Characterization of Conductive Polymer Inks based on PEDOT:PSS

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Abstract

Since the discovery of conductive polymers in the mid-1970, they have been very popular and widely researched among scientists worldwide. Nowadays, polymeric materials exhibiting electrical conductivity are very promising for applications in low-cost and disposable electronics. In addition, some polymeric materials can be solution processable, which makes the implementation of existing printing technologies to electronics manufacture possible. Among conductive polymers, the properties and performance of polyaniline (PANI) and poly(3,4-ethylenedioxy-thiophene)-poly(styrene sulfonate) (PEDOT: PSS) inks are studied and optimized for deposition by different printing methods. The present work focuses on properties of PEDOT: PSS based polymer inks. Electrical conductivity of PEDOT: PSS films can be increased by addition of alcohols; ethylene glycol was used in this work to enhance conductivity. Other modifications made to aqueous solution of PEDOT:PSS were addition of ethanol and non-ionic surfactant. Applicability of the PEDOT:PSS ink to printing process was addressed with consideration of surface tension, surface roughness of the deposited films and their electrical conductivity depending on the ink formulation. The reduction of surface tension of water based solution of conductive polymer was studied by two different methods. The resulting inks were characterized in terms of static (pendant drop) and dynamic surface tension (maximum differential bubble pressure) and dynamic contact angle (sessile drop). Surface topography of PEDOT:PSS films was studied using white light interferometry and atomic force microscopy. Surface uniformity has significantly improved for inks with addition of ethylene glycol. It was observed that the addition of ethylene glycol increased the conductivity of the films almost 20 times as measured by four-point probe technique.

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Introduction

Nowadays, more and more electronics manufacturers are embracing printing technologies as a high-potential manufacturing method for mainstream electronic components. However, to fully utilize the benefits of printed electronics, manufactures need advanced materials that are well suited for specific electronic applications and also printing systems, and are available in commercial quantities. Functional materials needed for printing of electronic components include conductors, semiconductors and dielectrics.

Ink conductivity can be achieved by different mechanisms, such as incorporating metallic or other conductive particles into a non-conducting polymer matrix, or by using polymers that exhibit electrical conductivity in a suitable solvent. Among conductive polymers, solvent based (xylene, toluene) polyaniline inks (Makela, 2005, Hrehorova, 2005) and water-based poly (3,4-ethylenedioxy-thiophene)-poly(styrene sulfonate) (PEDOT: PSS) inks (Fenoll, 2005, Zielke, 2005) are widely studied for applications in organic electronics. Several different printing methods are employed in these studies, such as flexography, offset and gravure printing, as well as ink-jet printing.

The present work focuses on characterization of PEDOT: PSS based polymer inks. PEDOT: PSS is commercially available as a water-soluble polyelectrolyte system with good film-forming properties, high visible light transmittance, and excellent stability (Groenendaal, 2000). Some applications of PEDOT: PSS include antistatic coatings, conductive layers in organic light emitting diodes (OLEDs), capacitors and thin film transistors (Kirchmeyer, 2005). PEDOT: PSS complex is prepared by oxidative polymerization of ethylenedioxythiophene (EDOT) in aqueous dispersion using sodium peroxodisufate as the oxidant. A template polymer (usually polystyrene sulfonic acid – PSS) is present during the polymerization (Groenendaal, 2000). The PSS in the resulting complex acts as a source for the charge balancing counter ion. Moreover, it keeps the PEDOT chains dispersed in water, forming stable, easy to process, deep blue microdispersions (Kirchmeyer, 2005). The chemical structure of PEDOT: PSS is shown in Figure 1.

As already mentioned, PEDOT: PSS is commercially available as aqueous dispersions. The water-based nature of such polymer systems gives rise to the issues of substrate wetting and ink spreading. Water has a high surface tension and thus water based inks are very often formulated with alcoholic co-solvents and/or surfactants in order to lower surface tension for printing. The addition of alcohols lowers the surface tension monotonically with increasing concentration, due to a preferential adsorption of the organic molecule at the liquid-air interface. Surfactants, however, quickly reduce the surface tension at very low concentrations up to the critical micelle concentration (CMC), due to a strong adsorption of the surfactant at the liquid-air surface. At concentrations higher

than the CMC, the surface tension is practically constant, because any additional amount of surfactant will form micelles in bulk (Huibers, 1996).
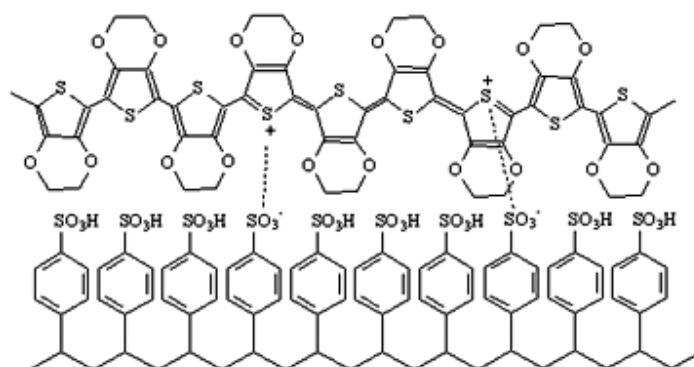

Figure 1: Chemical structure of poly(3,4-ethylenedioxy-thiophene)-poly(styrene sulfonate) complex (PEDOT: PSS).

Although the static surface tension is widely used in the printing industry to predict wetting behavior of printing inks, especially water based printing inks, it is also important to characterize interfacial surface tension under dynamic press conditions where the ink is under constant compositional change. A new liquid-air interface is created characteristically in the order of milliseconds. Dynamic surface tension of inks containing surfactants and other polymers is determined by diffusion, adsorption and desorption processes and it is typically higher than equilibrium (static) surface tension.

Analysis of wetting behavior of different functional fluids and their interaction with polymeric substrates is an important subject in order to develop and optimize various materials for electronics manufacture. The quality of the interface between functional layers in an electronic device is crucial for its performance (Fahlman, 2002). In general, the wetting process is reflected by the contact angle, defined as the angle that a liquid makes with a solid surface. The equilibrium relation of a three phase system can be described by the Young – Dupre equation (Young, 1855, Dupre, 1869):

$$\gamma_{lv} \cos \Theta = \gamma_{sv} - \gamma_{sl}$$

where Θ is the contact angle and γ is the surface/interfacial tension at the liquid-vapor interface (lv), solid-vapor interface (sv) and solid-liquid interface (sl).

As already discussed, there are several different ways to reduce surface tension of water based systems. With PEDOT: PSS dispersions, addition of secondary alcohols has yet another positive effect on the resulting films. It has been reported that electrical conductivity can be enhanced by addition of different

organic compounds (Ashizawa, 2005). The conductivity improvement is strongly dependent on the chemical structure of the compound. Among the alcohols, ethylene glycol and glycerol were found to be the most efficient. Enhancement of conductivity is believed to be a result of an increased interchain interaction caused by conformational change of the PEDOT chains from the coil structure into expanded-coil or linear structures (Ouyang, 2004).

In this work, we studied the effect of addition of ethylene glycol, ethanol and surfactant on dynamic and static surface tension of PEDOT: PSS dispersions. Dynamic contact angle of resulting ink was measured in order to examine its wetting behavior on poly(ethylene terephthalate) (PET) substrate before and after corona treatment. Surface topography and conductivity of resulting films on glass substrates as well as on PET were also measured.

Materials and Experimental Procedures

Materials

The conductive polymer (Baytron[®] P) dispersion was obtained from H.C.Starck GmbH & Co, which contains 1.2-1.4% of PEDOT: PSS in water. Three different types of PEDOT: PSS based inks were prepared. Other materials, such as ethylene glycol, ethanol and TWEEN80 (nonionic surfactant) were purchased from Sigma Aldrich. Ethylene glycol was used in the formulation of PEDOT: PSS based inks to enhance conductivity. Ethyl alcohol and TWEEN80 were used to decrease surface tension of the PEDOT: PSS dispersion. Table 1 shows the tested ink compositions and ID's that will be used throughout this article.

Table 1: Composition of tested PEDOT: PSS based inks.

Ink ID	Ink Composition
PEDOT: PSS	Pure PEDOT: PSS (Baytron[®] P)
EG-PEDOT: PSS	Ethylene Glycol in PEDOT: PSS (50% v/v)
EtOH-EG-PEDOT: PSS	Ethanol in EG-PEDOT: PSS (25% v/v)
TWEEN80-EG-PEDOT: PSS	Surfactant Tween80 in EG-PEDOT: PSS (0.31 wt %)

Procedures

A SensaDyne Tensiometer was used to measure dynamic surface tension of the inks during addition of ethylene glycol, ethanol and surfactant to the PEDOT: PSS dispersion. This test is using the maximum differential bubble pressure method (Klaus, 1983) based on creation of air bubbles in the fluid, at the end of

two orifices with different diameters. The differential pressure of the formed bubbles is measured and the surface tension of the liquid is directly proportional to the pressure difference.

Measurement of the static surface tension of inks was done using the contact angle analyzer FTA200 from First Ten Angstroms. The values of ink surface tension were calculated from the pendant drop (Andreas, 1938) shape of the ink.

Wetting behavior of inks was tested by measuring dynamic contact angle using the FTA200. The values of contact angle were calculated from the sessile drop (Nutting, 1941). PET (DuPont) was used as a substrate for contact angle measurements. Corona treater (SOA, Inc.) was applied in order to increase surface energy of the PET substrate (Thomas, 1982).

In order to observe the changes in surface topography of PEDOT: PSS based films; the tested inks were solution casted onto a glass slides and dried for 30 minutes at 120 °C. White Light Interferometry in the Vertical Scanning Mode (WYKO RST-Plus microscope) was used to study topography of the resulting films. White light interferometry is a non-contact method for optical surface profilometry of various surfaces (Caber, 1993). In vertical scanning mode (VSI), the interferometric lens scans the surface at varying heights by vertical movement through the focus and captures interference data at fixed intervals. The interference signal for each point of the sample surface is recorded, providing information about the fringe modulation, which is consequently used to calculate the surface height profile (Veeco, 1999). Another method for surface topography characterization employed in this study was Atomic Force Microscopy (AFM). Autoprobe CP machine (Thermomicroscopes, USA) operated in a tapping mode and with typical scan sizes from 30 x 30 µm2 down to 2 x 2 µm2 was used to study the morphological features at different levels of structural organization and depending on the preparation conditions of the samples. Root mean square (RMS) roughness was then measured and used as a parameter characterizing perfectness of the polymer film on glass.

The conductivity of PEDOT:PSS based inks casted on glass was measured using Keithley 2400 multimeter in four-probe mode. Measured resistance, cross-sectional area, and length of tested film sample can be used to calculate resistivity, ρ (Ω-cm). The inverse of resistivity yields conductivity (S/cm).

Results and Discussion

Surface Tension of PEDOT: PSS based Inks

Firstly, ethylene glycol was added to the PEDOT: PSS dispersion. This addition caused decrease of static surface tension of PEDOT: PSS ink from 70.7±0.7 to 59.3±0.2 dyn/cm as measured by the pendant drop method. However, surface tension of EG-PEDOT: PSS measured under dynamic conditions is higher than

the static (equilibrium) surface tension and depends strongly on time of interface existence - surface age. For shorter surface age, the alcohol molecules have less time to migrate onto the newly created interface and thus the surface tension is higher than that measured under equilibrium conditions (Figure 2).
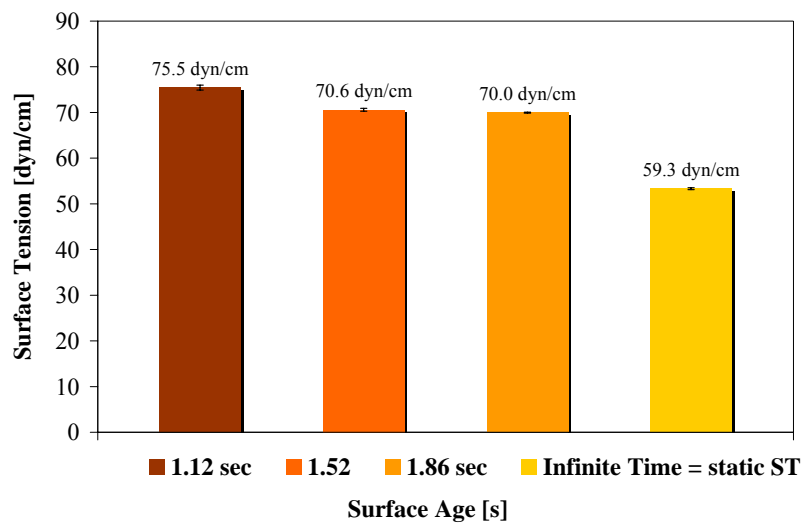

Figure 2: Dynamic surface tension of EG-PEDOT: PSS ink.

Figures 3 and 4 show the change in dynamic surface tension and bubble frequency of EG-PEDOT: PSS ink during addition of ethanol and nonionic surfactant TWEEN80, respectively. It can be seen, that addition of alcohol into the system caused gradual decrease in surface tension within the measured range of ethanol addition. It has been reported (Sharma, 1989) that the surface tension decreases relatively slow or is almost constant when the ethanol content in ethanol/water mixture is exceeding 20 vol%. Therefore and also due to low concentration of polymer, we have used only up to 20 vol% of ethanol in this work. In the case of the surfactant TWEEN80 (Figure 4), the initial drop in surface tension is more dramatic and further addition of surfactant caused rather slow decrease in surface tension, indicating that the system is above the CMC of the tested surfactant at the measured bubble frequency. This conclusion is also confirmed by a steady bubble frequency observed.
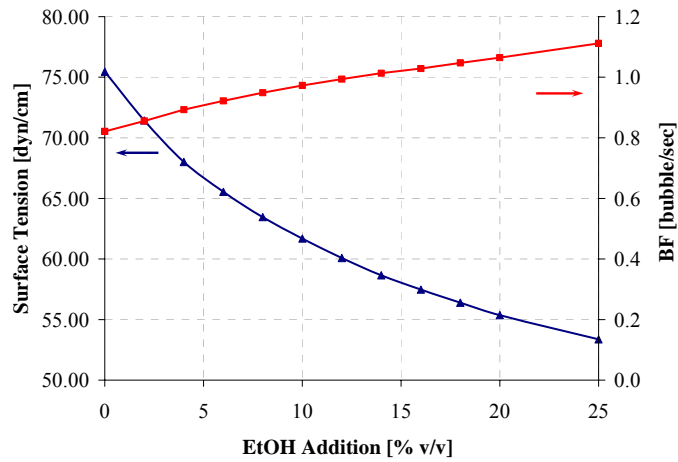
Figure 3: Surface tension and bubble frequency changes during addition of ethanol to EG-PEDOT: PSS ink.
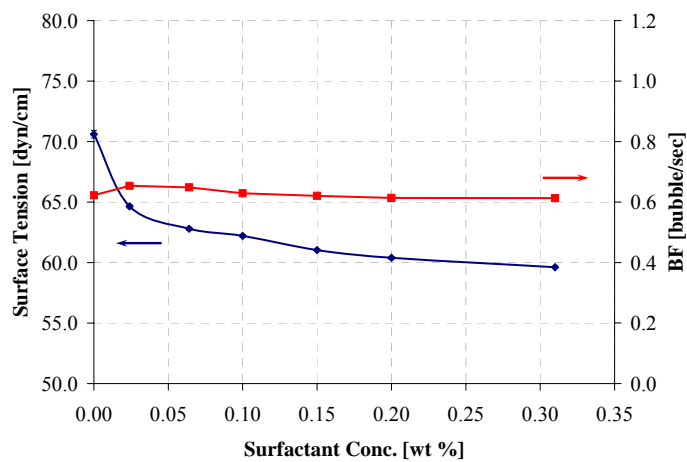

Figure 4: Surface tension and bubble frequency changes during addition of TWEEN80 to EG-PEDOT: PSS ink.

Static surface tensions of the tested inks are shown in Table 2. The "rule of thumb" in the printing industry is to have the surface tension of ink at least 10 dyn/cm lower than the surface energy of the substrate to be printed on. Typical

values of static surface tension for water-based inks used in gravure or flexo printing are in the range of 28 - 45 dyn/cm (Podhajny, 1989). The lowest surface tension was found for EtOH-EG-PEDOT: PSS ink. However, printing of such ink might be still problematic for some polymeric substrates with lower surface energy.

Table 2: Static surface tension of tested PEDOT: PSS based inks.

Ink ID	Static Surface Tension [dyn/cm]
PEDOT: PSS	70.7 ± 0.9
EG-PEDOT: PSS	59.3 ± 0.2
EtOH-EG-PEDOT: PSS	37.4 ± 0.2
TWEEN80-EG-PEDOT: PSS	41.8 ± 0.1

Dynamic Contact Angle

The dynamic contact angle was measured for all prepared inks on corona treated PET substrate. As expected, the lowest contact angle was found for the ink with the lowest surface tension (EtOH-EG-PEDOT: PSS). It can be seen from Figure 5, that contact angle of pure PEDOT: PSS ink and inks containing only alcohols stabilizes after a short time (around 1.5 sec), corresponding to initial spreading of the ink drops on the substrate. In the case of surfactant-containing system, the contact angle has not reached the stable value even after 30 seconds and continued to decrease. Figure 6 shows the contact angle of TWEEN80-EG-PEDOT: PSS ink on PET substrate after 2, 5 and 10 minutes of observation.
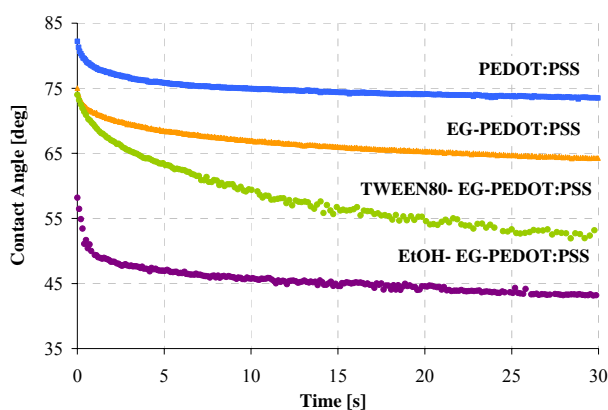

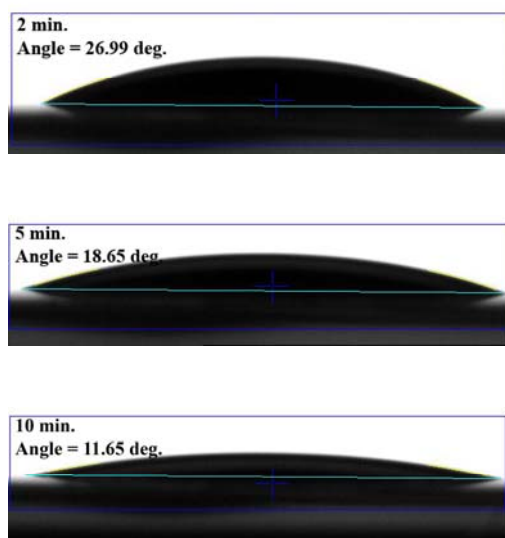**Figure 5:** Dynamic contact angle of PEDOT: PSS inks on PET substrate.

Figure 6: Contact angle of TWEEN80-EG-PEDOT: PSS ink on PET substrate**.**

Surface Topography

In order to avoid effect of the substrate and study only the effect of ink formulation of surface topography, conductive polymer films were solution casted on glass slides. It can be seen from Figure 7, that addition of alcohols into the PEDOT:PSS system significantly improves uniformity of the film surface at the millimeter scale (2.5×1.9 mm^2) as measured by vertical scanning interferometry (VSI). However, AFM scans made at micrometer scale (10×10 μm^2) show smoother surface of PEDOT:PSS films. EtOH-EG-PEDOT:PSS film show appearance of some larger domains, which can be a result of conformational change of polymer chains and swelling of PEDOT:PSS complex indicating stronger interchain interactions caused by alcohol addition (Ouyang, 2004). It was found that the RMS roughness of PEDOT:PSS film measured by VSI was reduced from 902 nm down to 67 nm by addition of ethylene glycol and ethanol. Simultaneously, the RMS roughness measured by AFM shows only 2.3 nm for PEDOT:PSS and 12.9 nm for EtOH-EG-PEDOT:PSS. A similar effect on RMS roughness measured by AFM was found for addition of glycerol into the PEDOT:PSS system (Snaith, 2005).
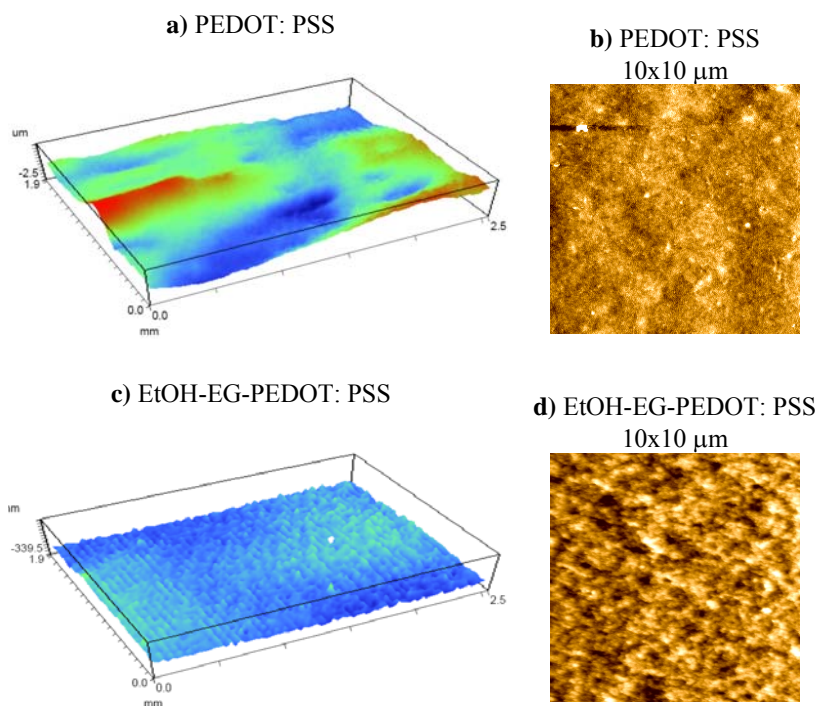
a) PEDOT: PSS

b) PEDOT: PSS
10x10 μm

c) EtOH-EG-PEDOT: PSS

d) EtOH-EG-PEDOT: PSS
10x10 μm

Figure 7: Surface topography of PEDOT: PSS and EtOH-EG-PEDOT: PSS
ink film on glass substrate as studied by a), c) VSI and b), d) AFM.

Conductivity

The electrical conductivity of the PEDOT:PSS based inks was calculated from
resistance measurements on casted films. As it was previously reported, addition
of ethylene glycol to PEDOT:PSS dispersion enhances conductivity of the
resulting films up to 200 S/cm (Ouyang, 2004). In our case, addition of 25 vol%
of ethylene glycol resulted in conductivity increase from 5.3 to 92.1 S/cm.
Addition of ethanol to EG-PEDOT:PSS caused a decrease in conductivity. On
the other hand, the presence of surfactant TWEEN80 in EG-PEDOT:PSS has led
to slightly increased conductivity (Table 3).

Table 3: Conductivity of tested PEDOT:PSS based inks.

Sample ID	Conductivity [S/cm]
PEDOT:PSS	5.3 ± 0.1
EG-PEDOT:PSS	92.1 ± 0.1
EtOH-EG-PEDOT:PSS	62.4 ± 0.2
TWEEN80-EG-PEDOT:PSS	115.6 ± 2.1

Conclusions

Organic electronics are already being introduced into the market. A way to reduce the cost of organic electronics would be development of roll-to-roll production methods, where individual components of integrated circuits are deposited onto the plastic or even paper substrates. Conductive polymers are just one class of organic materials that can be used for active components of low-cost electronic devices. An essential requirement for materials to be printable is to be processable through solution state. Despite the fact that there are already several "top" candidates from the group of conductive polymers selected for such applications more research is needed in the field. Wetting property of polymer solutions on various surfaces and the quality of the resulting surface layer are of crucial importance. There are many different arrangements of polymer/polymer interfaces for scientists to be examined and controlled in order to find the most suitable combination of materials for printed electronics applications.

This work was focused on modification of PEDOT:PSS aqueous solutions by addition of alcohols (ethylene glycol and ethanol) and non-ionic surfactant. PEDOT:PSS based inks were first characterized in terms of dynamic and static surface tension and dynamic contact angle on PET substrate. It was found that addition of ethylene glycol to PEDOT:PSS solution lowers the static surface tension by 11 dyn/cm. Further decrease can be achieved by addition of ethanol or surfactants. Dynamic contact angle measurements have revealed that the surfactant-containing ink did not reach equilibrium contact angle within the time of measurement and continued to decrease. Surface topography studies reveled that addition of alcohols into PEDOT:PSS solution helped in improving the resulting film roughness on a millimeter scale, however the opposite effect was detected at the micrometer range.

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