Conductivity of inkjet-printed PEDOT:PSS-SWCNTs on uncoated papers

Peter D. Angelo, Gregory B. Cole, Rana N. Sodhi and Ramin R. Farnood

KEYWORDS: Inkjet printing, PEDOT:PSS, Carbon nanotubes, Conductive ink, ToF-SIMS

SUMMARY: Poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate), or PEDOT:PSS, as well as single-walled carbon nanotubes, were incorporated into an inkjet ink. Handsheets were prepared which contained varying amounts of TiO₂ filler, internal sizing agent, fixation agent, and either softwood or hardwood kraft pulp. The ink was jetted onto the handsheets to form conductive layers with apparent conductivity as high as 0.018 S/cm on internally alkylketene dimer-sized softwood kraft handsheets with no other additives. Internal sizing increased conductivity at low filler loadings by preventing PEDOT:PSS from penetrating into the substrate, resulting in a conductive ink film on the surface of the sample. Unsized handsheets allowed more rapid absorption, and therefore deeper penetration, of the PEDOT:PSS ink, which resulted in a more diffuse conductive layer. The inclusion of a polyethylenimine retention aid for TiO₂ filler decreased conductivity significantly even in unfilled sheets by interaction with PSS counterions. A positively charged fixation agent, poly(diallyldimethylammonium) chloride, reduced PEDOT conductivity through the retention of non-conductive PSS anions.

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Over the last several years, the use of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), also known as PEDOT:PSS, in printed electronics has attracted interest due to its high optical transmittance, tunable electrical conductivity, and ease of processing by wet methods such as spin-coating or inkjet printing (Ouyang et al. 2003). PEDOT:PSS, in printed electronics, has a broad range of applications, from solar cells to displays and sensors. PEDOT:PSS layers rather than printed ones (Denneulin et al. 2008; Agarwal et al. 2006, 2009). As the substrate itself appears to cause variability in conductivity, however, either coated or printed layers are likely to interact with it in a similar fashion. In general, the roughness of the substrate plays a major role in the conductivity of any films deposited on it. Furthermore, in the case of paper, chemical interactions such as adsorption to the cellulosic components of paper (Montibon et al. 2009) or the inorganic coatings (Agarwal et al. 2006) can lead to wide variability in conductivity. Polyelectrolytes contained in the paper may also alter conductive layer structure and performance (Agarwal et al. 2006, 2009). Paper, being hygroscopic, also tends to absorb the aqueous PEDOT:PSS suspension into its fibres. These and other physicalchemical interactions make paper-based conductive PEDOT films complex systems with unpredictable electrical properties.

To enhance the conductivity of PEDOT:PSS films, the addition of single-walled and multi-walled carbon nanotubes (SWCNTs and MWCNTs) has been considered in the literature (Kymakis et al. 2007; Moon et al. 2005; Bhandari et al. 2009; Mustonen et al. 2007, Agarwal et al. 2006, 2009). In particular, Mustonen et al. (2007) showed that aqueous dispersions of PEDOT:PSS-SWCNTs can be deposited relatively uniformly by inkjet printing to form translucent conductive films.

Inkjet printing of PEDOT:PSS is highly desirable because the precision and flexibility offered by an inkjet printer is ideal for fine patterning of printed electronics without the use of labour- or time-intensive methods such as photolithography and vapour deposition. Stable inkjet inks are carefully formulated blends of components which control rheology, dispersion, foaming, microbial growth, and pH (Karsa 2005). Extensive research has been devoted to the preparation of inkjet inks using PEDOT:PSS as a conductive species, on a variety of printers (Garnett, Ginley 2004; Sankir 2008; Lopez et al. 2008). In our previous work (Angelo et al. 2009; Angelo, Farnood 2010a, 2010b, 2010c), we have prepared PEDOT:PSS-SWCNT inks and considered the optimization of conductivity, mechanical properties, and optical properties in jetted films of this material. Although paper has been used as a substrate in these studies, the effect of paper furnish on the conductivity of printed PEDOT:PSS-SWCNT films has not been
addressed. It was expected that the connectivity and hence
the conductivity of the printed ink would be affected by the
paper structure and constituents, i.e. fibres, fillers, sizing
agents, and so forth.

In this work, the role of the paper’s components in the
distribution of inkjet-printed PEDOT:PSS-SWCNT inks
and conductivity of the resulting layers is investigated. Handsheets with varying pulp type, filler content, internal
sizing, and fixation agent were prepared in the laboratory.
PEDOT:PSS-SWCNT inks were printed on the samples
using an inkjet printer and bulk resistance of printed
samples was obtained using a two-point measurement
technique. Using this approach, the interaction of paper
with inkjet-printed PEDOT:PSS-SWCNT films was
systematically investigated.

Materials & Methods

Handsheet characterization

Northern bleached softwood (SW) and hardwood (HW)
kraft pulps were used in this work. 40 g of oven-dried (OD)
pulp was soaked in 500 ml of deionized water for 12 h. The
excess water was pressed out of the pulp in order to
calculate consistency, which was 23-25% for both pulp
types. Pulp was then refined in a Noram refiner for 5100
revolutions after which 24 g (dry pulp weight) of refined
pulp was added to 2 L of water, and was then mixed in a
Durant disintegrator for 15000 revolutions. The resulting
slurry was made into handsheets containing 1.5 g dry pulp
per sheet, using a non-recirculating Noram sheet former
according to TAPPI Standard Method T-205. TiO₂ (≥ 99%,
Sigma-Aldrich) filler and alkylketene dimer (AKD) internal
sizing agent (Hercon 115, Hercules) were added to the pulp
slurry. Filler was added in 15 w/w% and 30 w/w%
(relative to the dry pulp weight) loadings. Internal sizing
agent was added at 0.8 w/w% on OD pulp basis. A
polyethyleneimine-based retention aid (Polymin SK, 30
w/w% active ingredient in water, BASF) was added to
sheets containing filler (0.83 g in a sheet containing 15
w/w% filler and 1.66 g in sheets containing 30 w/w% filler)
during sheet forming. An ink fixation agent, poly(diallyldimethylammoniumchloride) or PDADMAC
(Sigma-Aldrich), was added at 2 w/w% (OD pulp basis)
during sheet forming. Handsheets were air dried in a
conditioning room at 25°C and 75% relative humidity for
24 h. All sheets were calendared at 80°C, 100 kPa and 3
nips using a Beloit Wheeler laboratory calendar, couch side
up.

Handsheets were characterized for thickness using a TMI
micrometer at 10 different points on the sheet. Average
sheet thickness over a fixed area was also used to estimate
sheet density and thereby sheet grammage. Actual retained
filler content was determined by burning a portion of each
sheet of a fixed weight in an oven at 500°C for 1 h, at which
point the fibres were completely ashed. The weight of the
filler in the sheet was determined by the difference in ash
weights between a filled and unfilled sheet. The actual
weight percent of filler retained in the sheet was estimated
by dividing ash weight by the original sample weight
(before burning). Micrographs of the unprinted handsheets
were obtained using a JEOL-7001 JSM scanning electron
microscope (SEM). Filler and surface pore distribution
were observed using the backscattered electron (BSE)
detector on the SEM to improve contrast between the filler
and fibres. Contact angle was estimated using an aqueous
solution of crystal violet dye (test ink) prepared according
to TAPPI Standard Method T431 for measuring ink
absorbency into paper. The test ink had a surface tension
of 62 mN/m. 30 µL of this ink was dropped with a calibrated
micropipette onto a handsheet, and the resulting drop was
immediately photographed from the side using a Canon
Rebel XT-ME DSLR camera with a MP-E 65 mm macro
lens. Finally, absorbency of the sheets was observed by
measuring the time for complete absorption of a 30 µL
sample of the same test ink into the surface. During this
test, the samples were placed directly under a 60 W
incandescent lamp elevated 30 cm from the test specimen’s
surface. Complete absorbency was defined according to
Test Method T431 as the point at which light reflection
from the droplet on the surface was no longer visible.

PEDOT:PSS-SWCNT ink formulation and printing

Details of the formulation of a PEDOT:PSS-SWCNT ink
with suitable fluid properties for inkjet printing have been
provided in our previous work (Angelo, Farnood 2010a)
based on guidelines described elsewhere (Daniel 2007; de
Gans 2004). All reagents were supplied by Sigma-Aldrich
Canada. The basis for the ink was PEDOT:PSS suspension
(1.3 w/w% in water). SWCNTs (50-70% CNT basis, 1.2–5
nm width, 2.5 µm length) in water and sodium lauryl
sulfate (0.04 w/w% SWCNTs, 0.1 w/w% sodium lauryl
sulfate) solution were dispersed into the inks using an
ultrasonic mixer. The final optimized ink composition
was 35 w/w% DI water, 34 w/w% PEDOT:PSS suspension,
17 w/w% glycerol, 10 w/w% DMSO, 3 w/w% SWCNT
solution, 0.5 w/w% SLS, and 0.5 w/w% defoamer. This
ink met the criteria for stable drop formation and jetting
(FUJIFILM-Dimatix 2006), with a viscosity of 2.2 cP,
surface tension of 30.2 mN/m, and average particle size of
200 nm.

8 mm × 8 mm solid square patterns of PEDOT:PSS-
SWCNT ink were inkjet-printed onto each handsheet using
a FUJIFILM-Dimatix DMP2831 piezoelectric printer and
cartridge (10 pl drop volume). Jetting behaviour was
optimized by adjusting the drive voltage-time waveform for
the piezoelectric printhead, to produce stable, spherical
drops. 3 layers of ink were printed on the couch side of
each sheet, and printed samples were immediately dried at
100°C for 20 min on a hot plate.

Conductive film characterization

Time-of-flight secondary ion mass spectrometry (ToF-
SIMS) was used to map the distribution of PEDOT and PSS
ions and ion fragments relative to the paper fibres.
Table 1a. Negative ToF-SIMS ion fragments.

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<th>Species</th>
<th>Source</th>
<th>Ion</th>
<th>m/z</th>
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<td>Ink (PSS)</td>
<td>C₈H₆O₅⁻</td>
<td>183</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Ink (PEDOT)</td>
<td>C₈H₆O₅⁻</td>
<td>139</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₈H₆O₅⁻</td>
<td>138</td>
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<tr>
<td></td>
<td></td>
<td>C₂O₂S⁴⁻</td>
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<tr>
<td></td>
<td></td>
<td>C₂O₂S⁴⁻</td>
<td>136</td>
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</table>

Table 1b. Positive ToF-SIMS ion fragments.

<table>
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<th>Ion</th>
<th>m/z</th>
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</thead>
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<tr>
<td></td>
<td>Surfactant</td>
<td>Na⁺</td>
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</tr>
<tr>
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<td>Fibres</td>
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<td>127</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂H₃O₃⁺</td>
<td>145</td>
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<tr>
<td></td>
<td></td>
<td>C₂H₃O₃⁺</td>
<td>161</td>
</tr>
<tr>
<td>Additives</td>
<td>PDADMAC</td>
<td>C₆H₇N⁺</td>
<td>126</td>
</tr>
<tr>
<td></td>
<td>Retention aid</td>
<td>C₆H₇N⁺</td>
<td>43</td>
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</table>

and filler. An ION-ToF ToF-SIMS IV apparatus was used to perform the measurements. A Bi primary ion gun was used to induce ion ejection and fragmentation. Images of the samples’ surfaces were obtained using the high-spatial-resolution detector. The imaged areas had a size of 100 μm ×100 μm, with a spatial resolution of 390 nm. Both positive and negative ion spectral maps were obtained. A full peak list is shown in Table 1; identification of the cellulosic fragments was based on the work of Fardim & Holmborn (2005), Sokhi et al. (2008) and Delandes et al. (1998). It is important to note that the secondary ion masses listed were variable by several mass units due to protonation or deprotonation of the fragments, a common occurrence in ToF-SIMS analysis of organic species (Lua et al. 2005).

The thickness of the conductive layer was estimated by imaging cross-sections of the printed samples, and observing the dark-coloured PEDOT-SWCNT layer on the surface and in the bulk of the sheet. Samples were fastened between two glass slides with double-sided tape and a cross-section was cut along the edges of the slides using a surgical scalpel. Images were captured using a Leica DMLA optical microscope and attached camera. Several images were captured at various focal depths and stacked to generate an in-focus section using CombineZ software (Hadley 2009). The section was then converted to a greyscale image – the dark-coloured ink appeared as a darker grey. The image was then colour-inverted, and the grey levels at or above the ink colour were highlighted using thresholding in ImageJ software, highlighting only the inked region. The highlighted inked region was then measured as a %–area of the entire image. Multiplying the %–area by the image dimension parallel to the layer thickness gave an average layer thickness for the sample.

Sheet resistance, R, was measured using a two-point method, described by Heaney (2000). To perform this measurement, two bus bars of carbon paint were applied along opposite edges of the printed squares, and a silver contact was painted on each. The two-point method with bus bars as contacts was used due to the irregular penetration depth of the conductive ink observed in the sample. The bulk resistance was determined across the printed samples using a multimeter (Innova Electronics Corporation). Also, a mega-ohmmeter (GenRad 1863) was used to measure the resistance of the unprinted base paper sheets prepared in the same fashion. Ohmic behaviour of the ink films and the base sheets was confirmed by increasing the input potential of the megaohmmeter when applied to the samples and noting that the resistance did not change significantly between applied voltages of 0.1 – 100 V. Finally, any effect of retained moisture on resistance was examined by measuring resistance across several sheets before and after 30 minutes of dessication in a vacuum oven at 40°C and 1 Torr. Resistance did not vary as a result. Conductivity, σ, was estimated by measuring the film thickness (h) from cross-section images, as described above. According to the definition of conductivity in terms of resistance and film thickness:

\[ \sigma = \frac{1}{R \times h} \]

For homogeneous materials, σ is a fundamental material property. However, because the PEDOT-SWCNT ink penetrated into the paper structure, σ was an apparent property which depended on the variations in the structure of the conductive layer.

**Results & Discussion**

**Handsheet properties**

For this study, 24 separate handsheets were prepared (Table 2). Also, control handsheets, containing retention aid but no filler, were prepared, to assess the effect of retention aid itself on conductivity. The handsheets containing AKD generally had greater grammage values. At the same filler levels, the HW handsheets retained more filler than the SW sheets. Higher filler retention in HW sheets was likely due to differences in the fibre morphology and hence in the sheet structure (Gullichsen, Paulapuro 1999). BSE imaging of the handsheets’ surfaces confirmed that the wider SW fibres created sheets with larger surface pores and larger clusters of TiO₂ filler, whereas narrow HW fibres formed handsheets with many smaller pores and more uniformly distributed TiO₂ (Fig 1). There were also significantly larger clumps of filler in the sized sheets when compared to the unsized sheets, where filler was distributed evenly among the fibres. It is possible that the AKD internal sizing served as an additional retention aid during sheet forming, leading to both the higher filler amounts (Table 2) and larger concentrations of TiO₂ (Figs 1g, 1h), and greater sheet grammage. Based on Table 2, the conductivity of the base sheets varied in the range of about 1–4 nS/cm, but in general was insignificant compared to the conductivity of the printed PEDOT:PSS-SWCNT films, as described in subsequent sections. Therefore, the paper components themselves would not be capable of significant charge transport and that their physicochemical interactions with
the PEDOT-SWCNT ink were the determining factor in conductivity variation in the printed sheets. Table 2 also shows that the surface properties of the sheets were noticeably affected by the pulp type and the presence of additives. The unsized HW sheets generally showed more rapid wetting and ink absorbency than the corresponding SW samples. This suggested the presence of a relatively fine pore network in the HW sheets capable of rapid absorption of aqueous inks, which was absent in the case of sheets containing large, flat SW kraft fibres. As expected, surface wetting and absorbency were greatly reduced in the presence of AKD sizing (Fig 2). Absorbency was particularly low in sheets containing sizing, which in the case of the printed PEDOT:PSS ink lead to increased retention of conductive material at the sheet surface. There were also moderate decreases in contact angle, indicating improved wetting, with increases in filler content. This was caused by the reduction in volume of sized fibres – i.e. more of the sheet was composed of TiO$_2$ particles which were not sized, and therefore more easily wetted by the ink. Table 2 also suggests that the cationic fixation agent, PDADMAC, was able to bind to the ink as it penetrated through the substrate, resulting in improved wetting, but not necessarily in a faster rate of absorbency, as ink would be bound in the upper layers of the sheet rather than soak into the untreated fibres. Therefore, depending on the distribution of PDADMAC in the sheet, the ink absorbency might increase or decrease with the addition of fixation agent.

Conductivity of printed handsheets

Printing of the liquid PEDOT:PSS-SWCNT ink onto the porous, absorbent handsheets naturally resulted in the penetration of the conductive species into the paper. This had an effect on the connectivity and hence conductivity of printed PEDOT:PSS-SWCNT patterns. The conductivity of printed SW and HW handsheets can be found in Fig 3. Conductivity of these samples was four (4) orders of magnitude smaller than the bulk conductivity of PEDOT (Crispin et al. 2003), but was comparable to that reported in our earlier work on paper-based PEDOT-SWCNTs. Despite slight differences in ink absorption rate and surface structure (Table 2), there was little if any difference between SW and HW handsheets in terms of conductivity.

TiO$_2$ filler and retention aid

The plot of measured conductivity versus actual retained filler content (shown as “Ash” in Table 2) in Fig 3 shows that with the addition of TiO$_2$ (and therefore retention aid) conductivity of printed HW and SW handsheets decreased by nearly two orders of magnitude. However, this decline was primarily due to the presence of the retention aid, as the control sheets – containing appropriate amounts of Polymin SK but no actual TiO$_2$ – performed similarly to those with both filler and retention aid. The dashed horizontal lines in Fig 3 show the measured conductivity on these Polymin SK-loaded control sheets, which is similar to that in the handsheets containing both Polymin SK and TiO$_2$. This suggested a chemical or physical interaction between the conductive components of the ink and the Polymin SK which compromised conductivity. It is worth noting that conductivity was slightly higher in sheets containing Polymin SK and TiO$_2$ over the control sheets containing only Polymin SK, because of the interaction of the Polymin SK with TiO$_2$, which reduced the amount of Polymin SK interacting with the ink components. The above observations suggest that an interaction between the Polymin SK and the PEDOT:PSS-SWCNT ink took place resulting in compromised electrical performance.

Fig 1. SEM BSE micrographs of handsheets’ surfaces. None of the sheets shown contain fixation agent. (a) HW, 0% filler, unsized; (b) HW, 0% filler, sized; (c) HW, 30% filler, unsized; (d) HW, 30% filler, sized; (e) SW, 0% filler, unsized; (f) SW, 0% filler, sized; (g) SW, 30% filler, unsized; (h) SW, 30% filler, sized.
The most likely interaction is the neutralization of the excess ionic charge provided by the PSS counterion in the ink, a function for which polyethyleneimide (PEI), the active component of the retention aid, is known (Neimo 1999). Furthermore, due to this strong interaction with the PEDOT:PSS complex, non-conductive PEI was likely incorporated within the conductive layer, dramatically reducing conductivity of the layer as a whole. This type of interaction has been previously exploited by Lin et al. (2007) for modulation of PEDOT:PSS conductivity by five orders of magnitude at a ratio of PEDOT:PSS to PEI of 1:1. However, in the case of printed handsheets, PEI was dispersed throughout the sheet in a relatively low concentration, and hence had a less drastic effect on conductivity was observed. Furthermore, this effect was mitigated by washout of retention aid during the handsheet forming process, producing the plateau at $10^{-4}$ S/cm observed in Fig 3. These results suggest that the effect of the filler itself on conductivity was evidently negligible compared to PEDOT interaction with PEI. ToF-SIMS mapping of PEDOT, TiO$_2$, and PEI (Figs 4 and 5) confirms that the presence of isolated clusters of TiO$_2$ did not disturb the spatial distribution of PEDOT in the handsheets. This observation implied that these clusters of TiO$_2$ were also saturated with the conductive ink, and the filler species did not interrupt the conductive path. Hence, in the absence of retention aid, finely divided filler particles are expected to have little or no effect on the conductivity of paper-based printed PEDOT-SWCNT films. However, with the addition of a strongly positively-charged retention aid, filler can increase conductivity by binding to the retention aid, thereby diminishing its interaction with the PSS counterion. ToF-SIMS images of printed handsheets also revealed that PEDOT and PSS were located in exactly the same regions (Figs 5a and 5b), but were less concentrated where PEI was localized (Fig 5c). The resulting non-uniformity of the conductive layer would have an adverse effect on the conductivity of filled handsheets. Comparing Fig 5c and 5d, it appears that a very small amount of PEI is actually interacting with the TiO$_2$, and the majority resides in or on the fibres, where it can readily interact with the PSS. In fact, ToF-SIMS peaks for Ti$^{4+}$-PEI ($m/z = 91$) and TiO$_2$-PEI ($m/z = 123$) were very weak, suggesting that little PEI was adsorbed or bonded to the surface of the filler, leaving the rest to freely interact with PSS in or on the fibres. These observations are consistent with the hypothesis that PEI-PSS interaction was primarily responsible for increased electrical resistance.

**PDADMAC fixation agent**

The addition of fixation agent, PDADMAC, decreased conductivity of the printed handsheets, and this effect was more pronounced at higher filler addition levels (Fig 6). With a similar effect to the retention aid, this was likely caused by the interaction of the cationic PDADMAC with the PSS counterion and the introduction of non-conductive PDADMAC into the PEDOT film. However, the lower

### Table 2. Handsheet properties.

<table>
<thead>
<tr>
<th>Pulp (filler w/w%)</th>
<th>AKD (w/w%)</th>
<th>PDADMAC (w/w%)</th>
<th>Grammage (g/m$^2$)</th>
<th>Conductivity (nS/cm)</th>
<th>Contact angle (°)</th>
<th>Ink absorbency (µl/min)</th>
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<tr>
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<td>✔</td>
<td>0.049</td>
<td>95</td>
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<td>53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>✔</td>
<td>16.1</td>
<td>100</td>
<td>2.35</td>
<td>97</td>
</tr>
</tbody>
</table>
Fig 2. Contact angle of test ink on HW pulp, 30% filler: (a) no additives; (b) sized; (c) fixed; (d) fixed and sized.

Fig 3. Conductivity as a function of added filler for handsheets with SW pulp (squares), and HW pulp (circles). Dashed lines (a) and (b) represent the conductivity in handsheets containing retention aid but no actual TiO$_2$. Error bars represent standard deviation.

Fig 4. Distribution of TiO$_2$ in HW and SW handsheets (unsized, no fixation agent). (a) HW, 0% filler; (b) HW, 30% filler; (c) SW, 0% filler; (d) SW, 30% filler.

Fig 5. Relative distribution of PEDOT:PSS, PEI, and TiO$_2$. Sheets contained SW fibres, 30 w/w% filler during sheet forming and no internal sizing or fixation agent. (a) PEDOT; (b) PSS; (c) PEI; (d) TiO$_2$. 
Fig 6. Estimated conductivity of PEDOT-SWCNT printed ink on SW fibres: (a) unfurnished (b) PDADMAC fixation agent. Error bars represent standard deviation.

concentration of PDADMAC versus PEI resulted in a smaller decrease in estimated conductivity. In addition, the highly-charged, cationic nature of PDADMAC may also have caused agglomeration of the PEDOT or SWCNTs after printing due to destabilization of these suspensions through interaction with the PSS and lauryl sulfate dispersants. Such an interaction would create a non-uniformly distributed conductive ink and hence a lower sheet conductivity. The non-uniform distribution and the apparent agglomeration of both PEDOT and PSS in the ToF-SIMS maps of handsheets containing PDADMAC supported this theory (Fig 7). With increasing filler levels, the detrimental effect of PDADMAC also became more pronounced as the contact angle decreased (Table 2). A lower contact angle implied better wetting and penetration of PEDOT:PSS into the sheet, and hence reduced conductivity.

Internal AKD sizing

The most notable effect on conductivity aside from that of PEI was that of internal sizing (Fig 8). In every case, the addition of sizing agent resulted in an increase in conductivity. As shown in Table 2, internal sizing decreased ink spreading and absorption by increasing the contact angle of the ink. Therefore, a more uniform ink layer (containing fewer non-conductive fibres/filler particles) with higher connectivity and conductivity was obtained. Moreover, the ink absorption rate was reduced by several orders of magnitude in the sized sheets, allowing a longer time for the ink to rest on the surface during drying of the PEDOT-SWCNT ink. Cross-sectional images confirmed the presence of a relatively thin PEDOT-SWCNT layer on the sized sheets. Fig 9 shows the cross-sections of printed SW handsheets (30% filler) for an
internally AKD sized handsheet and an unsized handsheet. In the case of the sized sheet, the PEDOT-SWCNT ink (blue-coloured) is concentrated near the surface of the sample while in the latter case ink is distributed throughout the sheet thickness.

The positive effect of AKD sizing appeared to be more pronounced for handsheets containing retention aid and/or fixation agent. In other words, AKD sizing appeared to largely eliminate the adverse effects of PDADMAC and PEI that are distributed throughout the sheet, by reducing the amount of contact of the conductive ink with these molecules.

Because of this correlation between ink “holdout” in the printed sheets and the performance of the conductive layers, paper with minimal porosity and high hydrophobicity (for aqueous inks, at least) should be considered ideal for electrically conductive paper production. The performance of such materials might be improved by the deposition of larger amounts of ink, as the initial print passes would fill the pores and become absorbed into the fibres and filler clusters, providing a less absorbent surface for subsequent print passes. However, this approach would of course consume more ink and require more processing time to achieve similar performance to appropriately sized sheets.

The significant improvement in conductivity across all the sheets resulting from internal sizing is likely more easily and economically achieved by sheet pretreatment.

Another variable that might assist in improving conductivity, in the same vein, is sheet smoothness. A rougher sheet, whether it be sized or not, provides greater surface area for ink absorption and improved wetting, and is expected to result in a considerably more irregular conductive film and a lower conductivity. In fact, a brief examination of printed PEDOT-SWCNT layers for uncalendered handsheets revealed that their conductivity was close to those of the base sheets themselves (not shown). The universal calendering of the handsheets used in these experiments provided a high degree of smoothness, improving the ink holdout and conductivity of printed samples.

ToF-SIMS mapping of the ink components on the sized handsheets further confirmed the improved ink retention on the sheet surface. It is evident in Fig 10 that internal sizing allowed the PEDOT ink to coat the surface of the sheets to a greater degree, rather than being absorbed into them, resulting in a larger proportion of interconnected PEDOT-SWCNT regions. However, there was still not a completely contiguous PEDOT/PSS/SWCNT layer on the surface of the sized sheets, and fragments of cellulosic materials and filler were clearly visible in the spectral maps. As is also shown in Fig 9, even sized sheets absorbed the ink to a certain degree. However, it is worth noting that the intensity of the PEDOT signal in the ToF-SIMS maps of sized sheets was significantly higher indicating a higher concentration of conductive ink on the surface of the sized samples.

![Fig 9. Cross-sections of printed SW handsheets (30% filler): (a) internally AKD sized; (b) unsized.](image)

<table>
<thead>
<tr>
<th>% covered by PEDOT</th>
<th>(a) sized HW: 45.9%</th>
<th>(b) unsized HW: 25.6%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c) sized SW: 40.2%</td>
<td>(d) unsized SW: 25.1%</td>
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</tbody>
</table>

Fig 10. ToF-SIMS images of PEDOT distribution in unfilled, unfixed sheets. % coverage by PEDOT was estimated using grey-level thresholding.
Once again, the addition of PDADMAC and retention aid to the sized handsheets reduced conductivity (Fig 8). Therefore, the AKD sizing was not able to fully prevent the contact of the conductive ink with the PDADMAC and PEI distributed throughout the sheet. Indeed, both PEI and PDADMAC were detected by ToF-SIMS analysis on the sheet surface.

Conclusions

Moderately conductive paper was successfully produced by inkjet printing of PEDOT:PSS-SWCNT ink. The flexibility of inkjet printing, which allows for rapid patterning and is well-adapted to the use of paper as a substrate, makes it ideal for this application. The process represents an alternative to the use of metallic inks or metallicized paper fibres for conductivecellulosic materials. However, several layers of ink or adequate level of surface treatment may be required to achieve a desirable electrical conductivity.

Internal sizing can improve the ink holdout and therefore result in a higher conductivity by forming a thin layer of PEDOT:PSS on the surface of the paper. Papermaking additives, such as retention aids and fixation agents, could interact with PSS and/or other ink components and lower the connectivity and hence the conductivity of printed PEDOT:PSS films.

However, these values of conductivity are estimated from the dimensions of the ink layers. It should be emphasized that the key obstacle to objectively quantify the conductivity of printed PEDOT:PSS on paper arises from the irregularity and unpredictability of the ink distribution. Therefore, ideally, to optimize the performance of conductive papers, the uniformity of the paper itself needs to be controlled as tightly as possible. It is likely that the best result that can be offered for a given paper type is a range of conductivity values, which cannot be compared in an absolute sense to the conductivity of typical PEDOT-SWCNT structures, such as films. However, sized, unfilled paper provides a promising alternative and novel substrate for PEDOT-SWCNTs to be used as moderately conductive electrode or charge-injecting materials. It should be emphasized that this study deals with uncoated sheets; surface treatment of paper in the form of surface sizing and coating is an alternative opportunity that warrants its own systematic study.

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Literature


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