Extremely Flexible and Stretchable Carbon Nanotube Composites for Conformal Electronic Devices

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ABSTRACT

Electronic devices are increasingly being used in products that are not expected to be rigid and flat [1,2]. Many strategies have been implemented to create electronics that can work under stress and strain that would fracture ordinary silicon architecture [3,4]. Effective strategies, including zigzag and pre-stretched substrates, can only be effective in one dimension. For true flexibility, the conductive material itself must be designed to function under strain. Using composite materials allows conductive materials to gain some flexibility from the matrix without breaking the connections [5,6,7].

Brewer Science, Inc., has previously developed carbon nanotube–based inks for screen printing, stencil printing, Aerosol Jet® printing, ink-jet printing, drawbar coating, and spray coating [8]. These materials exhibit high flexibility but very limited ability to stretch enough to meet requirements of many applications in wearable electronics. Brewer Science's inks have been used to make explosives sensors, temperature sensors, humidity sensors, inductor coils, electrodes, and antenna structures.

We report on an innovative class of printable carbon nanotube composites that maintain connectivity through strain as large as 400%. Through the use of an additive to our carbon nanotube ink, the conductivity of our materials is 47% of the original material conductivity at 100% strain. These materials can be screen printed and cured with standard screen-printing equipment for use in strain sensors with a very large operating range. Integration of such flexible and stretchable conductors and connectors will be a key enabler for wearable electronics.

Keywords: nanotube composites, stretchable electronics, strain sensors, carbon nanotubes, screen printing

1 INTRODUCTION

As electronics become more ubiquitous in our daily lives, more durability is expected of our electronic materials. Common metallic conductors are prone to stress fractures and fail under moderate strain. For stationary silicon-based electronics, this is an acceptable outcome, but for electronics to become integrated into our life, they need to survive the wear and tear of repetitive flexing.

In addition, large-scale production of these materials will require techniques faster than chemical vapor deposition and lab-scale manufacture of these materials. Ideally, production would be accomplished with technologies already available in large-scale manufacturing facilities such as screen printing, drawbar coating, and roll-to-roll deposition.

Carbon nanotubes are a flexible conductor with very high tensile strength individually [9,10]. As a result, piezoresistive properties of composites made with these materials will be dependent primarily on the junction between the carbon nanotubes [11,12]. These materials should be capable of repeated strain without degradation of their electrical properties. Beyond simple resilient electronic interconnects, the materials themselves can become part of devices that measure strain, pressure, and acceleration.

This paper documents our development of a screen-printable carbon nanotube composite that can undergo strain as great as 400% without an electrical disconnect. This material is, to our knowledge, the only printable carbon nanotube composite that is designed for such large strain. Using this technology, we are able to print strain sensors onto existing materials and apply them as strain sensors or electrical interconnects for wearable devices for strain measurement on merchandise that is already on the shelf. We envision use of this technology on large surfaces that continuously measure strain for structural integrity.

2 EXPERIMENTAL

Carbon nanotubes for this research were purchased unfunctionalized from our vendor. The base ink for our experiments is our CNTRENE® 3020 A9-R material, which is manufactured by our documented process. Binding additives are combined with this ink by physically mixing directly into the dispersed ink until the mixture is homogeneous. The resulting ink is printed the same day to prevent variations that may occur due to separation and instability. In our experience, the ink is viable for 3 days.

Printing was accomplished in one of two ways. Screen printing was done on an Atmel AT-60PD automated screen printer with a steel 175-mesh screen. Additionally, many of our test samples were printed by using a laser cut stencil and a doctor blade, which allowed for thicker prints with less topology than the screen would allow.

Resistance measurements were performed with an Elenco Model M-2666K digital multimeter connected with alligator clips. Strain was induced manually and measured against a ruler. Due to difficulties with attaching the alligator clips to the soft materials, it was impractical to achieve identical length segments for each trial, so overall resistance of these experiments is not reported.

Cast silicone substrates were either Sylguard® 184 or Smooth-On Ecoflex® Supersoft 5 materials. For silicone substrates that were not cast, we used an FDA-compliant silicone rubber sold by McMaster-Carr.

3 RESULTS AND DISCUSSION

3.1 Printing onto Stretchable Materials

There were two major hurdles that we had to overcome to produce a stretchable conductive ink. One issue is the very low surface energy of the silicone substrates that we wanted to print. Initially, our plan was to use an ink-jet or drawbar formulation because, in our experience, these formulations had very high durability to abrasion and deformation [8]. Despite several attempts to treat the surface for printing, we were unsuccessful in obtaining a good print with these materials (Figure 1).

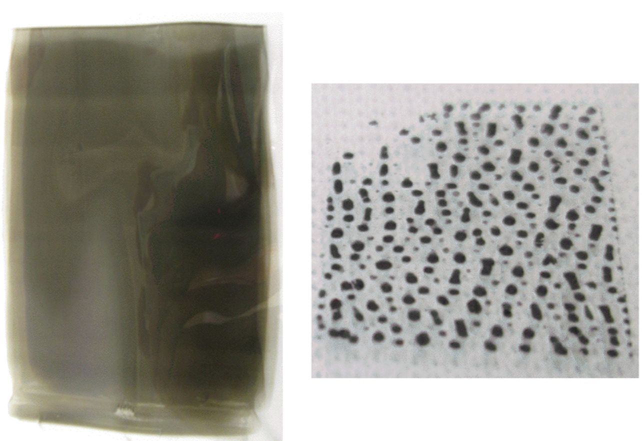

Figure 1: (left) A drawbar coating of CNTRENE® 3015 C8-R material with sheet resistance of 37 ohm/sq increased to 50 ohm/sq after repeatedly creasing the substrate. (right) A print on ozone-treated silicone dewetted.

We were able to resolve the wetting issue in two ways. Most importantly, by using our viscous screen-printing ink, CNTRENE® 3020 A9-R material, we were able to print directly onto these substrates. The thixotropy of this ink is such that once it is printed, it cannot retract from the surface despite the solvent incompatibility. Additionally, we found that we could print onto a temporary surface such as Teflon® film, then cast our PDMS over the print to transfer the film to the PDMS.

3.2 Formulating for Stretchable Inks

Using our unmodified commercial screen-printing ink, we had some success with prints that could undergo a minimum amount of strain by utilizing patterns that reduce stress in the direction of the strain. The mesh pattern created by printing with a 60-mesh nylon screen was enough to allow repeated strains of 20% with only slow degradation of the resistance (Figure 2). The mesh creates a p4m wallpaper group that can be stretched either with the grid or at a 45° angle to it. When the substrate was strained at 45° for 20 cycles, the resistance for a 2-cm length averaged 1 kohm at 0% strain and 3.3 kohm at 20% strain. In this case, the failure occurred at the adhesive used to hold the electrical contacts onto the substrate. For the substrate strained with the grid, the initial 0% resistance was 434 ohms; however, as the substrate was strained, repeated disconnections were observed. A consistent measurement of the resistance could not be made, since each strain resulted in an increase in the 0% strain resistance.

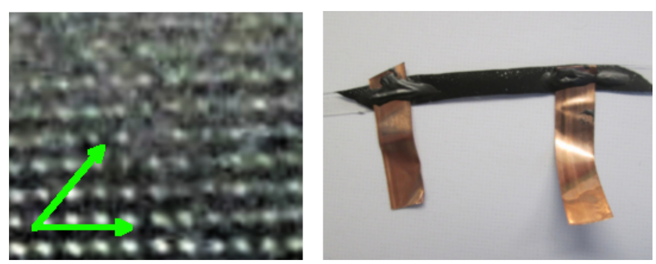

Figure 2: (left) A close-up of the mesh pattern left by a 60-mesh screen print on a silicone substrate. The arrows indicate the two directions that were strained. (right) An example test setup for the measure resistance vs. strain.

3.3 Stretchable Composites

In addition to difficulties with our inks not being resilient to stretching in all directions, it was found that thicker coats resulted in flaking and adhesion problems after the film was dried. This issue was particularly noticeable for patterns that were stencil printed where the mesh pattern is absent. To solve this problem, we began to experiment with some proprietary binders. Binders significantly improved adhesion and strain response; however, they significantly decreased the conductivity of the resulting ink. Our goal was to find an ideal concentration to maximize strain tolerance.

We ran our experiments by adding 0%, 1%, 4.7%, 9.1%, and 20% of our binder and running multiple trials to find where our ideal composition would be (Figure 3). To our surprise, the 0% and the 1% binder composites began each experiment with lower measured conductivity than the 4.7% and the 9.1%. Because the 0% mixture is identical to CNTRENE® 3020 A9-R material, which has a measured conductivity of 4000 S/m on non-stretchable substrates, we interpreted these results as fractures that were occurring during some part of the printing process. Sylgard 184 has a CTE of 310 ppm/°C, which would account for significant strain during the cure time in the oven.

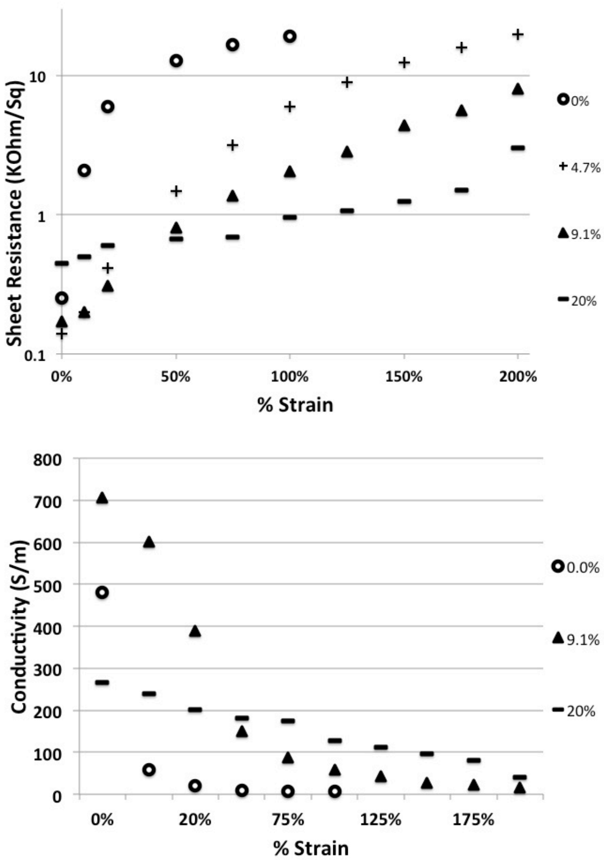

Figure 3: (top) Sheet resistance vs. % strain for composites with 0%, 4.7%, 9.1%, and 20% composites. (bottom) Conductivity vs. % strain for 0%, 9.1%, and 20% composites. Conductivity was calculated based on thickness measurements at 0% strain with the assumption that only the dimension of strain would change.

3.4 Operation as a Strain Sensor

As a simple test of this material as a strain sensor, we designed a circuit utilizing an Arduino Uno® microcontroller hooked up to the 5-volt port. A 1-mm line of our composite was printed onto a silicone substrate, and the substrate was stretched between 50% and 100% by hand.

We found that after an initial breaking-in period, the strain gauge produced consistent results over repeated strain.

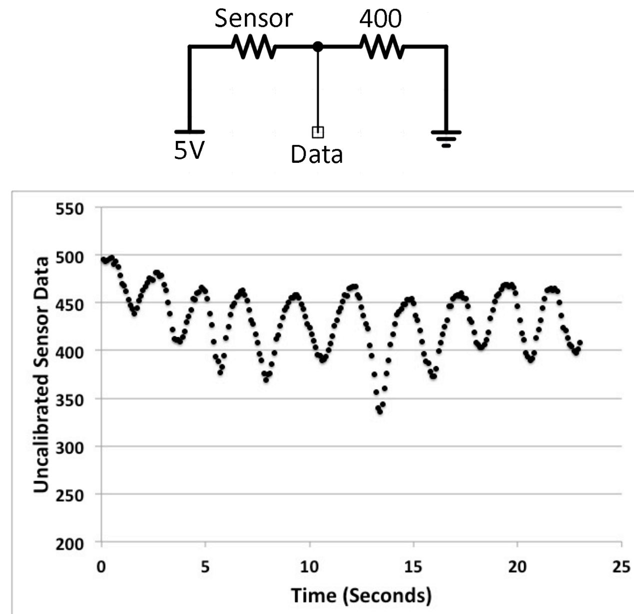

Figure 4: (top) Circuit diagram for analysis. (bottom) Data from strain measurements.

4 SUMMARY

We have demonstrated that we can print a carbon nanotube–based ink that can undergo a large amount of strain. The surface energy of the silicone substrates used was not useful for our ink-jet or drawbar inks; however, rheology of our screen-printing ink made it printable. Our standard carbon nanotube ink has a minimal ability to withstand strain if the pattern is printed in such a way that the direction of strain is complementary to the mesh of our screen printer.

The addition of a binder to the ink was necessary to achieve large strain without fracturing. This was particularly true for thicker coats, which had a tendency to flake off under strain. By varying the ratio of our binder in the formulation, the amount of strain tolerated by the composite could be adjusted. We were able to strain our samples as much as 400% without breaking the circuit. Our best-performing composite for strain greater than 75% contained 20% binder by weight. This material could be implemented as a simple strain gauge that demonstrated repeatable stretching without degradation.

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