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Abstract

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Printing Nanomaterials Using Non-Contact Printing

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Abstract — We report on the use of inkjet, extrusion, and capillary printing of poly(3,4 ethylenedioxythiophene)/ poly(sodium 4-styrene-sulfonate) (PEDOT/PSS) to create structures that could be used in a flexible, implantable bionic device. Resistance values as low as 250 kΩ are demonstrated, with little deviation under as much as 1.5% strain. The results show PEDOT/PSS can be a suitable material for printed bionic devices.

Keywords - PEDOT/PSS; inkjet; extrusion; capillary; printing; flexible

I. INTRODUCTION

The development of patterned structures containing conducting polymers is of interest to those involved in developing electronics, sensors, electrochromics, and even bioplatform technologies. We are particularly interested in the development of such bioplatforms for nerve [1] and muscle growth [2]. Printing is a class of techniques used to transfer functional materials onto suitable substrates with spatial control to create patterned structures. Printing techniques include roll-to-roll, screen, inkjet, and extrusion printing. Both roll-to-roll (gravure) and screen printing require contact with the substrate, which in some cases might not be desired. Additionally, these techniques can produce artifacts such as hairs, image distortions, and streaking [3]. Inkjet and extrusion printing involve no contact with the substrate; and while each of these techniques works best with materials having specific ranges of viscosity, surface tension, and particle size, the requirements overlap such that little or no modification of the materials is required to create a patterned structure.

The ability to fabricate structures containing conducting polymers poses some challenges given the inherent lack of processability of these materials. The development of a range of approaches to create conducting polymers of nanodimensions that are stable in dispersions has markedly improved processability [4]. Such nanodispersions can be made compatible with a number of printing approaches including inkjet printing [5,6].

Conducting polymers are widely studied as a substitute for metals in electrical devices. They can be functionalized for specific applications, and are generally easier to process than metals. Furthermore, biological systems are inherently flexible and wet, so metal is not ideal for applications in such an environment. PEDOT is an inherently conducting polymer with conductivities up to 1000 S/cm. When doped with PSS, it forms a nanodispersion and has been found to exhibit no cytotoxicity *in vivo* or *in vitro* [7]. At low concentrations, PEDOT/PSS can be inkjet printed. At higher concentrations, the polymer forms a gel which can be extrusion printed. If we consider a subcutaneous glucose sensor to be a typical implanted bionic device, with resistances ranging between 2.8 – 5 MΩ [8.9], then conducting polymer bionic devices should exhibit lower resistances to be useful. We will show that printed PEDOT/PSS structures meet these resistance requirements.

Biopolymers are generally components of an extra-cellular matrix (ECM), or biologically compatible polymers that can comprise an artificial ECM. Chitosan (CH) and hyaluronic acid (HA) are two such polymers. Chitosan is a polysaccharide used in applications such as wound dressing and biomedical implants [10,11]. HA is a component of the ECM, and can improve cell adhesion [12]. We combined these two materials and cast films to use as substrates on which to print PEDOT/PSS tracks [13].

Here we describe the design and development of several different printing options aimed at fabricating structures with micrometer resolution for stable conducting polymer nanodispersions with varying physical (surface tension, viscosity) properties. We have paid particular attention to the ability to print this nanodispersion on to flexible biopolymer platforms. These materials and the resulting structures have been characterized by profilometry, atomic force microscopy (AFM), current-voltage (*I-V*) measurements, viscometry, goniometry, strain evaluation, and optical microscopy.

II. RESULTS & DISCUSSION

A. Hardware

1) Inkjet Printing

A Fujifilm Dimatix DMP-2600 inkjet printing system was used for all inkjet deposition. Nanodispersions are jetted out of piezoelectric nozzles 22.5 µm in diameter, and parameters such as piezo voltage and temperature can be adjusted to suit the ink.

2) Extrusion Printing

The extrusion printing system is based on a CNC milling machine, and consists of three axes. A rotational motor can be attached to add a fourth axis. The software interface is the open source package EMC (Enhanced Machine Controller), which includes a graphical user interface with a g-code interpreter. The system runs on Ubuntu (Linux) version 8.04. For extrusion printing, an EFD (Engineered Fluid Dispensing) Ultra Dispensing Station gas flow regulator is used to provide controlled pressure to the syringe.

3) Capillary Printing

Capillary printing was done using the extrusion printing system, but with capillary force drawing the nanodispersion out of the syringe rather than gas pressure. The primary constraint of this printing technique is that it generally requires a rigid substrate with a very smooth and flat surface.

B. Printing PEDOT/PSS

The PEDOT/PSS dispersion was prepared by chemical synthesis. EDOT monomer was added to an aqueous solution of PSS at a mass ratio of 1:2.5. Ammonium persulfate solution was added as the oxidant, followed by iron (III) perchlorate solution as catalyst. The PEDOT/PSS gel was obtained by centrifuging the dispersion at 3000 g twice (35 minutes, then 75 minutes) with decanting at each stage. The physical properties of each of these "inks," and their compatibility with the available printing techniques are summarized in Table 1.

1) Inkjet Printing

Tracks of PEDOT/PSS were inkjet printed on a CH/HA biopolymer film. The viscosity of the PEDOT/PSS ink was ~11 cP, the surface tension was 0.27 mN/cm, and the average particle size 44 nm. The contact angle of PEDOT/PSS on a glass microscopy slide is 30.0° ± 0.5°. AFM analysis of the printed structures showed a height of 72.5 ± 8.2 nm per printed layer, and track widths of 50 ± 5 µm. The resistance of a single inkjet printed track (2 cm) was approximately 200 MΩ.

2) Extrusion Printing

Tracks of PEDOT/PSS gel complex were extrusion printed on a CH/HA biopolymer film and a CH film on polyethylene terephthalate (PET). The viscosity of the gel was ~227 cP. Profilometry analysis of the printed structures showed a height of 6.9 ± 0.9 µm for a single printed layer, and track widths of 232 ± 12 µm. The resistance of a single extrusion printed track (3.9 cm) was approximately 250 kΩ. The current-voltage (*I-V*) measurements of a single line printed on CH/PET showed little variance under tensile strain, which we estimated to be 1.5%, as shown in Figure 1. Conducting tracks embedded in soft tissue might be expected to experience strains of several percent, while conducting polymers typically fracture at about 2-6% [14,15]. Greater strains can be achieved using zig-zag or helical tracks [16]. The optical microscopy image of the line is shown in Figure 2.

3) Capillary Printing

Tracks of PEDOT/PSS were printed by capillary force onto a glass microscope slide using a 150 µm tip. The ink properties were the same as for inkjet printing. The current-voltage (*I-V*) measurements show a linear decrease in the current as the number of tracks decreases (Figure 3). Profilometry analysis of the printed structures showed a height of 548 ± 57 nm for a single printed layer, and track widths of 454 ± 19 µm (Figure 4). The resistance of a single capillary printed track (1.8 cm) was approximately 533 kΩ.

TABLE I. PEDOT/PSS INK PROPERTIES

Ink & Properties	Printing Technique		
	Inkjet	***Extrusion***	***Capillary***
PEDOT/PSS *viscosity*: 11 cP *surface tension*: 0.27 mN/cm *particle size*: 44 nm *concentration*: 18.4 mg/mL	+	-	+
PEDOT/PSS gel *viscosity*: 227 cP *surface tension*: unable to determine *particle size*: 44 nm *concentration*: 36.8 mg/mL	-	+	-

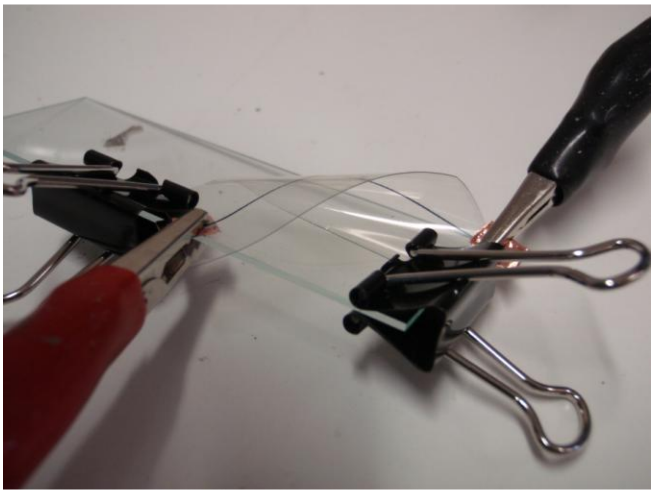

Figure 1. Extrusion printed PEDOT/PSS line on CH/PET in twist.

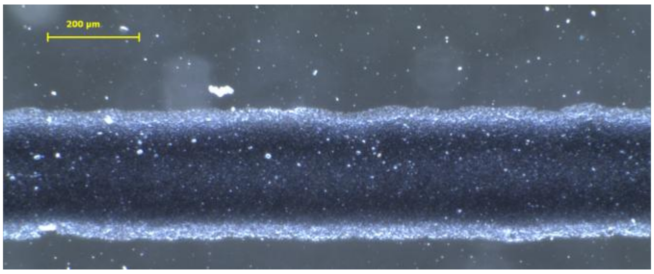

Figure 2. Optical microscopy image of a PEDOT/PSS extrusion printed line on CH/PET.

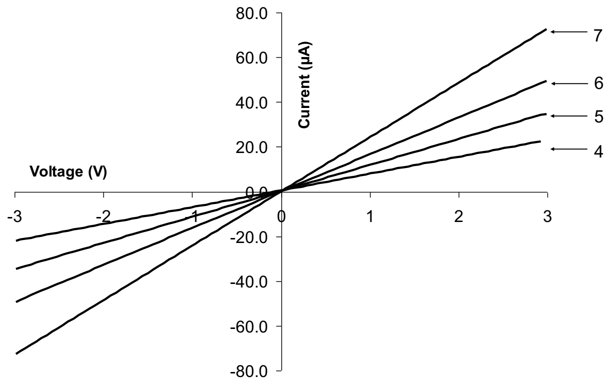

Figure 3. Current-voltage *(I-V)* characteristics of PEDOT/PSS capillary printed tracks on glass, with the number of tracks indicated on the right.

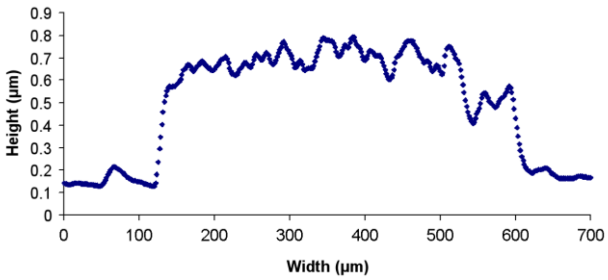

Figure 4. A representative profile of a capillary printed PEDOT/PSS track.

III. CONCLUSION

We have investigated printing functional nanomaterials using a custom-built printing system, based on a CNC milling machine, and using a syringe or inkjet cartridge assembly for deposition. We have printed structures using PEDOT/PSS nanodispersions and concentrated gel. We have shown that by extrusion printing PEDOT/PSS gel onto a hydrophilic CH substrate on PET it is possible to achieve flexible, conducting PEDOT/PSS structures that maintain their electrical characteristics when subjected to strain. Our experiments have shown that extrusion printed PEDOT/PSS structures exhibit appropriate resistance values for possible biological applications. However, for inkjet printed structures the conductivity of the material would need to be substantially improved. We have demonstrated the use of capillary force as a printing technique for PEDOT/PSS nanodispersions, but the substrate requirements limit the usefulness of this method for implantable bionic devices.

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