A Novel Screen-Printed Multi-Component Nanocomposite Ink with A Pressure Sensitive Electrical Resistance Functionality *

Alexander J. Webb, Sarah J. Dempsey, David Bloor, Adam Graham, Paul Laughlin, David Lussey, Marek Szablewski and Del Atkinson

***Abstract*— Here, a novel functional ink is described that is composed of multiple nanoscale components and exhibits pronounced touch pressure sensitive electrical properties ideal for applications in switching, sensing and touch sensitive surfaces. The ink can be screen-printed and the as-printed ink displays a large and reproducible touch pressure sensitive electrical resistance and, in contrast to some other composite materials, the resistance changes occur down to the smallest applied pressures. Detailed scanning electron microscopy shows the complex nanoscale structure of the composite that is critical for the electrical behavior. Current-voltage measurements, under static compressive loading, show monotonic non-linear behavior at low compression and ohmic behavior at higher loadings.**

I. Introduction

Printed electronics is an important area of commercial and academic activity. Examples of established functional applications include photovoltaics and RFID tags.[1,2] Another area of significant technological importance is that of printed touch sensitive components where applications include switching and location sensing. A key addition to touch sensitive components is the capacity to discern applied force, this would add a third dimension to the current x-y location functionality of current touch sensitive interfaces. Printable concepts for functional force and position sensing for resistive touch pad technologies have been previously demonstrated, however, they required additional printing and lithographic patterning on top of a resistive layer, in the form of a regular array of structural features, needed to enable the combination force sensing with the location sensing capacity.[3,4]

Ink-jet and screen-printed composites are available, primarily being applied for conductive tracks and electrodes, chemical sensors and thin film transistors.[5-8] This work presents a novel screen-printed composite ink, with electrical properties highly sensitive to compressive stress.

II. Experimental Techniques and Methods

The ink comprises acicular titanium dioxide needles, typically 1.6 µm by 100 nm, coated with a semi-conducing surface layer of antimony doped tin dioxide, and approximately spherical wide band-gap (essentially electrically insulating) titanium dioxide nanoparticles of mean diameter 200 nm, dispersed in an insulating polymer ink, such as a polyvinyl resin like Polyplast Type PY383.[9] The spherical nanoparticles have a dispersant surface coating, such as the commercially available Triton X, which aids their dispersion throughout the polymeric base and ensures a uniform distribution between the acicular particles. The conducting acicular and insulating spherical particles are blended in to the polymer ink until a homogeneous suspension is obtained. The ink was printed using a conventional manual load semi-automatic flat bed screen printer, with a 1 µm tolerance. After printing, the ink was dried at 90 °C for 30 minutes.

Test devices were made by printing the ink on to a polyethylene terephthalate (PET) substrate. The devices were constructed by successively printing a conducting silver track and carbon electrode, followed by a layer of the functional ink, on to a lower element of PET. The upper element comprised a silver track and carbon electrode printed on a complimentary PET substrate. The upper electrode was brought into registry with the lower element to form the test device. The device schematic and final appearance are shown in Fig. 1.

The structure of the as-printed ink was studied using a Hitachi SU70 Analytical scanning electron microscope. The devices were used in tests to determine the sensitivity of the inks' electrical resistance to compressive stress. This was undertaken using a Lloyd LRX test station using a Tricor Rubber Tip Model 933A force probe, conforming to ASTM standard F1578 that is intended to replicate the response of finger pressure on the device. The test devices were also

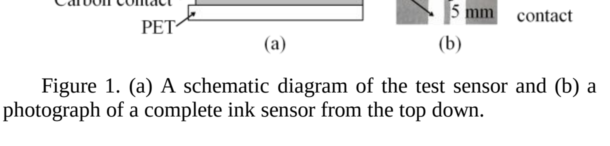

Figure 1. (a) A schematic diagram of the test sensor and (b) a photograph of a complete ink sensor from the top down.

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subject to current-voltage sweeps at fixed compression using a computer controlled Keithley 2420 and a custom compression rig based on a micrometer mechanism.

The voltage across the test device was varied from 0 V to 10 V at 0.1 V steps over 100 seconds, then decreased to 0 V at the same rate. This whole process was repeated for 10 cycles. Control devices comprising just silver and carbon electrodes on the PET were subject to I-V tests and showed only ohmic behavior and no pressure sensitivity.

III. Results and Discussion

The inks used in this study were made with filler particle concentration and size optimized for touch and location sensing. The results presented here are representative of all the samples studied.

A. *Physical Structure*

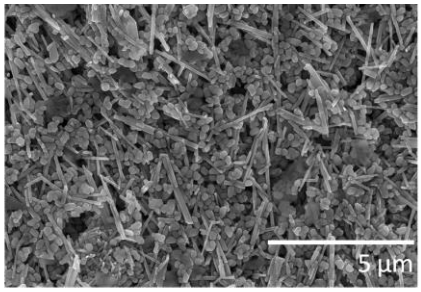
The structure of the as-printed ink, revealed by high-resolution SEM imaging, is shown in Fig. 2 (a). The acicular particles, while having the tendency to clump into aggregates of a few particles in some places, are widely dispersed across the surface, orientated randomly both on and into the ink surface. The approximately spherical nanoparticles, however, are more uniformly dispersed, and prevent the acicular particles from aligning with one another into a liquid crystal like structure, and likely prevent preferential alignment of the acicular filler during the printing process. Voids present in the ink layer lend to the inks' compressibility. This physical structuring is of great importance for the pressure sensitive conduction mechanisms. Fig. 2 (b) and Fig. (c) show histograms for the dimensions of the acicular filler particles and the diameter of the insulating nanoparticles.

B. *Electrical Behavior*

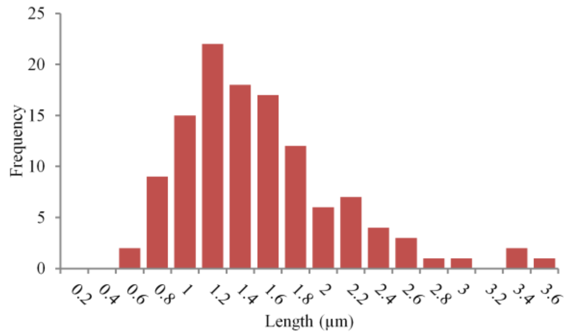
The touch pressure sensitivity of the electrical resistance as a function of compressive stress is shown in Fig. 3.

The initial resistance of the ink typically exceeds 10 MΩ. This indicates negligible contact between the ink surface and upper contact until a force is applied. A large decrease in resistance is observed for forces below 0.01 N. This response is likely due to increasing contact between the upper electrode and acicular particles lying out of the plane of the ink surface. By 0.1 N, the resistance has fallen to circa 7.5 kΩ. The rate of decrease with increasing force slows, indicating that intimate contact has been established between the electrode and the ink. This behavior contrasts with that of other composites which are largely insensitive to force below 5 N.[10,11] The resistance typically drops to circa 10^2 Ω with just 3 N of applied compression. At higher forces, compression of the ink body causes diminution of the void spaces in the ink layer and increasing close contact of the acicular particles. The resistance falls more gradually as the applied force increases. These changes are reflected in the nature of conduction in the device, as discussed below.

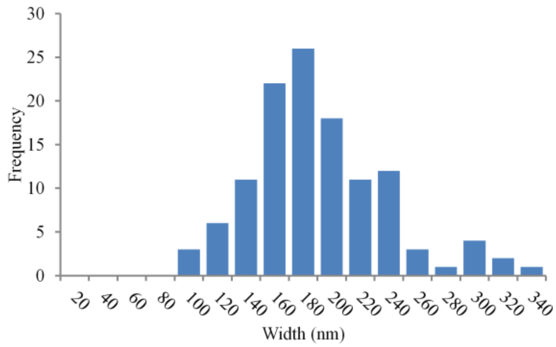
As part of the current-voltage analysis of the ink, the test devices were placed under a constant pressure. Some creep behavior was observed, with the resistance settling to a constant value after approximately ten minutes. At low



(a)



(b)



(c)

Figure 2. (a) A wide view of the ink surface, showing clumps of acicular semi-conducting particles and approximately spherical insulating nanoparticles dispersed across the surface. Voids in the printed ink are seen across the surface (b) Histogram of acicular particle length (c) Histogram of nanoparticle width.

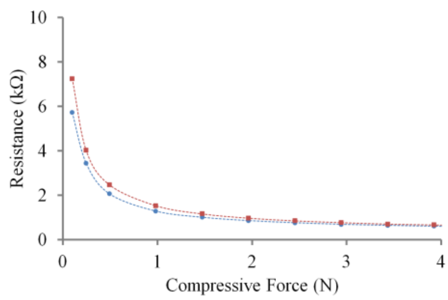


Figure 3. Data showing the relationship between the electrical resistance of the ink and applied force, averaged over 5 tests. Blue circles are data from the first compression to 10 N, red squares are data from after 1 million compressions.

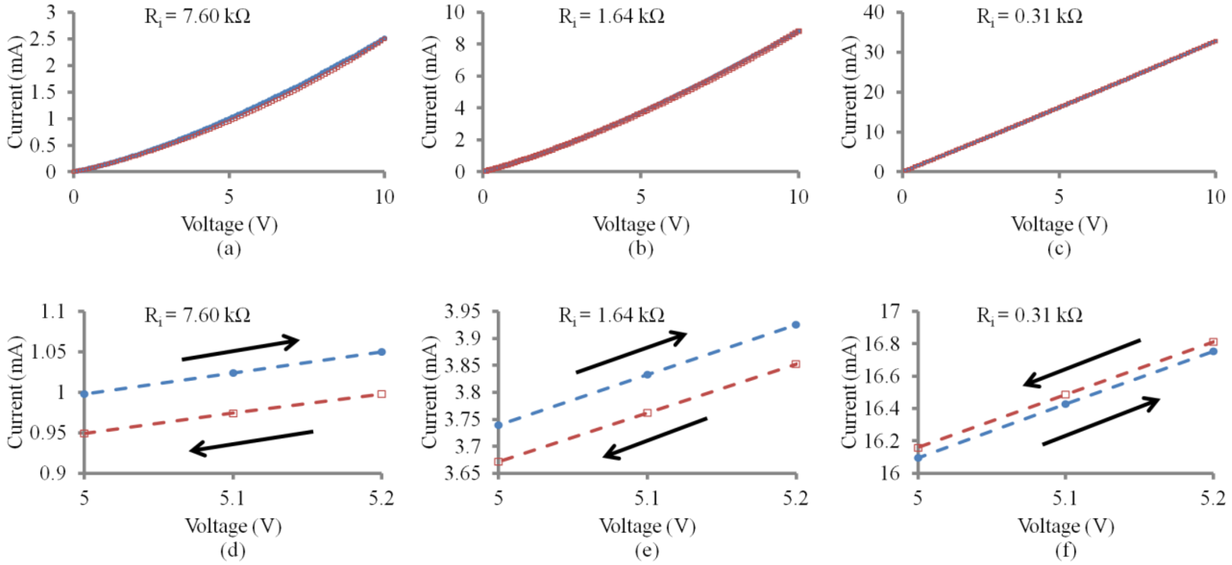


Figure 4. I-V curves taken at (a) low compression, (b) mid compression and (c) high compression. Blue solid circles indicate the ramp up of voltage, red open squares indicate the ramp down. As the compression is increases, the I-V characteristic becomes ohmic. Magnified areas of the I-V curves are shown in (d), (e) and (f). There is a small degree of hysteresis at all compressions, but the hysteresis reverses at the highest compressions. Error bars representing the error on the current measurements are smaller than the data points.

compression, the I-V characteristic is non-linear, with an increasing gradient at higher voltage. This is shown in Fig. 4 (a). At mid compression, Fig. 4 (b), the I-V is still non-linear. In contrast, the I-V is largely linear at high compression, though a very small non-linear contribution remains as shown in Fig. 4 (c). A small degree of hysteresis is observed in the I-V data at both low and high compressions, but is reversed at the highest compressions, shown in Fig. 4 (d), (e) and (f).

Work on composites with non-linear I-V characteristics, by He and Tjong (2011 and 2012), suggest a combination of linear ohmic percolative conduction and quantum tunneling internal field emission conduction mechanisms, given in (1), can describe the observed I-V characteristics well.[12,13]

$$J(E)_{TOTAL} = \sigma_0 E + AE^n \exp(-B/E) \tag{1}$$

Where $J(E)_{TOTAL}$ is the total current density, σ_0 is the linear conductivity (from percolative direct electrical contact between filler particles), A is a parameter related to the tunneling frequency and contains many correction factors, such as the field enhancement factor, E is the electric field, B is a value related to the potential barrier height and n is a constant that varies between 1 and 3, depending on the mode of tunneling, equaling 2 in the special case of Fowler-Nordheim tunneling.

Fitting of the model to the data in Fig. 5 (a) and (b) is good. The residuals in Fig. 5 (c) and (d) show that, while this model does not explain everything, it is certainly a good foundation to build upon in understanding the conduction mechanisms present in the ink. Values for the linear conductivity and parameter A were extracted for analysis with varying compression, shown in Fig. 6 (a) and (b). We see that both undergo a similar increase during initial contact up to 0.1 N force. Between 0.1 N and 1 N force, parameter A rises dramatically, while the linear conductivity rises at a shallower gradient. Above 1 N, however, we see a quenching of parameter A and a sharp increase in the linear conductivity.

The behavior of the parameters σ_0 and A reflect the processes dominant in conduction through the ink. At 0.1 N, full contact between the ink and the electrode is established. Between 0.1 and 1 N the ink is compressed and the acicular particles get closer together This increases the number of direct electrical connections, but more significantly increases the efficiency of field assisted tunneling by narrowing of the tunneling barriers. By 1 N, compression has led to a majority of acicular particles being in intimate contact. Above 1 N, direct electrical contacts come to dominate conduction. The contribution of quantum tunneling to charge conduction through the ink is greatly reduced. Hence the ink is driven into a more ohmic conducting state.

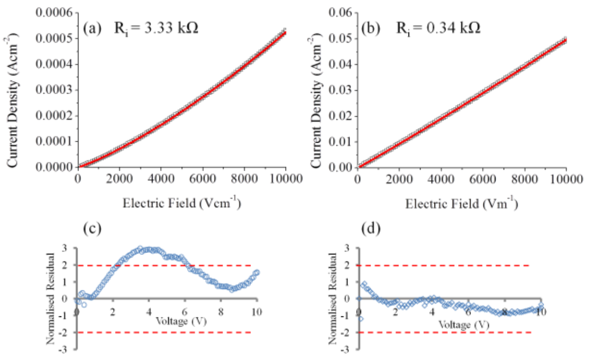


Figure 5. Fits of equation (1) to I-V data taken at (a) lower compression and (b) higher compression. The solid red lines in (a) and (b) are the model fit, the open black squares are the I-V data. Below each fit is a plot of the normalized residuals for (c) low compression and (d). The dashed red guide lines indicate the +/-2 cut off for a good fit.

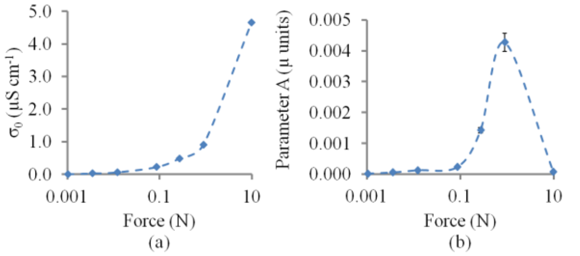


Figure 6. The behavior of (a) the linear conductivity and (b) parameter A in relation to the applied force on a logarithmic scale

IV. CONCLUSION

A functional multi-component, nanocomposite ink has been developed which displays electrical behavior with a very high and reproducible sensitivity to touch pressure. The behavior of electrical resistance in response to compressive stress showed three distinct regions. Below 0.1 N, initial contact between the surface of the ink and the upper electrode is established. Above 0.1 N, the ink undergoes compression and the contribution to charge conduction from direct, percolative connections and field assisted quantum tunneling are increased, but the tunneling dominates. Above 1 N, compression of the ink leads to most of the acicular filler particles being in direct contact. This causes conduction through direct contacts to dominate, quenches quantum tunneling and results in a more ohmic I-V characteristic. It is the combination of semi-conducting, high aspect ratio acicular particles and insulating nanoparticles in an insulating polymer ink, used as a binder to wet the particles, that forms a structure critical for this electrical behavior and high sensitivity. The choice of nanoscale filler particles has enabled this ink to be printed with conventional screen printing technology. The development of this nanocomposite ink presents a unique opportunity for three dimensional touch interfaces for location and force sensing.

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