3D INKJET PRINTING OF DIGITAL COMPOSITES FOR TAILORED DIELECTRIC PROPERTIES

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Introduction

A challenge to formulate composites with high solid loading is the vast change in rheology that occurs when the solid loading increases. This change in rheology could prevent such composites from being processed in certain processes, for example high load content inks are challenging for piezo-based inkjet-printing due to the associated high viscosity [1].

In piezo-based inkjet printing of digital composites, instead of fabricating structures from a reservoir of an already-blended material, digital composites can be deposited from different reservoirs [2,3] each contains a material that can be deposited at high resolution (drop diameter is ~50µm and a thickness of < 10µm) using additive manufacturing process known as material jetting in order to produce a digital blend on the substrate as shown in Figure 1.

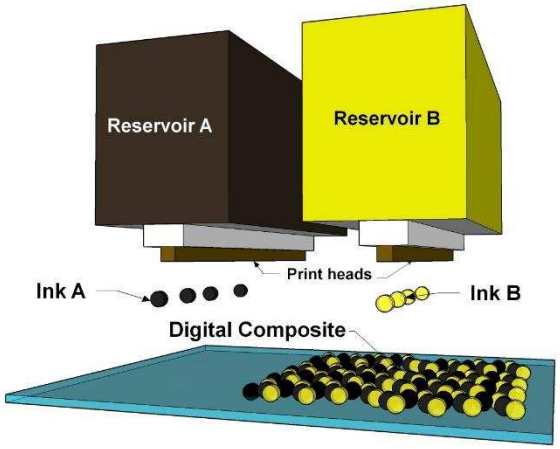

Figure 1, Schematic diagram of the digital composite printing apparatus.

Material jetting (MJ), based on inkjet printing technology, holds a high potential for depositing multiple materials in a single process. MJ has been used as a fabrication method to deposit a wide range of functional inks with a diverse spectrum of properties [4,5]. The fact that inks are ejected from print-heads with a large number of micro-nozzles offers scalability through a droplet on demand (DoD) regime, one that is commonly enabled through piezoelectric inkjet print technology. This regime is key to enable the deposition of different materials contemporaneously.

To produce highly tailorable dielectric structures using MJ the materials used to form the digital composite should have intrinsically different electrical properties [1,3]. In this study we used a UV curable polymer ink as an electrically insulative material and carbon black ink as an electrically conductive material.

Experimental Methods

Inks: A water-based carbon black ink (graphite) from Methode Development Co. (3800 Series) and an in-house formulated diacrylate UV curable monomer ink were used. Tri(Propylene Glycol) DiAarylate (TPGDA) was purchased from Sigma Aldridch and used as received. 2,4-diethylthioxanthone (DETX) and Ethyl 4-(dimethylamino) benzoate (EDB) were used as the incorporated photo-initiation system. TPGDA was mixed with 1wt% of DETX and EDB respectively at room temperature in an amber vial and then stirred at 800rpm until the initiators were fully dissolved. The prepared ink was then degassed by purging Nitrogen through for 15 minutes to help minimize inhibitions brought by pre-dissolved oxygen.

A silver nanoparticle (AgNP) ink from Advanced Nano Products (SilverJet DGP-40LT) was used as an electrode material in order to measure the dielectric constant of the digital composite.

Fabrication: Silver ink was printed on glass slides to form thin films of highly conductive electrode for dielectric measurement purposes. TPGDA and carbon black inks were loaded into Dimatix (DMP-2831) printheads and inkjet-printed on top of the silver films. Chessboard-like patterns were used to form the digital composite as shown in Figure 2.

Figure 2, Chessboard-like pattern to form the digital composite.

The ratio of carbon to polymer droplets in the pattern was 1:1 as shown in Figure 2. TPGDA cells were first printed followed by carbon to fill the gaps between the TPGDA cells. The two materials form 1 layer of digital composite. To manipulate that ratio and tailor the dielectric properties digitally the number of carbon layers were increased to increase the loading ratio of carbon. This was enabled because the thickness of dry carbon layer is around 1 µm whereas the thickness of each cured TPGDA layer is around 8 µm, hence 1:1, 1:2, 1:3 and 1:4 TPGDA layers to carbon layers were printed. The weight of each solid droplet of the inks was measured and the weight percent of each digital composite was measured.

Dielectric characterization: To measure the dielectric properties of the digital composites the printed carbon-TPGDA layers were placed under an aluminum plate. The capacitance of the digital composite was measured between the printed silver film and the aluminum plate using ModuLab XM instrument from Solartron.
The dielectric constant (ε) was calculated from the capacitance (C) values and the dimensions of the structures as follows:

$$\varepsilon = \frac{Cd}{\varepsilon_0 A} \quad (1)$$

where (d) is the total thickness of the digital composite, (ε_0) is the permittivity of free space and (A) is the area of the digital composite.

Results and discussions

Ink printability: To evaluate the printability of the inks a rheology indicator (Z) was used as follows:

$$Z = \frac{\sqrt{\rho D \gamma}}{\mu} \quad (2)$$

where μ is the viscosity, ρ is the density, γ is the surface tension and D is the diameter of the nozzle from which the liquid is ejected. Although the value of a printable Z number is still under investigation [4-6] inks of Z values $1< Z < 10$ are considered to be in the printable range [6]. Table 1 shows the properties of all inks used in the study and the Z number as calculated from equation 2.

Table 1, Properties of inks used in the study with printability indicator Z.

Ink	Density (g/mL)	Viscosity (mPa.s)	Surface tension (mN/m)	Z
Carbon*	1.01	12	37	2.33
TPGDA	1.03	10.03	30.78	2.57
AgNP*	1.04	13	36	2.15

*data as provided by the supplier

Ratio of materials: To determine the ratio of materials in the digital composite and calculate the weight percent of the carbon to polymer a known number of droplets from each ink were printed onto a glass substrate. The net weight of the dry droplets was divided by the number of deposited droplets to calculate the weight of each droplet. The weight of each solid TPGDA and carbon droplet was 7.39 ng and 3.71 ng, respectively. The thickness of each solid layer of the materials was measured using white light interferometry and found to be around 8 µm and 1 µm for TPGDA and carbon black, respectively. This explains the weight difference as the polymer droplet is heavier than the carbon droplet.
Dielectric properties: Digital composites were printed as shown in Figure 2 with a planer geometry of 10 x 10 mm for each sample. To manipulate the weight percent of carbon in each sample the ratio of carbon to TPGDA layers was increased from 1:1 to 1:4 as described in the experimental methods section. The net weight percent of carbon in each sample was 28.8%, 44.7%, 54.8 and 61.8%.
The dielectric constant was calculated as described in the experimental methods section. Figure 3 shows the dielectric constant of each digital composite sample as it changes with the percentage of carbon black at 1 kHz frequency.

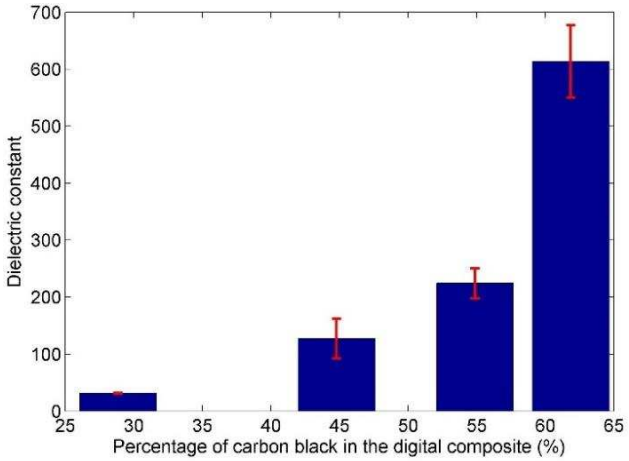

Figure 3, Dielectric constant change against carbon content at a frequency of 1 kHz.

The impedance of the samples decreases as the percentage of carbon is increased as shown in Figure 4.

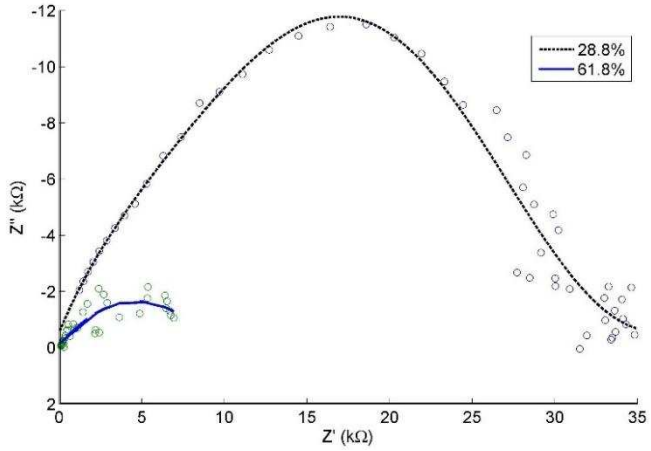

Figure 4, Impedance of digital composite samples of 28.8 wt% and 61.8 wt% carbon loading.

This impedance indicates to a percolation effect between the carbon cells which can be reduced by sandwiching the digital composite between two printed films of TPGDA layers. Such configurations and a variety of other patterns will be investigated in further studies.
The tailored high dielectric properties obtained in this study can be very desirable for many applications such as manipulating electromagnetic waves and energy storage applications.

References:

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