Additive Manufacturing of Electrically Conductive Materials

MAE 410 (001)

Modern Manufacturing Processes

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Literary Review

Additive manufacturing (AM) is a relatively new practice but has spread throughout the manufacturing world quickly. It is a method of manufacturing where material is added in layers to create a product. This allows for more precision with certain features, as well as more customization in parts (Debroy et al, 2018). Different from subtractive manufacturing, which is cutting away from the part itself, additive manufacturing allows for less waste to be produced. The four main types of additive manufacturing are photopolymerization, extrusion, powder based, and lamination. Table 1 details the different processes for additive manufacturing, the different techniques, the materials generally used in each, and advantages/limitations.

3D-printing process	Technique	Materials	Advantages	Limitations
Photopolymerization	Stereolithography (SLA)	Photopolymers	Simple	Single material
	Material jetting	Photopolymers	Multimaterial structures	High cost
	Continuous liquid interface printing (CLIP)	UV-curable resins	High speed	Single material
	Two-photon polymerization (2PP)	UV-curable resins	Sub-100 nm resolution	Low yield of production
Extrusion	Fused deposition modeling (FDM)	Thermoplastics (ABS, PLA, PC, PA, *etc.*); glass (new); metal (new)	Simple, multimaterial structures; low cost (for thermoplastic materials)	High cost (for glass and metal)
	Robocasting (DIW)	Plastics, ceramic, food, living cells, composites	Versatile	Requires post-processing; low resolution
Powder based	Selective laser sintering (SLS)	Thermoplastics, metals	No need for support material	Limited mechanical properties of object; high cost
	Selective laser melting (SLM)	Metals	No need for support material	High cost
	Electron beam melting (EBM)	Metals	No need for support material	High cost
	Binder jetting	Any material in particulate form	No need for support material; versatile; lower cost than laser-based methods	Limited mechanical properties
	Selective inhibition sintering (SIS)/inhibitor jetting	Metal	Sintering is performed only once after printing; lower cost than laser-based methods	Low resolution; limited mechanical properties
Lamination	Laminated object manufacturing (LOM)	Paper, metal, plastic, *etc.* as laminated sheets	Versatile	Limited mechanical properties; some design limitations

Table 1, Summary of Additive Manufacturing methods

Photopolymerization uses liquid polymer and exposes it to UV light in order to harden it. The process utilizes a moving platform with liquid polymer being slowly exposed to a UV laser light, and the laser hardens the material based on the CAD model given. Extrusion additive manufacturing deposits the semi-liquid model material from a nozzle head layer by layer in the pattern programmed. After the material is deposited it hardens, allowing the next layer of material to be deposited on top. This generally uses thermoplastic materials; however, it can also be used for a variety of others. Powder based additive manufacturing is similar to photopolymerization, however the liquid polymer would be replaced by powder. The powder is placed in a thin layer on the build surface, and then a binding system is used to create the desired pattern in the powder. This can be liquid glue, laser beams, or more. This is mainly used for metal and alloy particles and is being continuously improved to create higher quality parts. Lamination additive manufacturing utilizes laminated materials, or materials created in sheets, and stacks them on top of each other. It is then cut with a laser beam to create the desired shape.

Using additive manufacturing for electrochemistry could revolutionize the industry, as the complex customized systems made are expensive and unique. Using additive manufacturing, the electrodes could be made in specialized shapes and material composition based on the conductivity and desired use. One of the first attempts at printing conductive materials was made using a carbon-nanofiber epoxy mixture, and recently graphene has been used for direct 3D printing of carbon-based conductors. Combined with acrylonitrile-butadiene-styrene (ABS) and polylactic acid (PLA), conductive 3D models were successfully manufactured using Fused Deposition Modeling. (Ambrosi & Pumera, 2016)

Additive manufacturing for specifically metallic materials is an even more recent development, as it originally was used on more polymeric materials. Two common techniques used for additive manufacturing of metallic materials, selective laser melting and electron beam melting (Hirt et al, 2017).

With copper being one of the most commonly used conductive metals, it would be beneficial to have the ability to use additive manufacturing in combination with copper. However, with the selective laser melting process, the normal laser used is near infrared. This has a low absorption rate with copper, making it less ideal to use. However, when the laser wavelength is changed, it can increase the absorption rate. An experiment was performed to analyze the increased effectiveness of the new laser wavelength. The new laser is a 200W blue diode laser, with a wavelength of 400 nm. The experiment used a pure copper powder and the new laser. The setup of the selective laser melting system is shown below in Figure 1:

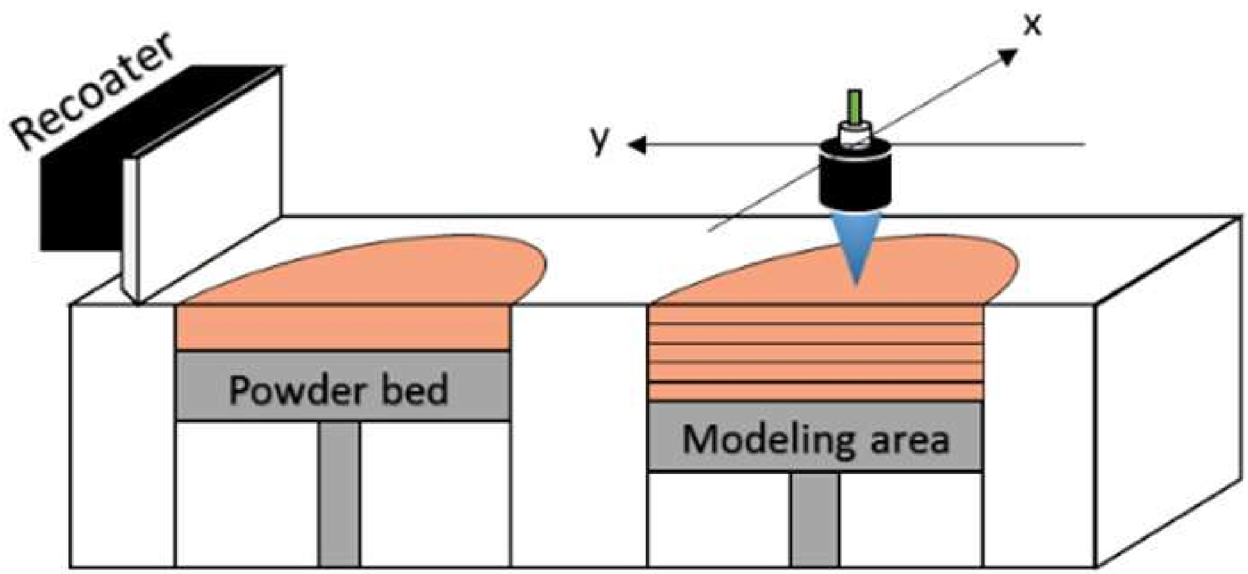

Figure 1, Selective Laser Melting System Setup

The conclusions of this experiment proved that the blue diode laser was more effective in the selective laser melting process. It produced layers with higher density, and less voids (Hori et al, 2021).

Other materials can be combined with electrically conductive materials in order to create a conductive part. A study was done at University "Politehnica" of Bucharest, Romania by a professor and PhD student to look into this. It can be done using fused deposition modeling, where filament is extruded to create layers of material. It is usually a thermoplastic material like acrylonitrile butadiene-styrene (ABS), polylactic acid (PLA), or thermoplastic polyurethane (TBU), but carbon powder and graphene can be added to make materials that can conduct electrical current. The materials created from this can be used in electromechanical systems and electrical circuits to create different types of sensors. They created sensors to be placed at the end of a “finger” structure and tested them against different forces of grips. The results of the test are shown in Figure 2 below in multiple plots. The sensors were tested against different types of fruits and vegetables, and the state switch delay was measured for different scenarios. The creation of these materials is referred to as Fused Filament Fabrication (FFF) and would be ideal for use in robotics (Zapciu & Constantin, 2016).

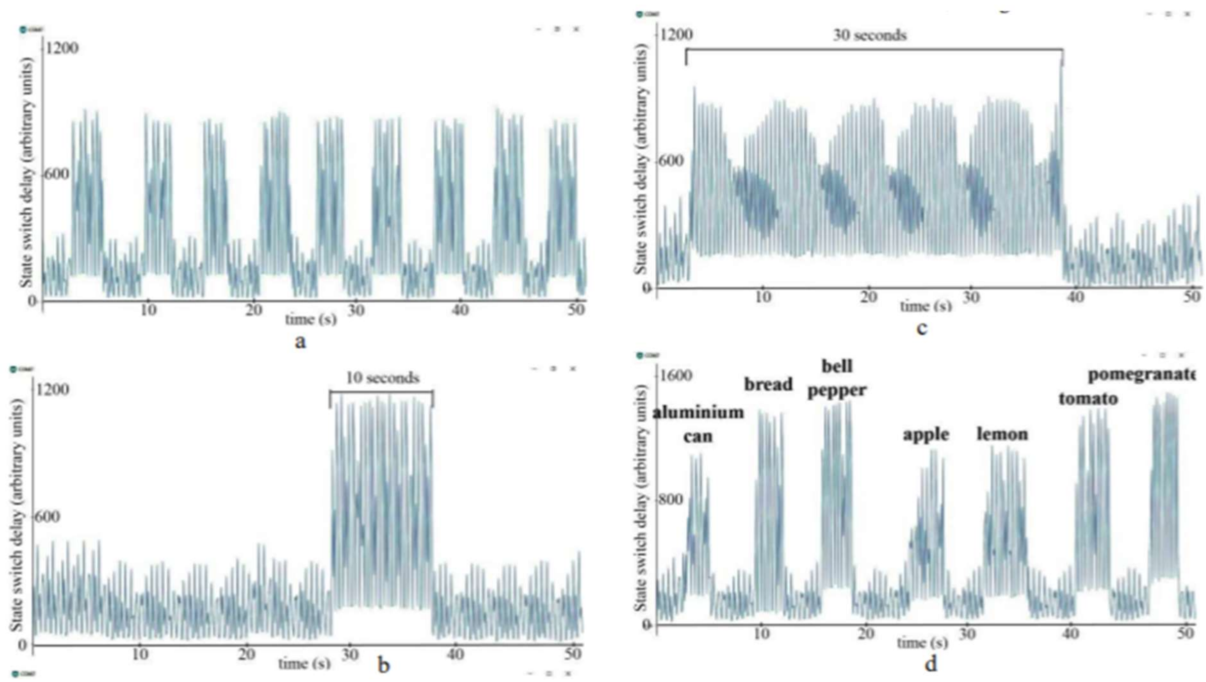

Figure 2, Results of Capacitive touch test; (a) repetitive test of finger contact with tomato; (b) 10 second gripping simulation of a tomato; (c) 30 second gripping simulation of a tomato; (d) gripping of various objects tested

Another study was conducted by the Fraunhofer Institute for Chemical Technology on Molded Interconnect Devices, and the ability to integrate an electrical circuit directly into a complex mechanical part. Initially, molded interconnect devices used injection molding of a thermoplastic part, and then the electrical components were added on top of the part. With the innovation of new techniques combining the thermoplastic with another nanocomposite, the electrical conductivity can be integrated into the part. This allows the electrical conductivity to go throughout the entire part, as opposed to only on top of the thermoplastic. This was tested using two different case studies, one of a “lightstick” which consists of a LED light inside an ABS casing connected to an electrical circuit, and the other was a set of capacitive sensors. The study was successful in proving the effectiveness of the nanocomposites and shows that it can be applied in larger scales to many industries (Morais et al, 2018).

One of the specific products that utilizes additive manufacturing for conductive materials is sensors, and a review of 3D printable conductive material for electrochemical sensors was done in the Electrochemistry Communications journal. Ordinarily, electrodes developed with 3D printing utilized the printing of metals which were then electroplated, which is an expensive and lengthy process. Instead, using carbon-based materials could provide a more feasible was to manufacture these electrodes. Using carbon nanotubes, graphene, and carbon black in combination with thermoplastics. The manufacturing of these conductive materials is very delicate, as the ratio of thermoplastic to conductive material needs to be precise. Many applications for the sensors created using the 3D printed electrodes are in the medical field. Figure 3 below details the 3D printed electrodes tested in this study. (Hamzah et al, 2018)

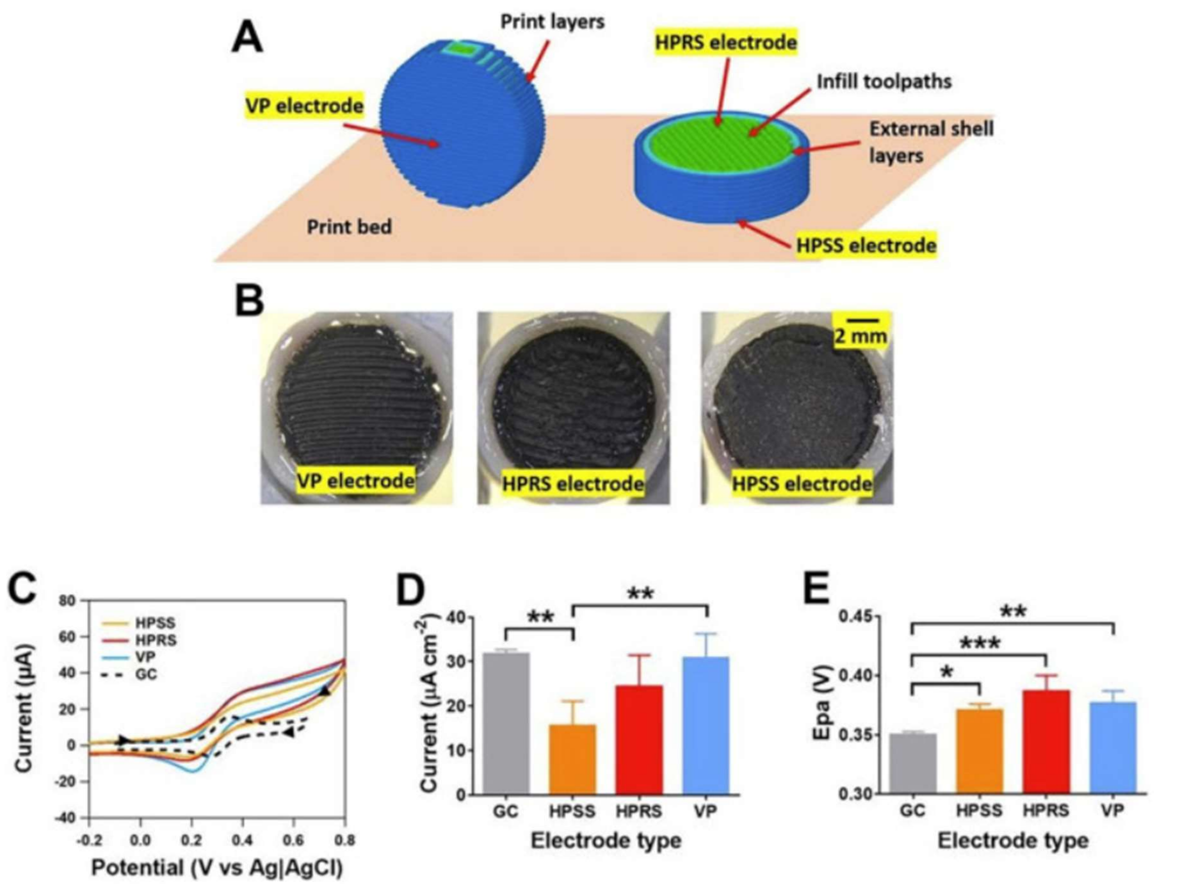

Figure 3, 3D Printed Electrodes
(A) Shows the different approaches of the horizontal smooth surface (HPSS) and rough surface (HPRS), and vertical (VP) prints using ABS/Carbon black material. (B) Photos of 3D printed ABS/Carbon black electrodes printed vertically and horizontally. (C) Voltammograms of glassy carbon (GC), VP, HPSS, HPRS, and VP for 1mM ferrocene carboxylic acid in 0.1M NaOH measured at a scan rate of 100mV/s. (D) Responses of anodic peak current. (E) Anodic peak potential (Epa) for 1mM ferrocene carboxylic acid.

Another study was done to test the 3D printing applications of thermoplastic composite filaments with polypropylene and carbon black. In order to prepare the print of this material, the rotor and header of the extruder were set between 200 ºC – 230 ºC. The rotor speed was set at 40-50% of its maximum. The percentage of carbon black in the polypropylene composite was determined by thermogravimetric analysis. This involved the temperature of the preweighted sample being increased to 700 ºC, and the degradation of the polypropylene was observed at 300 ºC and completed at 500 ºC. The carbon black remained stable at 600 ºC. The mass percentage of carbon black present in the sample was taken between 520 ºC and 600 ºC, and this was used as the percentage of carbon black in the original sample. A Fused Deposition Modeling printer was used for this study. The electrical resistance of printed wires was tested based on the percentage of carbon black in the composites found using the thermogravimetric analysis. The results of the tests showed that the resistivity was highest when the weight percentage of carbon black was less than 10% and decreased to below 0.01 Ω m when the weight percentage exceeded 30%. The filament was then used to create 2D and 3D circuits, as well as temperature sensors successfully. (Kwok et al, 2017)

The ability to use additive manufacturing and 3D printing to manufacture conductive materials is incredibly useful for rapid prototyping. A study done for the Journal of Materials Processing Technology goes into detail about the rapid prototyping of conductive components. The purpose is to expand the limits of rapid prototyping and allow for a more diverse range of materials to be used. They use carbon nanofibers in epoxy resin, and use a powder based additive manufacturing method. The plaster-based powder is bonded by a liquid binding agent, then the structure is cured by a hardening material, in this case it is an epoxy resin infused with carbon nanofibers. Before being combined with the epoxy, the carbon nanofibers are heat treated at 1500 ºC in order to increase electrical conductivity. The mixtures were prepared in two different ways, one of which contained mostly aggregates, and the other was a highly dispersed mixture. The samples manufactured were cured at 80 ºC for one hour, and then the resistivity was tested against the mass fraction of carbon nanofibers. The volume resistivity tested showed that conductivity occurred at a lower mass fraction for the aggregated mixture than the highly dispersed mixture. The same results were obtained when the surface resistivity was tested against the mass fraction. The results of this study show that electrically conductive materials can be integrated into the rapid prototyping world, and there are multiple ways to do that. Both the aggregated and dispersed mixture provided conductive samples. (Czyżewski et al, 2009)

Focusing more on the different types of conductive materials that can be used in additive manufacturing, there are a few different types for different uses. In the general sense, there are metal-based materials, and everything else. Using micro/nano scale 3D printing can alleviate some cost, as well as increase productivity. Metal-based materials provide very high levels of electrical conductivity, and are useful in producing electrodes, connectors, and conductors. There are three main groups for metal-based materials: liquid metals, metal nanoparticles, and in-situ reactive metal inks. Liquid metals have low melting temperatures and high conductivity and can be used in direct writing and inkjet printing. Metal nanoparticles are most frequently used for manufacturing conductive pieces, as they are placed into composite inks. Metals like gold, silver, and copper are used in this method. Using nanoparticles often requires high temperature treatments like laser-based annealing, thermal annealing, and joule hearing, which limits the applications of this method. In situ reactive metal inks use a material extrusion process to create structures. Silver inks have been tested at multiple temperatures and exhibit high conductivity levels at all. Nonmetal conductive materials used are carbon-based materials, lithium ions, and zinc. A few carbon-based materials commonly used are carbon black, carbon nanotubes, carbon nanofiber, and graphene. Carbon conductive grease, a type of carbon black particle, can be used to print stretchable sensors to detect different hand positions. Graphene oxide with polylactic acid was used to print stretchable parts as well, with high conductivity. The conductivity from carbon-based structures is not always consistent, as they are mixed with insulating polymers and the carbon-based materials are dispersed throughout. Micro batteries are produced using lithium ions and zinc, which can increase the energy density of the batteries by maximizing the space through additive manufacturing. Micro batteries were printed out of $Li_4Ti_5O_{12}$ (LTO) and $LiFePO_4$ (LFP) which had high energy and power density but had lower electrical conductivity. When graphene was added to the materials, the batteries performed better. (Chang et al, 2018)

Market Analysis

Multi3D

Multi3D is a company that produces conductive pellets and filament. Their filament is a metal-polymer composite made of biodegradable polyester and copper. It has an average resistivity of 0.006 Ω cm measured using a multimeter. This was done by applying silver paste to the ends of the filament to mitigate contact resistance, and then measuring the resistance using the multimeter. They offer two types of filaments, regular conductive and high temperature conductive. They offer the regular filament in diameters of 1.75 mm and 2.85 mm. The filament extrudes at 130-160 ºC, and they recommend a printing speed of 10-30 mm/s. Applications for this filament consist of many types of circuits; LED signs, Bluetooth lamps, interfacing sensors with Arduino, gaming controllers, and more. They claim that almost any circuit that can be run with a resistor of 10 Ω or more can be made with the filament. It retails for $196.00 for 100 g of filament and decreases in price for buying in bulk. The filament was tested at different sizes for the amount of current it could handle, and the relationship is shown in Figure 4 below.

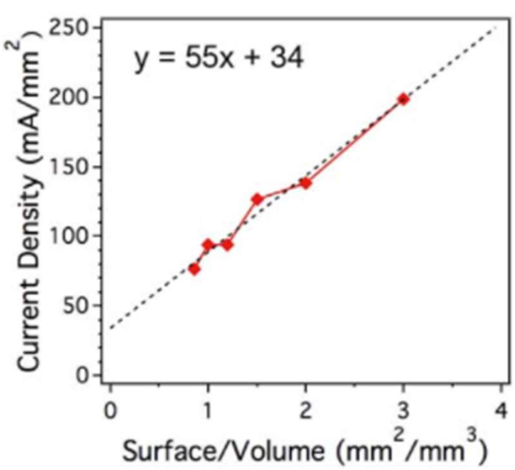

Figure 4, Electrifi Filament Current Density vs Surface/Volume

The “failure” of the filament was defined as the point where the resistance increased by 50% of its initial value. As shown, the higher surface/volume ratio allows for a higher current density. They also go into detail about the flow rate, infill pattern, and shell thickness for the Electrifi filament. Shown in Table 2 below are the results of the testing performed.

Shell thickness (mm)	Infill pattern	Flow rate (%)	Resistivity (Ω cm)
0.4	zigzag	100	0.022
0.4	zigzag	110	0.017
0.4	zigzag	120	0.017
0.8	Parallel lines	100	0.016
0.8	Parallel lines	110	0.012
0.8	Parallel lines	120	0.013

Table 2, Electrifi Filament 3D Printing Parameters

The high temperature conductive filament is still undergoing testing; however, it is expected to have a melting temperature of above 125 ºC and a volume resistivity of under 0.01 Ω cm. This could allow for more industrial or military applications. They offer Electrifi conductive pellets also made of biodegradable polyester and copper, which are useful for injection molding and 3D printing. They have a resistivity of 0.006 Ω cm as well, and retail for $70.00 per 100 g. They can be used for high volume manufacturing of electronics, as well as rapid prototyping for electronics and radio frequency components. They have published papers about several types of 3D printed electronic devices that can be done with the Electrifi filament and pellets, including inductors, capacitors, RF filters, antennas, batteries, and more.

3Dresyns

3Dresyns is a European company that produces many types of 3D printing materials. They have an entire section of electrically conductive 3D resins available. The resins available are silver based, hydrogel based, made with copper additives, graphene additives, and may variations of those. They have many applications, mainly in electronics as seen before, antennas, RFID tags, flexible cables, transparent electrodes for touchscreens, and more. they advise buyers that using the conductive products requires either stereolithography, digital light processing, or LCD 3D printers as the materials are quite complex.

3Dresyn AgNSEK1 is a non-soluble electrically conductive silver-based 3D resin, which has a sheet resistance of less than 0.44 Ω/square, and a resistivity of less than 7 micro Ω m. The conductivity of this resin is over 150 kS/m, and it requires a curing temperature of 120-140 ºC for 5-10 minutes after 3D printing. When added to the AgSEK1, which is the water-soluble version of the resin, the water resistance and solubility can be adjusted based on the needs of the user. It retails for $566.50 per 50 grams.

AgNSEK2 is a clear, electrically conductive nano silver 3D resin. It is used for touch screens, physical volume displays, and more. It has a resistivity of 380-390 milli Ω m, and sheet resistance of 1.9-2.1 kilo Ω/square. It requires curing after 3D printing for 5-10 minutes at 120 ºC. This product contains silver nanowires and is printable with stereolithography, digital light processing, or LCD 3D printers. It is valued at $226.59 for 50 grams.

AgSEK1 is a soluble and swellable conductive silver-based resin. It is used for antennas, RFID tags, flexible cables, and more, and is soluble in alcohol and water. It has a sheet resistivity of less than 0.42-0.44 Ω/square, and a resistivity of less than 6-8 micro Ω m. Its conductivity is greater than 100-200 kS/m. It requires curing for 5-10 minutes after printing at a temperature of 120-140 ºC. It is valued at $566.50 per 50 grams. AgSEK2 is clear soluble nano silver 3D resin, used for transparent touch screens and more. It has the same properties as AgNESK2, and also has a conductivity of 2.5-2.6 S/m. It retails for $226.59 per 50 grams.

PEDOTEK1 is a conductive hydrogel resin that needs no other conductive additives. It has a sheet resistance of less than 4500 Ω/square, conductivity of less than 1.1 S/m, resistivity of less than 0.1 Ω m. It retails for $339.89 per 250 grams. PEDOTEK1 Bio is similar to PEDOTEK1, however it is biocompatible. It has a sheet resistance of less than 100 Ω/square, conductivity of less than 0.5 S/m, and resistivity of less than 20 Ω m. It retails for the same price as PEDOTEK1.

3D-ADD AgEK1 is a biocompatible conductive nano silver additive. It can be used with other 3Dresyns to provide high conductivity. It has a conductivity of over $2x10^6$ S/m when used pure or in dip coatings, resistivity depending on dilution in other resins but can be up to 10^1-10^{13} Ω m, and conductivity depends on dilution in other resins as well can range from 10^{-1}-10^6 S/m. It has a high nano silver content of over 60%. It retails for $226.59 per 25 grams. 3D-ADD CuEK1 is a conductive nano copper additive, similar to AgEk1 in uses. Its volume resistivity is 7 mΩ/square, and conductivity depends on dilution in other resins but can range from 10^{-14}-10^2 S/m or higher. It has a high nano copper content of over 60%. It retails for $226.59 per 25 grams. 3D-ADD GrapEK1 is a conductive nano carbon graphene additive similar in uses to the silver and copper additives previously mentioned. It has a sheet resistance of 9-11 Ω/square, and conductivity depending on dilution in other resins but can range from 10^{-14}-10^2 S/m or higher. It has a high carbon graphene content of over 50%, and retails for $226.59 per 25 grams. 3D-ADD GraphEK2 Bio is another conductive nano carbon graphene additive, however it is biocompatible. It requires a low drying temperature and has a sheet resistance of less than 60 Ω/square.

Tuball

Tuball is a company that specializes in graphene nanotube additives to different materials for additive manufacturing. They create combinations with many different materials in order to produce all types of conductive structures. They boast that their graphene nanotubes only need a 0.01% dosage to make materials conductive. The nanotubes are also great for use in Lithium-ion batteries, for both the anodes and cathodes. They benefit the anodes with an increased life cycle, high energy density, increased SiO content, and increased capacity. The cathodes are benefitted with a higher discharge power, higher energy density, higher adhesion, and improved safety.

Tuball has a line of materials called Matrix, which consists of pre-dispersed concentrate of graphene nanotubes. They are designed to provide electrical conductivity to various materials with no negative effect on the mechanical properties of the original material. It is used to add anti-static and electrostatic discharge properties. It is independent of humidity, versatile, and has a variety of applications in different fields. The different concentrates offered are compatible with many different materials: acrylic, ethylene propylene diene monomer rubber, epoxy, LSR, RTV and HCR Silicones, Melamine, Phenolic, Polyester, Polyurethane, Polyvinylchloride, Tires and Rubber Goods, and Vinyl-ester. They have products in the beta stage of testing that are compatible with more materials: Polyethylene, Polypropylene, Polyvinylchloride, Polystyrene, Polyamide, Polycarbonate, natural rubber, polybutadiene rubber, styrene-butadiene rubber, ethylene propylene diene monomer rubber, nitrile butadiene rubber, hydrogenated nitrile butadiene rubber, FKM rubber, and liquid silicone rubber.

Tuball has an entire Research and Development sector called OCSiAl working with Tuball to research the uses and applications of the graphene nanotubes. They go into detail about the different types of graphene nanotubes, and what they actually are. The nanotubes are graphene sheets rolled into a tube, and they come in single wall nanotubes or multi wall nanotubes. Table 3 below details the difference between the two.

MWCNTs Multi Wall Carbon Nanotubes	SWCNTs Single Wall Carbon Nanotubes
Rigid and short	Flexible and long
Effective concentration of 0.5–5%	Effective concentration from 0.01%
Can only be used to produce black conductive materials	Allow the production of conductive materials of any color
Cannot be used to produce transparent conductive materials	Allow the production of transparent conductive materials
Can degrade mechanical properties because of the high concentrations required	Preserve or improve the mechanical properties of materials

Table 3, MCWNTs vs SWCNTs

Graphene nanotubes are such a recent discovery because of the lack of technology for their mass production. It was expensive to use them, making it less desirable to do so. However, they are compatible with almost all materials, and the length to diameter ratio is over 3000:1, meaning they can be quite long and small. They can withstand up to 1600 ºC in a vacuum and are 100 times stronger than steel. OCSiAl created the first industrial technology for synthesizing graphene nanotubes and worked with Tuball to market the first graphene nanotubes for mass applications.

Specific applications are detailed by industry, and the aerospace industry has multiple applications for conductive materials. The lithium ions detailed above can be used in airplanes, and composite pressure vessels can be made with the Matrix 301 additive for evacuation systems. Anti-static support equipment can be made with Matrix 815 additive, and conductive grease for battery assemblies can be made with the Matrix 601 additive for helicopters. Matrix 601 is also used with Matrix 605 for cable accessories in spacecrafts. They are used on the inner side for conductive and insulation, and the outer side which has a surface resistivity of 5000 Ω/sq. The Matrix 608 additive is used in gaskets and hoses for spacecrafts as well.

In the automotive industry it has applications for the exterior, interior, structure, battery, and tires of automobiles. On the exterior, the Matrix 204 & 301 additives are used for conductive primers for electrostatic painting. The interior has mostly anti-static applications. The battery can use the Lithium-ion battery discussed previously, as well having anti-static applications with the Matrix 608 additive.

Chasm

Chasm is another company specializing in carbon nanotube technology, and they supply products to additive manufacturing companies around the world. They have different mixtures of materials containing carbon nanotubes.

Their AgeNT materials are transparent conductive films used to create transparent touch sensors and buttons, heaters, antennas and more. There are five versions of AgeNT materials, all ranging in application, and conductivity. They have a formula based on a metal mesh substrate combined with the carbon nanotubes, as well as a model using a silver nanowire substrate. They also have a patented V2V ink vehicle that delivers flexible transparent conductors, meant for use in harsh environments. AgeNT materials are printed onto Chasm substrates using screen printing and the excess ink is etched away creating the desired circuits.

NTeC materials are specific additives where carbon nanotubes are grown onto other particles. They can be grown onto graphite, carbon black, cement, silicon, and more. It is integrated into cylindrical battery cells, coin cells and pouch cells. It can be mixed into a slurry as well and applied on top of other materials. It has a lower internal resistance than bare graphite, higher thermal conductivity, and greater lithium-ion storage. It is grown by mixing a solid catalyst with graphite, then placing the mixture in a rector for the carbon nanotube growth. They grow directly onto the graphite particles and produces a high yield with low cost. It is finally purified to produce higher grades using a thermal purification method. Figure 5 shows regular graphite particles compared to those with carbon nanotubes grown on them.

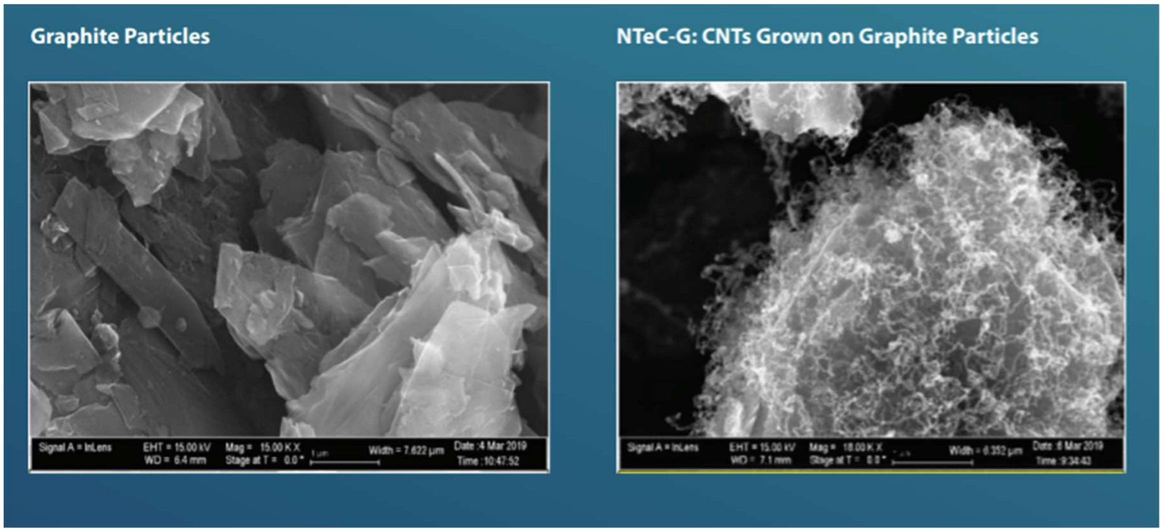

Figure 5, Regular Graphite Particles vs Carbon Nanotubes Grown on Graphite Particles

Signis is another type of material produced by Chasm made of single wall carbon nanotubes. It is produced using Chasm's proprietary CoMoCAT synthesis process. There are a few different versions of the Signis products: SG65i is semiconducting single-wall carbon nanotubes enriched in chirality, with a carbon purity of greater than 95% of the weight, and semiconducting carbon nanotube content of 95%. It comes in powder form but can be made in other forms such as wet cake, dispersions, coating formulas, inks, and more. SG76 is another semiconducting single-wall carbon nanotube enriched in chirality. It has a carbon purity of more than 90% of the weight and comes in powder form. It can also be supplied in the same forms as SG65i if needed. CG300 is a form of conductive single-wall carbon nanotubes, and it is Signis's most conductive single walled carbon nanotube product. It has a carbon purity of over 95% of the weight and comes in a powder form as well. It can also be made in the same forms stated above for SG65i if needed. CG100 is an economical single-wall carbon nanotube, which offers good electrical conductivity for a reasonable price. It has a carbon purity of over 90% of the weight and comes in the same forms as the products before.

Chasms fourth product sector is Chasm H_2O, which uses the carbon nanotubes for water purification. It uses the carbon nanotubes in a roll-to-roll fabrication method, locked in a UV-cured polymer matrix to form a membrane. It transports water molecules with higher speed, and almost perfect sanitation. It is degradation resistant, used in reverse osmosis desalination and other forms of water purification. They are also energy efficient, as they require less pressure and energy than traditional reverse osmosis membranes. They are used for water and wastewater reuse, rinse water, ingredient water, high purity water, and potable drinking water. The carbon nanotubes are produced using the CoMoCAT process, then dispersed into curable monomer fluid and roll-to-roll coated onto a substrate. They are then placed into vertical alignment and cured with UV to lock the matrix. The final membrane post-processing is a proprietary process.

Protopasta

Protopasta is a large producer of 3D printing filament, and they came out with an electrically conductive composite PLA. It retails for $49.99 per 500g spool, and has applications of LEDs, touch sensors, and more. It comes in either 1.75- or 2.85-mm diameters and can either be bought in loose coils or spools. It can print with standard PLA compatible printers. The volume resistivity of the molded resin not 3D printed is 15 Ω-cm, the volume resistivity of the 3D printed parts along layers x/y is 30 Ω-cm, and along the z layer is 115 Ω-cm. The resistance of a 10 cm length of 1.75mm diameter filament is 2-3 kΩ, and for a 2.85mm diameter filament is 800-1200 Ω. The material properties and print settings are shown in Table 4 below.

Material Properties

Properties	Value/Description
Base material	PLA
Characteristics	low odor, non-toxic, renewably sourced
Molecular structure	Amorphous
Additives	Carbon black / Polymer
Max particle size	N/A
Density	approx. 1.24 g/cc
Length	Approx. 332 m/kg (1.75 mm) & 124 m/kg (2.85 mm)
Min bend diameter	mm 25 (1.75 mm) & mm 50 (2.85 mm)
Glass transition (Tg) onset	N/A
Melt point (Tm) onset	approx. 155 deg C (310 deg F)
Max use	N/A

Use limit is geometry, load & condition dependent

Print Settings
(Based on Ultimaker s5 .15mm Profile)

Setting	Value
Nozzle Temperature [°C]	215
Heated Bed Temperature [°C]	60
Print Speed [mm/s]	25-45
Flow Rate/Extrusion Multiplier [%]	100
Extrusion Width [mm]	.45 (.05mm larger than nozzle size)
Volume Flow Rate [mm³/s]	2-3

Results may vary based on print settings as well as print quality

Table 4, (a) Material Properties (b) Print Settings

Heraeus Epurio

Heraeus Epurio is a German based company that produces materials for capacitor, display, and photoresist applications. They have a plethora of different types of materials ranging in applications and uses. Clevios is an extremely thin electrically conductive polymer coating made up of polythiophene and polyanion offering a very high conductivity of 1000 S/cm. It is available in several forms, as a momer for in-situ polymerization, a neat water-based dispersion, or a formulation mixed with solvents and additives. It is transparent, has good thermal and UV stability, and is scalable to industrial needs. Clevios requires thermal drying in a hot-air convection oven or using infrared, which is more effective than the traditional convection oven.

Touch panels are just one of the many applications of the Clevios conductive polymers. They offer a low sheet resistance of 15 Ω/square and can be made into curved surfaces and 3D shapes. Compared to the usual indium tin oxide material used to create touch screens, the Clevios conductive polymers are incredibly more flexible and energy intensive. Shown below in Figure 6 is a graph of the flexibility of the different materials compared to the sheet resistance of each.

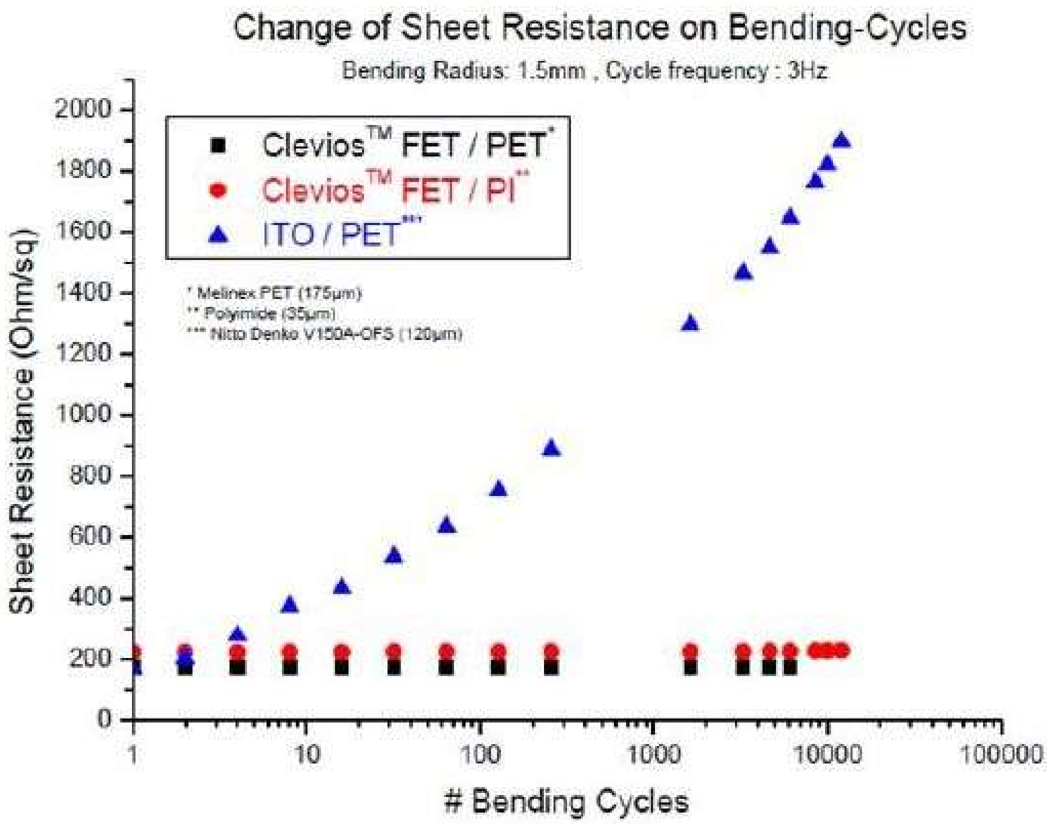

Figure 6, Change of Sheet Resistance on Bending Cycles

As seen above, the Clevios product hold their resistance for over 10,000 bending cycles, when the indium tin oxide originally used starts increasing in resistance after about 5 bending cycles. There are different versions of Clevios that can be used for touch panels, and each have different pros and cons. The highest conductive material is PH1000, which has the conductivity of 1000 S/cm. The sheet resistance in coating can go as low as 150 Ω/square. F 100T is used in harsh environmental conditions, and F ET is a ready to use coating formula with sheet resistance of 200 Ω/square. Heraeus also offers materials with extremely low sheet resistances for larger displays. HY E is a material used for foldable touch sensors, seen in the real world as foldable smartphones. It is a blend of silver nanowires and the PEDOT:PSS material in all Clevios conductive materials.

Other interesting applications of the Clevios materials are transparent electrodes, conductive adhesives, electroluminescence lighting, organic solar cells, polymer capacitors, antistatic coatings, printed electronics and more.

Methodology Review

It is clear through the literary review and market analysis that conductive materials in additive manufacturing play a huge role in the lives we lead today. Circuit boards are in every computer and smart phone, touch sensors are everywhere in technology, and technology is only getting smaller. The ability to produce conductive materials using additive manufacturing can lead to higher production rates, and lower prices.

As stated in the literary review, there are many different forms of additive manufacturing. The forms seen used for conductive materials were electron beam welding, selective laser melting, and fused deposition modeling. 3Dresyns recommends the use of stereolithography, digital light processing, or LCD 3D printers for their products. Fused deposition modeling is a very common form of additive manufacturing, as it is extremely accessible. The company Protopasta discussed in the market analysis produces all types of filaments to be used in fused deposition modeling, including the electrically conductive filament shown. It can be purchased for personal or industrial use and has many applications.

While copper is a highly conductive material and is used generously throughout the world for that purpose, it was not something easily found in research. A couple articles had been written about it, but additive manufacturing of metals is not a common practice. The addition of conductive carbon materials to already existing thermoplastics was a lot more common. Almost all of the articles in the literature review touch on different additives, and it can be seen throughout the market review that carbon-based additives are highly sought out and desired. They are less expensive to obtain and produce and can be manipulated easier. There are some companies that used silver-based additives, and research has been done on them. In the literary review, Chang et al wrote about silver, gold, and copper additives to filaments in order to add conductivity. In the market analysis, 3Dresyns has multiple additives that are silver based. Multi3D offers a ready to use filament, as well as pellets for injection molding and other forms of 3D printing, made of biodegradable polyester and copper. They offer the filament in a regular conductive form, as well as a high temperature resistant form. Chasm and Heraeus both had silver nanowires/substrates in their materials as well. Unlike the limited information found on metals, the research and products found with carbon-based additives was plentiful.

Materials like graphene, carbon black, and multiple types of nanotubes and nanofibers are used in combination with thermoplastics to create conductive materials for additive manufacturing. Studies were done by Ambrosi & Pumera, Zapciu & Constantin, Morais et al, Hamzah et al, Kwok et al, Czyżewski et al**,** and Chang et al all concerning these types of conductive materials. Ambrosi & Pumera focused on a carbon-nanofiber epoxy mixture as well as graphene used as an additive. Zapciu & Constantin worked with carbon powder and graphene mixed with different types of thermoplastics to create touch sensors. The sensors capacitance was then tested by gripping different objects. Morais et al focused on implementing nanocomposites added to thermoplastics to create LED lights. Hamzah et al looked at the effects of using carbon nanotubes, graphene, and carbon black in combination with thermoplastics to create the conductive materials. Kwok et al combined polypropylene with carbon black and used a fused deposition modeling 3D printer to analyze electrical and thermal conductivity. Czyżewski et al use carbon nanofibers in epoxy resin with a powder based additive manufacturing method to analyze the electrical conductivity of the material after printing. Chang et al tested various types of conductive materials. They used metal nanoparticles placed into composite inks, which have to be heat treated with high temperatures after production. They also produced in situ reactive metal inks, carbon conductive grease (a type of carbon black material), and graphene oxide with polylactic acid (makes stretchable parts). They also studied the addition of graphene into lithium-ion batteries, and the benefits that has on them.

On the market analysis side, almost every company found had thermoplastic additive materials or sold already mixed carbon materials with thermoplastics. 3Dresyns has a conductive hydrogel resin called PEDOTEK1, which is a conductive material in itself that needs no additives. All other 3Dresyns products have metal additives or metal components to them. Tuball specializes in graphene nanotubes, which are a type of carbon nanotube. They have single-walled nanotubes and multiwall nanotubes, the differences of which are detailed in Table 3 in the Market Review section. They market mostly graphene nanotube concentrates, which can be added into a multitude of materials and used for additive manufacturing in different ways. Chasm also concentrates in carbon nanotube production but have a few different forms of the nanotubes. They have their AgeNT, NTeC, Signis, and Chasm H_2O products, all of which differ in manufacturing process and application. The AgeNT products are transparent conductive films utilized for touch screens frequently, NTeC products are additives where carbon nanotubes are grown onto other particles, which can be seen in Figure 5 in the Market Analysis section. The Signis products are single wall carbon nanotubes produced using Chasm's proprietary CoMoCAT synthesis process. Finally, the Chasm H_2O products are carbon nanotubes in a roll-to-roll fabrication method, cured with UV to create a membrane used to filter water. Protopasta, a huge manufacturer of 3D printing filaments, has their electrically conductive filament. It is an electically conductive composite PLA and can be used in any PLA compatible 3D printer. This opens the door for many people to use the product, as PLA printers are highly accessible to the public. It allows personal research to occur with the product, and those without the funding of a large company to create projects using electrically conductive additive manufacturing. This is especially useful for university students or those who have hobbies in creating electrical systems, as they can use this filament to make simple or complex circuits. Heraeus Epurio's conductive material, Clevios PEDOT:PSS, is an extremely thin electrically conductive polymer coating made up of polythiophene and polyanion. It has many industrial uses, and most notably can be used to create flexible touch sensors, aka foldable touch screens. This is a novel use, as society is mostly used to touch screens being extremely fragile. Most everyone who has owned a touch screen piece of technology has cracked it before, and the idea of creating a flexible touch screen that may be shatter resistant is extremely desirable.

The applications of additive manufacturing of conductive materials are extensive and discussed in both the literary review and market analysis. These materials are certainly revolutionizing the manufacturing field, and the applications are always growing. Carbon-based conductors can be created and placed into electrical circuits, highly sensitive transparent or opaque touch sensors can be created, as well as stretchable touch sensors. Electrodes can be created more efficiently and with less cost. Flexible cables and wires can be created, which could be a game changer in the cable industry. Accounting for the bend radius in wires and cables is something extremely important in that industry and increasing that bend radius opens the door to new possibilities. The conductive materials can be used in circuits as inductors and capacitors for LED signs, Bluetooth lamps, interfacing sensors with Arduino, gaming controllers, and more. They can be used to create RF filters, antennas, conductive adhesives, organic solar cells, polymer capacitors, antistatic coatings, printed electronics and more. They also have uses in lithium-ion batteries, where they increase the effectiveness of them. They also have positive effects on the longevity of the batteries. Used in both the anodes and cathodes of the batteries, conductive materials generally improve the lithium-ion batteries.

As shown throughout this paper, the effect of electrically conductive materials on the additive manufacturing sector is great. Companies are doing continuous research to enhance these materials, and they are used throughout multiple sectors in the world. From aerospace, to automotive, to water purification, conductive materials can be seen everywhere. This is a booming topic in industry, and it would not be out of hand to expect it to take over. With the use of carbon-based materials, it is extremely accessible to produce. Cutting out the metals from electrically conductive materials opens up cheaper, and more environmentally friendly, options for this industry. Overall, electrically conductive materials in additive manufacturing are positioned to take over the industry if they have not already done so.

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