

**NOVEL NANOMATERIAL INK COATING METHOD FOR
FUNCTIONAL 3D-PRINTED PARTS**

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

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Nanocomposites have many useful and functional properties, yet additive manufacturing has only recently begun to take advantage of many of these properties. This work details a nanomaterial ink coating method for 3D printer filament to produce functional 3D-printed parts. This method allows 3D-printed parts to have full functionality that is not possible with conventional 3D printing methods, only previously simulated by surface modification.. Additionally, since nanomaterials should be used in a cost-effective and property-enhancing manner, maximum loading parameters are shown to prevent “streaking” of carbon nanotubes in the part, which leads to property degradation and printer malfunction. Our method, which represents a large advance in additive manufacturing technology, is applicable to seemingly all nanomaterials capable of withstanding typical extrusion temperatures.

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NOMENCLATURE

PLA	Poly-lactic Acid
CNT	Carbon Nanotube
3D-Printing	Three-Dimensional Printing
AM	Additive Manufacturing
FDM	Fused Deposition Modeling

CHAPTER I

INTRODUCTION

Nanocomposites have many useful and functional properties, yet additive manufacturing has only recently begun to take advantage of many of these properties. The practice of thermoplastic 3D printing has been well-established and is constantly being expanded and explored.[1] Nanotechnology has also been recently exploding, piquing the interest of many research groups.[2] However, the combination of these two fields, functional nanomaterials 3D-printing, has not been as large, but is beginning to be realized.[3-5] In this thesis, we demonstrate a novel nanomaterial ink coating method for 3D-printer (fused-deposition modeling) filaments that maximizes use of nanomaterials while minimizing nozzle clogging issues. This method distributes nanomaterials as a thin coating around the filament, but not dispersed throughout the entirety of the filament, which is the typical nanofiller routine.[6] The typical nanofiller, such as silica beads, carbon fiber, carbon nanotubes, or graphene, uses much more nanomaterials by comparison and is more difficult to print due to nozzle clogging issues.[4, 7, 8] This coating takes advantage of the fact that the interfacial properties of the 3D-printed layers dominate the overall mechanical and electrical properties of the printed part.[9] This method localizes nanomaterials to filament interfaces which allow nanomaterial-induced functional properties that persist after printing. Therefore, this method can be used to realize multiple functional properties depending on the nanomaterial used. We examine the effects of ink (and film) composition on the coating and printing of nanomaterial-coated filaments and demonstrate that this works for a variety of nanomaterials. There is a tradeoff between (i) insufficient nanomaterial present for functional properties and (ii) too much nanomaterial affecting print quality.

Typically, the focus of the combination of 3D-printing and nanomaterials has been using nanofillers to either improve mechanical or electrical properties,[4, 7, 8, 10, 11] using nanomaterials such as carbon fiber, carbon nanotubes, metallic nanoparticles, or ceramic nanofillers. Nanocomposites can also be used for EMI shielding.[12] The nanofillers are spread (ideally) homogenously throughout the print filament, which is both more costly and ineffective compared to nanomaterials highly concentrated at the interfacial layers.[9] Localizing nanomaterials to layer interfaces minimizes cost and maximizes effective use of the nanomaterial. This localization is important because the desired functional property can often be realized with surface modification, which means that nanomaterials can be used only where needed to achieve the same desired effect. The weak point of 3D-printed parts is still the interfaces, independent of the nanofiller used. Interfaces dominate properties, so our method uses the interfaces to help maximize properties and use less material.[9] We show correct coating and printing parameters to optimize the process. We also show maximum nanomaterial loading parameter space for printing.

Nanofillers are also notoriously difficult to print with. Using this novel ink coating method allows ease of printing that is not seen when a filament is filled with another material. This method may be applied to all nanomaterials capable of withstanding extrusion temperatures. This method allows the printing of functional 3D-printed parts, with properties post-print comparable to pre-print values.

CHAPTER II

METHODS

Ink Preparation

Preparing a CNT-Polylactic acid (PLA) or other nanomaterial-PLA ink has been a standard process that our research group has done for multiple years. There are two important parameters to consider when making an ink: the solids concentration, defined as milligrams (mg) of solids per milliliter (mL) of solvent, and the weight percentage of nanomaterial. The first step we take in preparing an ink is to add PLA (Essentium Engineering Grade PLA, 1.75 mm) to a glass bottle with the proper amount of chloroform. Chloroform is used because of PLA's great solubility in chloroform. The polymer solution is then placed in a 2.8 L Fischer Scientific bath Ultra-sonicator to expedite dissolution. After the PLA has completely dissolved, the CNTs are added to the solution. It is important to note that one needs to measure the amount of nanomaterial properly so that the desired functional properties are not lost during post-processing steps. Lastly, the solution is then placed in a Q-Sonica Q700 ultra-tip sonicator with a quarter-inch micro-tip and is then sonicated on a basis of 30 minutes for every 50 mL of solution. Because these are not colloidal dispersions, but are CNTs dispersed in a polymer solution, the CNTs can crash out of solution within a short period of time. We suggest to perform coating within 48 hours of the ink's preparation.

Ink Coating

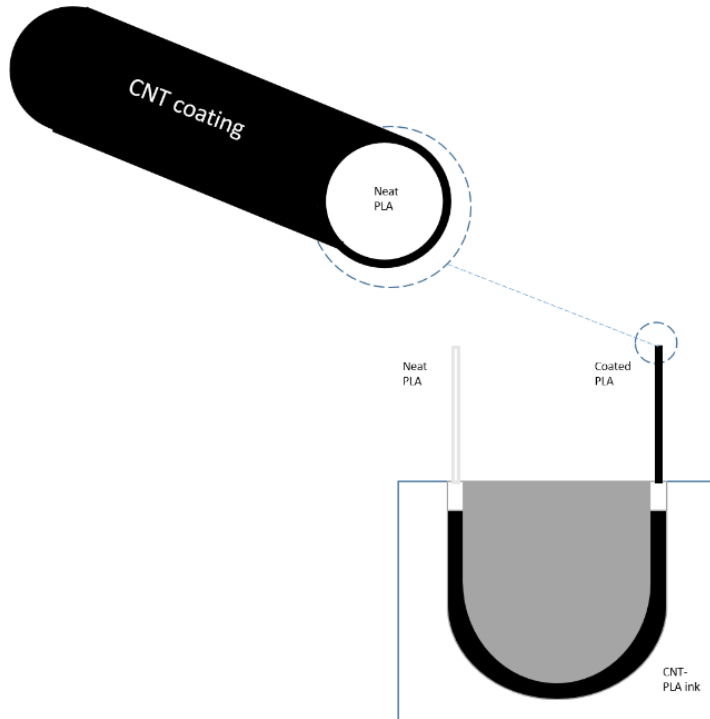


Figure 1. Schematic of coating process.

Once the ink has been made, the PLA filament is coated with the goal of printing a functional 3D-printed part. As seen above in Figure 1, neat PLA filament is fed into a coating apparatus built in our lab. While feeding the filament from one side, it is then pulled out the other side at a slow, constant rate. Through this process the ink is exposed to a shear rate of approximately 400 s^{-1} in order to replicate ink rheology measurements. However, problems may arise during the coating method. The main problem is the amount of time the filament is coated. If the filament is pulled out too fast, there is a possibility of having a non-uniform coating, resulting in a loss of the nanomaterial's properties. In contrast to a fast draw rate, a slow draw rate could degrade the PLA. This is due to the fact that chloroform is present in the ink, which dissolves PLA. Because of this, longer exposure time to the ink would result in a coated, yet degraded piece of filament. It can be seen that the draw rate during the coating process affects the success of printing a

functional 3D-printed parts. Ultimately it was found that a draw rate of approximately 400 s^{-1} led to a uniform coating and lack of dissolved filament. For this paper, inks used for filament coating were at constant solids concentration, 50 mg mL^{-1} , and varied weight percents.

Ink Characterization

Cup-and-bob rheology was performed on the inks using Anton-Paar MCI300 rheometer. Rheology was performed several inks varying solids content. Four milliliters of ink were measured and poured into the cup and loaded into the rheometer. The sample's potential hysteresis was erased by running a constant pre-shear of 400 s^{-1} for 30 seconds. The sample was then engaged in logarithmic shear ramp from 0.1 s^{-1} to 400 s^{-1} with viscosity measurements being taken every 5 seconds for a series of 20 intervals.

Printing Process

3D-printing was done on a Stacker 3D-printer. PLA was printed at 250° C , with a heated bed temperature of $60 - 70^\circ \text{ C}$. Samples printed were built in the positive z-direction. The samples consisted of an extruded rectangle, with 1 layer around the edge and a hollow center. Figure 2 shows the setup of the 3D-printer.

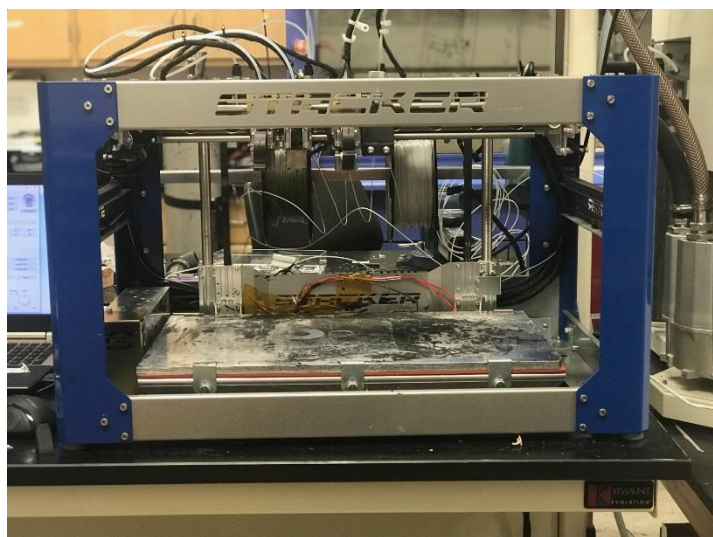


Figure 2: Stacker 3D-printer setup. The print bed is a heated aluminum print bed. The setup is controlled by a laptop to the left.

Electrical Characterization

A four point probe was used to characterize the DC conductivity of both pre-printed filament and the printed 3D objects. The samples were placed on a four-point-probe stand (from Lucas Labs) and measured through a differential voltage system (Keithley 2000 digital multimeter, two Keithley 6514 electrometers with a current source from a Keithley 6221). Volume resistivity (inversely conductivity) was calculated through the given formula:

$$\rho = \frac{\pi}{\ln 2} \cdot \frac{V}{I} \cdot t \cdot k \quad (1)$$

where ρ is volume resistivity, V is the voltage measured in volts, I is the current measured in amps, t is thickness measured in meters, and k is a correction factor based on the ratio between the thickness of the sample to the probe spacing. It was found that this correction factor is approximately 1. Currently we use the thickness as calculated in Sweeney et al. [9] for both the pre- and post-print structures.

CHAPTER III

RESULTS

Ink Coating Analysis

Cup and bob rheology confirmed the expected increase in viscosity with an increasing solids content of the filament. Figure 3 shows the shear thinning behavior of the ink as shear rate increases. It makes sense that an increasing amount of polymer, PLA, would increase the viscosity of a PLA-CHCl₃ solution.

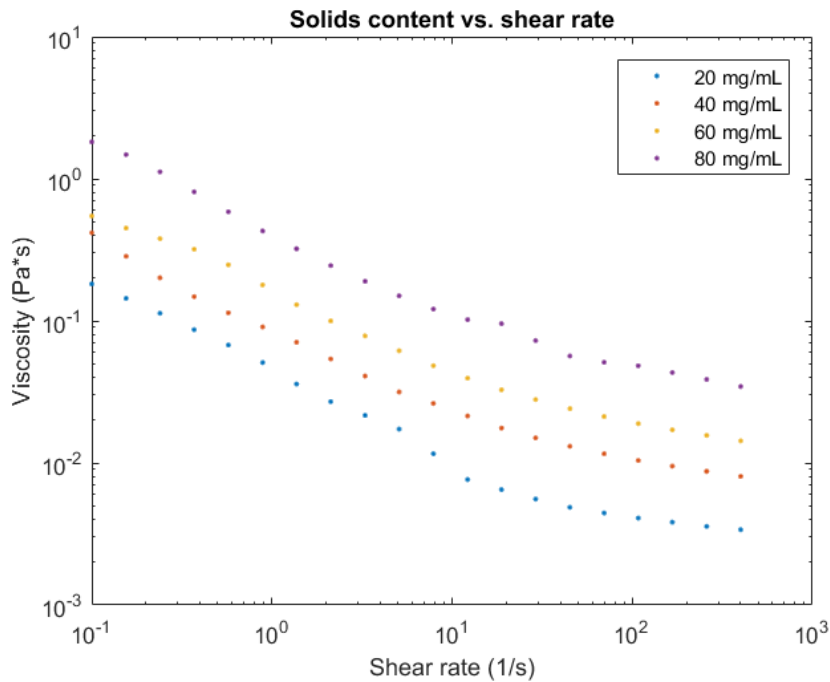


Figure 3: Solids content vs Shear Rate for Ink Rheology

The rheology of the ink coating is important to the printability of the part as well as the functionality. The CNT wt% was kept consistent because CNT wt% typically has less flexibility of range in industrial applications. Material applications will normally require a specific CNT

wt% to get the desired functional properties, and the solids content of polymer composites can be more easily varied.

Concerns with 3D-Printing

There are many concerns we have observed in our study that affect the quality of the print, and we address several of these concerns subsequently. As with all chemical reactions, the rate of polymer degradation will increase with temperature as it follows an Arrhenius trend.[13], which is why printing above recommended temperatures causes problems. In the case of PLA, the degradation mechanism is primarily the hydrolysis of the ester linkage within the polymer.[13] As a result of this, degradation products may build up within the nozzle and eventually begin to clog it. Furthermore, these degradation products are more thermally resistant and will require a heavier cleaning process to remove them. This degradation problem applies to all polymers printed via fused deposition modeling. Clogging may also arise from nanomaterial flow within the coating. Ways to address clogging may be through using a blowtorch on the nozzle, a fiber on the range of 100-500 microns (depending on the size of the nozzle) to push out material, or cleaning filament (e.g. eSun Cleaning Filament). We also have observed inhomogeneous flow while printing our CNT-coated material. We believe this to be derived from two different issues: one resulting from a clogged nozzle, as previously discussed, and the other from high loadings of CNTs within the coating. The reason for this would be due to different melt rheological properties between the coating and the neat filament. This will be discussed later. Lastly, we found that bed adhesion is crucial when printing a part, for if the initial extruded material does not adhere to the bed then the entire print will not be successful. A heated bed greatly increases adhesion as it allows for polymer mobility rather than the freezing of chains as extruded material comes into contact with a cold bed. This is why most recommended bed temperatures are at or

above the T_g of the thermoplastic. In addition to a heated bed, we observed that laying a solution of polymer also aided with bed adhesion. This is a result of cohesion between printed polymer, PLA in our case, and the deposited PLA solution on the bed.

3D-Printing Results

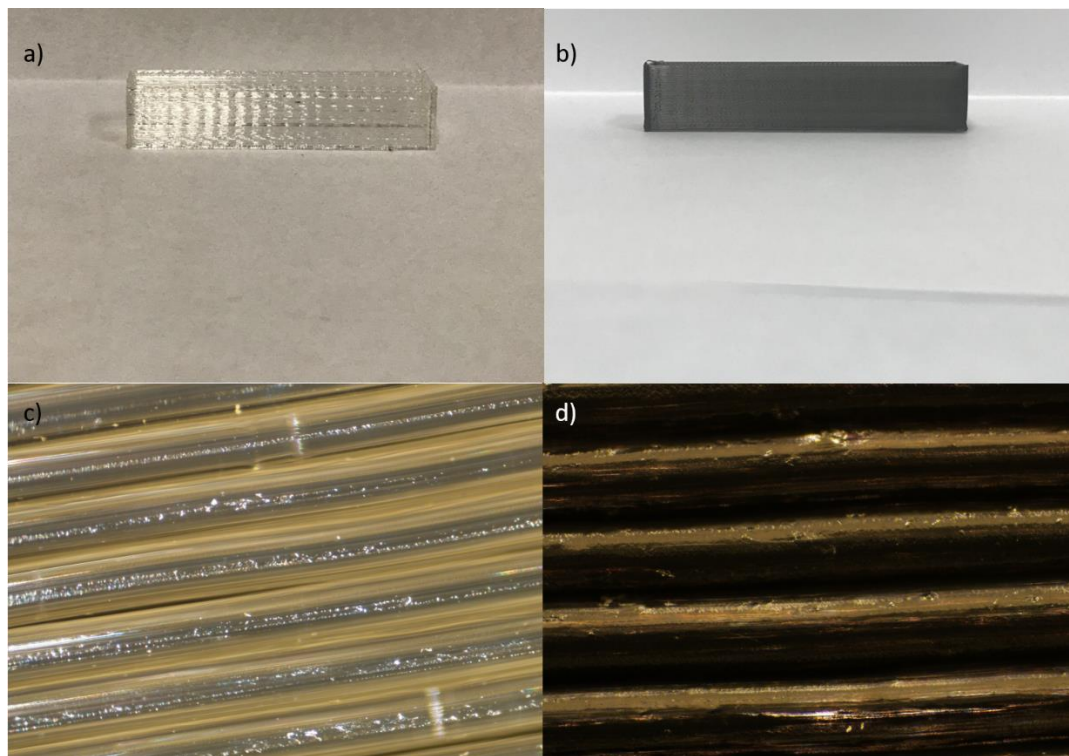


Figure 4. Side-by-side comparison of 3D printed wall from neat PLA and CNT-coated PLA. a) neat PLA 3D-printed wall. b) CNT-coated PLA 3D-printed wall. c) and d) are images from optical microscopy of these 3D-printed walls.

Figure 4 shows a comparison a neat PLA print and a 15 wt% CNT-PLA print. This figure shows that our nanomaterial ink coating method can successfully be used to print with nanomaterials without the negative “streaking” effects. Similar to our conductivity and coating analysis, we studied the effect of coated material during 3D-printing through the use of CNT-coated PLA. As seen in the conductivity analysis, decreasing CNT wt % in the coating results in lower filament conductivity. However, there is a tradeoff between nanomaterial loading and print quality. While the increase in CNT loading would make the printed part more conductive, the higher loading

would lead to significant differences between the melt rheological properties of the coating and the neat filament. Because of this, “streaking” will occur. We define streaking as inhomogeneous flow during the printing process that results in a non-uniform part. Consequently, streaking could result in uneven functionality within a part since some interfaces may have nanomaterial while others may not.

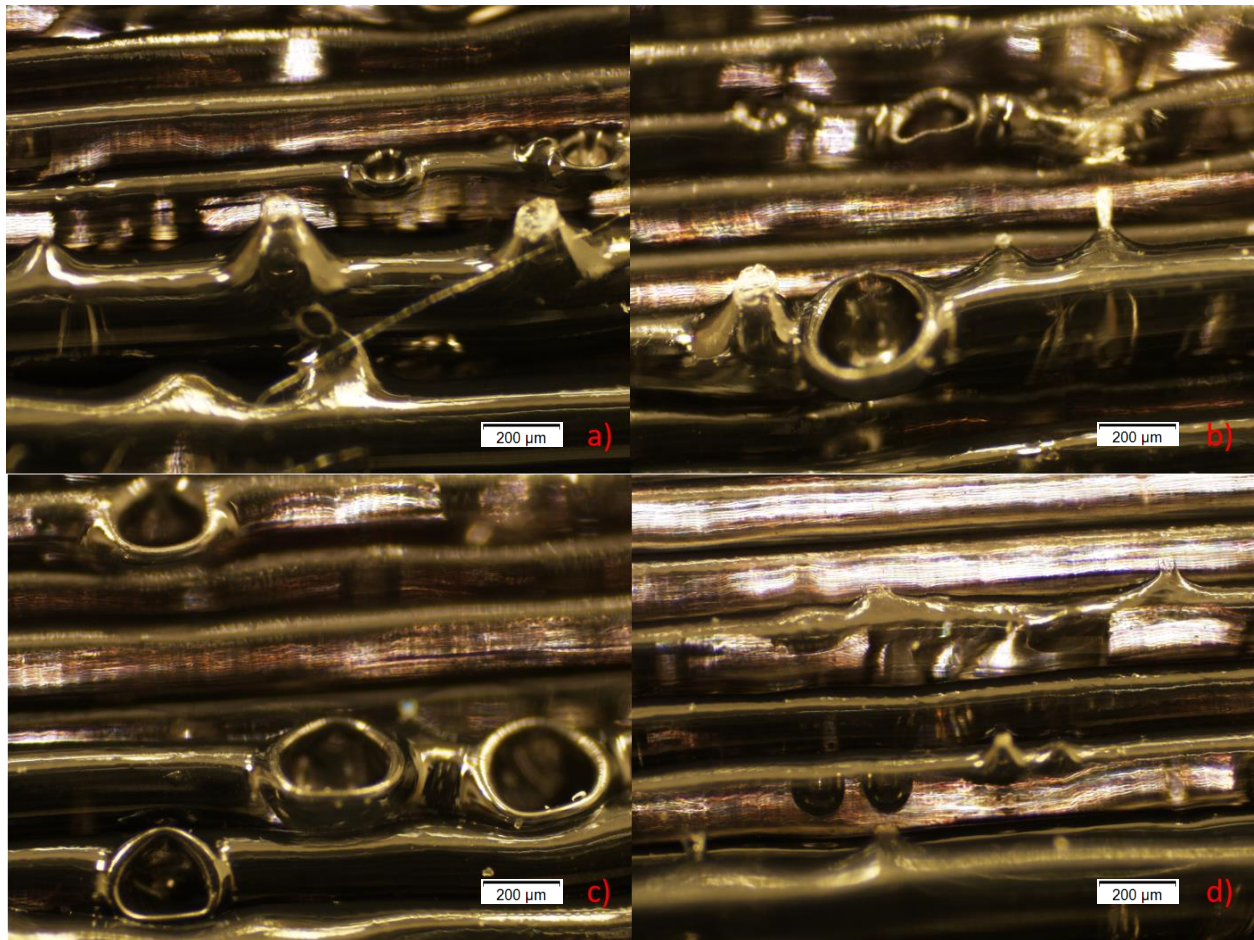


Figure 5: Images a-d show examples of streaking throughout printed layers. These layers were printed using 10 wt% CNT-PLA filament and images were taken under a 5X optical microscope. These layers are 0.25 mm tall.

Figure 5 shows examples of streaking in a 10 wt% CNT-coated filament. This occurred in the upper region of the printed part, but Figure 6 shows that inhomogeneities are present throughout the part, not just limited to “streaking.” This shows that printing is difficult with high weight percent CNT loadings.

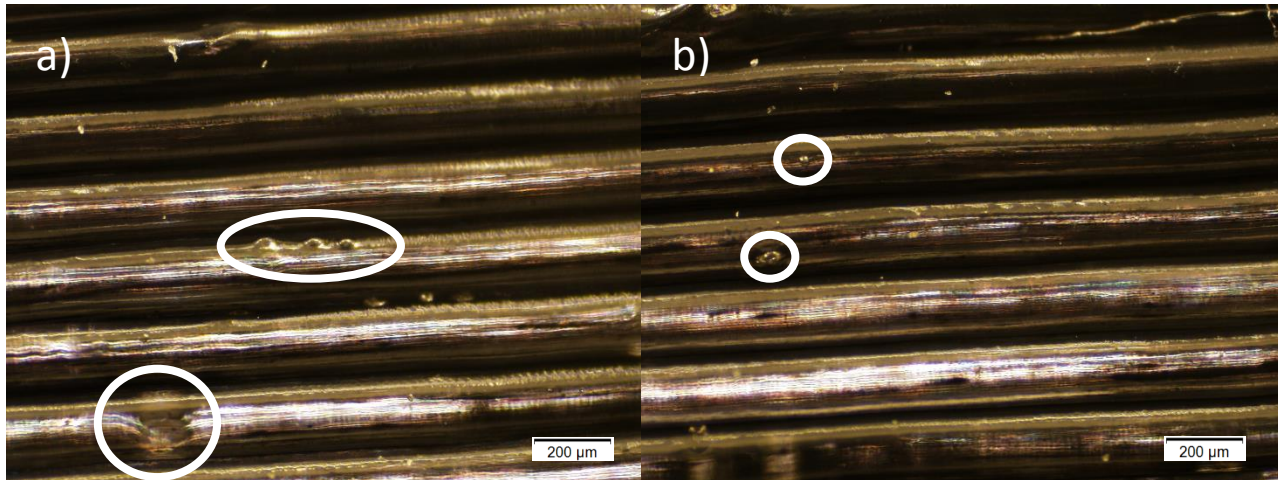


Figure 6: Examples of minor inhomogeneities from printing high weight percent CNT-PLA. Examples a) and b) were printed with 10 wt% CNT-PLA filament.

Overall, we show the capability of printing homogeneous structures using proper CNT loading and printing parameters, and we also show the dangers of high weight percent loading resulting in “streaking.”

Electrical Characterization

Pre-printed Filament Characterization

Upon measuring the volume resistivity of the filament, conductivity was then plotted against CNT wt%. The weight percent's in the coating varied from 2.5, 5, 10, and 15 wt%.

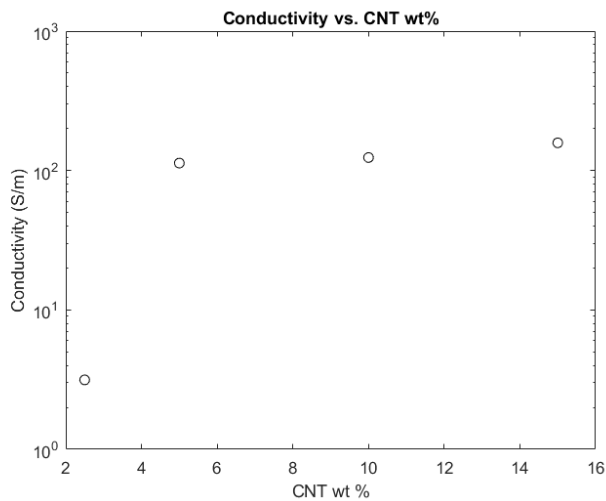


Figure 7: DC conductivity of Pre-printed CNT-PLA filament.

Figure 7 shows that after 5 wt% the conductivity begins to plateau with increasing CNT wt%. This is expected due to coated filament samples being above percolation, meaning that the addition of CNTs in the coating will not significantly change the conductivity.[14]

Post-Printed Part Characterization

Table 1: Post-print Conductivity of PLA

Sample	Neat PLA	5 wt% CNT-PLA	10 wt% CNT-PLA	15 wt% CNT-PLA
Pre-Print Conductivity (S/m)	N/A	1.13×10^2	1.24×10^2	1.58×10^2
Post-Print Conductivity (S/m)	2.78×10^{-8}	6×10^{-6}	7.5×10^{-6}	0.47

Table 1 shows a correct trend of increasing conductivity with increasing wt%, which is what we expected. These results compare successfully to the pre-print conductivity. However, there is a significant drop in conductivity between pre- and post-print. Brandon et al. showed that there should not be such a loss of conductivity, so more studies are needed to further quantify and explain this reduction in conductivity. However, the 15 wt% clearly shows the feasibility of making conductive 3D-printed parts with this ink coating method.

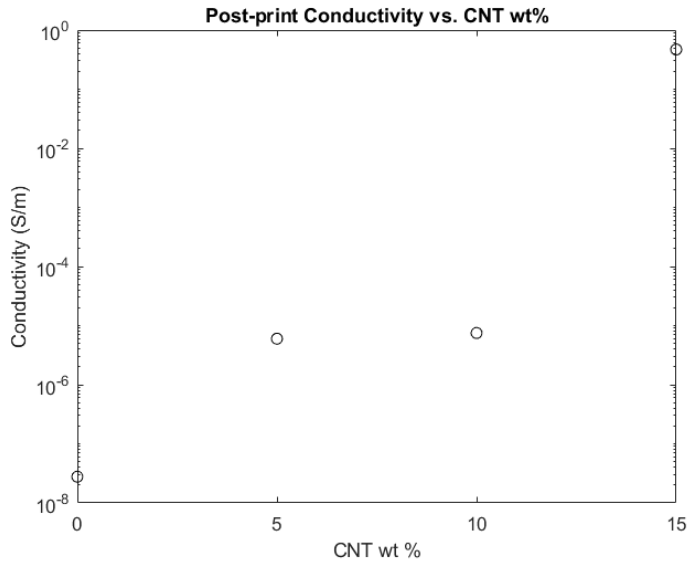


Figure 8: Post-print Conductivity of CNT-PLA Filament

Figure 7 demonstrates the proper increasing trend of the printed part conductivity with increasing weight percent. Figure 8 shows a visual representation of both the pre- and post-print conductivity and their differences.

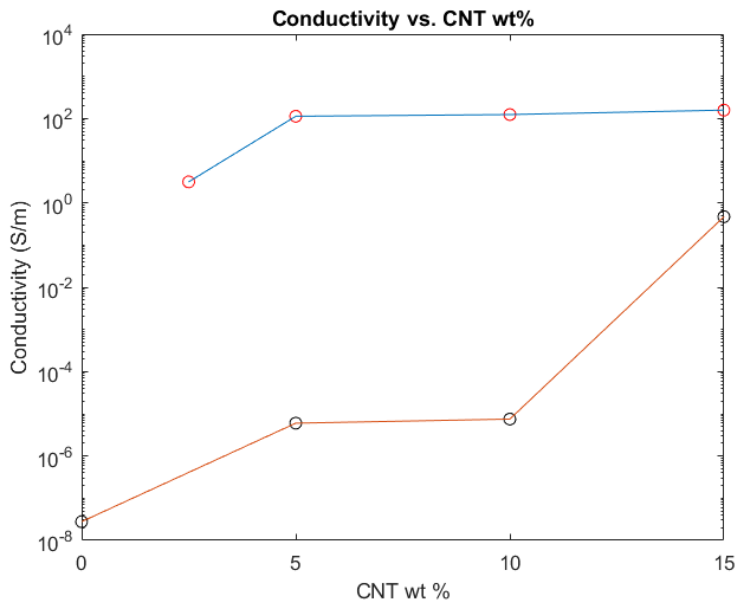


Figure 9: Overall electrical conductivity of CNT-PLA filaments

The graph shows orders of magnitude difference in the pre- and post-print conductivity of samples, which was not expected. More work is needed to identify and solve this problem.

CHAPTER IV

FUTURE WORK

Conductivity Change Analysis

Our work did not demonstrate similar conductivity (same order of magnitude) between pre- and post-printed samples of CNT-PLA filament. However, it was shown in Sweeney et al. [9] that post-printed parts still had high conductivity, as proven by its continued microwave-receptiveness. We aim to fix the issue either with the measurement itself or processing errors to maintain the same order of magnitude conductivity between pre- and post-printed samples. We hope to conclude exactly how 3D-print processing affects conductivity and other functional properties with our nanomaterial ink coating method.

Melt Rheological Studies

To properly predict the pattern of streaking that occurs during printing high nanomaterial loading filaments, we will need to gather data on melt rheological behavior of the CNT-PLA coatings. By comparing melt behavior of the coatings to neat polymer, we can determine whether CNT loadings truly affect melt behavior to cause such a problem like streaking. This study would allow us to further improve the printing process and discussion on streaking.

Additional Nanomaterial Applications

In addition to carbon nanotubes, this ink coating method is applicable to other nanomaterials. We plan to demonstrate the extension of this method to graphene, silver nanowires, and boron nitride nanosheets. Graphene can be used as a strain-sensor to be able to detect when a printed part reaches a critical strain. This possibility stems from graphene's piezoelectric properties [15] that will be taken advantage of embedded in a 3D-printed part. With silver nanowires' high

conductivity,[16] we should be able to print transparent, conductive traces based on the electrical conductivity of silver nanowires.

CHAPTER IV

CONCLUSION

A novel nanomaterial ink coating method was presented that maximizes nanomaterial use and reduces cost of achieving functional 3D-printed parts. We show maximal loading case parameters for a homogenous printed part as well as the consequences for exceeding these maxima. We demonstrate this “streaking” effect at 10 wt% CNT-coated filament. There is more work to be done, such as explaining the drop in conductivity, using melt rheological properties to predict printing behavior, and applying this method to other nanomaterials and other functionalities.

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