Polymeric Materials for Printed Electronics and Their Interactions with Paper Substrates

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Abstract

The primary goal of printing electronics is to create structures and devices that are functionally similar to conventional electronics, but at greater speed, lower cost and less production complexity. The applications that will be affected by lower cost of electronics include RFID tags, solar cells, displays, chemical sensors, etc. In this work, effects of paper properties and their effect on sheet resistivity of gravure printed PEDOT:PSS layers were evaluated. Among paper properties, it was observed that absorptivity and ink penetration had negative effect on conductivity. The higher the ink penetration into the substrate surface the lower the conductivity. Moreover, surface energy of the substrates needs to be in balance with surface tension of the conductive inks.

Introduction

Nowadays, printing is seen in a new light for the fabrication of advanced functional materials, such as electronic components. There are many commercially available polymeric materials suitable for deposition by printing. Solution processable conductive and semiconductive polymers are already leading to low cost sensors and cheap, disposable electronics. In electronics, the quality of the interface between individual layers is crucial, because it functions as a conveyor of charge carriers across or along the interface. The smoothness and uniformity of printed semiconductor and dielectric layers is essential for optimal device performance.

In this work, PEDOT: PSS based inks were used to print conductive layers. This conductive polymer is commercially available as a water-soluble polyelectrolyte system with good film-forming properties, high visible light transmittance, and excellent stability[1]. Some applications of PEDOT: PSS include antistatic coatings, conductive layers in organic light emitting diodes (OLEDs), capacitors and thin film transistors[2]. It has been reported that electrical conductivity of PEDOT:PSS can be enhanced by the addition of different organic compounds[3]. The conductivity improvement is strongly dependent on the chemical structure of the compound. Among the alcohols, ethylene glycol and glycerol were found to be the most efficient. Enhancement of conductivity is believed to be a result of an increased inter-chain interaction caused by conformational change of the PEDOT chains from the coil structure into expanded-coil or linear structures[4].

The vast majority of organic transistors have been prepared using doped silicon wafers as the substrate, basically with the purpose to demonstrate the concept of utilization of organic materials in electronics[5]. However, to realize large scale and roll-to-roll production of printed electronics, flexible substrates will be required. With the technology of flexible electronics becoming closer to device prototyping and commercial production, it is clear that the choice of substrates with desirable properties is essential in order to make this technology viable. Different applications, such as displays, disposable electronics or intelligent packaging, will demand different sets of substrate properties.

Flexible substrates pose a number of challenges. Dimensional stability of the substrate is very important in order to ensure precise registration and resolution. Many types of substrates are also incompatible with some solvents used for organic materials[6]. Surface smoothness and cleanliness of the flexible substrate are both essential to ensure the integrity of subsequent layers and formation of a high quality interface for better device performance.

Of the flexible plastic substrates, the most commonly used are polyesters[7,8] (PET, PEN) and polyimides[9]. Although paper is of big interest for printed electronics, there are very few reports to date[10,11].

Experimental Part

Conductive polymer ink used in this study was prepared from commercially available Baytron® P HS (H.C.Starck GmbH & Co.). This aqueous solution contains 2.6 - 3.2% of PEDOT:PSS complex. In addition to BAYTRON® P HS, the ink formulation included 27 wt% of ethylene glycol for conductivity enhancement[4] and 16% of ethanol used to improve substrate wetting and ink spreading[12].

Commercially available label stock paper papers were used as substrates for printing PEDOT:PSS layers. A laboratory scale gravure proofer (K-printing proofer by RK Print-Coat Instruments Limited) was employed for printing. Conductivity of printed layers was measured using a Keithley multimeter model 2400 in a four-probe sensing mode. Sheet resistivity, ρ_s, was calculated from measured resistance, R, and dimensions of printed conductor (width, w and length, l) according to the following equation:

$$\rho_s = R \times \frac{w}{l}$$

Three different label stock papers were used, L1, L2 and L3 (Table 1). Table 2 summarizes measured paper substrate properties together with corresponding methods and instruments used.

Table 1: Basic properties and end use of tested paper substrates

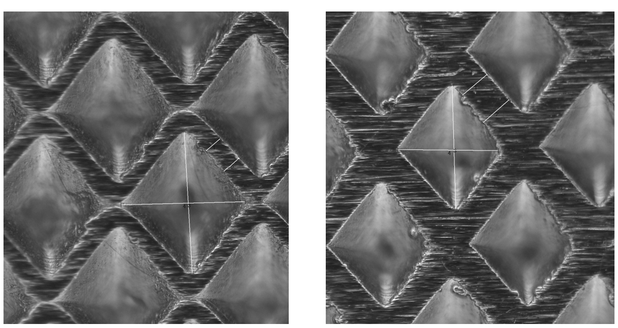
Substr. ID	Basis Wt. [g/m^2]	Thickness [μm]	Applications
L1	73	70	Flexible packaging
L2	74	69	Pressure sensitive labels
L3	81	71	Pressure sensitive labels

Table 2: List of tested paper properties, methods and instrumentation used

Measured Property	Method	Instrument
Roughness	Air Leak Method	Parker Print Surf (PPS)
Porosity	Air Leak Method	Parker Print Surf (PPS)
Dynamic Contact Angle	Sessile Drop Method	First Ten Angstroms FTA200
Surface Energy	Owens-Wendt Method	First Ten Angstroms FTA200
Dynamic Liquid Penetration	Ultrasonic Transmission Measurement	Emco Dynamic Penetration Tester DPM30
Topography	Atomic Force Microscopy	Autoprobe CP by Thermomicroscopes
Image Analysis	Optical Measurement	KDY ImageXpert

Results and Discussion

It was previously reported that inkjet printed ink film thickness of PEDOT:PSS ink can be controlled by adjusting luminosity values or in other words darkness of the color. Higher luminosity values led to lower ink film thickness and consequently higher sheet resistivity[13]. In gravure printing, color darkness (tone scale) is typically controlled by gravure cells dimensions. Cells with bigger opening and depth will deposit thicker film. Standard gravure printing plate used for printing of PEDOT:PSS ink in this work included four different tone steps (100-90-80-70%), where the 70% tone steps had the smallest opening of the cells or the thickest cell wall thickness (Figure 1) and thus it was expected that it will deposit the lowest amount of the ink onto the substrate.



100% 70%

Figure 1: Digital microscope images of gravure plate engraving at 100 and 70% tone steps. Cell wall thickness was measured to be around 30 microns for 100% and 50 microns for 70% tone.

Figure 2 shows the effect of tone step value on sheet resistivity of printed PEDOT:PSS layers on three different paper substrates. As expected, lower tone step value resulted in the highest sheet resistivity. It can be seen that experimental values fit the exponential function closely. By considering paper substrate type, a significant effect on sheet resistivity was observed. The lowest sheet resistivity was measured for L3, and then L1 and L2. For 100% tone step, the sheet resistivity for L3 was 4.8±0.2 kΩ/sq. The L1 and L2 have significantly higher sheet resistivity, 459±92 and 784±85 kΩ/sq., respectively, which is almost 100 fold increase of resistivity by changing paper substrate from L3 to L1.

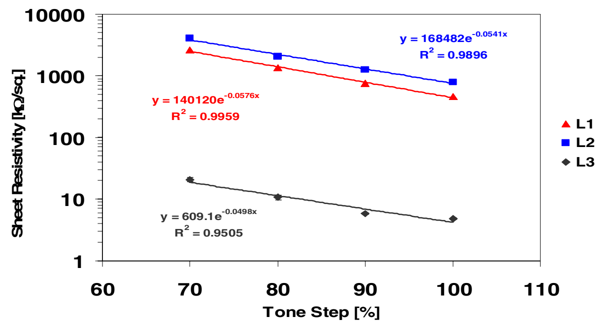


Figure 2: Effect of tone step value on sheet resistivity of PEDOT:PSS layers printed on three different label stock papers.

Table 3 presents some basic properties of the tested substrates, such as PPS roughness and compressibility (K), PPS porosity and bulk. Compressibility coefficient was calculated from roughness values taken at two different clamping pressures. It can be seen that in terms of roughness, L1 and L3 are very similar and L2 has higher roughness. In terms of compressibility, all three substrates are very similar. Considering the bulk of tested papers, it can be seen that L3 is the least bulky or in other words, it is the densest since the bulk is just the inverse of density.

Table 3: Properties of tested paper substrates

Substrate ID	PPS Rough. [μm]	K	PPS Porosity [ml/min]	Bulk [cm^3/g]
L1	1.28 ± 0.05	0.80	2.54 ± 0.27	0.96
L2	1.47 ± 0.05	0.82	2.67 ± 0.14	0.93
L3	1.25 ± 0.03	0.81	2.28 ± 0.15	0.88

It is typical with water based systems that the surface energy of the substrate as well as the ink is very important for proper wetting and spreading. Therefore, surface energy, σ, was calculated using Owens-Wendt model[14] to further evaluate paper substrate properties. Contact angles were measured with two testing liquids, water and methylene iodine and were used in calculation. Estimated values of surface energy as well as contribution from polar and dispersive forces are shown in the Table 4. The highest value was found for L2 substrate. L1 and L3 substrates exhibit comparable surface energy values.

Table 4: Estimated values of surface energy and dispersive and polar force contributions

Sample	σ [mN/m]	Dispersive	Polar
L3	43.3	38.4	4.9
L2	49.7	36.6	13.1
L1	42.6	38.4	4.1

During the measurements of contact angle for estimation of surface energy, different changes in water drop volume were observed for the tested substrates. Figure 3 shows that L2 absorbs the water the most and L3 the least. This is in good correlation with PPS porosity values and might be one possible explanation of significantly higher conductivity of printed polymer film on L3 substrate.

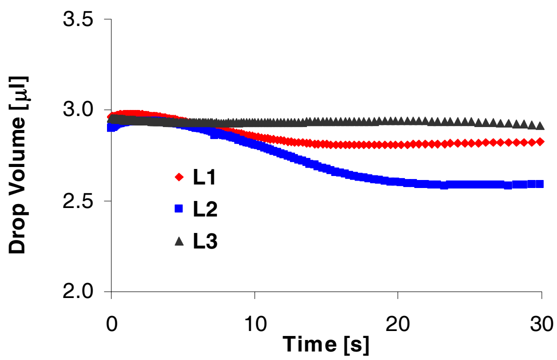


Figure 3: Change drop volume in water with time for tested substrates.

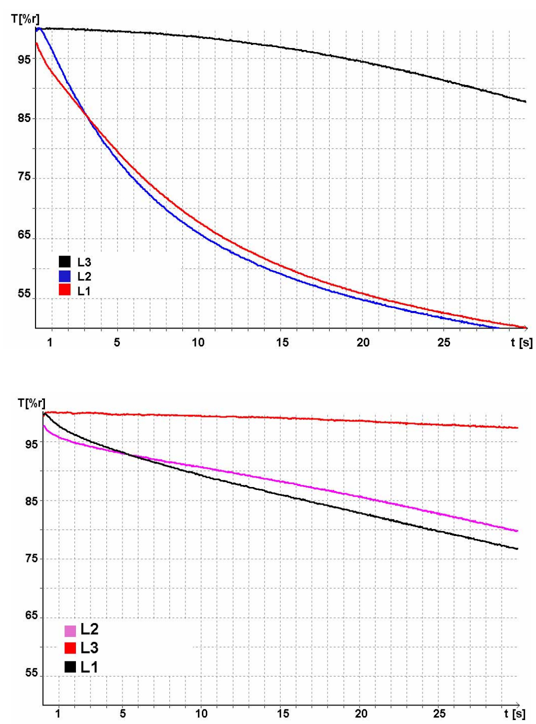


Figure 4: Dynamic liquid penetration curves for tested substrates; top - water and bottom - solvent system.

Liquid penetration was also tested by ultrasonic transmission measurement. Two testing liquids were used, DI water and solvent system containing DI water, 27 weight % of ethylene glycol and 16 weight % of ethanol. Results are shown on the Figure 4. It can be seen that L3 substrate exhibits the lowest penetration of both testing liquids. Dynamic penetration curves for the L1 substrate initially show a hold out and then liquid penetration. Substrate L2 shows immediate liquid penetration in both testing liquids. This test is a good indication of ink absorption into the paper surface structure and, based on the sheet resistivity measurements; it can be used as one of the testing methods for evaluation of paper substrates for printing of functional inks.

Paper surface topography was measured using atomic force microscopy and the 3D images are shown on the Figure 5. It can be seen that substrate L1 has a smoother surface (RMS = 27 nm) than L3 (RMS = 34 nm). However on the other side, substrate L3 showed areas with high smoothness and sealed surface (white ci

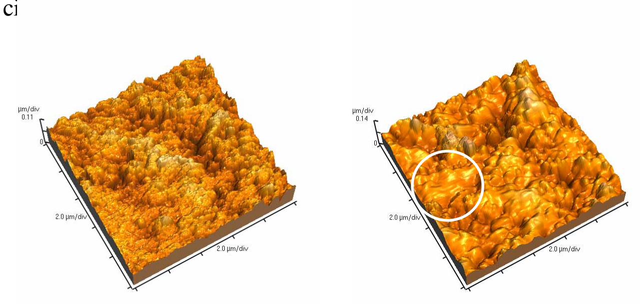


Figure 5: Surface topography for substrates L1 (left) and L3 (right) as measured by AFM

Figure 6 shows the optical images of gravure printed PEDOT:PSS based ink on the tested substrates. Polymer film does not cover the substrate completely and it can be seen that printed layers exhibit a branched inhomogeneous morphology. Such morphology is typically observed due to the phenomenon known as “viscous fingering instability”[15]. This occurs when a viscous fluid (in our case polymer solution) is displaced by lower viscosity fluid (air). Similar branched structures were observed with offset printed PEDOT:PSS on a plastic substrate[16] and it was reported that the size of the fingers can be optimized by printing speed and amount of ink volume. In this case, morphology of printed layers is also significantly influenced by choice of substrate. Evidently, the widest fingers, or best polymer spreading occurs on L3 and the narrowest for L2 substrate, which also had the highest sheet resistivity. It can be also seen that shear forces during printing induced the fingers orientation preferably in print direction. For printing of integrated circuits, sufficient conductivity of contact electrodes as well as their surface morphology is very important for higher performance[17]. Possibly, low absorptivity of the L3 substrate allows for better polymer spreading resulting in higher conductivity.

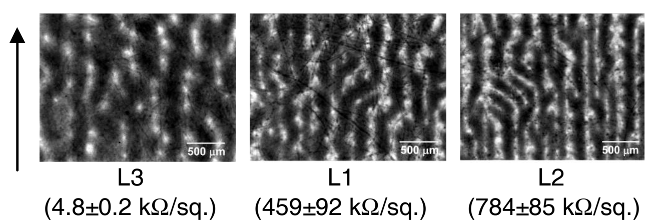


Figure 6: Optical images of printed PEDOT:PSS ink on different substrates illustrating the viscous fingering effect (arrow on the left indicates the print direction).

Conclusions

Paper substrates are of interest in printed electronics, however, they posses a number of challenges. This work focused on comprehensive study of paper properties and their effect on sheet resistivity of gravure printed PEDOT:PSS ink. There is need for better understanding of functional ink-paper interaction and novel paper substrates with optimized surface structure and chemistry for better performance of final printed electronic components. This work showed the importance of paper properties and their effect on sheet resistivity of printed conductive polymer layers. Among tested properties and used methods, dynamic liquid penetration tests correlate well with experimental results, and thus can be used to evaluate ink-paper interactions and predict printing behavior. Moreover, surface energy of the paper substrate also plays an important role and must be in balance with surface tension of the ink.

Author's Bio

Erika Hrehorova received her PhD and MS degrees in Paper and Imaging Science from the Department of Paper Engineering, Chemical Engineering and Imaging at Western Michigan University. Moreover, she received the MS degree in Polymeric Materials from the Department of Chemical Technology of Wood Pulp and Paper at Slovak University of Technology. Her main research focus is concentrated on printing inks for gravure and flexography, more specifically substrates and conductive polymer inks for printed electronics.

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