Resistive Gravure Inks Made With Soy Protein

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soy polymer, ink formulation, sheet resistivity

Abstract

The major challenge faced by the printed electronics (PE) industry is to formulate low-cost, renewable, easily available alternatives for current solvent based conductive inks based on precious metals. This work is aimed to formulate the alternative inks based on renewable "green" raw materials such as soy polymer, in combination with conductive graphites and conductive carbon fillers. Water-based conductive acrylic and soy inks were formulated for the gravure printing process. Blends of graphene and conductive carbon fillers were used to replace the expensive silver. Simultaneously, a study was conducted to determine the potential of soy polymers as resin system to replace acrylic resins.

Introduction

The global market demands high quality and low cost fabrication methods for manufacturing of electronic devices that are both faster and cheaper compared to traditional production methods. Printed Electronics (PE) is an upcoming technology, where conventional printing methods are employed to print electrically functional devices. There is a worldwide effort to make these processes available for commercial use, and some are already being successfully commercialized (1-3). PE brings together previously separate fields, printing and electronics. Using conventional printing processes, inks based on metal nanoparticles and metallo-organic complexes are used to produce building blocks of electronic products such as transistors and diodes (4). The advantage offered by PE in the manufacturing of these components is a drastic decrease in the cost of electronic devices. Applications of PE have been demonstrated previously in the manufacturing of batteries, LED's, displays, speakers, sensors and fully printed RFID labels (3). Conventional printing processes are additive in nature and offer great advantages over the traditional processing methods for electronic device manufacturing. Flexible electronic devices are manufactured by depositing a single or multiple layers of functional materials on polymer

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substrates, including paper. The important challenge for PE is the formulation of the functional inks. Formulation of functional inks is similar to graphic inks, but in addition, they should provide good printability of the printed pattern, good compatibility with the substrate and low-temperature processing in order to be compatible with flexible substrates (1) shows the comparison of conventional processing and printed electronics. Advances in the field of ink technology, such as particle and binder manufacturing have enhanced performance of inks in terms of conductivity, flexibility, line resolution and their compatibility with various substrates. Recently, functional inks suitable for screen, gravure and flexographic printing processes are being developed for printed electronics.

Conventional Processing	Printed Electronics
Subtractive processing (photolithography and wet/dry etching for layer definitions)	Additive processing (printing) for layer definitions
Controlled / Vacuum environment	Ambient temperature and pressure conditions
Typically requires a high temperature for processing	Requires low temperature for processing thus allowing use of flexible and plastic substrates

Table 1: *Comparison of Conventional Processing and Printed Electronics (5)*

Functional inks may be conductive, semi-conductive, and dielectric. To formulate conductive ink, silver is the primary choice due to its high conductivity (σ=6.3x10^7 Ω^{-1} m^{-1}) (3), stability and performance. Other highly conductive metals that have also gained popularity are copper (σ =5.96x10^7 Ω^{-1} m^{-1}) (3), gold (σ =4.4x10^7 Ω^{-1} m^{-1}) and aluminum (σ =3.78x10^7 Ω^{-1} m^{-1}) (3). Silver is a very expensive material; therefore extensive research is being carried out to replace silver by less expensive metals or other conductive materials, such as variously processed carbons. Copper, aluminum, and zinc are less expensive as compared to silver. However, the main challenge is to avoid their oxidation at room temperature, which requires sophisticated reaction conditions, such as use of hydrocarbon solvents, low precursor concentration and inert atmosphere (3). Oxidation is a formation of dense, thin layer of metal oxide on the surface of metal particles, which results in loss of electrical conductivity and limits the use of these materials in the formulations of conductive inks (5-7). For applications that do not require very high conductivity, resistive inks based on graphene and carbon fillers can be used. Inks based on a blend of conductive carbon with graphene is one of the popular options that are being tested and researched (8). Pure graphene-based inks offer exceptional electrical conductivity with cost effective printability on a variety of printing systems, including roll-to-roll. Introduction of carbon fillers can reduce the amount of graphene required to create a conductive network in an ink film, resulting in saving of material and thus being more cost effective. Blends of graphene-carbon inks do not require high temperature sintering, they create robust films that do not crack or delaminate with repeated flexing and creasing. This enables true, flexible applications where bending, folding, handling, and dropping do not disturb the printed circuitry. Also, these inks do not form an insulating oxide layer; they are non-toxic and can be readily dispersed in solution (8).

A tremendous amount of research is being carried out at an industrial and at the university level to utilize the natural, renewable, and cheap sources of raw materials. The printing industry is not an exception to this change and it is systematically going away from nonrenewable petroleum based products. Traditionally, soy oil based inks have been widely utilized in lithographic printing processes to print newspapers and some commercial products. In the United States alone, use of soy oil based printing inks has increased from 5% in 1989 to 22.5% in 2001 (9). Soy proteins have been found useful in fluid inks, especially water-based inks (10). Soy protein based vehicle systems, which are a result of chemical modification of soybean protein help to serve as a carrier for the pigment and binder to the substrate. In water based soy inks, soy protein vehicle replaces a portion of acrylic resin, becoming homogeneous with the system. Being renewable resources, soybean-based raw materials also limit the emission of environmentally hazardous gases. Furthermore, it has been demonstrated by life cycle analysis that the use of renewable resources is more cost-effective and eco-friendly than petrochemical resources (10). Soy polymers are already used largely for paper coating applications offering high temperature resistance, high crosslinking and good adhesive properties (11,12). Considering the advantages offered by carbon-graphene blends, the aim of this study was to formulate different inks based on varying carbon-graphene and soy polymer content and to study their electrical conductivity, and printability.
Experimental procedure

The specification of graphite (Asbury Carbons) samples is given in the Table 2. They are characterized based on particle size and surface area. Synthetic carbon filler properties are given in the Table 3. Acrylic resins Joncryl 264 (BASF) and Joncryl HPD 296 (BASF) were used in ink formulations. PET film (DuPont) was used as a print substrate. Drawdowns were made with with Meyer rod #12 or gravure K-proofer. Printed samples were dried at 105º C in a hot air oven for 5 minutes to cure the ink layer. After cooling, sheet resistivity was measured with Keithley 2400 digital multimeter. Ink film thickness was measured by Technidyne Co, (New Albany, IN) instrument. Surface roughness of the printed films was measured using a Bruker GT-K white light interferometer.

Product	Type	Particle size [µm]	Surface area [m²/g]	Bulk Resistivity [Ω.cm]
TC 309	Synthetic Graphite	4.08	20.07	0.050
TC 301	Synthetic Graphite	8.00	11	0.045
3442	Natural Graphite	3.68	14.49	0.060

Table 2: *Specifications of graphite samples from Asbury Carbon*

Product	Type	LTI	Surface area [m²/g]
Nano 25	Synthetic Graphite	14-15	172.08

Table 3: *Properties of Nano 25 synthetic graphite µm*

A full factorial design of experiment was employed to prepare 16 different inks. Four different vanishes were made by adding 25 %, 30%, 35% and 40% of acrylic resins on weight of dry solids basis into ammonium DI water. These four varnishes are Varnish 1, Varnish 2, Varnish 3 and Varnish 4, respectively. Micro 850 and conductive carbon fillers (four levels – 0%, 5%, 10%, and 15%), along with additives and additional DI water were blended into the prepared varnish to formulate the finished inks.

The results from Phase I were used as reference for Phase II. The optimum proportion of graphene and fillers from Phase I (Ink ID V3F15 with sheet resistivity of 153.8 Ω/sq) was used and soy polymer based inks were formulated. Four inks were formulated as shown in the Table 4. Drawdowns were taken with Coating Applicator on PET film or gravure K-proofer. Once printed, the samples were immediately dried at 105º C in a hot air oven for 5 minutes. After cooling, the sheet resistivity was measured with a Keithley 2400 digital multimeter.

Ink #	Soy Content (%)	Acrylic content (%)	
1	100	0	
2	75	25	
3	50	50	
4	25	75	
5	0	100	Control (V3C15)

Table 4: *Soy polymer based inks*

Results and discussion After the formulation of four inks using graphene material as shown in Table 6, drawdowns were prepared with #12 Mayer rod (Gardco, Gardner Company Inc.) with each of the inks. Ten samples for each ink were prepared and thickness, resistivity readings were measured at 3 different locations. It was observed that the ink film thickness increased proportionately with increasing particle size of graphite material. TC 301 (synthetic graphite) and Micro 850 (natural graphite) material showed very close values of bulk resistivity and sheet resistivity (5). However, sheet resistivity was observed lower with Micro 850 (655.08 Ω/sq) and hence it was selected for further studies. Figure 1 shows the graphical representation of sheet resistivity with four graphite materials.

Carbon Type	Avg. IFT (µm)	Sheet Resistivity (Ω/Sq.)	Bulk Resistivity (Ω.cm)
TC 301	17.1	723.1	1.24
TC 309	15.6	1077.5	1.68
3442	13.7	1757.2	2.41
Micro 850	18.8	655.1	1.23

Table 5: *Resistivity properties of graphite inks*

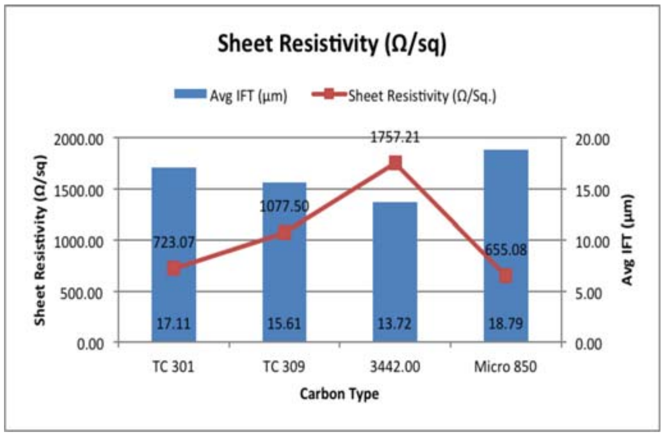

Figure 1: *Sheet Resistivity (Ω/Sq) of four graphite materials, (IFT: Ink Film Thickness)*

Effect of Conductive Carbon Fillers on Sheet Resistivity

After selecting Micro 850 graphite material, inks were formulated as per proposed DOE, and drawdowns were taken on the PET film with coating applicator. Printed films were dried in the convention oven and thickness of the ink film was measured on Technidyne Instrument.

Varnish Type 1 (25% resin solid content): Due to low resin content, very poor cohesion and adhesion was observed with inks formulated with Varnish type 1. Due to poor binding between graphene and carbon fillers, very high resistivity values were achieved (Table 6).

Ink ID	Avg. IFT (µm)	Sheet Resistivity (Ω/Sq.)	Bulk Resistivity (Ω.cm)
V1/F0	36.08	1795.9	6.48
V1/F5	34.6	1435.1	4.96
V1/F10	31.6	1099.5	3.48
V1/F15	34.05	1187.1	4.04

Table 6: *Resistivity values with inks formulated with Varnish type 1*

Varnish Type 2 (30% resin solid content): Ink formulated with Varnish Type 2 showed drastic improvements in terms of resistivity. Due to continuous ink structure, more conductive material is available for electron flow, leading to lower resistivity values (Table 7).

Varnish Type 3 (35% resin solid content): Improved resistivity values compared to Varnish Type 2, especially with V3F15 (15% conductive carbon filler) ink. More compact binding between conductive particles, lower ink film thickness, and higher concentration of nanosized carbon fillers showed excellent sheet resistivity values (Table 8).

Ink ID	Avg. IFT (µm)	Sheet Resistivity (Ω/Sq.)	Bulk Resistivity (Ω.cm)
V2/F0	37.9	235.4	0.89
V2/F5	35.4	192.9	0.68
V2/F10	34.0	192.4	0.65
V2/F15	26.2	205.0	0.54

Table 7: *Resistivity values with inks formulated with Varnish Type 2*

Ink ID	Avg. IFT (µm)	Sheet Resistivity (Ω/Sq.)	Bulk Resistivity (Ω.cm)
V3/F0	35.3	216.5	0.76
V3/F5	32.6	193.5	0.63
V3/F10	31.9	190.2	0.61
V3/F15	29.1	153.8	0.45

Table 8: *Resistivity values with inks formulated with Varnish Type 3*

Varnish Type 4 (40% resin solid content): A saturation limit was reached for resin content, as higher concentration is limiting the available conductive material for electron flow. Hence, higher resistivity values was observed with inks formulated with Varnish Type 4 (Table 9).

Ink ID	Avg. IFT (µm)	Sheet Resistivity (Ω/Sq.)	Bulk Resistivity (Ω.cm)
V4/F0	36.16	216.46	0.78
V4/F5	30.15	194.33	0.59
V4/F10	26.87	190.40	0.51
V4/F15	31.97	153.81	0.49

Table 9: *Resistivity values with inks formulated with Varnish Type 4*

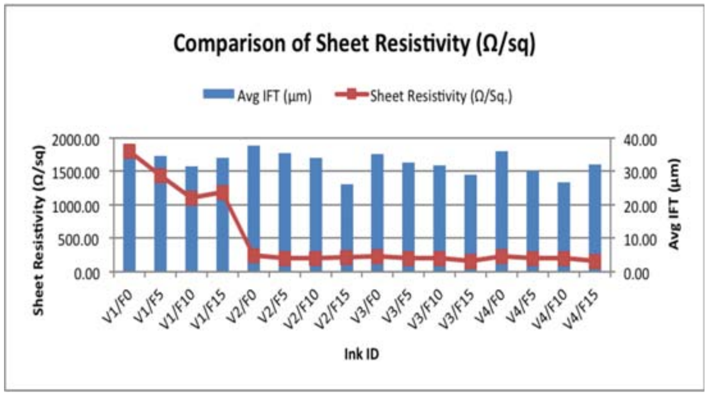

Figure 2: *Comparison of Sheet Resistivity and Ink Film Thickness*

Figure 3: *Cured film V3F15 vs. Soy Polymer Ink*

The optimum formulation parameters from Phase I (Ink ID V3F15) were selected for Phase II. Acrylic resin content from V3F15 was replaced gradually with soy polymers. Four inks were formulated as shown in the Table 5. Once the soy inks were formulated, drawdowns were taken on PET film with coating applicator, and immediately dried in conventional oven. The major defect observed with soy polymers was "sheet curling" (Fig.3). Sheet curling is a defect observed in mostly solvent or water based ink printing, where due to solvent retention or under-curing of inks, residual solvent/water causes printed sheet to lose its dimensional stability. Soy polymer inks showed extreme curling effect (Figure 3). Along with sheet curling, soy based inks also showed poor adhesion to the PET film and cracking of ink film.

Table 10 shows sheet resistivity of soy polymer inks compared to acrylic V3F15 ink. Even though all inks had the same percentage of conductive material in the formulation, due to properties exhibited by resin material, drastic differences were observed in the sheet resistivity values. Ink 1 (100% soy polymer) showed sheet resistivity of 1322.2 Ω/sq compared to V3F15 sheet resistivity of 153.8 Ω/sq. Poor film formation and poor adhesion was the primary reason for very high resistivity values. As soy polymers were of larger particle size and higher molecular weight, continuous films could not be formed with soy polymer of large degree of polymerzation.

Ink ID	Avg. IFT (µm)	Sheet Resistivity (Ω/Sq.)	Bulk Resistivity (Ω.cm)
Ink 1	37.7	1322.2	4.98
Ink 2	35.2	1162.1	4.09
Ink 3	33.4	1057.2	3.53
Ink 4	31.7	987.2	3.13
Control (V3F15)	29.1	153.8	0.45

Table 4: *Sheet resistivity of soy polymer inks compared to V3F15*

In addition to the electrical properties, surface roughness of the printed films was also measured using a Bruker GT-K Interferometer. The differences in the surface topography of soy polymers inks are shown in Figure 4. The Sa value depicts the average roughness over an area (a 3D parameter). Surface roughness Sa of Ink 1 (100% soy ink) is 14.2 µm, for Ink 2 (75% Soy/25% Acrylic) Sa is 1.1 µm, for Ink 3 (50% Soy/50% Acrylic) Sa is 0.65 µm, and for Ink 4 (25%Soy/75% Acrylic) Sa is 0.59 µm. On the other hand, (Figure 5) shows surface roughness for ink V3F15, where Sa is 407.4 nm. This huge difference in surface roughness could be due to the particle size, solvent retention, and swelling of soy polymers, which in turn impact the electron flow in the printed ink layer, leading to very high sheet resistivity.

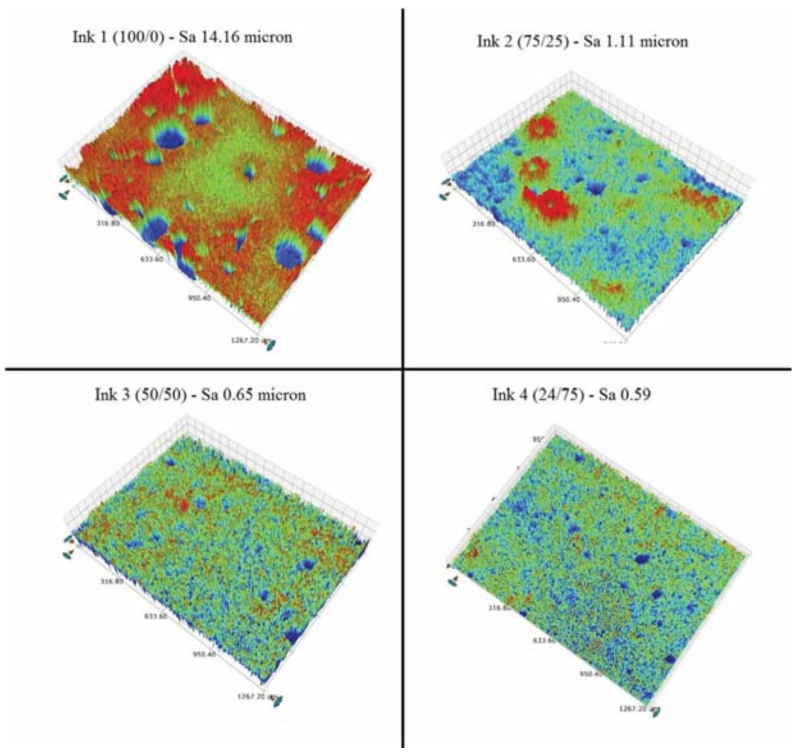

Figure 4: S*urface roughness of soy polymer inks*

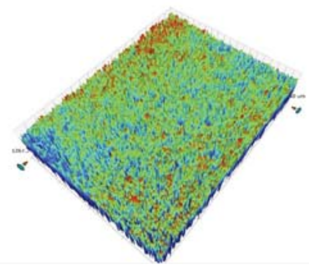

Figure 5: *Surface roughness of V3F15 ink, Sa 407.382 nm*

Conclusion

The sheet resistivity achieved by graphite Micro 850 was significantly increased by varying resin type and ratio and introducing conductive carbon fillers. It was showed that sheet resistivity is highly dependent on the varnish type (or resin content) in the ink. At the same time, it was observed that ink film thickness has a low impact on the sheet resistivity. Ink ID V3F15 showed lowest resistivity, and used as "control" parameter for Phase II of the work. Phase II involved evaluation of soy polymers in the functional inks to potentially replace petroleum based acrylic polymers.

Acrylic resins were replaced by soy polymers at four levels to formulate four different inks. Most likely due to high degree of polymerization of soy polymer, its high solvent retention, high surface roughness, and poor adhesion, soy based inks showed very high sheet resistivity as compared to acrylic resins. Even though soy based inks have shown very promising results in graphic inks (13), more research is required to evaluate their potential in the functional printing.

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