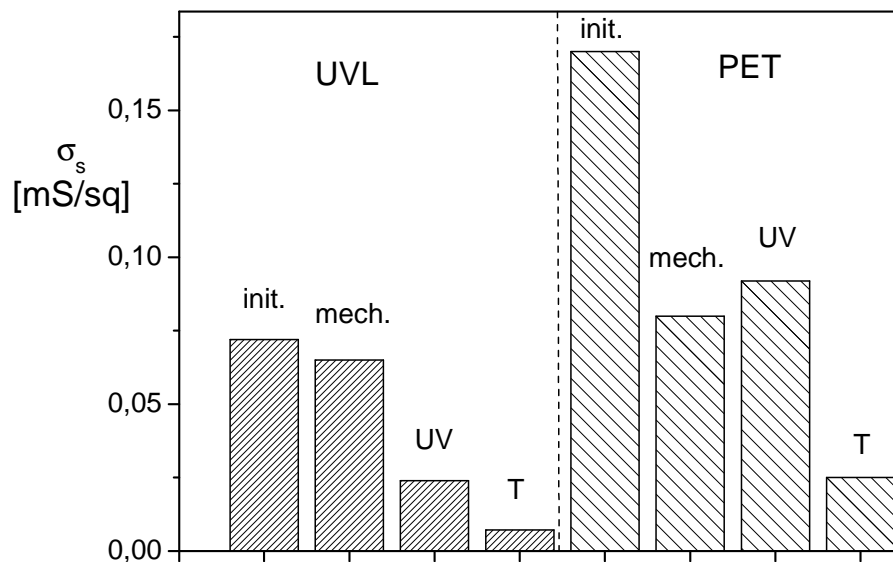


Figure 8: Specific surface DC conductivities of inkjet printed lines PEDOT:PSS/DMSO onto 2 glossy substrates (6 times printed) initial and after mechanical, UV and thermal treatment

Conclusion

PEDOT:PSS complex with 5 % of DMSO formed layers with conductivities of 5000 S m^{-1} or 0.2 mS sq^{-1} in surface specific measure for features printed by plotter or 10x by inkjet, that is about 1000 times less than metal systems get. Commercial PEDOT:PSS water solution (1.3 wt. %) need to be diluted more by water (2:1) for inkjet printing by EPSON.

Surface roughness (or smoothness), wetting and imbibition were key factors of features quality. The highest surface conductivities of lines were achieved at glossy non-imbibitive substrates with sufficient wetting (UV lacquered paper and plasma treated PET foil for laser printer). Plasma treatment and IPA addition caused the increase of conductivities of lines and areas, as well as the homogeneity and overall quality of lines.

AFM measurements in contact and tapping modes (STM as well) have proven formation of clusters of PEDOT:PSS macromolecules after addition of specific solvents (DMSO). The reflectance spectra support the expectation that the addition of solvent changes the supramolecular structure and does not change the electronic properties of macromolecule itself.

Resistance of the printed conductive features at glossy substrates were tested by mechanical, UV-A and thermal treatment. The found resistances are comparable with those of common inks on relevant substrates

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References

- Chang Y, Lee K, Kiebooms R, Aleshin A, Heeger AJ (2009) *Synthetic Metals* 105: 203–206
- Kallberg E (2006) *Intelligent Papers*, PhD. thesis, Univ. of Jyvaskyla, Finland
- Kim JY, Jung JH, Lee DE, Joo J (2002) *Synthetic Metals* 126: 311
- Lee HH, Chou KS and Huang KC (2005) *Nanotechnology* 16: 2436
- Mäkelä T, Jussila S, Kosonen H, Bäcklund TG, Sandberg HGO, Stubb H (2005) *Synthetic Metals* 153: 285
- Pingree LSC, MacLeod BA, Ginger DS (2008) *J. Phys. Chem. C* 112: 7922–7927
- Soltman D, Subramanian V (2008) *Langmuir* 24: 2224
- Svanholm E (2007) *Printability and Ink-Coating Interactions in Inkjet Printing*, PhD. thesis, Faculty of Technology and Science, Karlstad University, Sweden
- Timpanaro S, Kemerink M, Touwslager FJ, De Kok MM, Schrader S (2004) *Chemical Physics Letters* 394 (2004): 339–343
- Yoshioka Y, Jabbour GE (2006) *Inkjet Printing and Patterning of PEDOT-PSS*, in *Conjugated Polymers, Processing and Appl.*, Eds. T. A. Skotheim, J. Reynolds, CRC Press