Benchmark Study of Screen Printable Silver Inks on a PPE Based Substrate

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***Abstract*— In this study, two silver inks are screen printed and their performance on a PPE polymer compound is evaluated. Both physical and chemical surface pre-treatments are used to modify substrate surface roughness and energy. Electrical performance of printed structures is evaluated by sheet resistance measurements. In addition, a crosscut adhesion test is used to evaluate mechanical performance of printed patterns. Low sheet resistances can be obtained with used materials. However, there is a significant difference in adhesion level. By substrate surface pre-treatments, adhesion level can be improved, and tape test ink removal can be decreased even from 15% to 0%. These results indicate that PPE substrate may be utilized in production of high quality printed electronics applications.**

Keywords*— *PPE; printed electronics; screen printing; surface treatment

I. Introduction

Printed Electronics (PE) enable fabrication of cost-effective, large-area wireless applications, which may be integrated into novel electronics substrates, such as stretchable thermoplastic polyurethane [1,2] or 3D molded interconnect device (MID). These applications can be utilized in various industry fields, such as automotive industry or health care, where integration of electrical devices directly into supportive structures can provide significant benefits, as devices do not require additional space and no external wiring is required. Significant benefits of PE technology lie in cost-effective wireless sensor applications, such as radiofrequency identification (RFID) and Internet-of-Everything (IoE), since sensors and antenna structures may be integrated in everyday environment, thus enabling efficient device functionality without need for user control [3].

Fabrication of sufficient high frequency (HF) structures sets specific requirements for the used materials. First, conductor materials with low resistivity are required, since low DC sheet resistance is essential to ensure proper HF functionality. In addition, several requirements are set for the substrate material. Substrate materials used in HF applications include for example polyethylene terephthalate (PTFE; Teflon) and polyphenylene oxide (PPO). Low relative permittivity and dissipation factor make these materials attractive for HF applications, since signal will not be attenuated by the substrate [4].

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In this study, a novel polyphenylene ether (PPE) polymer compound, is studied in PE applications. This substrate has been developed for especially HF applications. In addition, substrates may be fabricated by injection molding, which enables manufacturing of innovative 3D substrate shapes, i.e. 3D antennas [5]. Therefore, this polymer is an attractive alternative for substrate material in printed HF structures.

From printing point of view, the main challenge of PPE substrate material is its hydrophobic nature. Hydrophobic substrate may not be wetted properly, which is likely to cause issues with print quality and possibly with mechanical performance of printed structures. Therefore, surface modification may be necessary to improve substrate wettability and to ensure good adhesion between ink and substrate.

In this study, highly conductive commercial silver inks are used to print conductive structures on PPE substrate. High metal contents enable high DC conductivity, which is essential for low-loss HF signals. In addition, the effect of substrate surface pre-treatments (oxygen plasma, sulfuric acid, and potassium hydroxide) on substrate parameters and ink-substrate interactions are inspected.

II. Experiments

A. Materials

Square-shaped (10 cm x 10 cm) PPE substrates Preperm® L260 (3 mm thickness) from Premix were used in this study. Key parameters of this substrate material include low relative permeability ($\varepsilon r = 2.6$) and low dissipation factor (DF = 0.0006) [6].

For printing of test patterns, two screen printable silver inks were selected: CRSN2442 from SunChemical and DuPont 5064H. Ink parameters used as selection criteria are listed in Table I. Both inks are solvent-based and their viscosities are suitable for screen printing. Metal content of both inks is higher than 60 wt%, which should provide sufficient electrical performance. In literature, these inks have been compared to each other for example by Muck [7] and Kavcic [8], where ink properties were studied in RFID applications printed on paper substrates. Sheet resistances below 100 mΩ/□ were obtained even on extremely porous paper substrates.

TABLE I. INK PARAMETERS [9; 10]

Ink	Ink parameters			
	Ag (%)	*Solvent*	*Viscosity (cP)*	*sheet resistance (mΩ/□@25 µm)*
CRSN2442	69 - 71	Propylene di-acetate	2,000 – 3,000	10
5064H	63 - 66	C11-ketone	10,000-20,000	<14

B. Substrate pre-treatment methods

Due to the hydrophobic nature of PPE substrates, surface energy increasing pre-treatments were selected to enhance substrate wetting. Both physical and chemical treatments were used to inspect the effects of different treatment types.

Oxygen plasma was used as a physical treatment, since this treatment is widely known for its surface energy increasing abilities. Furthermore, this treatment is widely used as an adhesion promoter [11-13]. In this study, an Oxford Plasma Technology RIE System 100 plasma printer was used for plasma treatments. Used treatment parameters are presented in Table II.

TABLE II. PLASMA TREATMENT PARAMETERS

Treatment	Time (min.)	Exposure power (W)	Chamber pressure (mTr)	Gas (O_2) amount (sccm)
1	1	25	56.0	30.0
2	1	50	56.0	30.0
3	1	75	56.0	30.0

Three chemical treatments were used to modify substrate surface 1) Sulfuric acid (H2SO4) with 98 % concentration, 2) Potassium hydroxide (KOH) with 1.0 M concentration, and 3) KOH with 30 % concentration [11; 14]. Substrates were dipped in chemical containers for etching. Afterwards, chemical remnants were wiped off with deionized (DI) water. Treatment parameters used in these treatments are presented in Table III.

TABLE III. CHEMICAL ETCHING PARAMETERS

Sulfuric acid etching				
1 min.	2 min.	5 min.	10 min.	15 min.
KOH 1.0M				
1 min.	2 min.	5 min.	10 min.	15 min.
KOH 30%				
-	-	5 min.	10 min.	-

C. Printing and post-treatment

Test patterns were printed in cleanroom conditions using a manual single-sheet TIC SCF300 screen printer. A screen with NBC UX79-45 polyester mesh (opening 81µm, theoretical wet thickness 27.7µm) was used in printing.

After the printing phase, samples were cured in oven according to datasheet recommendations. 5064H was cured at 130 °C for 20 minutes, and CRSN2442 was cured in 150 °C for 30 minutes.

D. Characterization

To inspect the effects of the used surface treatments, several characterization methods were utilized. Dyne pens with a range from 30 mN/m to 60 mN/m were used for measurement of substrate surface energies before and after treatments. In addition, an optical profilometer Veeco Wyko NT1100 was used to measure the surface profiles of different substrates.

After printing, conductivity and adhesion of fabricated samples were analyzed. Two different test patterns were designed, one for conductivity measurements and other for adhesion measurements. In Fig. 1 are demonstrated the test patterns used in this survey. Pattern Fig. 1A) includes 10 basic conductor structures used in four point probe (4PP) measurements to determine sheet resistances. A Keithley 2425 sourcemeter was used in these tests. Sheet resistance Rs was then determined based on obtained results and conductor dimensions:

$$R_S = R\frac{w}{l}, \quad (1)$$

where R is measured conductor resistance, l is theoretical conductor length (32 mm) and w is theoretical conductor width (1.3 mm) (Fig. 1A)).

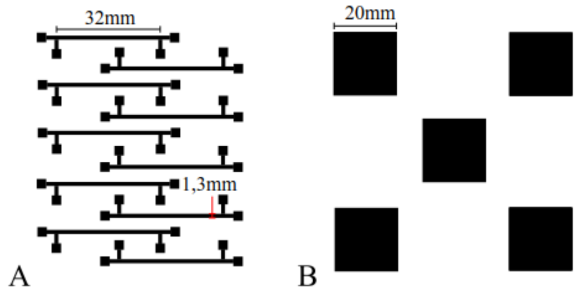

Fig. 1. Designed test patterns for A) sheet resistance measurements B) adhesion evaluation.

In addition to sheet resistance measurements, adhesion of different substrate-ink combinations was evaluated to compare mechanical strength of used inks, and also to inspect used surface treatments' effect on adhesion of ink-substrate interface. Adhesion test pattern (Fig. 1B)) was designed for these experiments. A crosscut test was used for adhesion evaluation, according to ASTM D3359 standard [15].

III. Results and Discussion

A. Substrate surface

In Table IV, measured surface energies of fabricated test samples are presented. It was observed that initial surface energy of the used substrate material is rather low, approximately 30 mN/m, but may be more than doubled, depending on the used surface treatment. Both oxygen plasma and H2SO4 seemed to increase surface energy significantly, whereas KOH treatment seemed to have no effect on the wetting abilities of PPE substrate, regardless of the base concentration. Explanation may lie in the solvent resistance of the substrate material, since the strongest KOH concentration was only 30 %.

Furthermore, it was observed that increment of surface energy by H2SO4 was saturated after 5-minute etching, a 5-minute treatment was used in further experiments. With KOH, 5-minute treatment was also used, since surface energy was not changed by any treatments.

TABLE IV. Measured Surface Energies

Reference (PPE)					
mN/m	30-32				
Oxygen plasma treatment					
mN/m	≥60				
H_2SO_4 etching					
	1 min.	*2 min.*	*5 min.*	*10 min.*	*15 min.*
mN/m	38	46	56-58	58-60	58-60
KOH 1.0M etching					
	1 min.	*2 min.*	*5 min.*	*10 min.*	*15 min.*
mN/m	32-34	32-34	32-34	32-34	32-34
KOH 30 % etching					
	-	-	*5 min.*	*10 min.*	-
mN/m	-	-	32-34	32-34	-

In addition, plasma treatment increased surface energy beyond the Dyne pen range already with exposure power of 25 W, and therefore analysis of surface profile was necessary to find differences between plasma treatments. It was observed that increment of exposure power led to more effective etching. This phenomenon is demonstrated in Fig. 2. Since 75 W exposure power seemed to lead to highest average roughness of the substrate, it was used in further experiments.

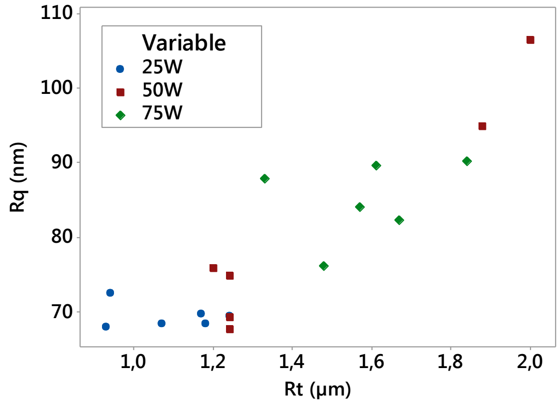

Fig. 2. Measured R_q/R_t with different plasma exposure powers.

After the initial surface characterization, new samples were fabricated with the chosen substrate surface pre-treatments. Surface profiles were measured again with optical profilometer and differences between each treatment were compared. Results of this measurement are presented in Fig. 3. Plasma treatment would appear to have most significant effect on the surface profile of the substrates, whereas no significant change was observed with chemical treatments.

B. Print quality

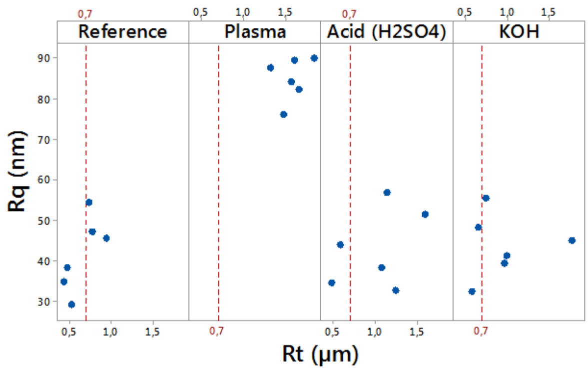

Fig.3. Measured R_q/R_t with surface pre-treatments.

Print quality was evaluated by line thickness inspection with the optical profilometer. Variation in line thickness depending on the used ink is demonstrated in Table V. It may be observed that thicker lines were obtained with SunChemical CRSN2442 ink than with DuPont 5064H ink. This is most likely due to the higher silver content of CRSN2442 ink. At the same time, lines are rougher. Surface treatments did not have any effect on line thickness or roughness.

Furthermore, it was observed that increment of line thickness led to rougher conductor surface in each inks data. This phenomenon is presented in Fig. 4 results. It seems that especially with CRSN2442 ink, increasing line thickness causes more surface roughness, whereas roughness of 5064H ink does not increase significantly. The importance of conductor surface roughness is emphasized especially at high frequencies due to skin effect [16]. In order to provide good quality HF conductors, process should be optimized.

TABLE V. MEASURED LINE THICKNESS AND ROUGHNESS FOR BOTH INKS

Ink	Thickness (µm)	Roughness (µm)	Samples
CRSN2442	22,81±2,13	3,08±0,67	29
5064H	19,33±3,01	2,15±0,33	32

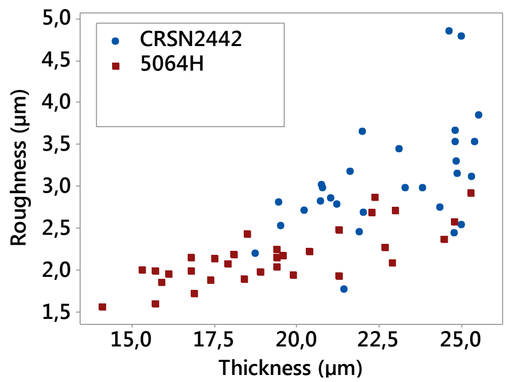

Fig. 4. Measured conductor line roughness per line thickness.

C. Sheet resistance

Calculated sheet resistances of printed patterns (Fig. 1A)) using (1) are presented in Fig. 5. It was observed that surface treatments seem to lower sheet resistance mean values, excluding H_2SO_4, which seems to have negative impact on the sheet resistance. On the other hand, there is more deviation in CRSN2442 results on treated substrates, whereas 5064H results include less deviation on treated surfaces. Due to the higher silver content, CRSN2442 values should be a bit lower than 5064H values. However, as measured sheet resistance values of Table VI indicate, CRSN2442 sheet resistance was similar or even higher than that of 5064H. This difference may have been caused by annealing parameters, since datasheet conditions were used.

Still, most of the measured values are between 10 mΩ/□ - 20 mΩ/□, and therefore both inks are likely to perform well at high frequencies, as stated in [17]. However, as observed in [17], low DC sheet resistance alone cannot guarantee required HF performance, since substrate surface roughness as well as the conductor uniformity and roughness affect HF attenuation.

D. Adhesion

On the contrary to the conductivity measurements, crosscut adhesion test revealed significant differences between used inks. Results are demonstrated in Fig. 6.

TABLE VI. MEASURED SHEET RESISTANCES

Ink/Substrate	Sheet resistance (mΩ/□)		
	Mean	***St.Dev.***	***Samples***
CRSN2442/PPE	17,28	1,13	20
5064H/PPE	18,86	3,21	20
CRSN2442/Plasma	15,47	2,71	20
5064H/Plasma	15,17	1,17	20
CRSN2442/H_2SO_4	23,78	3,17	20
5064H/H_2SO_4	39,36	10,34	16
CRSN2442/KOH	16,14	3,25	20
5064H/KOH	13,90	1,70	18

5064H adhesion was excellent even on the bare PPE substrate, whereas CRSN2442 adhesion is significantly worse. Comparison of treated samples indicates that plasma treatment is an excellent adhesion promoter for this substrate material, CRSN2442 adhesion was improved from levels 3B-4B (tape removal 5-15 %) to level 5B (tape removal 0%).

On the other hand, chemical treatments do not have any effect on the adhesion level. Reason may be found in the surface characterization results: chemical etching does not alter surface profile of the substrate. Therefore, it may be concluded that surface must be roughened to obtain better adhesion.

It may be observed that all of the ten fabricated samples of each ink-substrate pair are not included in the graph. This is due to the substrate imperfections, which cause ink removal from the substrate, and thus cannot be compared to other results. Therefore it may be concluded that molding process has a significant effect on mechanical performance of inks.

On the other hand, another adhesion test would be required to measure adhesion strength between inks and substrates, since the crosscut test is only aimed at quick evaluation of initial coating adhesion. In addition, number of fabricated samples is rather small, and therefore more samples would be needed for a more accurate adhesion classification. Furthermore, reliability tests are needed to inspect the aging tendency of the material interfaces. However, this test has provided a directional estimation of ink adhesion and surface treatment effects.

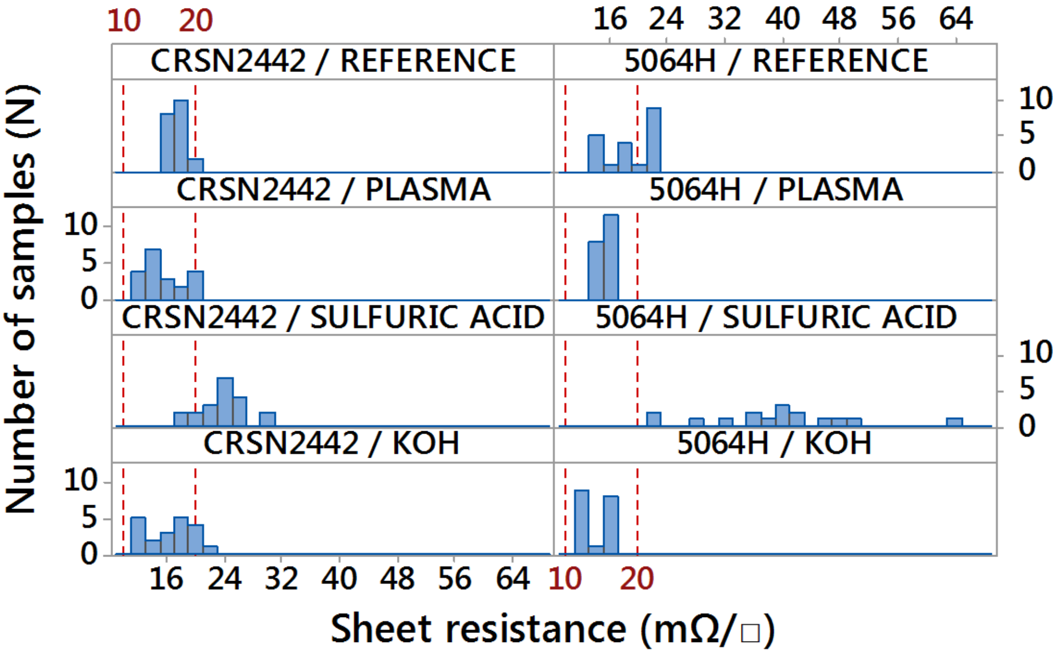

Fig.5. Measured sheet resistances.

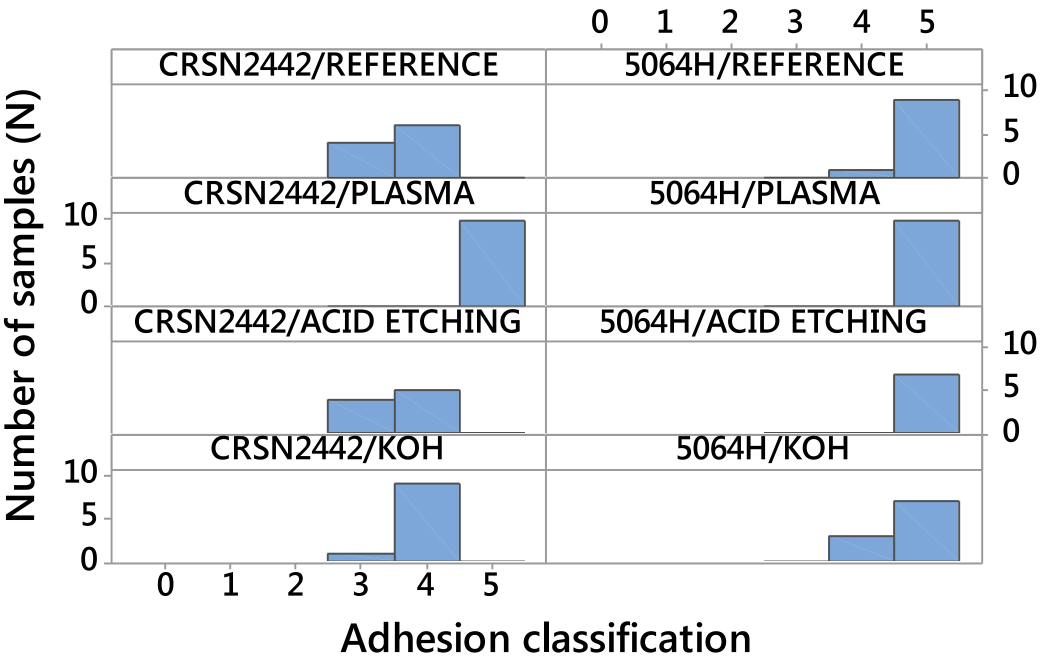

Fig. 6. Adhesion classification rates.

IV. CONCLUSIONS

In this paper, printability and performance of two commercial silver inks were evaluated on a PPE based polymer substrate. The purpose was to inspect surface treatment effects and to compare ink performance. This substrate is aimed at HF applications and therefore it is essential to find such conductive materials, which provide low sheet resistance and therefore enable sufficient HF performance in printed electronics applications.

In this study, obtained sheet resistances were between 10-20 mΩ/□, which indicates good conductivity. However, printed lines were rather rough, and therefore process optimization is needed to obtain good quality conductors. In addition, further characterization of HF properties is required. Even though suitable conductive material and surface treatment was found, more surface treatments and materials should be studied to find alternative ink-substrate combinations for wide variety of HF applications. In addition, long-term reliability of substrate-ink interfaces should be studied.

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