Advancements in Ink-Jet Deposition of Carbon Nanotube Materials for Printed Electronics

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Abstract

The printed electronics industry is increasingly expanding its role in the production of devices for the consumer electronics, defense, aerospace, and space industries. As device manufacturers look toward new materials that can be used on flexible substrates and can be applied with low-cost deposition techniques, such as ink-jet deposition, advancements in carbon nanotube–based materials are showing improved performance that can solve customer problems. While universities and companies have been working with carbon nanotube materials since the mid-1990s, the unique properties of carbon nanotubes could not truly be realized due to low concentrations of nanotubes in liquid form, as well as the inability of solvent systems to perform well in advanced ink-jet printing systems.

Brewer Science has been able to combine new functionalization processes and dispersive techniques that allow for much higher concentrations of carbon nanotubes in final formulations. In addition, Brewer Science has selected solvent systems that enable formulations to not only wet and adhere to popular customer substrates in use, but also perform drastically better on both R&D ink-jet printing platforms and production-type platforms. These advancements will allow carbon nanotube materials to compete with other well-established materials in the field of printed electronics.

Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima in 1991, researchers have attempted to utilize carbon nanotubes in a wide variety of applications by the manipulation of their unique electrical, chemical, and mechanical properties. As device manufacturers look at the concept of printed electronics as a cost-effective, high-throughput means for producing devices, compositions (inks) made using electrically conductive CNTs are gaining much interest.

As electronics manufacturers push to shrink device technologies to create smaller, faster chips, there is a segment of device manufacturing that is driven by cost control and high-throughput. In printed electronics, the devices do not need to be smaller or use high-cost processes such as lithography. Device manufacturers in this market segment are looking for very inexpensive, quick manufacturing processes with which to manufacture larger-scale devices, such as RFID antennas, electrodes, contacts, and traces. One deposition process that is garnering a great deal of attention is ink-jet printing. While the concept seems easy, as most people have used a desktop ink-jet printer to print documents at one point in their lives, printing functioning electronic devices by way of ink-jet deposition has many challenges, including finding the best materials for printing devices. Carbon nanotubes are one such material that device manufacturers are researching for conductive device elements by way of ink-jet printing.

Device-printing materials must meet many important criteria. The first is to find a formulation that can be ink-jet deposited. The second objective is for the formulation to not only adhere to plastic or similar substrates (for example, PET, polyimide, polycarbonate), but also to result in a cured film at lower temperatures (< 150^{o}C). A third criterion, in

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addition to the ink formulation being able to adhere to the substrate of choice and cure at lower temperatures, is for the ink to jet stably over an extended period of time. The nozzles must remain clog free and maintain consistent printing for the duration of the material charged to the cartridge. The fourth objective is to determine the highest possible concentration of CNTs in an ink-jet-depositable formulation which does not clog the print nozzles.

Experimental

CNTs can come in a variety of types, such as multiwalled, double-walled, and single-walled nanotubes (MWNTs, DWNTs, and SWNTs). For the work described here, each of these CNTs types was used to produce ink-jet-depositable samples for testing. The CNTs were purchased from leading raw material vendors. The CNTs were further processed using specific oxidative reactions based on the starting tube properties, for example, diameter and length. While conductivity is one of the testing parameters for this work, the functionalization processes were not held constant due to the fact that concentration and material stability were also major driving forces to be tested. Once the CNTs were processed and dispersed into a "feedstock" (target of 2 g/L), the materials were further formulated into ink-jet-depositable samples using specific combinations of the following organic solvents: ethanol, isopropanol (IPA), glycerol, ethylene glycol, propanediol, and triethylene glycol monomethyl ether. The concentrations of the final formulations to be tested ranged from 0.1-1.2 g/L in order to effectively test for conductivity, as well as printability.

While there are a variety of ink-jet tools that are used for consumer electronics, it was decided to use piezoelectric, drop-on-demand ink-jet printers.

Figure A gives a schematic of a piezoelectric head by the deformation mode (bending) used to generate the drops. Two different models of ink-jet deposition systems were tested.

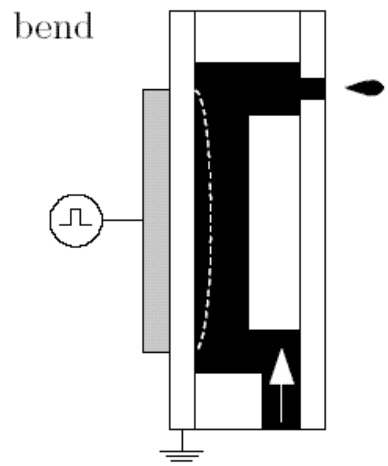

Figure A

Both systems will use a 16-nozzle disposable cartridge for sample testing.

Simple test structures that are 1mm x 1mm were used so that sheet resistance could be assessed by four-point probe. Since percolation threshold is a very important aspect of CNT films, a series of prints (1-10) were used to determine the number of prints versus concentration required to meet the percolation threshold.

Results

To begin, formulations comprised of solvents only were created to test for viscosity and surface tension so that the CNTs were not wasted. The viscosity was targeted to be 8-15 centipoise (cP), and the surface tension target was 30-40 dyn/cm^2. Once a target formulation was identified, the functionalized CNTs were added at varying concentrations, and the viscosity and surface tension were re-tested to see if the CNTs or the concentration impacted these variables.

The first type of CNT was formulated into concentrations of 0.1, 0.25, 0.75, 1, and 1.25 g/L in a simple glycerol, IPA, and water formulation. Table 1 compares the sheet resistance measured after a single print of a square test structure.

Table 1

Concentration	Sheet Resistance (MOhm/sq)
0.1	6.1
0.25	3
0.75	0.12
1	0.11
1.25	0.07

All of the samples showed good printing behavior, with all 16-nozzles firing consistent and stable droplets at a rate of 5 kHz. Figure B shows a representative sample of the droplets from the 1.0 g/L sample.

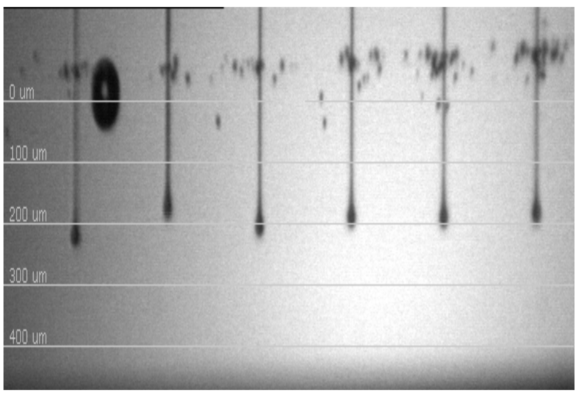

Figure B

In order to compare the sheet resistance between different CNTs, samples having a concentration of 0.1 g/L were produced and tested. Table 2 shows the comparative results.

Table 2

Sample	Sheet Resistance (MOhm/sq)
1	6.1
2	1
3	1

Because samples 2 and 3 showed the best sheet resistance head to head, additional samples were produced having concentrations of 0.25, 0.5, and 0.75 g/L. Prints of 1, 2, and 4 cycles were tested for sheet resistance, and the results are shown in Figure C below.

While Figure C does show that, by either increasing the concentration of the CNT ink or by printing more passes, the overall conductivity of

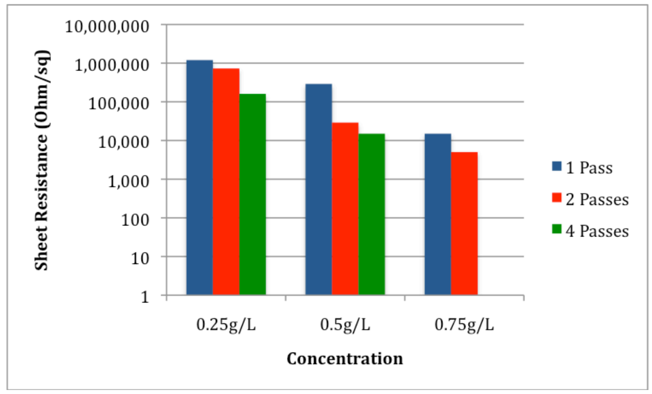

Figure C

the print can be improved. Even though the conductivity can be increased, a concentration of > 0.75 g/L or more than 4 passes must be used for the percolation threshold to be reached for the CNT type used.

Conclusion

Functionalized MWNTs, DWNTs, SWNTs have been incorporated into ink-jet-depositable formulations. It has been shown that stable dispersions of CNTs in these formulations can be as concentrated as 1.25 g/L yet still provide stable droplet formation and not clog any nozzles after a 24-hour period. It has also been shown that advancements in CNT ink technology, as it relates to ink-jet deposition, are capable of producing materials that can be used for printed electronics. While great strides have been made in optimizing dispersive techniques that enhance the unique properties of CNTs and in breaking the concentration barrier, improved inks must be developed that can adhere to plastic substrates and can be cured at both reduced temperatures and in shorter times.

While it was not specifically addressed in this paper, it was found that a formulation that was optimized for jetting performance on one ink-jet system did not typically work on a different system, and vice versa. While this cannot yet be explained specifically, early data suggest that CNT concentration and specific solvent surface tension play a large role in whether a formulation can be jetted consistently on a specific system.

Brewer Science will continue to address differences in deposition systems and how our formulations are affected.