Novel Method of Incorporating CNT into Additive Manufacturing Electronics Dielectric Material

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ABSTRACT

Flexible Hybrid Electronics (FHE) Parts that are additively manufactured give engineers and designers greater flexibility in geometry, complexity, and variety or customizability. In this work, UV curable dielectric materials for additive electronics and incorporated Carbon Nano Tubes (CNTs) within a formulated UV/LED curable matrix was used. It will be shown that inkjet printing CNT mixture in specific manner with a commercial UV curable dielectric improves mechanical and thermal properties of the final dielectric compared to the dielectric without the CNT mixture, including a significant decrease in the coefficient of thermal expansion, while keeping excellent electrical properties.

Key words: Dielectric, PCB, FHE, AME, CNT

INTRODUCTION

Printing electronics is a new and quickly growing alternative to traditionally manufactured electronics wherein an additive method is used to produce electronic circuits, passive circuitry, displays, sensors, and radio-frequency identification (RFID) tags utilizing conductive and sometimes dielectric materials. Numerous advances have been made in electronic printing technology in recent years bringing it closer to scalable manufacturing.[1-3] New and faster printing equipment has been engineered and modified for printing electronic traces using conductive inks rather than using copper etching on flexible and rigid substrates.[4,5] Flexible PCBs (FPCB) provide the same processing capability as a standard PCB, with added flexibility, and are better suited for large scale manufacturing applications. FPCB's are more reliable, can bend without breaking/sustaining damage, can withstand greater stress and harsher conditions, and can be adapted to smaller spaces due to thin copper and insulating layers.

If the PCB industry were able to produce complex multilayer circuitry quickly and easily without etching copper and without the numerous hands-on multi-lamination steps thus required, not only would this facilitate the design process, leading to quicker innovation, but it would revolutionize and tremendously enhance production, in addition to lowering manufacturing costs (especially for low volume production). Achieving this goal provides new functionality to electronics such as incorporation of printed passive electronics to be printed within the layers, reducing the total components placed on a circuit board. Designers could consider these added abilities in designs to increase the complexity of multilayer circuitry utilizing less space. This will allow manufacturers the capability to design and develop circuitry quickly and efficiently.

Widespread adoption of additive manufacturing (AM) has the potential to disrupt current production and supply chains, simplifying these processes, and moving manufacturing capacity closer to the consumer. Rather than an extensive network of storing and shipping parts, parts can be produced on site according to demand. Flexible Hybrid Electronics (FHE) Parts that are 3D printed give engineers and designers greater flexibility in geometry, complexity, and variety or customizability. With traditional manufacturing techniques there is a direct connection between degree of complexity and cost of production. Additive manufacturing eliminates the extra cost burden of additional complexity. Printing discontinued parts, across all industries, also reduces waste and extends the life of various electronics, tools, and machines. Printing electronics gives the user the ability to change designs immediately on the production line, and to design and create previously impossible objects. Additive manufacturing also has significant associated medical impacts. [6-8] Implants, prosthetics, hearing aids, and dental devices can be custom 3D printed. The impact of the technology developed and tested within this work is wide-reaching across several target gap areas including, but not limited to: improvements in materials for multilayer printing, specialized printed components, achieving high levels of performability and robust results. There is extensive overlap in the applicability of the materials and print systems tested in this work and marketability to a solve a variety of needs in the medical, automotive, aerospace, military and commercial manufacturing sectors.

One of the key advances in recent years in AM electronics has been in the conductive inks for inkjet printing. This advance is a main reason why scalable printed manufacture PCBs is now within reach.

Advances with reactive, particle-free silver conductive inks have proven to have high performance and reliability in inkjet applications.

The environmental benefits of additive manufacturing are even greater for printed electronics.[9] This printing method allows for more automation and less hands-on cleaning and heat laminating - also reducing energy. It will enable new designs of energy efficient smart sensors, IoT, and packaging materials.

In addition, there are many applications for FHE/PCB's in the aerospace industry, such as wearable electronics, RFID antennas, satellite communications, navigation and passive detection systems, radio communications, LED lighting systems, temperature sensors, power converters, control tower systems, IOT devices, and others. Furthermore, lack of a secure and domestic supply chain for PCBs poses a national security risk. Increasing the additive manufacturing of PCB boards domestically is critical to enabling the U.S. to manufacture technologically sophisticated devices within our supply chains. Because AM allows PCBs to be manufactured sustainably, economically, and in an environmentally-friendly manner, AM is the conduit for secure and sustainable domestic production.

Despite the technological advances and significant benefits of FHE's, (including, AM PCBs & FPCBs) further R&D is needed to develop materials suited to the conditions of various manufacturing environments and needs. The work here further addresses these needs by showing a method of improved printed dielectric materials using inkjet as the deposition method.

Carbon nanotubes (CNTs) are tubes made of carbon with diameters typically measured in nanometers. CNTs can be chemically modified, and have exceptional tensile strength and thermal conductivity because of their nanostructure and the strength of the bonds between carbon atoms. It has been shown that it is possible to improve mechanical and thermal properties of a polymer matrix by mixing small fraction 1-3% of CNTs into the formula.[10-12] Current use of nanotubes has mostly been limited to the use of bulk nanotubes, which is a mass of unorganized fragments of nanotubes.

In this work, UV curable dielectric materials for additive electronics and incorporating CNTs within a formulated UV/LED curable matrix was used. CNT within a formulated UV/LED curable matrix has been used to make a functional printable dielectric material to show improved performance. Specialized functionalized/dispersed and patented CNT dispersions from Molecular Rebar Design LLC were used.

PROCEDURE

Multilayer circuitry is based on depositing a conductive (usually inorganic) material and a dielectric or insulating material. Some of the challenges in printing multilayer circuitry are that materials (a) must stand up to reflow soldering and (b) have a variety of precise mechanical, thermal, and electronic qualities. Inkjet printing is emerging as having potential for printing FHEs. Inkjet can print digitally-encoded data captured from images and accurately deposit a conductive ink for the traces and pads, and dielectric ink for the solder mask or other advanced statistical machine translation (SMT) systems. Inkjet deposits dielectric ink between layers of circuitry leaving vias between the layers to be filled with conductive ink. Inkjet also allows the printing of unique identifiers, such as text or a bar code with a serial number within a single platform. These capabilities make inkjet the obvious choice for FHE manufacturing.

For this work, an inkjet system branded ElectroJet which includes dielectric materials and printing equipment capable of printing multi-materials in layers was used and shown in Figure 1.

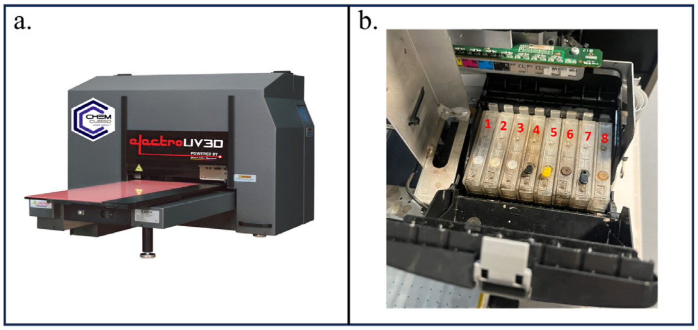

Figure 1: ElectroUV3D printer used in the ElectroJet printing system (a), and it's 8 channels with an individual cartridge dedicated to each channel (b).

Materials

One dielectric material to be used in this work is ChemCubed's Electrojet C3-DI-7 ink with a dielectric constant(εr) of approximately 3.5, deformation resistance, has electrical insulating properties, and be able to withstand thermal fluctuation from 20oC to 140oC. Another dielectric material, which has <1% multi-walled carbon nanotubes (MWCNTs) with an average length of 900 nm dispersed in compatible UV formulations, is labeled as C3-DI-CNT. The viscosity of C3-DI-7 and C3-DI-CNT is between 5 and 7 cPs.

Printing

ChemCubed has employed a novel printing technique (U.S. Provisional Patent Application Serial No. 63/327,884) to incorporate the nanotube solution into the dielectric. Instead of composing a singular solution with CNT's, ChemCubed prints the dielectric at the same time as the CNT solution causing mixing before curing. The C3-DI-7 and C3-DI-CNT were loaded in different channels within the same printhead of an inkjet printer. An UV LED light was aligned next to the printhead which lighted up while printing. For non-CNT dielectric samples, only the channel contained C3-DI-7 was used. For CNT dielectric samples, C3-DI-7 and C3-DI-CNT channels were being printed simultaneously, resulting in a 1:1 mix ratio of the two materials. The prints were than labelled as C3-DI-7-CNT. The samples were printed and cured layer by layer until a desired thickness was reached. Figure 2 shows a block diagram of the setup of the printhead and how the CNT samples were being printed. Examples of the printed samples can be found in Figure 3.

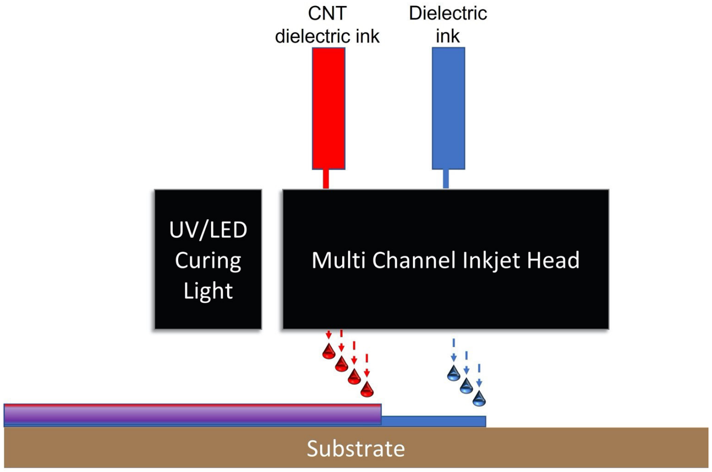

Figure 2: Block diagram of the setup of the printhead.

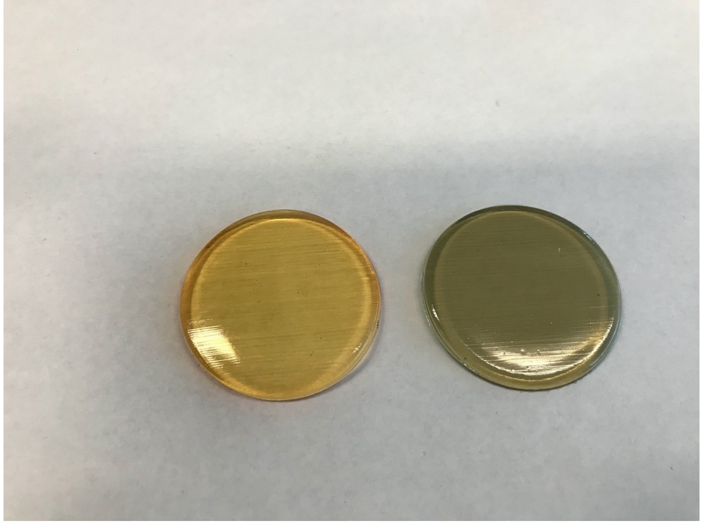

Figure 3: Examples of printed materials (D = 36 mm). Left: C3-DI-7. Right: C3-DI-7-CNT (mix of C3-DI-7 and C3-DI-CNT).

Testing

Samples has been printed for testing different properties according to corresponding ASTM standards, if possible. Type IV samples in ASTM D638 were used for obtaining Young's modulus, elongation, and tensile strength. The dielectric constant was measured using disk electrodes referenced from ASTM D150 with an electrode diameter of 25 mm. The dielectric strength was measured using a withstand voltage tester with the samples printed in sheets. The glass transition temperature (Tg) and melting point (Tm) were obtained by Differential Scanning Calorimetry (DSC). The thermal conductivity was measured using ASTM E1530 standard by a thermal conductivity meter. The coefficient of thermal expansion (CTE) was obtained by Dynamic Mechanical Analysis (DMA).

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties of the electric material were dramatically increased after CNT has been incorporated into the system. As shown in Table 1, both Young's modulus and tensile strength of the CNT dielectric material, C3-DI-CNT, increased by more than 100% compared to the non-CNT one, to be specific, 123.3% and 112.4%, respectively. The results indicate that the CNTs has been successfully well distributed in the dielectric material which reinforced the system with their strong mechanical properties. It also reveals a high bonding strength between the CNT and the dielectric material.

Table 1: Mechanical properties of C3-DI-7 and C3-DI-7-CNT.

	C3-DI-7	C3-DI-7-CNT
Young's modulus (MPa)	300	670
Tensile strength (MPa)	25.8	54.8

Thermal Properties

Table 2 summarizes the thermal properties of the dielectric materials which includes glass transition temperature (Tg), coefficient of thermal expansion (CTE), melting point (Tm), and thermal conductivity. From the table we can find that C3-DI-7 has two separate Tg values, which are around the Tg of its two main components, indicating a separation of polymer blocks. On the contrary, only one Tg was found on C3-DI-7-CNT. This is exciting since CNT not only increased the mechanical properties of the material, but also made it more uniform. Moreover, there was a dramatic decrease in CTE resulting in an over 2.5-fold difference. This is very important since large CTE leads to delamination either when printed on top of other materials or used as substrates. CNT, in this case, "stitched" the dielectric material and prevented it from having a large deformation when heated up. Nevertheless, a 10.3% increase in Tm and a 11.8% increase in thermal conductivity were observed indicating a better thermal stability.

Table 2: Thermal properties of C3-DI-7 and C3-DI-7-CNT.

	C3-DI-7	C3-DI-7-CNT
Glass transition temperature (°C)	69, 121	112.7
Coefficient of thermal expansion (1/K)	232	90
Tm, melting point (°C)	268.5	296.2
Thermal conductivity (W/mK)	0.17	0.19

Electrical Properties

As dielectric materials, both C3-DI-7 and C3-DI-7-CNT exhibited good electrical properties with dielectric constants of 3.5 and 4.1, respectively. An excellent dielectric strength greater than 50 MV/m was measured on both materials as well.

To have a clearer view of the comparison, a bar graph was plotted in Figure 4 with the property values of C3-DI-7-CNT normalized to the values of C3-DI-7.

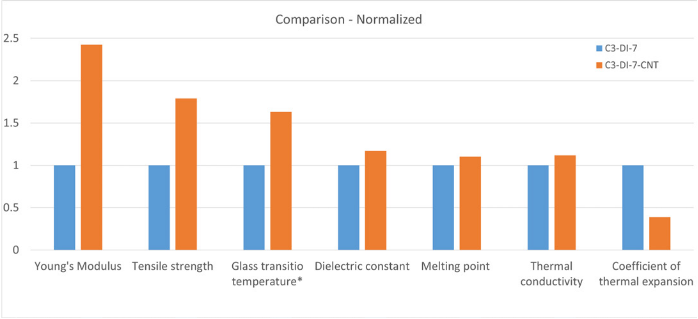

Figure 4: Comparison of different properties with C3-DI-7-CNT values normalized to that of C3-DI-7. *The lower glass transition temperature of C3-DI-7 was used here when compared to C3-DI-7-CNT.

CONCLUSION

In conclusion, we have successfully developed a method for adding CNTs to our dielectric material. The result CNT dielectric material, compared to the original one, showed a great improvement in mechanical and thermal properties while keeping excellent electrical properties.

The proposed mechanism is such that, by laying down a thin film, the nanotubes align themselves in the x-y plane. This causes a strong layering structure. There will be a few nanotubes on surfaces of each layer that would help with the interfaces in the z- direction, almost like stitching the layers. The tubes must be singular, maximizing surface area to have the desired effect. If they agglomerate or bunch up, they will have the opposite effect, and make the material weaker. This new revolutionary printable nanocomposite that will change the way circuits will be designed and manufactured.

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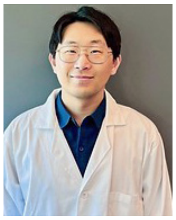
BIOGRAPHIES

Dr. Daniel Slep serves as chief executive officer for ChemCubed. Dan's background includes leading manufacturing, research and product development. In these positions, Dan has worked with multiple companies from startups to fortune 500s. Dan has served on multiple External Advisory Boards such as Rutgers Leading Disruptive Innovation and for Chemical Engineering at Stony Brook University. He lectures about topics such as Additive Manufacturing, Polymer Engineering and Nanotechnology. Dan's education includes a bachelor's degree in physics, as well as a master's degree and Doctor of Philosophy in material sciences. During his more than three decades in the printing Industry, Dan has published industry-related articles and scientific papers and is the inventor of multiple patents.



Dr. Fan Yang received his PhD and master's degree in Materials Science and Engineering from Stony Brook University. His research experience involves characterization of materials, modification of polymers, synthesis of nanoparticles, as well as experience in cell biology and developing biomaterials where he has numerous publications in leading scientific journals. Dr. Yang did his post- doctoral work at Stony Brook University. His experience with nanoparticles and polymer materials is a perfect fit for the ongoing research areas at ChemCubed