Paper Substrates and Inks for Printed Electronics

Laura K. Wood†*, Erika Hrehorova*, Thomas W. Joyce†*, Paul D. Fleming‡†*, Margaret Joyce†*, Alexandra Pekarovicova‡* and Valery Bliznyuk†**

**** Department of Paper Engineering, Chemical Engineering and Imaging, Western Michigan University, Kalamazoo, MI***
***** Department of Material Science and Engineering, Western Michigan University, Kalamazoo, MI***
† Center for Coating Development
‡ Center for Ink and Printability Research

Abstract
The present work explores the effects of paper properties on conventional silver-based conducting inks. The effects of smoothness, relative humidity, porosity, permeability and wettability on electrical properties of silver inks on different paper substrates were studied. Another objective of this work was to prepare and study polyaniline synthesized in the presence of different lignosulfonates.

Introduction
The industrial use of printed low-profile electronics in new technologies, such as paper batteries[1] and Radio Frequency Identification[2] (RFID), is expanding at a rapid rate. Paper and paperboard substrates are often employed in the manufacture of packaging materials. Also referred to as intelligent packaging, RFID could be used in tracking inventory from cradle to grave[3]. This includes raw materials production, manufacturing and assembly, purchases, deliveries, use, maintenance, and disposal or recycling[2]. Current research[4-7] in the area is focusing on the use of conductive inks in tag components to reduce the cost of implementation and make this technology economically viable.

With the increasing trend of integrating RFID tags into supply chains[3], companies are beginning to turn toward electronic printed RFID tags on label papers. To reduce production costs and enhance tag efficiency, the effects the paper substrates impose on electronic properties of the printed area must be examined. In particular, the roles of porosity, permeability, surface roughness and relative humidity are of great interest.

The use of renewable natural materials to develop or improve existing materials or technologies is one of the most important ideas of research. Polyaniline is representing a well known class of conductive polymers in materials science. It has been studied to great extent because of its good environmental stability, ease of synthesis and relatively good processability[8]. There is a number of acids that can be used for polyaniline synthesis and lignosulfonic acid is one of them[9].

Experimental
Effect of Substrate Properties on Conductivity
A water-based flexographic conducting ink (Precisia[5]) comprised of silver flakes was applied to several label-stock substrates. The influences of various substrate properties on the printed conductivity were examined. The rheological properties of a conducting silver-flake ink were studied prior to application.

Conducting Ink: The rheological properties of a conducting silver-flake ink were examined prior to application. A dynamic stress sweep was conducted on the material to determine its linear viscoelastic region (LVR), as well as the behaviors of the elastic modulus and the storage modulus. During a stress sweep, the sample is subjected to an increasing stress while constant frequency and temperature are maintained. A frequency of 1 Hz or 10 Hz is typically used. The sample's response to the stress is displayed and the LVR is determined. The elastic modulus (G') and the viscous modulus (G") are plotted against stress. The LVR is the stress range in which the G' and G" values are constant before they drop off due to deformation. When the sample is subjected to a stress within the LVR, the material will be able to recover from the deformation it undergoes. Outside of the LVR, the deformation cannot be completely reversed. In a frequency sweep, the frequency is varied while constant stress and temperature are maintained. The frequency sweep is run at a stress value within the LVR, as determined during the previous stress sweep. Frequency is a measure of the time needed to complete one oscillation and is defined as the inverse of time. The frequency sweep is used to determine the time dependency of the sample's deformation. A steady state stress sweep is carried out at a fixed frequency while the stress amplitude is varied. Steady flow is used to study the

viscosity change under increasing shear stress. It also gives the idea of how viscous or elastic the material is under shear stress.

Upon viewing the sample's apparent viscosity, the couette geometry was chosen. The couette is appropriate for low viscosity samples and is capable of a high shear rate. After installing the geometry and loading the sample, a conditioning step was performed to pre-shear the substance. The dynamic stress sweep was executed in a range from 0.001809 Pa to 100 Pa at a frequency of 1Hz and 25°C. The frequency sweep was performed on the sample at the predetermined stress of 0.1 Pa. The sweep ranged from 1 Hz to 100 Hz.

Substrates: Five substrate samples were provided by Stora Enso for analysis in conjunction with conducting silver-flake ink. These substrates are listed below in Table 1 along with their intended applications.

Table 1: Substrates

Grade	Description
LabelSet SP	Wet strength labels for beverage bottles
OptiTherm	Direct thermal tickets and tags
PointFlex	Flexible packaging
UniTherm	Pressure-sensitive thermal transfer applications with conventional pre-print applications
UniTherm Sharp	Pressure-sensitive thermal transfer applications with demanding conventional pre-print requirements

Each substrate was characterized in terms of its roughness, porosity (Parker Print Surf Tester, Mercury Porosimetry), and wettability (contact angle - First Ten Angstroms Dynamical Contact Angle Tensiometer). In addition, the permeability of each substrate was calculated from its Parker Print porosity value and its thickness using the following equation: [10, 11]

$$K = 0.048838 * Q * X \qquad (1)$$

Where K is the permeability in μm^2, Q is the flow rate in ml/min and X is the thickness in m.

Ink/Substrate Interactions

Conductivity: The silver-flake ink was drawn down on the substrate using a Flexographic "hand-proofer"[12] and the conductivity of each sample was then determined using a Keithley multimeter model 2400. Two flat alligator clips were placed 20 mm apart on the inked area and a voltage range of -0.1V to 0.1V was passed between the probes. Conductivity was calculated from the I-V curves using the following equation:

$$\sigma \quad \frac{L}{V} \quad \frac{I}{A} \qquad (2)$$

Where L is the length of the gap, I is electric current, V is applied potential difference and A is the cross-sectional area of the sample calculated as thickness × width of the sample.

Porosity: Each substrate was analyzed in the AutoPore IV Mercury Porosimeter. Porosimetry is the measurement of the porosity-related characteristics of a material. These characteristics include pore size, volume, distribution and density. The mercury porosimeter characterizes the porosity of a material by applying varying levels of pressure to a sample immersed in mercury. The pressure required to intrude mercury into the sample's pores is inversely proportional to the size of the pores. The pressure versus intrusion data is collected by the instrument, and volume and size distributions are generated using the Washburn equation[13].

Table 2: Mercury Porosimeter Parameters

Operational Parameters	
Penetrometer: #s/n – (13) 3 Bulb, 0.412 Stem, Solid	
Hg Parameters	
Adv. Contact Angle: 130 degrees	Rec. Contact Angle: 130 degrees
Hg Surface Tension:485 dynes/cm	Hg Density: 13.5335 g/mL
Low Pressure	
Evacuation Pressure	50 µmHg
Evacuation Time	5 mins
Mercury Filling Pressure	0.48 psia
Equilibrium Time	0 secs
Maximum Intrusion Vol.	100.000 mL/g
High Pressure	
Equilibrium Time	0 secs
Maximum Intrusion Vol.	100.000 mL/g

Wettability: The contact angle of the silver-flake ink with each substrate was determined using the First Ten Angstroms Dynamical Contact Angle Tensiometer. The tensiometer works by dispensing a single drop of a chosen liquid from a syringe onto a strip of the sample substrate. The camera takes a picture of this sessile drop and the image is analyzed by computer software. A low contact angle indicates high wettability and vice versa.

Roughnesss: UniTherm Sharp was calendered to four roughness levels and hand-proofed with silver flake ink. UniTherm Sharp was chosen for this procedure because it had the highest initial roughness value of the five substrates. Conductivity measurements were taken to determine the effect of roughness on the final printed product. Parker Print-Surf Roughness values were determined at a clamping pressure of 1000 kPa with a soft backing.

Relative Humidity: OptiTherm samples hand-proofed with silver-flake ink were conditioned at various relative humidity and temperatures. Relative humidity is defined as the ratio p_w/p_{ws} where p_w and p_{ws} are the vapor pressure and saturated vapor pressure at the appropriate temperature.[14] The conductivity of each sample was determined to explore the effect of relative humidity on a final printed product. A CARON 6030 Environmental Test Chamber was used to condition the samples to the desired temperature and humidity levels. The operating parameters of the humidity chamber are displayed in Table 3. In several measurements, the sample was removed from the chamber and exposed to ambient conditions after the conductivity was determined at the desired humidity level. Three subsequent measurements were taken (Open 1, Open 2, and Open 3) to observe the effect the sudden change in relative humidity had on conductivity of the printed sample.

Table 3: Humidity Chamber Parameters

CARON Model 6030 Specifications	
Temperature Range without lights	5°C to 60°C
Temperature Range with lights	10°C to 60°C
Heater	1160 Watts @ 115VAC
Compressor	1/4hp, 2940 BTU/Hr@7°C Evaporator
Temperature Control	± 0.1°C
Temperature Uniformity	± 0.3°C
Relative Humidity	20 to 98% RH
Humidity Control	± 2%
Electrical	115V/25A/60Hz 1Ph.

Polyaniline Synthesis and its Properties:

Aniline was oxidatively polymerized with ammonium persulfate (APS) in the presence of lignosulfonic acid prepared from different lignosulfonates (Table 4). The weight ratio of lignosulfonic acid and monomer was 1:1 and 1:4. The polymerization was carried out at 3-5 °C and the reagents were stirred for 3 hours. The resulting product was washed and centrifuged from acetone followed with water and dried under vacuum overnight at 60 °C. Identification of prepared polyaniline samples is presented in the Table 5. All the samples were characterized by means of FTIR Spectroscopy, Differential Scanning Calorimetry and Total Sulfur Content Analysis. Conductivity of polyaniline films (casted on the glass substrate) and pressed pellets was calculated from I-V characteristics measured using a Keithley multimeter model 2400 operated from a PC with Labview software. More detailed procedures can be found in the reference[4].

Table 4: Composition of lignosulfonates (LS) used for polyaniline polymerization

Name	Composition	Content	Total Sulfur [%]	Weight Average Molec.Wt.
REAX 88B	Lignosulfonic acid, sodium salt, sulfomethylated	100%	10.5	2900
EDF 350	Lignosulfonic acid, sodium salt, sulfomethylated	60-70%	13.7	5700
	Sulfuric acid, disodium salt	30-40%		
Polyfon O	Lignosulfonic acid, sodium salt	100%	6.8	2400

Table 5: Identification of prepared polyaniline samples

Sample ID	Starting LS	Weight Ratio of LS : Aniline
1.1	Reax 88B	1:1
1.2	Reax 88B	1:4
2.1	EDF 350	1:1
2.2	EDF 350	1:4
3.1	Polyfon O	1:1
3.2	Polyfon O	1:4

Results and Discussion:

Effect of Substrate Properties on Conductivity

Conducting Ink Rheology: The dynamic stress sweep is pictured below in Figure 1. Within the LVR, the G' (storage modulus) values were greater than the G" (loss modulus) values, indicating that the sample performed more elastic than viscous. A stress of 0.1 Pa was chosen for the frequency sweep. A crossover point, in which the paths of G' and G" crossed, was observed around the stress value of 1 Pa. This crossover point corresponds to the point in steady flow in which the viscosity dropped. After the initial drop of G' and G" outside of the LVR, a second plateau can be seen before G' and G" decrease further. The first drop may be attributed to the deformation of the structure created by the silver flakes. Likely, the second plateau is due to the structure of the remaining smaller particles present in the water-based ink. The second drop would be due to the destruction of the order of these particles.

A frequency sweep (Figure 2) was performed on the sample at the predetermined stress of 0.1 Pa. Here, the slope of the G' curve indicates the material's strength. A large slope reveals low strength, and a small slope indicates high strength. In this case, the G' curve remains fairly level until the frequency of 20 Hz is reached. At that point, G' drops off sharply. This result indicates that the ink maintains its strength until a frequency of 20 Hz, then the sample deforms quickly.

The steady state flow test (Figure 3) was conducted to determine the critical stress of the ink. As in the dynamic stress sweep, a second plateau of stability can be seen in the steady state flow. The critical stress of the ink occurs at approximately 1 Pa.

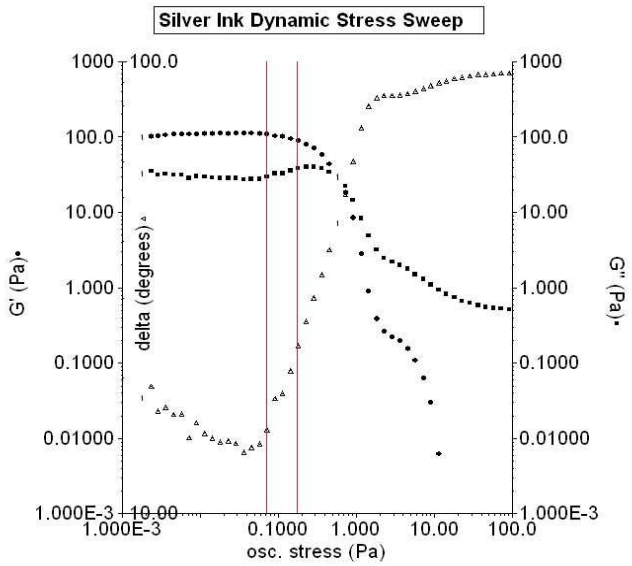

Figure 1: Dynamic Stress Sweep for Silver-Flake Ink

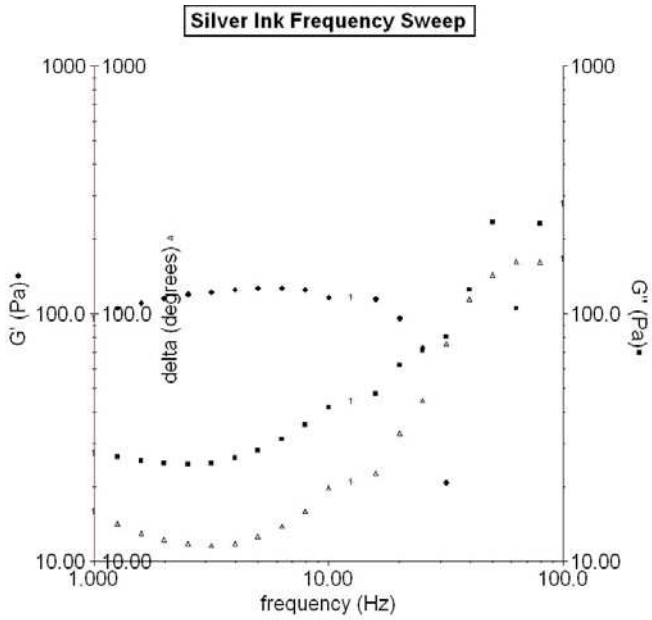

Figure 2: Frequency Sweep for Silver-Flake Ink

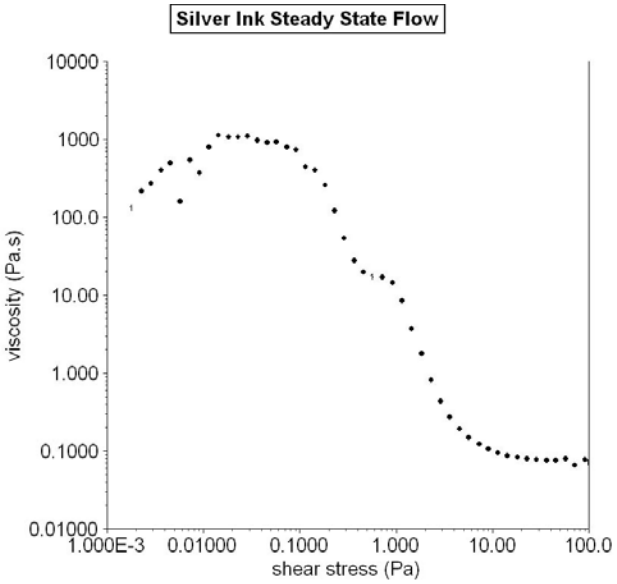

Figure 3: Steady State Flow for Silver-Flake Ink

Ink on Paper: Silver ink was hand-proofed onto five different paper substrates. Though each substrate was hand-proofed with ink in an identical manner, the thickness of the ink layer varied from substrate to substrate. The variations may be attributed to differences in ink holdout capabilities among the substrates, as well as a slight difference in manual force applied during application. These thicknesses were measured using a caliper and taken into consideration during the conductivity measurements. The LabelSet grade possessed the thinnest ink layer and the highest overall conductivity (Table 6).

Table 6: Conductivity of Silver-Flake Ink on Tested Substrates

Substrate	Length [cm]	Width [cm]	Thickness [cm]	Conductivity [S.cm^{-1}]
LabelSet	2	1.244	0.0003	2684
OptiTherm	2	1.239	0.0013	795
PointFlex	2	1.243	0.0005	2169
UniTherm	2	1.303	0.0009	1448
UniTherm Sharp	2	1.284	0.0010	1177

Roughness: UniTherm Sharp was calendered to four roughness levels and hand-proofed with silver flake ink. Parker Print-Surf Roughness[15] values were determined at a clamping pressure of 1000 kPa with a soft backing.

The results for different roughness values (Table 7) indicate that calendering has an overall detrimental effect on conductivity. Though the thickness of the ink layer showed no relevant difference, the conductivity of the printed area generally decreases with a decrease in surface roughness.

Table 7: Effect of Surface Roughness on Conductivity

Calendering Conditions	Roughness [microns]	Thickness [cm]	Conductivity [S.cm^{-1}]
None	1.58	0.001	1177
10# 1 Pass 1 Side	1.31	0.001	945
40# 1 Pass Each Side	1.25	0.001	786
10 # 2 Pass 1 Side	1.24	0.001	812
50# 3 Pass Each Side	1.15	0.001	852

Substrate Permeability and Porosity: The OptiTherm tag exhibited the highest permeability of the five substrates (Table 8). According to the mercury porosimeter results (Table 9), the PointFlex substrate has the highest percent porosity at 23.8%, closely followed by UniTherm Sharp at 23.1%. OptiTherm Tag displayed the lowest percentage at 18.6% porosity. The porosity and permeability data for the substrates are compared to their final conductivity in Table 8 for easier comparison. The high permeability, low porosity sample exhibited a low conductivity; whereas the low permeability, high porosity substrate exhibited a high conductivity.

Table 8: Parker-Print Porosity and Permeability of Substrates

	Permeability	
Sample	PPS Porosity [mL/min]	Permeability [µm^2]
LabelSet	1.65	5.74E-6
OptiTherm	5.74	5.13E-5
PointFlex	2.11	5.76E-6
UniTherm	2.23	8.03E-6
UniTherm Sharp	8.12	3.02E-5

Table 9: Mercury Porosimeter Data for Substrates

	Intrusion Vol. [mL/g]	Total Pore Area [m^2/g]	Avg. Pore Diameter [A]	Porosity [%]
LabelSet	0.2273	0.184	49324	22.9
OptiTherm	0.2163	0.099	87662	18.6
PointFlex	0.2487	0.092	108210	23.8
UniTherm	0.2410	0.039	244925	21.8
UniTherm Sharp	0.2552	0.046	221776	23.1

Table 10: Relationship between Substrate Permeability, Porosity and Conductivity

	Permeability [µm^2]	Porosity [%]	Conductivity [S.cm^{-1}]
LabelSet	5.74E-6	22.9	2684
OptiTherm	5.13E-5	18.6	795
PointFlex	5.76E-6	23.8	2169
UniTherm	8.03E-6	21.8	1448
UniTherm Sharp	3.02E-5	23.1	1177

Wettability: The contact angles of the silver ink with the substrates ranged from approximately 40 degrees (PointFlex) to 52 degrees (LabelSet). The high contact angle on the LabelSet sample correlates with its low permeability. However, the PointFlex sample exhibited a low contact angle despite its low permeability.

Table 11: Contact Angles of Conducting Ink with Substrates

Substrate	Contact Angle [deg]
LabelSet SP	52.0
OptiTherm	46.5
PointFlex	39.9
UniTherm	45.4
UniTherm Sharp	48.0

Relative Humidity: An increase in the relative humidity of the sample's atmosphere at a given temperature resulted in a decrease in the conductivity of the printed area (Table 12). However, once removed from the humidity chamber and exposed to ambient conditions, the printed substrate typically regained its original conductivity. Exceptions to this trend are seen at the high relative humidity conditions, where complete recoveries from the humid conditions were not accomplished. This is likely due to the physical warping that the samples experienced at high humidity levels.

Table 12: Effect of Relative Humidity on Conductivity

Conditions		Conductivity [S.cm^{-1}]			
Temp [°C]	Relative Humidity [%]	Avg.	Open 1	Open 2	Open 3
23	35	1081	n/a	n/a	1323
23	50	1073	1035	1027	1028
23	80	761	n/a	1095	1087
23	90	767	806	814	820
30	35	1286	1340	1328	1332
30	50	1051	1373	1373	1373
30	80	918	704	714	704
35	80	1399	1299	1282	1299

As seen in Table 13, an increase in temperature caused an increase in conductivity at the same relative humidity. As temperature increases, more moisture is present in the sheet at any given relative humidity. The relationship between temperature and relative humidity can be seen in Figure 4[12]. It is unknown why increased temperature results in increased conductivity, since more moisture would be present in the sheet. Additional research is required in this area.

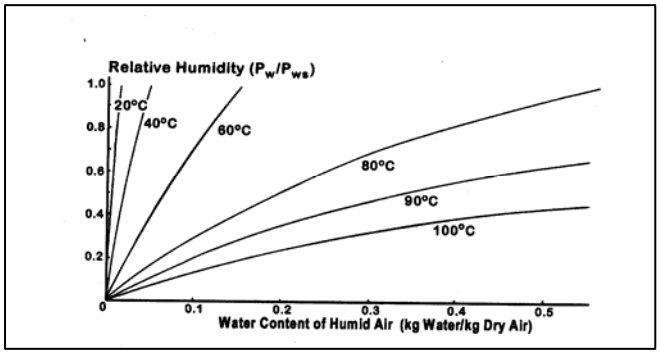

Figure 4: Relationship between Relative Humidity and Water Content of Humid Air

Table 13: Effect of Temperature on Conductivity

Temperature [°C]	Relative Humidity [%]	Conductivity [S.cm^{-1}]
23	35	1081
30	35	1286
23	50	1073
30	50	1051
23	80	761
30	80	918
35	80	1399

The effect of repeated increases and decreases in relative humidity at a constant temperature on conductivity was also investigated (Table 14). The initial increase in relative humidity caused a decrease in conductivity, as expected. The subsequent decrease in relative humidity caused the conductivity to drop further still. However, the second humidity increase resulted in a sudden increase in conductivity. The final humidity decrease again decreased the conductivity value. The reason for the spike in conductivity following the second humidity increase is unknown and should be further explored.

Table 14: Effect of Repeated Humidity Change on Conductivity

Run Number	Temperature [°C]	Relative Humidity [%]	Conductivity [S.cm^{-1}]
1	29	50	1484
2	29	85	1469
3	29	50	1370
4	29	85	1509
5	29	50	1423

Polyaniline Properties:

The infrared spectroscopy showed that FTIR spectra of polyaniline samples and their starting lignosulfonates showed overlay of FTIR peaks showing the presence of the template in the polymer, however in different extent. Figure 5 shows the changes in Tg's of samples as calculated from DSC thermograms. It is evident from the chart that the higher ratio of LS to aniline caused the higher decrease in Tg. In the case of sample 2.2, the slight increase in Tg was observed. Decrease in Tg is generally known as plasticization. Lignosulfonates grafted into the polyaniline chain can most probably move more easily because of less restrictions and crosslinking. On the other hand, very interesting is that lower amount of LS present in the polymerization caused smaller decrease in Tg or even slight increase.

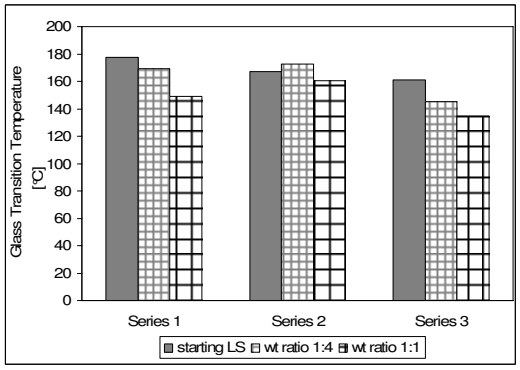

Figure 5: Glass Transition Temperature for tested samples of starting LS and prepared polyanilines.

Table 15: Conductivity of polyaniline samples

Sample ID	Conductivity (Films) [S.cm^{-1}]	Conductivity (Pellets) [S.cm^{-1}]
1.1	4.01×10^{-09}	0.0100
1.2	2.35×10^{-10}	0.0946
2.1	1.32×10^{-08}	0.0776
2.2	1.27×10^{-09}	0.1542
3.1	7.94×10^{-10}	-
3.2	1.92×10^{-10}	0.2913

Conductivities of polyaniline films and pressed polyaniline pellets are presented in Table 15. Low conductivity levels of polyaniline films are due to dedoping effect of the solvent used[4]. On the other hand, conductivity of pressed pellets is in the order of magnitude of 10^{-2} to 10^{-1} $S.cm^{-1}$. Unfortunately, it was not possible to measure the pellet sample 3.1 due to bad integrity of the pellet. The highest conductivity was found for the polyaniline sample 3.2; which was prepared in the presence of lignosulfonic acid from lignosulfonate Polyfon O.

Conclusion

The research conducted in this work yielded some interesting phenomena. Increased smoothness caused a decrease in the conductivity of the printed sample. A substrate possessing high permeability and low porosity exhibited a lower conductivity than a substrate consisting of low permeability and high porosity. The contact angle of the silver-based ink did not show a strong correlation to the permeability of the substrate. Finally, an increase in relative humidity resulted in a decrease in conductivity, and an increase in temperature caused an increase in conductivity.

Paper substrate properties impose significant effects on the conductivity of printed electronics. Understanding these effects is a first step towards producing an ideal printed electronic substrate to optimize product performance. Future research will further explore the relationship between temperature, relative humidity and printed conductivity.

Acknowledgement

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