The Properties of Conducting Polymers and Substrates for Printed Electronics

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Abstract

The present work deals with the preparation and properties of a conductive polymer and effect of paper properties on conventional silver-based conducting inks. Polyaniline was prepared using template guided polymerization in the presence of different lignosulfonic acids. Characterization of prepared polymers was performed using Fourier Transform Infrared (FTIR) spectroscopy and thermal behavior was studied using Differential Scanning Calorimetry (DSC). Electrical properties of polymers were studied in the form of polymer films as well as pressed pellets. Electrical properties of silver inks on different paper substrates were also studied.

Introduction

A major breakthrough in the area of conductive polymers was the discovery that polyacetylene could be easily oxidized (by electron acceptors) or reduced (by donors) in 1977.[1] Nowadays, conductive polymers are emerging as the basis of a number of new technologies, including plastic electronics, in which the intrinsic properties of the polymers are critical in determining device performance. Polyaniline is an important member in the family of intrinsically conductive polymers (ICPs) and it has been brought to attention because of good environmental stability, ease of synthesis and relatively good processability. It has been also studied to great extent because of its chemical, electronic and optical properties and thus representing a well known class of conductive polymers in materials science.[2]

The use of renewable natural materials to develop or improve existing materials or technologies is one of the most important ideas of research. Lignin is a complex natural polymer, which can be isolated from lignocellulosic materials. This aromatic network polymer has found applications in numerous industrial areas because of its versatile dispersing, binding, complexing, and emulsifying properties. The basic building blocks of lignins are variously substituted phenylpropane units, linked together via different chemical bonds, such as ether, alkyl and aryl linkages.[3]

Commercial lignosulfonates (LS) are obtained either from spent sulfite liquor or by sulfonation or sulfomethylation of kraft lignin. The sulfomethylation reaction (with formaldehyde and sodium sulfite or sodium bisulfite) adds the sulfomethylene group ($--CH_2SO_3Na$) to the lignin phenolic unit. Sulfuric acid, sulfur trioxide, or sulfur trioxide-dioxane complex may also be used to sulfonate the phenolic unit of the lignin.[4] Lignosulfonates are commercially available in form of sodium or ammonium salts, which can be easily converted to lignosulfonic acid by using proton exchange resins. Lignosulfonic acid is a highly water soluble polymeric acid, which can be used as a template for the polyaniline or polypyrrole polymerization[5] (Figure 1).

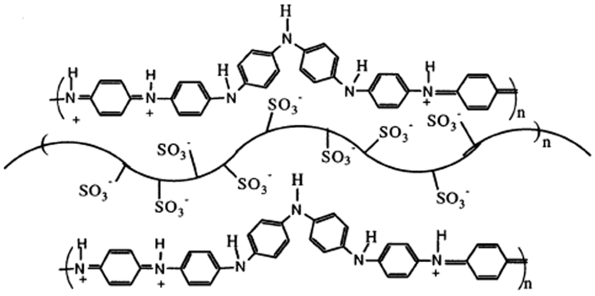

Figure 1. Schematic illustration of the formation of polyaniline-lignosulfonic acid (LSA) complex.[5] (LSA is positioned between two polyaniline chains)

The industrial use of printed low-profile electronics in new technologies, such as paper batteries and Radio Frequency Identification (RFID), is expanding at a rapid rate.[6] Paper and paperboard substrates are often employed in the manufacture of packaging materials. With the increasing trend of integrating RFID tags into supply chains,[7] 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.

Experimental

Synthesis of Polyaniline

Three types of different lignosulfonates (MeadWestvaco) were used in this work (Table 1). Materials such as aniline and ammonium persulfate (APS) used in polyaniline synthesis were purchased from SigmaAldrich.

Prior to use, the lignosulfonates were protonated using the proton exchange resin (DOWEX HCR-W2, Dow Chemicals) in order to prepare lignosulfonic acid from its sodium salt. The pH of the resulting lignosulfonates solution after protonation was 1.6 – 1.8. Aniline was oxidatively polymerized with ammonium persulfate (APS) in the presence of lignosulfonic acid. The weight ratio of lignosulfonic acid and monomer was preferably between 1:1 and 1:4, as it was found in preliminary work to be the best for dispersibility and conductivity, respectively.[8] The polymerization was carried out at 3-5°C and the regents were stirred for 3 hours.

Table 1: 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

The resulting product was washed and centrifuged from acetone followed with water and dried under vacuum overnight at 60°C. The dark green/black polyanilines doped with lignosulfonic acid were stored in dark container for further measurements during this project.

Characterization of Polyanilines

FTIR

Infrared spectra were obtained for all prepared polymer powders in pressed KBr pellets using a Bruker Equinox 55 FT-IR Spectrometer. For spectral comparison, infrared spectra of pure lignosulfonates were also obtained.

Differential Scanning Calorimetry

DSC analyses were preformed using a Perkin Elmer DSC 1 analyzer equipped with Pyris™ Software 7.0. For DSC scans, the samples (5-10 mg in closed aluminum pans) were hold at 30°C for 1 minute and then heated to 500°C at the rate 20°C/min to find transition temperature range. For more precise thermal analysis, further scans were performed in the temperature range from 50°C to 300°C at the rate of 10°C/min. Nitrogen atmosphere was used at the rate of 20 mL/min.

Conductivity

Electrical characteristics of the prepared polyanilines and raw lignosulfonates were studied in the form of the polymer films on the glass substrate. Lignosulfonate films were prepared using a standard spin coating procedure at the coating speed of 2000 rpm for 60 seconds. Polyaniline films were prepared by casting from polymer solution in solvent mixture N-Methyl-2-Pyrrolidone (NMP) and 2-Amino-2-Methyl-1-Propanol (AMP) in weight ratio of 2:1. In order to measure electrical characteristics of the polymer films, the silver microelectrodes were PVD (Physical Vapor Deposition) patterned using the wire shadow-mask method. After deposition of the Ag electrodes in high vacuum chamber, the wire mask was removed leaving a 200 μm gap between electrodes. The thickness of the electrodes was at least 100 nm and thickness of the polymeric film was measured using AFM. The samples were measured for their I-V characteristics using a Keithley multimeter model 2400 operated from a PC with Labview software. The conductivities of prepared polyaniline powders were also measured in the form of pressed pellets prepared using the ICL's E-Z Press™ hydraulic lab press. The following equation was used to calculate conductivities:

$$\sigma = \frac{L \times I}{V \times A} \quad (1)$$

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 film.

Effect of Substrate Properties on Conductivity

A water-based flexographic conducting ink (Precisia) comprised of silver flakes was applied to several labelstock substrates. The influences of substrate properties on the printed conductivity were examined. The rheological properties of a conducting silver-flake ink were studied prior to application. The results are presented elsewhere.[9] Five substrate samples were provided by StoraEnso for analysis in conjunction with conducting silver-flake ink. These substrates are listed below in Table 3 along with their intended applications. 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

$$K = 0.048838 * Q * X \quad (2)$$

where K is the permeability in μm^2, Q is the flow rate in ml/min and X is the thickness in m. Results from the characterization tests are detailed in Ref. [9].

Table 2: 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

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 Equation (1). The effect of substrate roughness as well as the relative humidity on conductivity was determined.

Table 3: Substrates Description

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

Results and Discussion

FTIR

Figure 2 shows the FTIR spectra of prepared polyaniline samples 1.1 and 1.2, which were synthesized in the presence of sulfomethylated lignosulfonic acid (Reax 88B). The FTIR spectrum of the starting lignosulfonate contains peaks at 3429 cm^{-1} due to OH stretching in phenols; aromatic skeletal vibrations peak at 1600 cm^{-1}; at 1458 cm^{-1} is due to CH stretching of methyl or methylene groups. The peak at 1045 cm^{-1} is the result of OH stretching of primary alcohols. Peaks at 1185 and 512 cm^{-1} are due to the S=O stretching in sulfonic acids and SO_2 scissoring, respectively. The polyaniline samples 1.1 and 1.2 are similar and show some overlaps with starting lignosulfonate spectra. However polyaniline sample 1.1 shows the peak at 1040 cm^{-1} that is not present in sample 1.2, which may indicate the presence of primary OH groups from lignosulfonates in polyaniline at higher weight ratio of lignosulfonate to aniline during polymerization. Furthermore, the peak at 1300 cm^{-1} is due to C-N band stretching and peaks at 1490 and 1566 cm^{-1} are coming from stretching of C=N bands of a quinoid structure typical for polyaniline. Comparison of all polyaniline samples and their starting lignosulfonates showed overlay of FTIR peaks showing the presence of the template in the polymer, however in different extent. The sulfonate groups of LS acid, S=O stretching peaks are shifted to lower wavelengths and the SO_2 scissoring peak is present in all prepared polyanilines.

Figure 3 shows the comparison of FTIR spectra of polyaniline samples prepared with weight ratio of different lignosulfonic acids to aniline 1:1. The quinoid structure stretching (1560 and 1490 cm^{-1}) and C=N bond stretching (1300 cm^{-1}) is in complete agreement with those of polyanilines doped with protonic acids.[13]

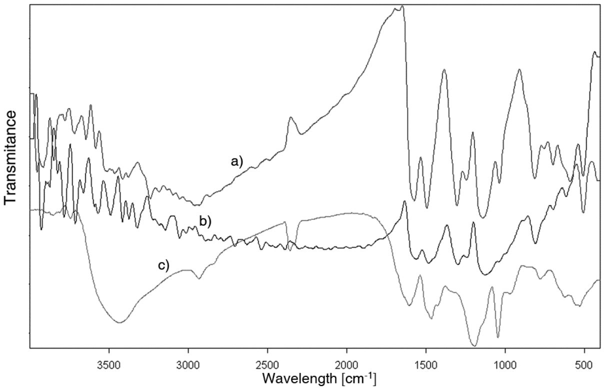

Figure 2. FTIR spectra of polyaniline samples a) 1.1, b) 1.2 and c) lignosulfonate Reax 88B.

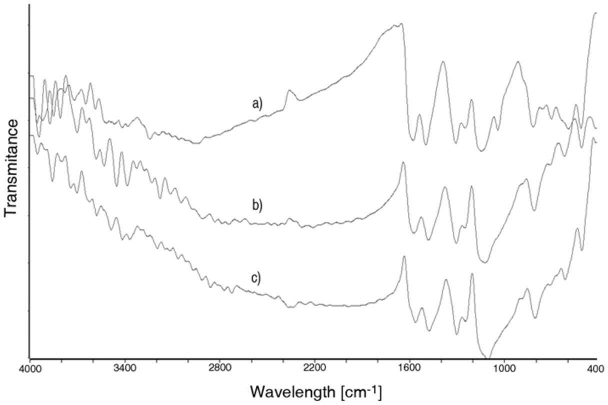

Figure 3. FTIR spectra of polyaniline samples a) 1.1, b) 2.1 and c) 3.1.

Differential Scanning Calorimetry

Figures 4, 5 and 6 show the stacked DSC thermograms measured for tested powder polyaniline samples under a nitrogen atmosphere. The thermograms are showing several endothermic peaks, with one dominant endothermic transition. It is typical for crosslinked polymers to observe the thermal transition over a wider range of temperatures due to more restricted movement of polymer chains.[14] Furthermore, the higher the crosslinking the higher the glass transition temperature T_g.[15] The glass transition temperature (T_g) is calculated from thermograms as a temperature, at which the one-half of the change of heat capacity, ΔC_p, occurred.[16] The determination of T_g is also illustrated in the Figures 4, 5 and 6. There is a hysteresis peak associated with thermal transition itself and perhaps can be due to destruction of any residual order in otherwise amorphous polymers.[16] The T_g of lignin depends on the conditions under which it was isolated and is between 100- 190°C.

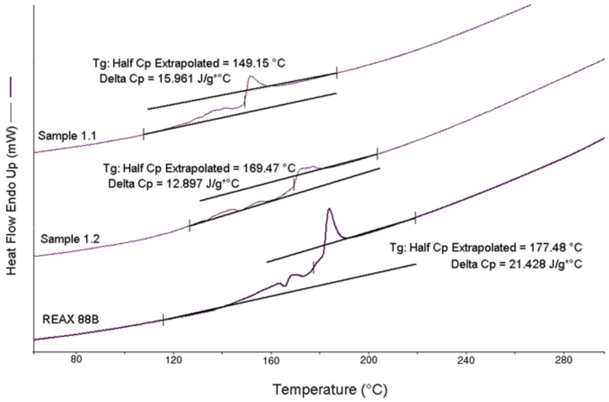

Figure 4. DSC curves for polyaniline samples 1.1 and 1.2 prepared in the presence of lignosulfonate REAX 88B.

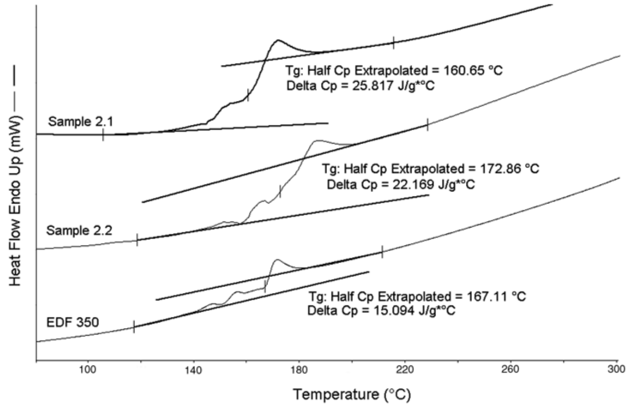

Figure 5. DSC curves for polyaniline samples 2.1 and 2.2 prepared in the presence of lignosulfonate EDF 350.

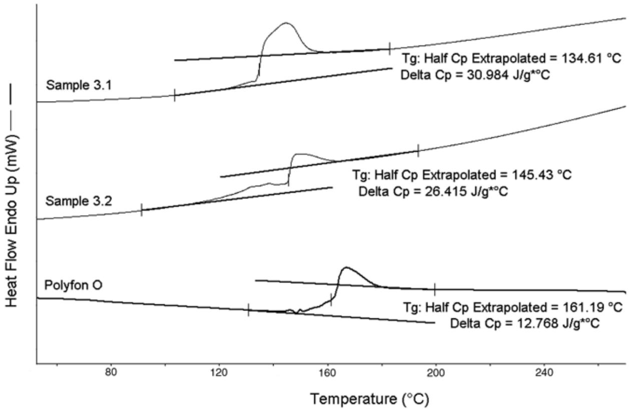

Figure 6. DSC curves for polyaniline samples 3.1 and 3.2 prepared in the presence of lignosulfonate Polyfon O.

High T_g is most probably due, in large part, to hydrogen bonding of phenolic hydroxyl groups in the main chain as well as the presence of aromatic rings in the chain and overall complex chemical structure[17] It was observed that the glass transition temperature of starting lignosulfonates is higher than the T_g of polyaniline samples containing LS template. Polyaniline samples prepared in the presence of lignosulfonic acids show changes in T_g depending on the weight ratio of LS acid and aniline during the polymerization reaction. For a better comparison, Figure 7 shows the changes in T_g'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 T_g. In the case of sample 2.2, the slight increase in T_g was observed. Decrease in T_g 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 T_g or even slight increase. Further characterization analyses are necessary to determine the chemical and physical structure of prepared polymers and its effect on thermal behavior. Preliminary works showed that polyaniline complexes prepared in the presence of polymeric sulfonic acids are more thermally stable than HCl-doped polyaniline and dedope only at pH higher than 9 as compared to pH 4 for HCl-doped polyaniline. This indicates that interactions between the two polymers result in more stable polymer complex.[18]

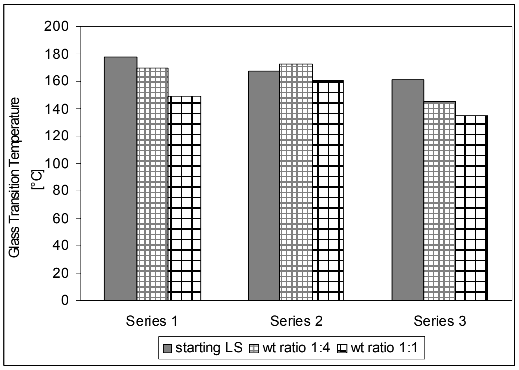

Figure 7. Glass Transition Temperature for tested samples of starting LS and prepared polyanilines.

Conductivity

For preparation of polyaniline film by casting onto the glass, the solvent mixture of NMP and AMP was used, because of only partial solubility of polyanilines in pure NMP. In previous work[19] it was found, that it is very difficult to remove NMP completely during film casting and the resulting polyaniline film contains a considerable amount of NMP, about 10-18% by weight. This is due the presence of the hydrogen-bonding interaction of the C=O group in NMP with the NH group in polyaniline. Since the C=O group can hydrogen bond with the proton in the acid dopant and it is expected that the residual NMP in the film will affect the doping level strongly.

In agreement with the statement above, due to casting from NMP solution, polyaniline was in its dedoped state confirmed by low conductivities values in the range of 10^{-10} to 10^{-8} S.cm^{-1} (Table 4). On the other hand, conductivities of pressed pellets differ substantially. The weight ratio of LS to aniline 1:4 during polymerization yielded higher conductivity than ratio 1:1. Lignosulfonic acid serves as a dopant at lower concentrations up to 1:4 (LS: aniline).[20]

Table 4: 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

However, at higher concentrations, it may act as the impurity causing restrictions to charge transfer along the polyaniline chain and consequently causes decrease in conductivity.

Conductivities of pressed polyaniline pellets are presented also in Table 4 and are in the order of magnitude of 10-2 to 10-1 S.cm-1. Unfortunately, it was not possible to measure the sample 3.1 due to bad integrity of the pressed 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.

Effect of Substrate Properties on Conductivity

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. 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 5).

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. Parker Print-Surf Roughness[21] values were determined at a clamping pressure of 1000 kPa with a soft backing.

Table 5: 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

The results for different roughness values (Table 6) indicate that calendering has a detrimental effect on conductivity, likely as a result of sheet consolidation. Though the thickness of the ink layer showed no relevant difference, the conductivity of the printed area decreases overall with a decrease in surface roughness.

For relative humidity effect, the OptiTherm samples hand-proofed with silver-flake ink were conditioned at varying humidity at 23°C. The CARON 6030 Environmental Test Chamber was used to condition the samples to the desired temperature and humidity levels. Samples were contained in a small humidity capsule during conductivity measurement to maintain the proper atmospheric conditions. After the conductivity was determined at the desired humidity level, the sample was removed from the capsule and exposed to ambient conditions. Three subsequent measurements were taken (Open 1, Open 2, and Open 3) to observe the effect the sudden decrease in relative humidity had on conductivity of the printed sample.

Table 6: 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

An increase in the relative humidity of the sample's atmosphere resulted in a decrease in the conductivity of the printed area (Table 7). However, once removed from the humidity capsule and exposed to ambient conditions, the printed substrate substantially regained its original conductivity. In the case of the 90% relative humidity sample, complete recovery from the humid conditions was not accomplished. This is likely due to the physical warping that this sample experienced at the high humidity condition. Further experiments are underway concerning changes in temperature as well as relative humidity, as well as hysteresis.

Conclusion

Conductive polymers represent interesting materials for various applications. Polyaniline is one of the most studied conductive polymers and there are already many suitable polymeric acids for its synthesis. Lignosulfonic acid can also be used as a template in polymerization of aniline. The resulting product is a complex of polyaniline and lignosulfonates. Further work will concentrate on finding of suitable resins and additives and preparation of conductive inks from this polymer.

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 investigate a larger span of relative humidity at higher temperatures and hysteresis effects will be studied.

Table 7: Effect of Relative Humidity on Conductivity

Conditions		Conductivity [S.cm^{-1}]			
Temperature [°C]	Relative Humidity [%]	Inside Chamber	Open 1	Open 2	Open 3
23	60	1073	1035	1027	1028
23	80	761	n/a	1095	1087
23	90	767	806	814	820

Acknowledgement

Authors would like to thank Department of Chemistry for the help with characterization of the samples. We also thank the Western Michigan University Office of the Vice President for partial financial support for this work.

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