The Material Testing of Nanoparticle Doped 3D Printed ABS to Decrease Resistance and Create a Conductive Pathway

Sara M. Damas* and Dr. Cameron J. Turner *

*Department of Mechanical Engineering, Clemson University, Clemson, SC 29634
Fluor Daniel Engineering Innovation Building, 218 S Palmetto Blvd, Clemson, SC 29631

Abstract

The technology to 3D print by low-cost fabrication has been around since the 1970's. Thanks to one of its founding fathers, Scott Crump, as of 1989, it is possible to 3D print in low-cost fabricated layers to obtain a solid component. The demand for 3D printed products has only gone up since. Nickel, copper, carbon, and electric paint nanoparticles were bound to Acrylonitrile Butadiene Styrene (ABS) using N-Methyl-2-Pyrrolidinone (NMP) by fused deposition modeling (FDM). When ABS is doped with nanoparticles, conductive properties are introduced to the filament which can then be used for strain measurements. This study concluded: When compared to the other nanoparticles, nickel produced the lowest resistance when doped into the ABS. Multiple layers of the NMP and nanoparticles yields a lower resistance, which subsequently yields higher conductivity. The methodology outlined in this paper successfully created individually isolated conductive pathways, where indeed NMP does improve the conductive performance of the nanoparticles.

Introduction

Additive manufacturing (AM) is unlike traditional methods of manufacturing. Traditional manufacturing methods such as milling and lathing subtract material and produce waste. Due to the need of little to no tooling, 3D printing provides the final product quickly to consumers. The additive manufacturing process begins with the use of computer-aided design (CAD) to produce a 3D model. This model is saved in a .stl file format, which is a triangulated representation of the model. Then software such as MakerBot Desktop, is used to slice the data file. These "slices" refer to the layer by layer instructions to the printer on how to produce the 3D model. The 3D printer creates the model and post processing such as sanding, filing, polishing, curing, material fil, or painting may occur. As an alternative to traditional CAD programs, 3D scanning and imaging is becoming increasingly popular.

There are 3 common research methods researchers approach studying additive manufacturing coupled with nanoparticles. In the first method of testing, the binder used in testing is kept constant while changing the coupled nanoparticles. In the second method of testing, the binder is varied and the type of nanoparticle is kept constant. In the third method of testing, the type of nanoparticles and binder selected are kept constant, instead the testing environment (such as temperature and humidity) is varied. This allows researchers to observe the environmental effects of the curing of the test samples.

This research followed the first method of additive manufacturing. N-Methyl-2-Pyrrolidinone (NMP) was used to bind the selected nanoparticles. In the first experiment, the researchers tested the conductivity of binder-copper solution of varying concentrations. In the second experiment, the researchers tested the conductivity of nickel, electric paint and carbon. In the third experiment, the researchers retested the materials from the first and second experiment. Finally, in the fourth experiment the substrate distances were tested. This extensive and detailed study concluded several points. The first point is nickel consistently showed to be the nanoparticle that yielded the least amount of resistance, and therefore, the highest conductivity. Second, layering multiple layers yields the best conductivity results. Third, the binder selected does indeed improve the performance of the nanoparticles. Fourth, the research was able to create individually isolated conductive pathways.

Background

There are now at least 13 different sub-technologies within the additive manufacturing umbrella. They are grouped into seven distinct process types. The first type is vat photopolymerization, where a liquid photopolymer in a vat is cured by light polymerization. An example of this process is stereolithography (SLA), and digital light processing (DLP). In the second type of additive manufacturing, material jetting, material is selectively deposited by a print head. The material is usually a photopolymer with a secondary "tacky" material such as wax. Other times post processing using a UV light can be used to solidify the photopolymer and cure the part. An example of material jetting is multi-jet modeling (MJM). The third type of additive manufacturing sub-technology is material extrusion. Thermoplastic material is extruded by a heated nozzle to make a 3D printed part. This can be considered as one of the first and most traditional ways of additive manufacturing. An example of material extrusion is fused deposition modeling (FDM). In powder bed fusion a thermal energy source, for example a laser, is used to fuse together particles of material. A layer of powder is in between the filament layers in order fill the void spaces that occur during printing. This reduces the need for supports. An example of powder bed fusion is electron beam melting (EBM), selective laser sintering (SLS), selective heat sintering (SHS), and direct metal laser sintering (DMLS). The fourth type of additive manufacturing uses liquid binders to adhere material particles together. Like powder bed fusion, powder is often used in between layers to add extra support. This process is repeated until the final product is created. Sometimes inks are injected throughout the layers to impact the color. Examples of this form of additive manufacturing include powder bed and inkjet head (PBIH), and plaster based 3D printing (PP). During sheet lamination, glue or ultrasonic welding is used to bond thin sheets of material such as plastic or metal. These sheets are layered on top of each other, and a laser or sharp edge is used to cut away unwanted excess material. Examples of this type of additive manufacturing process include laminated object manufacturing (LOM), and ultrasonic consolidation (UC). The last type of sub-technology in 3D printing is directed energy deposition. In this method focused thermal energy fuses material as it is deposited. Often this type of additive manufacturing couples with wire-based or powder-based approaches. An example of this method is laser metal deposition (LMD). (Mark Cotteleer, 2013) These forms of additive manufacturing have been extensively been researched and developed by researchers in various fields beyond engineering such as: Khaing detailed his research with direct metal lase sintering (M. W. Khainga, 2001), Silva and colleagues used selective laser sintering in 3D-printingof models for craniomaxillary anatomy reconstruction (D. N. Silva, 2008), and Allen and Sachs used binder jetting when they 3D printed metal parts for tooling and other applications. (Samuel M. Allen, 2000).

Looking more into depth of these types of additive manufacturing, fused deposition modeling (FDM) is easily repetitive, and the cost of equipment and materials is cheaper than stereolithography (SLA) and selective laser sintering (SLS). Many fears and uncertainties are associated with 3D printed parts such as its lack of structural stability, reliability, and material restrictions. However, with new 3D printing system technology and innovation, these fears can be overcome with multi material 3D printing. This type of printing insures that structural integrity, flexibility, and multiuse are preserved in the product. Multi-material 3D printing is used in many applications and most notably products such as circuit boards. (Multi-Material 3D Printing, n.d.) By 3D printing the product in one uniform system, tight tolerances can be met, better adhesion without damage to parts of the product can be insured and better accuracy and efficiency of the product and be achieved.

The art of multi material 3D printing has yet to be perfected. There is still much to be desired. The method of stereolithography (invented by Charles Hull), where light is used to fuse and cure UV-curable polymers, has been used to support the mixing of multiple materials. (S. Maruo, 2001) While this method provides a high resolution, changing material for each layer during 3D printing is time consuming. 3D printing technology has been pushed to advance in the realm of additive manufacturing as well. The Model 2, 3D printer even supports an internal library of materials, and extrudes them using multiple syringe-based extruders. (Jeffrey I Lipton, 2009) However, this system is infamous for its low resolution. Often, plastics and metals do not want to mix harmoniously. Therefore, new methods using binding are being investigated.

One of the methods includes a powder substance distributed on the 3D printing bed, then a 3D printer prints the product using one material. Then the product is impregnated with other materials, preferably metals in this second step. After completion the product is baked and therefore the powder detaches itself off the product and can be recollected to be used in future experiments. This methodology eliminates the need to 3D print support material. Therefore, it is more efficient and less wasteful than traditional 3D printing and provides a structurally sound industrial grade product. (What Is Binder Jetting, 2019)

Multi-material 3D printing becomes a unifying factor between two materials when the benefits of both their properties are combined. One of these methods includes inkjet printing combined with sintering in a separate furnace. Another popular method is metal injection molding using metal injection molding (MIM) powder. Cheaper alternatives include mixing of nanoparticles and a binder to form a solution that is injected to a 3D printed component. Inkjet technology has been bought and dominated by companies like HP looking to lead the path of research and innovation with their patents. However, it seems like manufacturing and material suppliers and vendors are the most interested in the binding of materials. This is because the ability to multi-material 3D print in house eliminates the need for third party vendors and allows for intellectual confidentiality. Companies can now engineer and conceptualize things like microchips, then print the prototype in house, instead of sending it to a 3D party to obtain a sample.

Much like the rest of the world, and similarly to how DVR's, music streaming platforms, etc. are all demand driven, the technology sector is not an exception. Manufacturers and innovators want samples now, and are subsequently driving a field and demand for inhouse fabrication of this type. One of these material suppliers is PyroGenesis which is seeing an explosive demand for MIM cut powder. Other vendors supply direct metal printing (DMP), XEJT offers nanoparticle jetting (NPJ) and Vader systems provides liquid material jet printing (LMJP) particularly with the use of magnetism in their molten metal. Most notably Digital Metal AB has begun commercial production for its 3D metal binder jet printers. MakerBot alone has sold over 22,000 since 2009. (Clay, 2013) Today, MakerBot has the "largest install base of 3D printers worldwide and runs the largest 3D design community in the world". (About Us, 2019) This will also allow amateurs and at home tinkerers to join in this emerging field. In addition, Digital Metal is incorporating metals such as stainless steel, titanium, silver and cooper in their technology. By using these methods of additive manufacturing, we minimize the need for supports, and thus waste less material. Benefits include, printing more accurate angles that are less than 45°, and the metal imbedded supports act as a heat sink and lessen the impact of cooling. (Petch, 2017) The below table summarized the applications that use 3D printed components and was taken from (Mark Cotteleer, 2013) basics of additive manufacturing report.

INDUSTRIES	CURRENT APPLICATIONS	POTENTIAL FUTURE APPLICATIONS
COMMERCIAL AER0SPACE AND DEFENSE	• Concept modeling and prototyping • Structural and non-structural production parts • Low-volume replacement parts	• Embedding additively manufactured electronics directly on parts • Complex engine parts • Aircraft wing components • Other structural aircraft components
SPACE	• Specialized parts for space exploration • Structures using light-weight, high-strength materials	On-demand parts/spares in space • Large structures directly created in space, thus circumventing launch vehicle size limitations
AUTOMOTIVE	• Rapid prototyping and manufacturing of end-use auto parts	• Sophisticated auto components

	• Parts and assemblies for antique cars and racecars • Quick production of parts or entire	• Auto components designed through crowdsourcing
HEALTH **CARE**	• Prostheses and implants • Medical instruments and models • Hearing aids and dental implants	• Developing organs for transplants • Large-scale pharmaceutical production • Developing human tissues for regenerative therapies
CONSUMER **PRODUCTS/RETAIL**	• Rapid prototyping • Creating and testing design iterations • Customized jewelry and watches • Limited product customization	• Co-designing and creating with customers • Customized living spaces • Growing mass customization of consumer products

Table 1 AM applications by select end markets

Now that it is explained why there is a demand in the field of engineering for multi-material 3D printing the contents of this paper will be explained. This paper explains the processing of binder jet multi-material 3D printing to improve upon the material property of conductivity. This was achieved in a series of several experiments. Adding nanoparticles in multi-material 3D printing adds multi-functionality by mixing thermal and electric conductivity to additively manufactured part (N. B. Crane, 2006). "Adding nanomaterials to additive manufacturing can improve mechanical properties lower sintering temperatures and improve dimensional accuracy" (John Changjin Bai, 2007).

This paper details a set of experiments testing different variables on trays. These traces were tested for conductivity. The results of the testing, including the effects of the material and binder on the 3D printed ABS, was observed and collected qualitatively and quantitively. The goal proves the best methodology in 3D printing binding and dope a substrate with the most viable nanoparticle found to obtain a conductive pathway. This conductive pathway will act as a substrate can his conductive enough to light lightbulbs and incorporate sensors.

Methodology

After analyzing previous literature, and the most current up to date research on the topic and field of multi-material 3D printing, experimentation began. 3D printed ABS trays were doped with various types of nanoparticles or binder solutions. The trays were tested for their conductivity with an electrical conductivity meter (EC meter).

Figure 1 Auto-ranging multimeter conductivity measuring device

1) Experiment 1: Pilot Testing of Copper Nanoparticles

For the initial experiment copper oxide nanoparticle (CuO, high purity, 99.95+%, 25-55nm) was purchased and combined at different concentrations of 7mL of NMP (N-Methyl-2-Pyrrolidinone). The concentrations of copper oxide nanoparticles were measured using the scale seen in *Figure 3 Scale used to weight copper nanoparticles*. The concentration increments of NMP were: 1.5 grams, 3 grams, 4.5 grams, 6 grams and the solutions were put in a glass vile container like below and stored underneath a hood in a chemical lab.

Figure 2 Glass vile container

Figure 3 Scale used to weight copper nanoparticles

Then several 3D printed circuit board like trays were created using ABS plastic, see *Figure 4 First Trial Circuit Board Tray*.


Figure 4 First Trial Circuit Board Tray

One of the channels on the trays (the trays were labeled with a marker) was layered with 0.5 mL of the NMP binder and left to cure for one week. This way the effects of the binder on the ABS alone can be observed. It was beneficial to understand if an extra layer of the binder allowed for better binding when curing. Then both the channels were injected with 0.5 mL of the mixed solution. At first a dropper like the one seen in Figure 5 was used. However, it was concluded that using a needle like dispensing tool such as the one seen in Figure 6 would allow a cleaner and more precise application.

Figure 5 Initial dropper used to measure and inject 3D printed trays with NMP and nanoparticle solution

Figure 6 Needle like dropper used to measure solutions and binder

The samples created using these tools, included a tray that had no solvent or solution (i.e. pure ABS), a tray with only solvent, these were both used as controls. Then 4 trays containing, 1.5 grams, 3 grams, 4.5 grams, 6 grams of copper nanoparticles and 7 mL NMP respectively. The final product of the first trial looked like so:

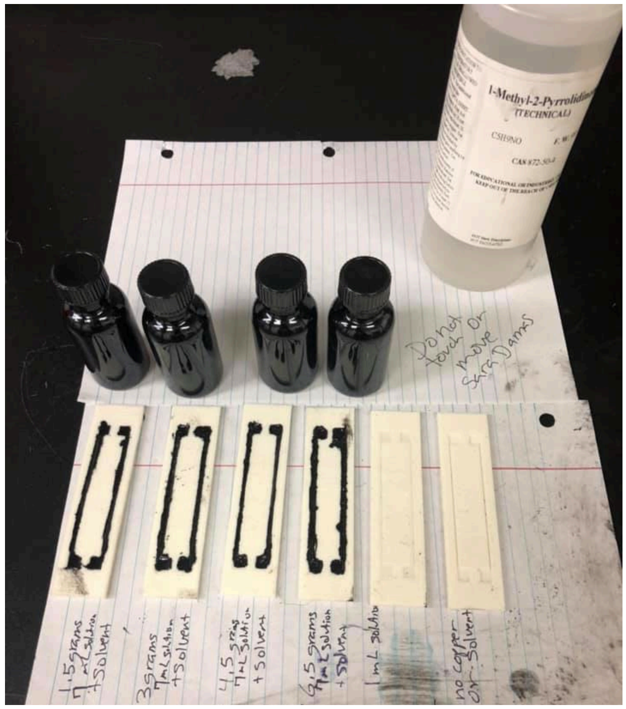

Figure 7 First Trial Samples

These samples were stored underneath a hood for "curing". Their conductivity was tested after 1 week and the result was inconclusive. Therefore, a second layer of solution was layered for each sample respectively. However, after curing for 2 more weeks the results were still inconclusive. Finally, a third layer of solution was layered for each sample respectively. However, even after two more weeks of curing in a hood and under a desk fan, the results were still inconclusive. Therefore, experiment 2 was conceptualized.

2) Experiment 2: Testing Nickel, Carbon, Electric Paint

For the second experiment, conductive pens and electric paint were bought from amazon. The nickel conductive pen contained a solution of nickel nanoparticles and acetone and was manufactured from MG Chemicals. The carbon conductive pen contained acetone, Butan-2-one, carbon black, and 1-Methoxy-2-Propanol Acetate and was also manufactured by MG Chemicals. The final product purchased was electric paint, which was composed of water, natural resin, conductive carbon, and humectant, processing aids and preservatives. Specific natural resin, humectant, etc. used was not listed as Bare Conductive, the manufacturer, lists them as a trade secret.

Five more 3D printed ABS circuit board like trays were made like the one seen in *Figure 4 First Trial Circuit Board Tray*. The first tray had nothing layered, the second tray had only solvent layered on its right channel and nothing in its left channel. The remaining 3 trays had solvent layered on their right channel of their circuit board like tray. Then after the solvent was cured underneath the hood for one week, nickel, cooper, and electric paint was layered on the right channel. After a week of curing the resistance of the left and right substrates was measured. (Even though the left substrate was bare, it was important to make sure no bleed through happened). In addition, the effects of the selected binder (NMP) could be observed when mixed with the selected metal material and ABS, vs. the metal material and ABS acting alone. After collection of the first set of data, BOTH substrates of each respective tray were layered with the respective material and left to cure for one week. This trial was basically mimicking what was done in the first trial but instead of cooper nanoparticles, nickel, carbon, and electric paint were used. Finally, the conductivity of the second layer was recorded.

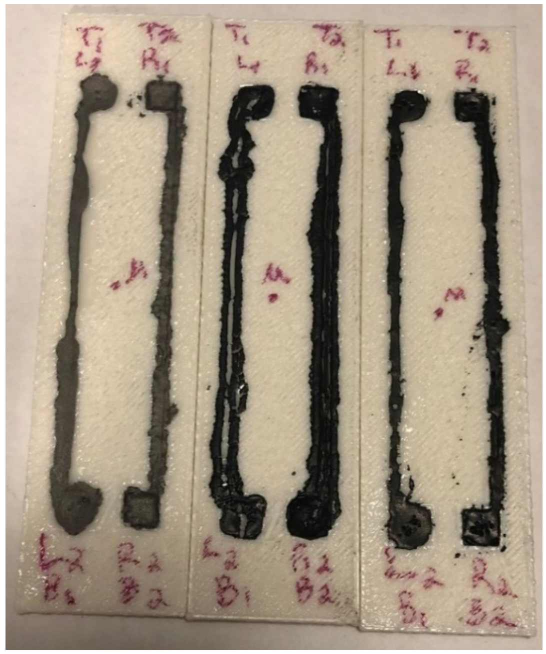

Figure 8 Experiment 2 layout. From left to right: nickel, carbon, and electric paint

The conductivity of this trial was captured after the samples had cured for a week. Then after the first data collection a second layer of each respective material was layered. Then after a week of curing, the second layer's data was recorded. The results of this trial will be discussed in the next section, "Results", of this paper. Most notably, what was understood from this trial is the side that had binder layered first on the ABS, then the metal nanoparticles layered on top had better conductivity than the side with no binder pre-layered on the ABS.

3) Experiment 3: Retesting All Concentrations of Copper, Nickel, and Electric Paint

Now that conductivity was confirmed in the binding of nickel, carbon, and electric paint and the binder was indeed helping increase the conductivity of the materials, trial 3 was initiated. Trial 3 served as a confirmation check between trial 1 and trial 2, and to replicate the results. Since, experiment 1 was a pilot trail and yielded inconclusive results. Nine 3D printed ABS trays, like the one pictured in *Figure 4 First Trial Circuit Board Tray*, were created. The first tray was left completely untouched. The remaining 8 trays had solvent layered on the right channel. The previous test concluded that the binder does indeed help with binding the two materials (ABS with nickel, ABS with copper, etc.) and provides better conductivity results, similar results were sought out in this experiment to further validate the findings. After the NMP cured for one week underneath a hood, the 7 trays were layered once with their respective materials. Tray 3: nickel, tray 4: carbon, tray 5: electric paint, tray 6: 1.5 grams cooper solution, tray 7: 3 grams cooper solution, tray 8: 4.5 grams cooper solution, tray 9: 6 grams cooper solution. The second tray only had solvent layered on it's right channel and no nanoparticles layered into its channels. Like the first tray, it was used as a control.

Figure 9 Experiment 3 layout. From left to right: nickel, carbon, electric paint, 1.5 g copper, 3 g copper, 4.5 g copper, and 6 g copper.

These samples were cured for 1 week and then their conductivity was checked and recorded. A second application of each respective material was then placed for each sample. Again, after a week of curing, the conductivity was checked and recorded. The results of this experiment are discussed in the next section. Experiment 3 solidified the methodology, proper materials, and confirmed that the binder does indeed positively interact with the nanoparticles and ABS, the experimentation was expanded. The next experiment explores how close the substrates can get without exhibiting bleed through.

4) Experiment 4: Testing Trace Distances

Experiment 2 and experiment 3 confirmed the findings of the effect of NMP when used to bind two materials. Conductivity was confirmed for several of the samples and data was quantified. Experiment 4 studied the spacing of the traces (channels) of the tray. Does the spacing of the traces effect the conductivity of the materials? Can trace proximity cause bleed through of nanoparticles between traces? What trace material and geometry will give the lowest resistance? For this experiment, four different trays were designed and printed. The first design of trays had a spacing of 1.4 mm between the traces, the second set had a spacing of 2.4 mm, then 3.4 mm and 4.4 mm respectfully. Drawings of the trays can be seen in: *Figure 10 Tray design with traces 1.4 mm-Figure 13 Tray design with traces 3.4 mm*.

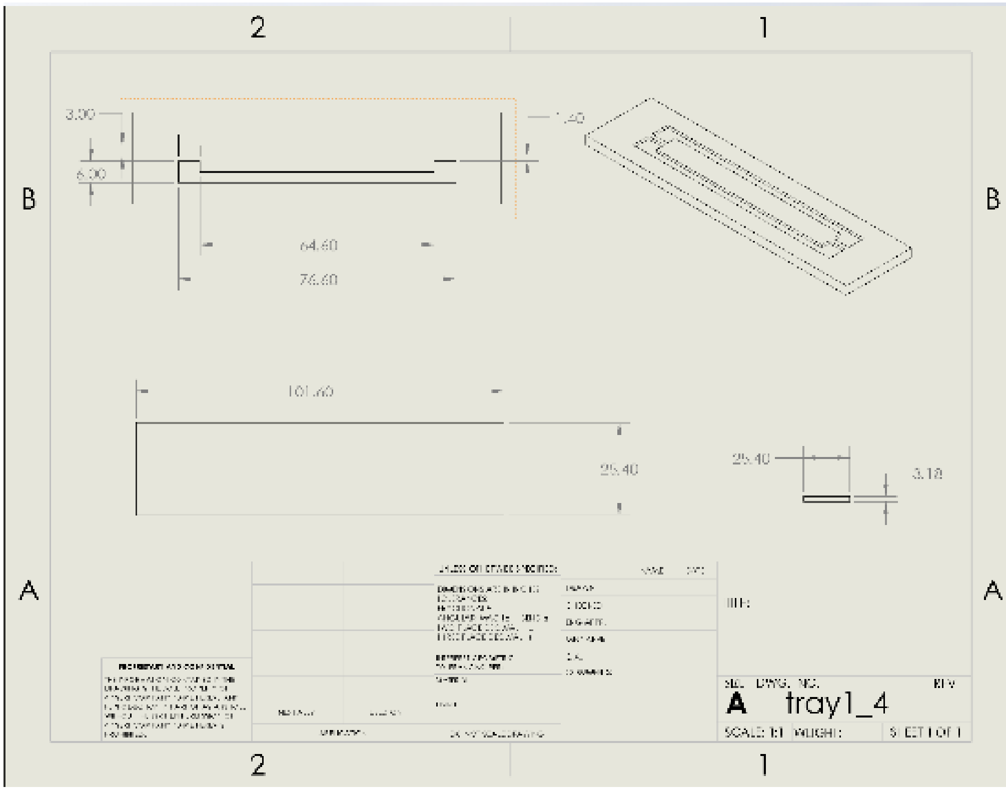

Figure 10 Tray design with traces 1.4 mm

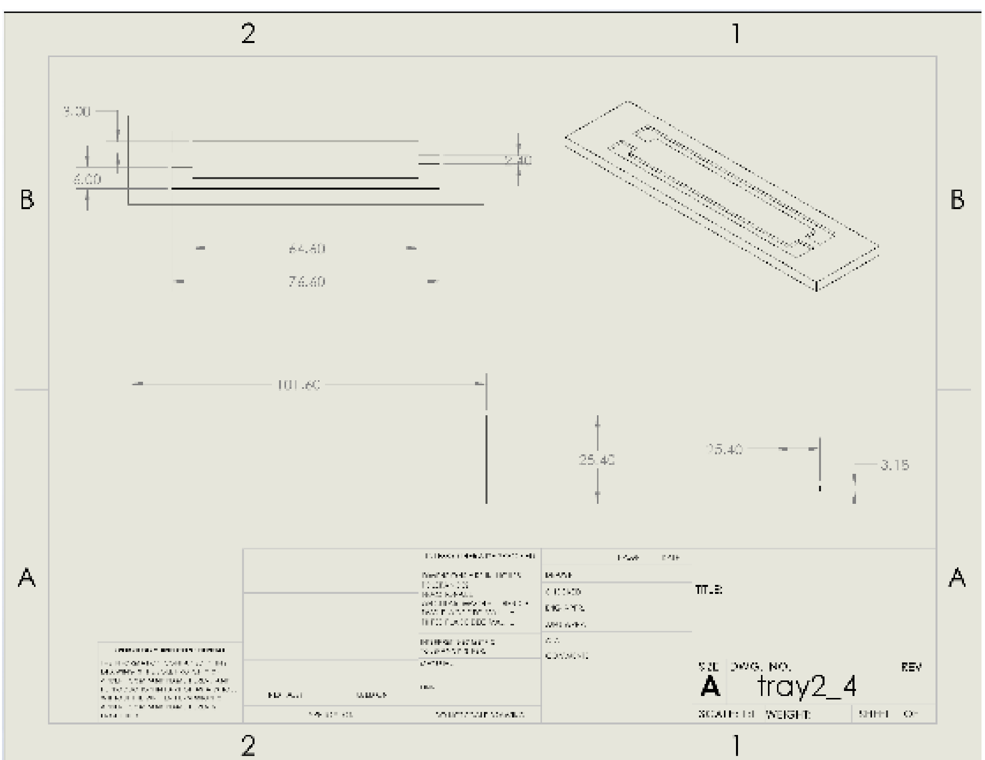

Figure 11 Tray design with traces 2.4 mm

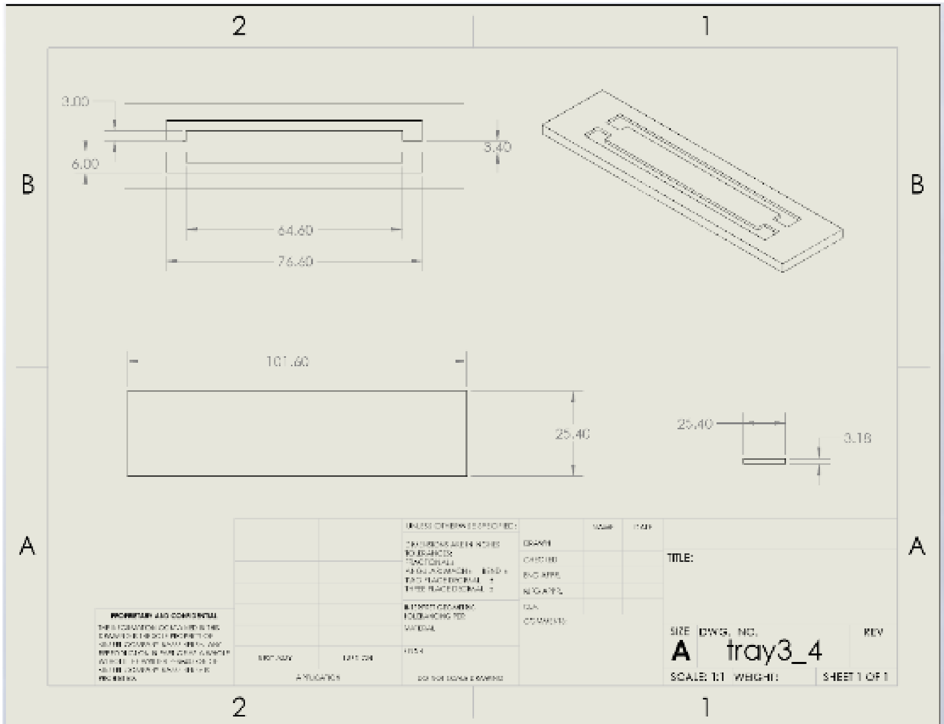

Figure 12 Tray design with traces 4.4 mm

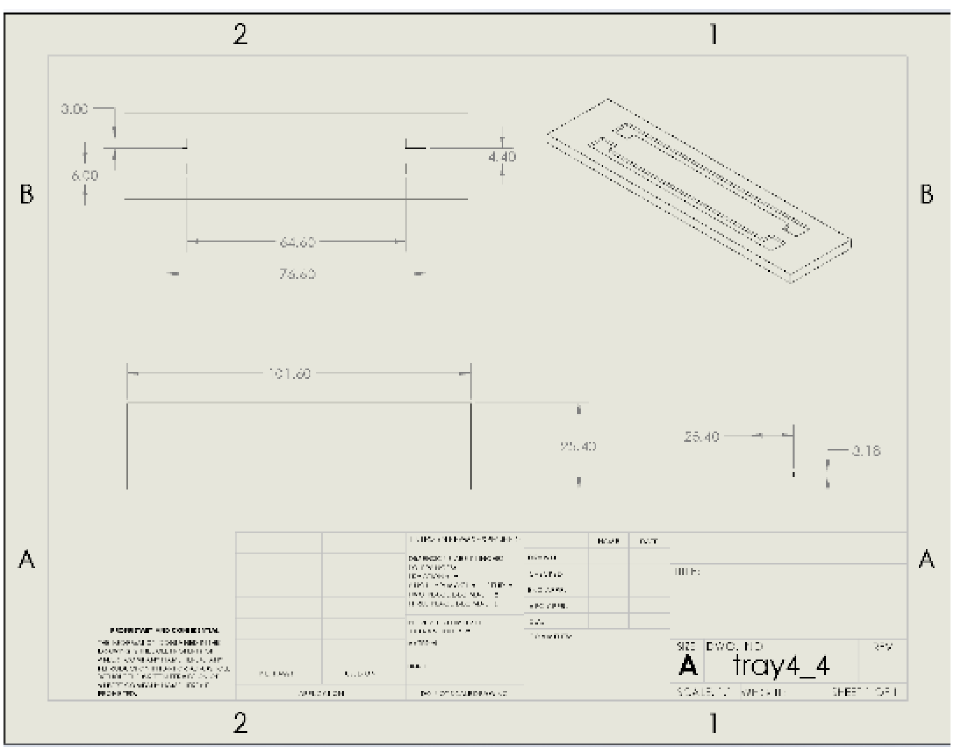

Figure 13 Tray design with traces 3.4 mm

Three types of nanoparticles were tested in this experiment: nickel, carbon, and electric paint. Therefore, 4 trays of the predefined varying trace distances were printed for each material being tested. Of course, 4 control trays of each trace distance were printed as well to ensure that the binder itself did not cause conductivity. In this experiment, the cooper solution that was created in experiment 1, was not used since it was proven that it produced inconclusive results in experiment 1 and experiment 3.

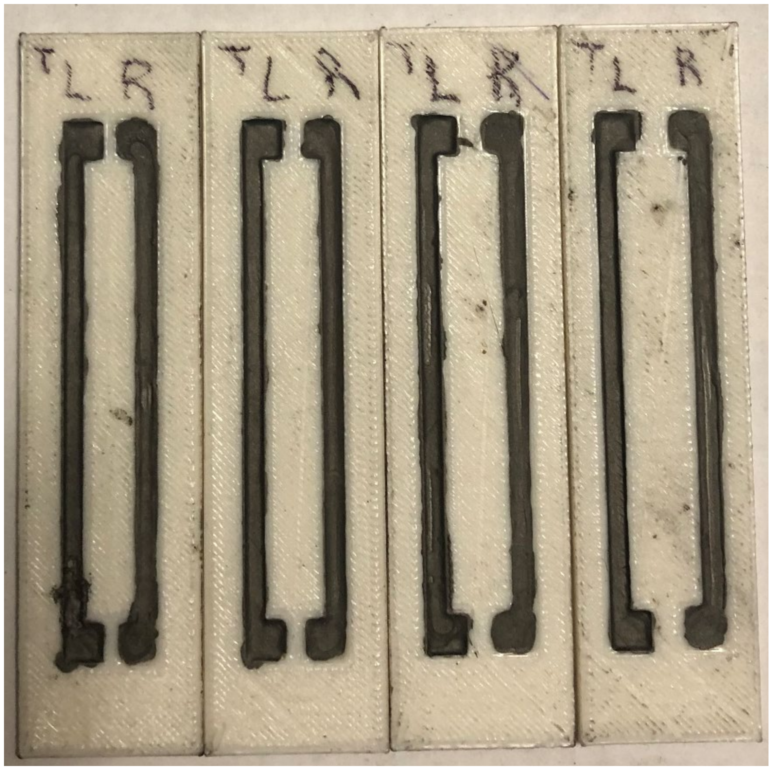

Figure 14 Example trays tested for conductivity with varying trace separations. From left to right: nickel 1.4, nickel 2.4, nickel 3.4, nickel 4.4

NMP was layered on the right channel of each set of trays. Then after a week of curing each material was layered in both channels. Then the data was collected after one week and like before the appropriate materials were layered again. All data was collected using the multimeter as mentioned before.

Trial 4 ended the testing and observation of the conductivity of nickel, carbon, electric paint, and copper nanoparticles. The data that was focused on for this experiment was the resistance of the right trace (bound trace) when compared at difference distances and different materials. A summary table was created with these results and discussed in the next section.

<u>Results</u>

1) Experiment 1: Pilot Testing of Copper Nanoparticles

Quantitative results of the first pilot experiment were not collected because the experiment kept yielding inconclusive results. However, it was noticed that the side with the pre-applied binder solvent had a smoother application of the copper nanoparticle substrate. In addition, as curing progressed more and more cracking was apparent in the samples. An example of the cracking can be seen in *Figure 15 Example of experiment 1 copper tray cracks* below.

Figure 15 Example of experiment 1 copper tray cracks

In addition to the cracking, the copper nanoparticles would return to their powder form. Therefore, several of the samples are coated in copper nanoparticle residue, due to transportation of the samples. (The picture in *Figure 15 Example of experiment 1 copper tray cracks* was taken a year after experimentation). It was concluded that the ratio of copper nanoparticles to binder could be one of the reasons why the results of the conductivity test of the first experiment were inconclusive. The nanoparticle laced binder could have been supersaturated. Another reason could be the type of binder paired with the nanoparticles. Since the in-house nanoparticle solution was not effective, pre-mixed nanoparticles were purchased for experiment 2 to be combined with the selected binder.

2) Experiment 2: Testing Nickel, Carbon, Electric Paint

The second experiment was the first experiment that yielded quantitative results. As can be seen from the example in Figure 15, the trays were labeled and measured in several locations. The trays were tested for conductivity from the left trace to the right trace (for example: L1 to R1 to make sure there was no bleed through).

Nickel	Unit (kΩ)	Unit (kΩ)	Unit (kΩ)												
	L1 to L2	R1 to R2	Standard Deviation	L1 to R1	L2 to R2	L1 to M	L2 to M	R1 to M	R2 to M	T1 to B1	T2 to B2	T1 to T2	B1 to B2	T1 to M	B1 to M
Layer 1	open circuit	**54.02**	3.48	open circuit											
Layer 2	0.0412	**0.0281**	0.00386												

Table 2 Averages of layer 1 and layer 2 for nickel conductive pen experiment 2

As can be noted from the table, the second application reduced the resistance of the nickel substrate substantially. When calculating the resistance reduction from 54.02 kΩ to 0.0281 kΩ, a 99% decrease in resistance can be seen. It can also be noted that the resistance of the right side (had binder pre-applied before nickel conductive pen) was slightly lower than that of the unbound left side. Therefore, the binder had a positive effect on the nickel nanoparticle binding with ABS. The binder was able to bind the two materials to yield a lower resistance.

Electric Paint	Unit (kΩ)	Unit (kΩ)	Unit (kΩ)												
	L1 to L2	R1 to R2	Standard Deviation	L1 to R1	L2 to R2	L1 to M	L2 to M	R1 to M	R2 to M	T1 to B1	T2 to B2	T1 to T2	B1 to B2	T1 to M	B1 to M
Layer 1	open circuit	**6.37**	0.0547	open circuit											
Layer 2	2.201	**1.08**	0.0475												

Table 3 Averages of layer 1 and layer 2 for electric paint experiment 2

The results from the conductivity from the electric paint was also very encouraging. Initially, the resistance of the trace with the pre-applied binder was 6.374 kΩ then it exhibited an 83% reduction in resistance to 1.078 kΩ. It is also worth noting that just like in the nickel sample, the electric paint sample exhibited better resistance on the trace that had the binder pre-applied.

Carbon	Unit (kΩ)	Unit (kΩ)	Unit (kΩ)												
	L1 to L2	R1 to R2	Standard Deviation	L1 to R1	L2 to R2	L1 to M	L2 to M	R1 to M	R2 to M	T1 to B1	T2 to B2	T1 to T2	B1 to B2	T1 to M	B1 to M
Layer 1	open circuit	7.02	0.109	open circuit											
Layer 2	4.004	**1.47**	0.0886												

Table 4 Averages of layer 1 and layer 2 for carbon conductive pen experiment 2

Just like the trends seen in nickel and electric paint, the carbon samples showed better resistance on the second layer application and when compared against no binder. When comparing the first and second layer, a 79% decrease of resistance was observed. When comparing the bound side versus the unbound side, the bound side a 63% decrease in resistance. Compared to all the other samples, the nickel samples yielded the lowest resistance results.

Material	Resistance of R1 to R2 Layer 2 (kΩ)
Nickel	**0.0281**
EP	**1.08**
Carbon	**1.47**

Table 5 Focused average results of experiment 2

A table was created highlighting the important final results of experiment 2. The lowest resistance was collected from the second layer of each of the respective samples and on the bound trace. To confirm these results and test the limits of bleeding through within the ABS 3D printed trays, experiment 3 was conceptualized.

3) Experiment 3: Retesting All Concentrations of Copper, Nickel, and Electric Paint

When quantifying experiment 3, which served as a redo and confirmation of experiment 2, the results were highly supportive of experiments 2’s findings. The binder did in deed help bind and increase the conductivity of the nanoparticle traces. The right side of the trays (side with binder) had a substantial decreased resistance compared to the unbonded side. The findings and averages are discussed below in detail. These average results were derived by taking resistance samples 5 times for each material tray. The controls, tray with no binder or material overlay, and tray with only binder, yielded no results, and therefore, no tables were generated of their results.

When looking at the average results of the first layer of the nickel samples, the right side had a resistance that is 51% lower than the left side. This was after only one week of curing. When comparing the right side of the tray from week 1 to week 2, a 99.88% decrease in the resistance proved that the binder helped cure the nickel nanoparticles to a lower resistance and hence better conductivity.

Nickel	Unit (kΩ)	Unit (kΩ)	Unit (kΩ)	Unit (kΩ)	
	L1 to L2	R1 to R2	L1 to L2 Standard Deviation	R1 to R2 Standard Deviation	All testing locations outside of substrate
Layer 1	30.4	14.8	0.339	0.206	open circuit
Layer 2	0.0182	0.0169	0.0002	0.0002	

Table 6 Averages of layer 1 and layer 2 for nickel conductive pen experiment 3

Overall, electric paint started off at a much lower resistance than that of nickel. Nickel started at a resistance between 14-31 kΩ, while electric pain started in the resistance range of 2-5 kΩ. When comparing layer 1 results of electric paint, the right side of the tray saw a 47.47% decrease in the resistance. That is comparable to nickel's decrease of resistance for the first layer which was 51%. While, electric paint yielded similar results to that of nickel, nickel is still slightly more favorable. When observing the bound trace, an 83.90% drop in the resistance was observed when comparing the electric paint's trace of layer 1 vs. layer 2. While that is a positive result, that is still not as high as nickel's 99.88%.

Electric Paint	Unit (kΩ)	Unit (kΩ)	Unit (kΩ)	Unit (kΩ)	
	L1 to L2	R1 to R2	L1 to L2 Standard Deviation	R1 to R2 Standard Deviation	All testing locations outside of substrate
Layer 1	5.072	**2.66**	0.037	0.166	open circuit
Layer 2	0.50	7 **0.429**	0.010	0.004	

Table 7 Averages of layer 1 and layer 2 for electric paint experiment 3

The results of the carbon sample took some effort and attention to environment to be understood. Naturally, when comparing the bound and unbound side, the bound side had a lower resistance and therefore, higher conductivity. However, when looking at the layer 1 results vs layer 2 results, layer 2 had a higher resistance than layer 1. The trend was untraditional compared to the other experiments and their samples. Something had interfered with the bonding of the nanoparticles and ABS.

Carbon	Unit (kΩ)	Unit (kΩ)	Unit (kΩ)	Unit (kΩ)	
	L1 to L2	R1 to R2	L1 to L2 Standard Deviation	R1 to R2 Standard Deviation	All testing locations outside of substrate
Layer 1	4.03	**1.27**	0.042	0.015	open circuit
Layer 2	5.72	**4.58**	0.052	0.004	

Table 8 Averages of layer 1 and layer 2 for carbon conductive pen experiment 3

Experiment 1 and experiment 2 were conceptualized, 3D printed, layered, and tested in the winter. Experiment 3 was done in the mixed weather of the spring. It was noticed that some days when entering the lab, the air conditioning would be on, and other days the air conditioning was off. Of course, with the conditioning and environmental climate changes, there are more drastic changed in the humidity in the air. The researcher was observing the effects of humidity, and environment changes on the carbon sample. This observation is consistent with the findings of previous researchers. (Amelia Elliott, 2016) adjusted her methodology when conducting her research to minimize the effects of environmental changes curing the samples faster. This research went a step further and shortened the curing time by using a furnace and a ramping temperature schedule for the samples. This would shorten the curing time of the samples so data can be collected as soon as possible before environmental effects can introduce uncertainty. Other researchers built an enclosed temperature/humidity controlled apparatus to store the samples in while they cured in natural air. (Jason Cantrell, 2017) didn't build an apparatus nor used a furnace to cure his samples. He cured them in open air but took note of the temperature in the room when testing the strength of his specimens. He conducted several experiments on the effects of temperature and humidity changes on the material properties of his nanoparticle bound samples

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While, this instance seen in the carbon sample can be paralleled to previous literature and can possibly explain the root of why an increase in resistance was seen between layer 1 and layer 2, it doesn't explain why similar reactions were not seen in nickel and the electric paint? To understand why nickel and electric paint possibly didn't react in the way that carbon did make qualitative observations of the nature of the carbon samples. When examining the carbon samples, the carbon can be seen to dry and crack as curing time progresses. Of course, any crack in the substrate will produce an open circuit and therefore, will not allow for conductivity. This is similar to the copper samples, who dried into a powder and produced an open circuit as well. Cracks in the carbon sample can be seen in the layout of the trace.

Figure 16 Drying of carbon sample

Just like how, all the copper samples could not give resistance data because the samples dried to a very loose powder, and resulted in an open circuit, the carbon under the right condition, sees a decline in conductivity due to its drying nature. The electric paint dries to more of a plastic putty, and the nickel takes the look of ink or paint.

Figure 17 Drying of nickel sample

Figure 18 Drying of electric paint sample

Therefore, the carbon material appears to be more sensitive to environmental conditions than nickel and electric paint. To further test this hypothesis the carbon sample was left to cure for a month straight. After four weeks the results can be seen below.

Carbon	Unit (kΩ)	Unit (kΩ)												
	L1 to L2	R1 to R2	L1 to R1	L2 to R2	L1 to M	L2 to M	R1 to M	R2 to M	T1 to B1	T2 to B2	T1 to T2	B1 to B2	T1 to M	B1 to M
Trial 1		189												
Trial 2		189												
Trial 3	open circuit	188							open circuit					
Trial 4		188												
Trial 5		187												

Table 9 Carbon individualized tray results from second layer after 4 weeks experiment 3

The left side of the sample with no binder dried to point that it cracked all the way through and lost all conductivity. The resistance of the bound right side increased. It is theorized that the binder more effectively entrains the nanoparticles in the ABS substrate material.

While, the experimental environment failed to decrease the resistance of the carbon when a second layer of material was added and cured for a longer period, it did not prohibit from the data proving that a binder does indeed help improve the binding and subsequently the conductivity of the nanoparticle/ABS substrate.

A comprehensive summary of the data discussed above can be seen in the table below.

Material	Percent decrease of resistance from unbound side to bound side (layer 1)	Percent decrease of resistance from unbound side to bound side (layer 1)	Percent decrease of resistance between layer 1 and layer 2	Percent decrease of resistance between layer 1 and layer 2
Nickel	51.4 %	7.57%	99.9%	99.9%
Electric Paint	47.5%	15.4%	90.0%	83.9%
Carbon	68.5%	20.0%	-42%	-261%

Table 10 Summary of resistance decrease and effect of adding a second layer in experiment 3

The last two columns explain how adding a second layer of nanoparticles does indeed benefit the substrate. Adding a second layer whether the material is bound or unbound improves the results because the 3D printed samples have voids in them and when you layer them you fill in the voids. The more layers the more the voids are packed. As explained before, temperature, and humidity effects affected the bonding of the carbon nanoparticles because these nanoparticles cured to more of a powder (powder has more voids in their particles) form than the nickel and electric paint samples.

4) Experiment 4: Testing Substrate Distances

The data collection of experiment 4 was consistent with the procedures in experiments 1, 2, and 3. A multimeter was used to collect resistance data. The goal of experiment 1, which was conducted as a pilot run to create a nanoparticle laced binder, was to determine if it was possible to bind CuO nanoparticles with ABS using NMP as a binder and achieve conductivity. Nanoparticles were successfully bound in experiment 2 (after the nanoparticle material was changed) and then experiment 3 confirmed that indeed the nanoparticles chosen do conduct, the binder does indeed decrease the resistance, and a second layer does indeed fill the voids in the 3D printed ABS trays. Since, those points were proven, only the averages of the bound side and second layer of the trays printed for experiment 4 were discussed. (All samples had a lower resistance in their second layer than their first, because they were done all in one stable season). Below is the summary data of layer 2.

Layer 2	R1 to R2 1.4 (kΩ)	ST.DEV Unit (kΩ)	R1 to R2 2.4 (kΩ)	ST. DEV Unit (kΩ)	R1 to R2 3.4 (kΩ)	ST.DEV Unit (kΩ)	R1 to R2 4.4 (kΩ)	ST.DEV Unit (kΩ)
nickel	0.0122	0.000248	0.00662	0.000147	**0.006**	0.000126	0.00846	0.000215
electric paint	**0.285**	0.00429	0.311	0.0137	0.337	0.0114	0.368	0.00979
carbon	1.31	0.0423	**1.19**	0.0249	1.95	0.486	2.00	0.0194

Table 11 Layer 2 experiment 4 summary

The lowest resistance that each material exhibited was identified bold in Table 11 *Layer 2 experiment 4 summary*. The substrate distance with the lowest resistance was identified to be 3.4

mm. All the samples were tested at varying locations on the trays like outlined in previous experiments and can be observed in *Figure 8 Experiment 2 layout. From left to right: nickel, carbon, and electric paint* and *Figure 15 Example of experiment 1 copper tray cracks*. When tested at these prelabeled locations, it was confirmed that none of the samples no matter what material bled and observed conductivity outside of the respective substrates. The material that yielded the lowest average resistance was nickel. This is hypothesized to be contributed to the drying form of this nanoparticle. It dries into a pen ink or paint like consistency. That drying form gives better material distribution within the substrate than the putty like drying form of the electric paint or potential cracking crevasses of carbon nanoparticles.

Note that a tray of just ABS and a tray with binder, were also laid up and tested. However, only nickel, electric paint, and carbon yielded results. Because experiment 1 and experiment 3 confirmed that the self-made concentrations of copper nanoparticles lose conductivity and due to their final curing form (powder), samples were not made to test them in this experiment since they would likely conclude to inconclusive results. Lastly, this experiment was conducted once and 36 samples were tested and averaged to obtain the summarized results. This experiment can be conducted multiple times and a 3D printer with tighter printing tolerance can be used to print traces that are closer than 1 mm apart, to fully understand the limitations of the trace separation distances before exhibiting bleed through between the traces.

Conclusion

The appeal of additive manufacturing is due to its minimalistic production of waste. In addition, this process uses little to no tooling. In return, this quickly and efficiently turns around a product to consumers. This research, "Experiments with a binder in fused deposition modeling (FDM) printing, to determine the best approach to providing/printing an electrically conductive material on a substrate."

In the first experiment (administered as a pilot experiment, that tested 6 samples), 3D printed Acrylonitrile Butadiene Styrene (ABS) trays, with a left and right substrate, were doped with a binder with various concentrations of copper nanoparticles (1.5 grams, 3 grams, 4.5 grams, and 6 grams respectively) on both the left and right side. However, after many failed attempts it was concluded that due to the drying nature, concentration, and binding combination, the nanoparticles cured to their original powder form, instead of binding to the ABS. It was concluded that it was unfeasible to lace CuO nanoparticles with the selected binder, NMP. Therefore, in the second experiment new nanoparticles were sought out.

The second experiment, 3 samples were made using the same methodology used in experiment 1 to test the binder effect on the conductivity of, nickel, carbon, and electric paint. The right side of the ABS trays was pre-applied with binder while the left was left bare. Then the nanoparticles were layered twice and left to cure. The testing concluded promising results and it was apparent that adding a second layer of nanoparticles decreased the resistance of all the samples, the binder did indeed help improve conductivity, and nickel yielded the lowest resistance at 0.0281 kΩ.

A third experiment was meant to repeat experiment 1 and 2 to confirm the results found. Nine samples were created, each one corresponding to the respective material type including the controls, one unbound sample and one pure ABS sample, in addition to (nickel, electric paint, copper 1.5 grams, etc.) Once again, a second layer of nanoparticles did indeed fill the voids in the 3D printed ABS trays, which lead to better material distribution and consequently, lower resistance and an increase in conductivity. However, an interesting phenomenon was observed. The resistance of the carbon sample had increased instead of decreased. This finding was consistent with previous literature detailing the effect of variation of humidity and temperature in the testing lab on nanoparticle bound sample's material properties.

The fourth experiment sought to determine the relationship between trace distance and nanoparticles. For this experiment 36 samples were created, because there were four geometries tested for each sample material type. The distance between the substrates was varied to determine the tolerance of the material and binder bleed through. Fortunately, in their tightest/closest trace distance none of the samples exhibited material bleed through. In other words, the samples only saw resistance within their traces. However, no trace distance seemed to be superior over the other. It seemed that the substrate distance did little to affect the resistance of the samples. Which is important when analyzing the integrity of the experiments and results of this study.

An electrically conductive pathway was achieved best when applying NMP to the ABS 3D printed trays, then layering two layers of nickel nanoparticles. The binder, NMP, softens the substrate of the ABS 3D printed tray, which allows for better adhesion between filament and nanoparticles. Nickel yielded the lowest resistance results consistently, when compared across experiments.

Even though this research was successful and yielding qualitative and quantitative results, much can still be learned and tested. As some engineers and scientist have done in previous works, a closed and climate controlled apparatus should have been built to eliminate environmental effects on the curing samples. An entire study, like the one conducted by (Jason Cantrell, 2017) can be done on the material property effects that temperature and humidity have on bound nanoparticle samples. It would be interesting to see what would happen if environmental effects were strategically forced on the samples, in the form of ramping humidity in a closed apparatus and then testing the samples.

A focused study can be done on the relationship between the substrate distance of the doped 3D printed trays. Using a higher resolution 3D printer, it can be tested how close can the traces get without causing bleed through? The MakerBot Replicator 2X that was used could only print at 1 mm minimum spacing. However, with the use of a higher resolution 3D printer closer traces can be printed.

If this testing was conducted again, a depositing nozzle would be programed to deposit a steady flow of nanoparticles instead of a human hand. This could eliminate the biggest human error that can be linked to this study. It would also ensure that all samples consistently had the best material distribution amongst their pathways and would eliminate clumping and potential breaks in the substrates.

Finally, this testing only explored improving the material properties of ABS. It would be interesting, and beneficial to the field of science, to understand how other filaments such as PLA would react to the FMD method of binding nanoparticles. It is possible that similar results could be duplicated, to see if localized strain hardening can be achieved along the conductive pathway of PLA doped with nanoparticles.

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