Printability, Compatibility and Electrical Performance of Functional Inks Printed on Flexible Substrates

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Abstract

The field of printed electronics has become a widely researched area with some applications already entering the market. Applications that could benefit by employing traditional printing processes for electronic manufacturing include printed organic light emitting diodes (OLEDs) for display and lighting applications, printed batteries and memory devices, solar cells, sensors, smart labels and radio frequency identification (RFID) and a wide range of low-cost electronic components and products. For successful roll-to-roll production of low cost electronics by printing, there is a need for compatible solution-processable functional materials and flexible substrates. Cellulous substrates offer flexible character; they are cost-effective, readily available and are environmentally friendly. However, using paper as a substrate for printed electronics might be a challenging task.

In this work, various flexible substrates, including paper and polymer film, were employed as a base for the printing of functional materials such as conductors, semiconductors and dielectrics. Printed features were evaluated in terms of printed quality and electrical performance.

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Introduction

Printed electronics is an emerging industry [Knobloch, 2008, Spitzer, 2009] and therefore there is a great need of research, mainly in the area of printable functional materials that are chemically and electrically compatible with each other as well as with flexible substrates. For printed electronics, the current focus is on the organic field-effect transistor (OFET). Similarly to conventional FET, an OFET functions as amplifying or switching component in integrated circuits. It can be fabricated in several different ways. Figure 1 shows four basic designs of staggered organic transistors differing by the gate electrode position (top gate and bottom gate) and placement of semiconductor (top contact and bottom contact).

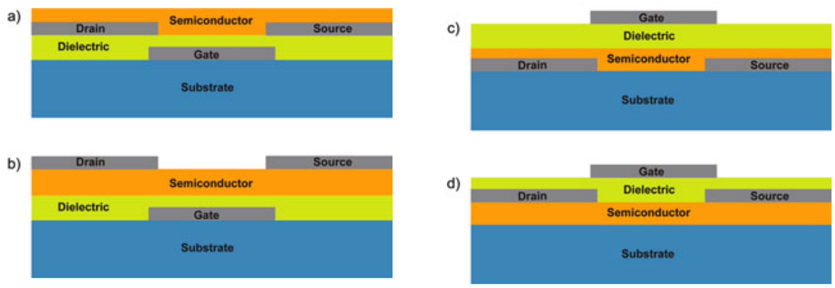


Figure 1: Illustration of different types of horizontal OFET architectures, a) bottom gate, bottom contacts b) bottom gate, top contacts c) top gate, bottom contacts and d) top gate, top contacts

The majority of publications regarding OFETs are using a combination of fabrication methods, such as solution processing (mainly spin coating or inkjet printing) together with sputtering, thermal evaporation or lithography (Manuelli, 2002; Veres, 2003; Kim, 2008; Halik, 2002; Kalb, 2007), which are not compatible with high throughput and roll-to-roll (RtR) manufacturing. It is desirable, that all layers are printed RtR and on flexible substrates. As it can be seen from Figure 1, there are four main materials required for OFET fabrication. These include conductor (for gate, source and drain electrodes), semiconductor, dielectric and substrate. For fully printed OFETs, it is important that all materials are compatible and do not attack each other as being deposited on substrate from solution and that they provide desired electrical characteristics (matching work function of conductor and semiconductor, high mobility of semiconductor, high capacitance of dielectric, low leakage currents, high ON/Off ratio, etc.).

To date, there are already several favorite candidates for each of the needed material types. Conductive inks are probably the most accessible functional inks on commercial scale. There are already a number of companies offering printable silver inks or pastes containing silver particles, graphite or intrinsically conductive polymers. These are formulated for a range of printing processes (gravure, flexography, inkjet and screen printing). Previously, our group reported on successful RtR printing of RFID tag antenna and other passive components directly on paper and board substrates using silver flake filled conductive inks and flexography (Kattumenu, 2008) and gravure (Rebros, 2008) printing. For semiconductive layers, several polymeric semiconductors showed a great potential. Probably the most widely studied polymeric semiconductor is poly(3-hexylthiophene) (P3HT) (Kline, 2005; Hugger, 2004; Kline, 2007). P3HT is also the most widely available among organic semiconductors and even large quantities can be obtained. Very attractive materials for dielectric layers are common polymers, because of their availability and ability to be processed from solution. Typical examples of polymeric dielectrics include poly(vinyl acetate) (PVAc), poly-4-vinylphenol (PVP), polyimide (PI), poly(vinyl alcohol) (PVOH), poly (methyl methacrylate) (PMMA), polystyrene (PS), epoxy based polymers, etc (Yildirim, 2008; Fikao, 2000; Byun, 2005). The substrate, on which the component is constructed, is also an essential part of the system and has an effect on device performance. Polymer substrates such as PET (polyethyleneterephthalate) or PEN (polyethylenenaphthalate) are probably the most widely used in printed electronics (MacDonald, 2007). However, paper substrates have also been used in printed electronics applications (Rebros, 2008, Hrehorova, 2007, Hodgson, 2007).

As mentioned above, majority of OFETs are fabricated by the combinations of solution processing with processes used in traditional electronics manufacture. This works focuses on evaluating the printability of conductive and semiconductive inks on different substrates. Moreover, printability of conductive inks on dielectric layer is also studied. Printability and electrical performance is correlated to the properties of substrates and/or underlying dielectric layers.

Materials and Experimental Part

Compatibility of a variety of functional materials has been studied in terms of their printability, surface properties, interaction with flexible substrate and electrical performance. Table 1 summarizes functional materials used during the study. These materials were chosen based on their performance, availability, and their potential for application in printed electronics. Functional materials were formulated into the inks appropriate for different deposition methods.

Table 1: List of materials used throughout the study

Material	*Material Function*	*Material ID*
Silver flake filled ink	Conductor	WB-flake
Silver nanoparticles filled ink	Conductor	NanoAg
Poly(3-hexylthiophene)	Semiconductor	P3HT
Polymethyl methacrylate	Dielectric	PMMA
PVDC-PAN-PMMA	Dielectric	Copolymer
UV Curable dielectric (proprietary)	Dielectric	UV
Poly-vinyl phenol	Dielectric	PVP

Overall, five paper substrates and one polyethylene terephthalate (PET) film were used for materials deposition (Table 2). Paper substrate Sub1 is a commercially available label stock substrate. Remaining paper substrates are modification of the substrate Sub1. The objective of the modification was to improve surface smoothness, control ink absorption and at the same time retain optimal surface energy of the substrates for sufficient wetting. Several non-pigmented coatings were formulated using latex binders of different chemical nature and film forming properties. The coatings were applied to the substrate Sub1 using a bar applicator (8-9 g/m^2 coat weight). PET film was chosen for comparisons because it is being widely used as a substrate for printed electronics.

Table 2: Paper substrates used throughout the study

Substrate ID	*Character of the coating*
Sub 1	Label paper
Coat 1	Styrene-Butadiene
Coat 2	Polyvinyl acetate
Coat 3	Polyurethane
Coat 4	UV conformal coating

A K-Printing Proofer (RK Print-Coat Instruments Limited) in gravure mode and the Dimatix DMP-2831, piezoelectric ink jet printhead system, were used to print functional inks to test their printability and functionality. Dielectrics materials were deposited on the PET substrate using a bar applicator. This method provided uniform and smooth film coverage appropriate for further overprinting with conductive inks.

Print quality of printed features was evaluated using an ImageXpert (KDY Inc.) image analysis system comprised of a motion table for sample positioning, two calibrated cameras for image capture and ImageXpert image analysis software (IX 10.0b63). The resistivity values of printed lines were measured using a Keithley 2400 digital multimeter in the 4-wire sensing mode.

Results and Discussion

Presented work was divided into three individual studies (cases). The Case #1 deals with the interaction between substrate and conductive inks. In the Case #2 printability and performance of semiconductive ink printed on different substrates are discussed. Finally, the effect of dielectric material on printability and conductivity of printed conductive inks is summarized in the Case #3.

Case #1

Objective of the Case #1 study was to evaluate the effect of substrate properties on printability and conductivity of printed conductive traces. All paper substrates were gravure printed with both, silver flake filed ink and silver nanoparticle filed ink.

Figure 1 summarizes data for surface properties of the substrates used during this experiment. By applying different coatings, surface energy of substrates Coat1 and Coat2 remain similar to the initial substrate Sub1. Substrates Coat3 and especially UV coated substrate Coat4 have substantially lower surface energy which can cause certain problems during the printing, especially for use with water based inks. The roughness measurement of coated sample reveals great improvement in the smoothness, compared to the original substrate Sub1, for substrate Coat4 and moderate improvement for substrate Coat2. The rest of modified substrates, Coat1 and Coat3, showed no improvement in the surface smoothness.

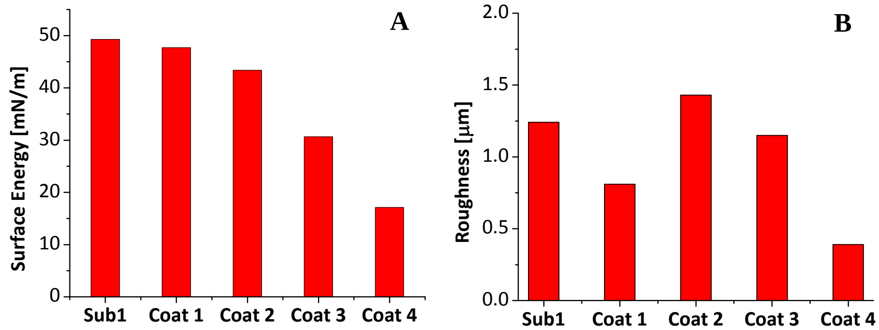
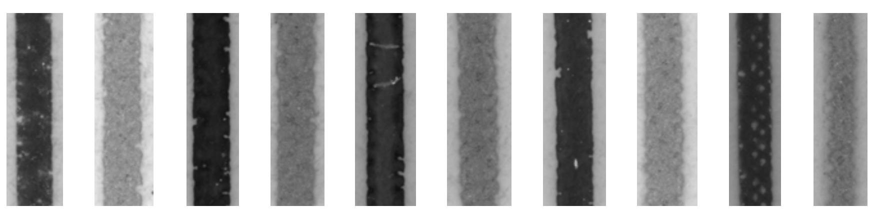


Figure 2: Properties of paper substrates; (A) Surface energy measurement, (B) Surface roughness measurement

After the substrate surfaces were characterized, two silver based conductive inks were printed on top of each substrate using laboratory gravure printer. Design included lines with nominal length of 30 mm and nominal width of 300 μm. After the printing, substrates were dried for 10 min. at 110 °C. Image analysis and electrical measurement were performed to obtain printability data for printed lines as well as to calculate their electrical performance.

Image analysis revealed poor ink coverage for nanoAg ink printed on substrate Sub1 and Coat4. Besides the coverage issues, cracking of printed silver layer was observed for some substrates. The features printed with WB-flake ink had better ink coverage compare to the nanoAg ink, with exception of Coat4 substrate were poor coverage was noticed as well. The edge raggedness (fidelity) of printed lines was fairly poor for both inks (Figure 3).



Sub1 Coat1 Coat2 Coat3 Coat4

Figure 3: Image analysis of printed features (in order WB-flake ink, nanoAg ink)

Another measured parameter of printability was the line width. Spreading of the printed lines was observed for both inks and all tested substrates; which is the deviation between nominal (designed) line width and actual (measured) line width (Figure 4). Even though all measured width variations, when comparing two ink systems, are within the standard deviation of each measurement, lines printed with WB-flake ink were consistently wider than lines printed with nanoAg ink for all substrates tested. The spreading of the lines was the least for substrate Coat4 due to the lowest surface energy and high smoothness of this substrate. For the rest of the samples spreading was fairly stable, about 52 μm for nanoAg ink and 56 μm for WB-flake ink.

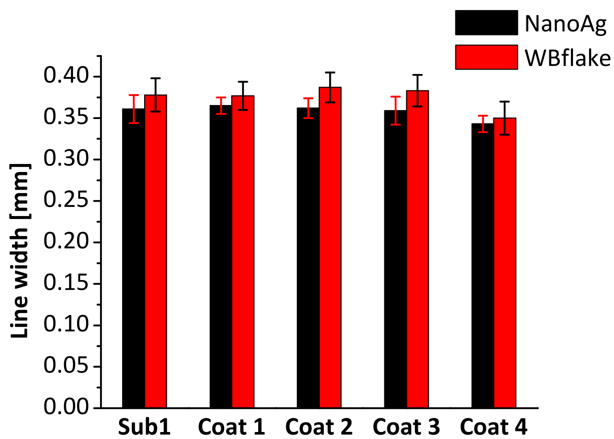


Figure 4: Measured width of printed lines (nominal width – 300 μm)

The electrical performance, expressed in sheet resistivity, is summarized in Figure 5. The best performance (the lowest sheet resistivity value) was calculated for substrate Sub1 in the case of WB-flake ink and for substrate Coat3 for nanoAg ink. Electrical resistance for lines printed with nanoAg ink on substrate Coat2 and Coat4 was not measurable; which indicates that conductive pattern is disconnected in a certain place.

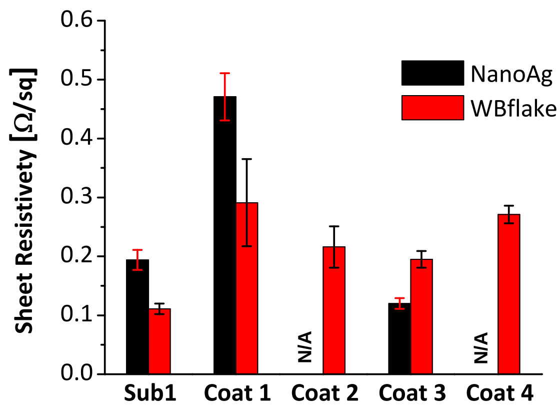


Figure 5: Electrical performance of printed lines

A reason why some samples were not conductive and/or they showed poor electrical performance of the printed lines on the paper substrates is emphasized on Figure 6. For substrates Coat1 and Coat2, cracks in printed lines formed probably during the drying step and caused discontinuity of the line and thus poor electrical performance. For the substrate Coat4, insufficient ink coverage was observed, with visible "missing dots" on the print (Figure 6).

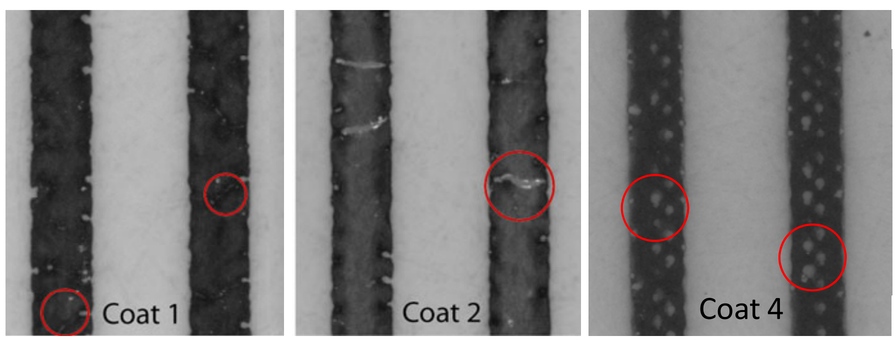


Figure 6: Printability defects of lines printed with nanoAg ink

The explanation of better conductivity for WB-flake ink lays in the thickness of deposited layers. Figure 7 compares conductive line printed with WB-flake ink and nanoAg ink as printed by gravure on PET substrate. From X- and Y-profiles it can be seen that the line thickness is higher for WB-flake ink. WB-flake ink also has significantly higher roughness than nanoAg ink. The peak-to-valley roughness for silver flake and silver nanoparticle ink is 2 μm and 0.5 μm, respectively. Thickness of WB-filled ink is 3 μm and 0.7 μm for nanoAg ink.

This significant difference in thickness of printed lines caused the deviation in sheet resistivity between the two inks. However all conclusions have to be made with accepting the fact that WB-flake ink contains 3 μm silver particles and nanoAg ink contains silver particles with dimensions from 20 to 50 nm.

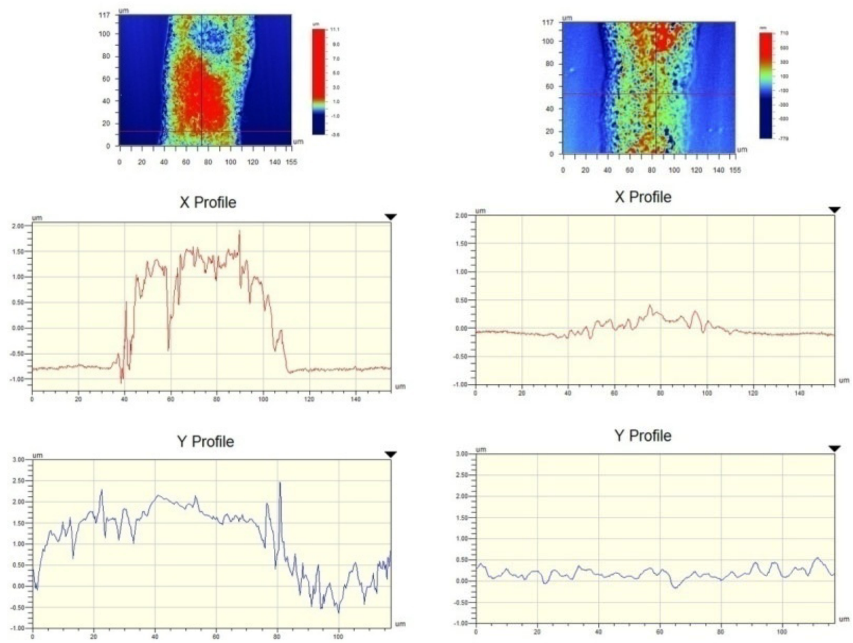


Figure 7: Conductive line gravure printed on PET substrate with silver flake (left) and silver nanoparticle (right) ink

Results from the Case #1 revealed worse performance of nanoAg ink printed on different substrates than WB-flake ink. At the same time, nanoAg ink offers more uniform and smoother ink surface, which are very important qualities when printing multilayer structures, where conductive ink will be overprinted with another functional material.

By comparing the results for different substrates, in some cases the printability of conductive inks was improved, but only in one case (nanoAg ink printed on substrate Coat3) electrical performance was improved as well. For the rest of the samples, there was no electrical performance improvement.

Case #2

In the Case #2, the effect of substrate properties on printability and conductivity of printed semiconductive ink was studied. Based on the results for Case #1, substrates Coat2 and Coat4 were removed for further consideration and only substrates Sub1, Coat1, Coat3 were investigated further. In addition, PET film was added as reference substrates for electrical performance comparison. The surface energy of PET film was comparable to Coat1 (45 mN/m) and the surface was the smoothest among all substrates (0.4 μm).

Semiconductive ink, P3HT, was printed with inkjet printer. After printing, the P3HT layers were dried at ambient conditions overnight. Nominal widths of printed lines were 40, 50, and 100 μm (Figure 8). Image analysis revealed the best line raggedness and the lowest spreading for Coat3 substrate. Even thought this substrate did not have the smoothest surface, the lowest surface energy promotes better holding of the line dimensions.

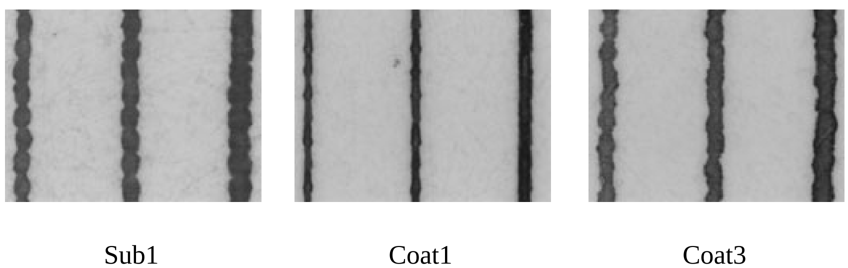
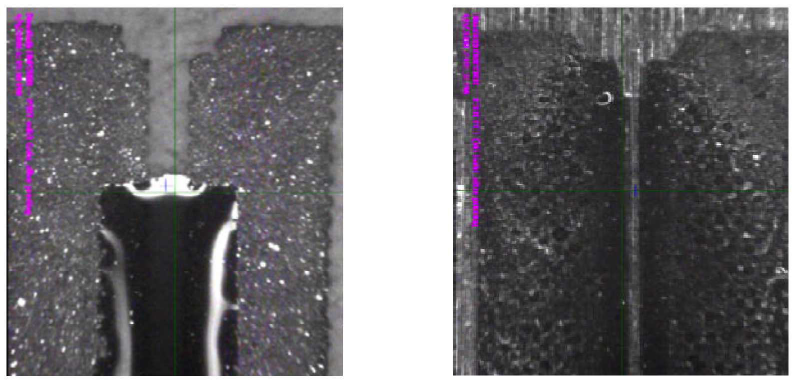


Figure 8: Printability of the lines printed with P3HT (nominal line width from the left on each image is 40, 50 and 100 μm).

The effect of substrate properties on electrical performance of semiconductive ink was evaluated by printing P3HT onto the paper substrates with different properties. A PET substrate was also used for the comparison. Contact electrodes for measuring the electrical performance were screen printed using silver based flake ink and P3HT was again inkjet printed on top of the electrodes and in the gap (Figure 9). Prior to P3HT printing, the distance between electrodes was measured and later used in the calculation of sheet resistivity. After printing and drying of P3HT ink, I-V curves were measured and used to calculate the sheet resistivity of the P3HT on each of the tested substrates using gap length and width. Results for the sheet resistivity are reported in the Figure 10.

The sheet resistivity values for P3HT were very high on some of the substrates (Sub1 and Coat3), which can be attributed to ink penetration into the substrate. Surprisingly, a high resistance was measured also for PET substrate. This might be due to poor wetting of the PET substrate, which caused the ink to spread more on top of the electrodes, leaving only a thin P3HT layer in the gap as shown in the Figure 9. In this case the substrate that demonstrated best printability performance showed also the best electrical performance.



P3HT printed on Sub1 P3HT printed on PET

Figure 9: Pictures from the fiducial camera integrated with the Dimatix DMP-2831 inkjet system taken right after printing

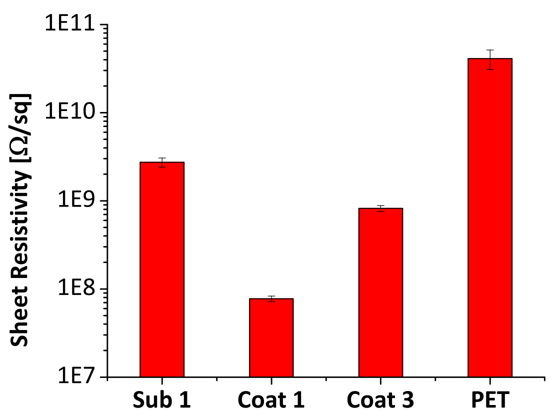


Figure 10: Sheet resistivity of P3HT inkjet printed on different substrates

By applying test coating Coat1 to original substrate Sub1, electrical performance and printability of semiconductive material was significantly improved. The second experimental substrate Coat3 showed only moderate improvement of P3HT performance at very similar printability performance as was on original substrate Sub1. The calculated electrical performance of P3HT printed on PET is questionable due to printability issues mentioned above.

Case #3

Objective of the Case #3 was to evaluate effect of dielectric layers on printability and conductivity of printed conductive ink. Based on the results from Case #1 nanoAg ink was chosen as a conductive ink to be printed on top of dielectric layers due to its smother surface necessary for printing of multilayer structures. Prior to printing, all dielectric materials were deposited on top of PET film with bar applicator. After the curing of dielectric layers, surface energy of the layers was calculated from contact angle measurements and Owens-Wendt model (Figure 11). The highest energy value was calculated for PMMA layers and the lowest value for UV dielectric layer. As it was seen in the Case #1, low surface energy may cause problems during the printing of conductive ink. Surface energy of copolymer and PV layers is very close to the energy value of control surface of PET.

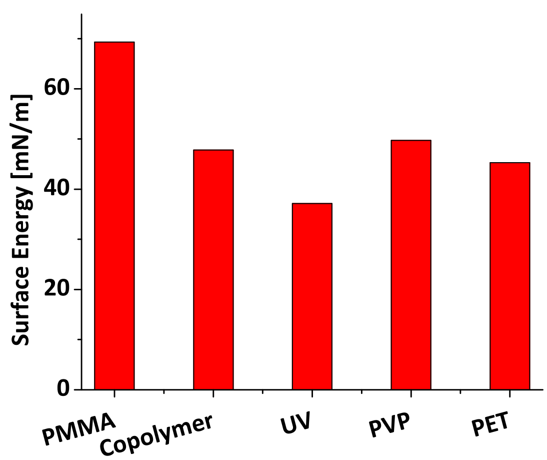


Figure 11: Surface energy values for dielectric layers

In the next step, nanoAg ink was gravure printed on top of each dielectric layer. Results from image analysis are summarized in Figure 12. It can be seen that printability trend followed surface energy values, with the best printability and ink coverage for the sample with highest surface energy value, PMMA. On the other side is UV dielectric layer with the lowest surface energy value and the worst printability and evidently poor ink coverage (Figure 12).

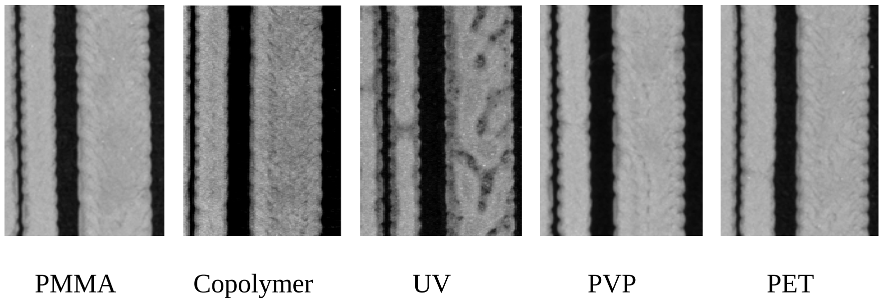


Figure 12: Printability of the lines printed with nanoAg ink on top of dielectric layers (nominal line width is 200 and 500 μm)

The last parameter to be considered in this case was electrical performance of nanoAg ink printed on dielectric layers (Figure 13). As was expected from printability results, very poorer performance was recorded for lines printed on UV layer when compared to PET, PMMA and PVP. Surprisingly, lines printed on top of copolymer dielectric showed the worst electrical performance. The reason for such behavior is not known and further studies would be necessary. The results however indicate that there is some sort of the interaction between the nanoAg ink and copolymer dielectric material. Lines printed on top of PMMA and PVP layers, showed comparable electrical performance than lines printed on top of the control PET substrate.

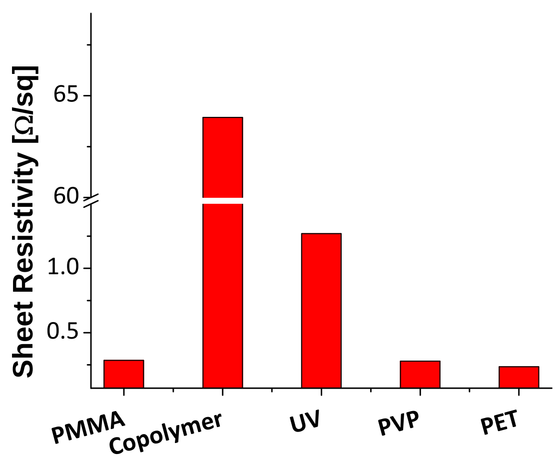


Figure 13: Sheet resistivity of nanoAg ink printed on different dielectric layers

Considering all the results from this case, PMMA and PVP materials seem to be the best choices for the dielectric layer, with good printability properties and in the same time with good electrical performance of a conductive ink printed on top of these layers. Both materials offered similar printability and electrical performance as control PET substrate.

Conclusions

Printing of multilayer electronic components for applications in printed electronics is a challenging process. Compromises have to be made between printability, performance and compatibility of printed functional materials to ensure stable final product. For example, for printing of multilayer components, silver flake filled inks are not suitable due to very high roughness of printed layers making it difficult to create smooth interfaces between subsequent layers. But at the same time, silver flake ink offers excellent conductive properties. In other case, good printability of silver ink on dielectric material does not guarantee desired electrical performance of deposited conductor. This study showed that printability and conductivity of printed conductive and semiconductive inks is strongly affected by surface the ink is printed on.

Nowadays, developments in the area of new solution processable functional materials are very promising. But there is a great deal of research that need to be done especially in deposition of these materials by printing, before all the advantages of using printing in electronics manufacturing can be fully utilized.

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