A Study on the Use of Extrusion-based Additive Manufacturing for Electrostatic Discharge Compliant Components from PEEK-Carbon Nanotube Composite

by

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ABSTRACT

Electrostatic Discharge (ESD) is a unique issue in the electronics industry that can cause failures of electrical components and complete electronic systems. There is an entire industry that is focused on developing ESD compliant tooling using traditional manufacturing methods. This research work evaluates the feasibility to fabricate a PEEK-Carbon Nanotube composite filament for Fused Filament Fabrication (FFF) Additive Manufacturing that is ESD compliant. In addition, it demonstrates that the FFF process can be used to print tools with the required accuracy, ESD compliance and mechanical properties necessary for the electronics industry at a low rate production level. Current Additive Manufacturing technology can print high temperature polymers, such as PEEK, with the required mechanical properties but they are not ESD compliant and require post processing to create a product that is. There has been some research conducted using mixed multi-wall and single wall carbon nanotubes in a PEEK polymers, which improves mechanical properties while reducing bulk resistance to the levels required to be ESD compliant. This previous research has been used to develop a PEEK-CNT polymer matrix for the Fused Filament Fabrication additive manufacturing process.

DEDICATION

I would like to thank my wife the most of all. She has been my biggest cheerleader through this journey and very patient while I worked towards this new goal. I appreciate the sacrifices she has made that has allowed me to embark on this journey of research and learning and I love her dearly.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Keng Hsu, for providing the opportunity to work with him on this project. The time spent on this project has been a challenging experience but very rewarding. I also appreciate all the time we spent discussing the possibilities of research in Additive Manufacturing arena.

I would also like to thank Dr. Darryl Morrell and Dr. Bradley Rogers for taking time out their busy schedules to a part of my supervisory committee. Their contributions went beyond just being a committee member they also encouraged me to embark upon a path in research during the completion of my Undergraduate degree.

I would also like to thank Dr. Thomas Sugar and Dr. Kevin Hollander the most for their enthusiastic encouragement. Their combined encouragement and letters of support are a primary reason why I returned to ASU to work on completing a Master's degree and maybe more. One of them told me "You will turn 60 someday. Do you want to be 60 with a PhD or 60 without a PhD?"

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INTRODUCTION

In the semiconductor industry static electricity and Electrostatic Discharge Damage (ESD) is a significant enough issue that an entire segment of the industry is working on solutions. ESD is such an issue that the American National Standards Institute (ANSI) has developed standards surrounding ESD compliance to establish a level of confidence when dealing with various suppliers of electronic components. Even with this focus on ESD reduction it was estimated in 2005 that losses in electronic hardware related to ESD damage cost the global electronics industry in excess of $84 billion dollars [1]. These costs amount to approximately 4% to 8% of total revenues and these costs do not include rework and warranty issues related to ESD. The costs incurred by the electronics industry has driven development of materials and processes to create products that attempt to eliminate the ESD damage entirely.

ESD damage occurs when there is a transfer of accumulated electrical charge. This transfer of accumulated electrical charge can occur from a person or due to a discharge from the device itself. There are several analytical models used to evaluate ESD events but the two models used most frequently in the industry to evaluate the potential effect of ESD on electrical components are the Human Based Model (HBM) and Component Based Model (CBM) [2]. Both models demonstrate that one of the best methods to reduce ESD damage to an electrical component is to have a resistive ground path with a sufficiently high enough resistance, approximately $10^6\ \Omega - cm$ [2], to slow the discharge rate thereby reducing the peak voltage experienced by the component. Some of the newer electronic designs have driven the sensitivity to ESD of the electrical devices to as low as 50 volts [3], the ESD standards use 100 volts as the minimum threshold for damage. The typical human can generate over 2000 volts in a normal factory environment without any ESD controls [4]. To combat these issues the production teams, technicians, engineers, and safety personnel, need to develop a system that is safe for the employees and the electrical components to reduce the potential for ESD damage. One area that these teams work diligently on is the packaging for the components during the manufacturing process.

ESD complaint JEDEC trays , Figure 1, are an industry standard tool for storage and processing of electronic components during the manufacturing process. They are typically built by machining or injection molding to meet the dimensional requirements of the electrical component they will be used with and are typically unique in their features to that specific electrical component.

Figure 1 JEDEC Matrix Trays

Not only are these trays used for storage of the sensitive electronics components, but they are also used for processing the components through various manufacturing processes including solder reflow ovens.

JEDEC trays can be ordered in various configurations to meet the manufacturing requirements of the electrical components they will be used with including trays that have a bulk surface resistance of $10^6\ \Omega - cm$ to minimize the chance of ESD damage to electrical components. The trays used for solder re-flow ovens also require the ability to survive a temperature approaching 250^o Celsius for approximately three minutes. Figure 2 shows a typical solder reflow oven temperature profile as the tray travels the length of the oven.

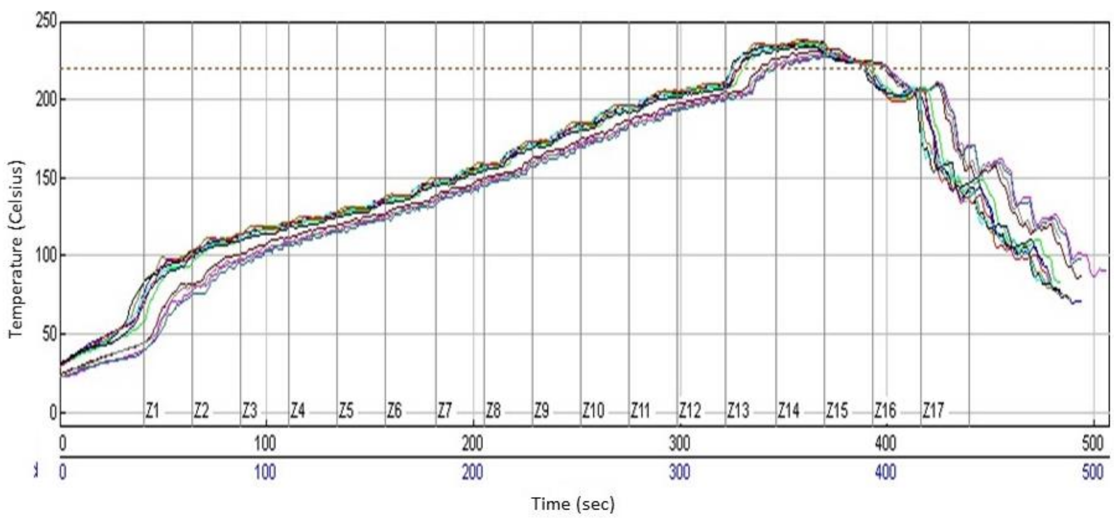


Figure 2 Typical Solder Re-Flow Oven Temperature Profile

Typical materials used in JEDEC trays in these harsh temperatures are a high-performance thermoplastic such as PolyEther Ether Ketone (PEEK), PolyEther Ketone

Ketone (PEKK), and Ultem. These high-performance thermoplastics have a heat deflection temperature of at least 195^o Celsius as tested per ISO 75/Be. Unfortunately, these high-performance thermoplastics are also natural insulators and do not have the required bulk surface resistance of $10^6 \ \Omega - cm$ as manufactured to protect the sensitive electrical components from ESD damage.

There are four primary methods that have been used to improve the bilk surface resistance, conductivity, of JEDEC trays manufactured from these high temperature thermoplastics [5]. The first method is to apply a coating, powder coating or paint, to the tray after it is machined, or injection molded. Unfortunately, these coatings tend to lose their effectiveness over time due to wear and will need to be subject to bulk surface resistance testing and reapplication of the coatings if the trays are used for an extended period of time. These coatings can be used to extend the life of trays that have been manufactured using carbon powder as a filler if the coating thickness does not affect the dimensional tolerances of the tray.

The second method is to mix carbon powder in the thermoplastic during the manufacturing of the raw material. Carbon powder is relatively inexpensive and does not adversely affect the manufacturing process at the raw material or detail level of the tray. Unfortunately, raw materials fabricated in this method tend to leave a powder residue during use. If the powder content in the raw material is too high, it will reduce the strength of the base polymer significantly. If the tray is used in a manufacturing area that is sensitive to contamination the carbon powder could create other failures in the manufacturing system. Carbon powder trays will increase their bulk surface resistance over time as the powder at the surface of the tray is worn during use. The powder does not create a matrix that is interconnected through the cross section of the tray.

The third method is blending short chopped carbon fibers in the raw material before extruding the raw material into an extrusion for machining or pellets for injection molding. The addition of the carbon fibers improves the raw material strength and stiffness. It will also improve thermal and electrical conductivity at low loading levels. Trays manufactured using carbon fiber fillers exhibit excellent wear properties. Even though the carbon fiber fillers are more expensive than the previous methods mentioned the excellent wear properties and the potential to have a bulk surface resistance the same through the cross section of the part is attractive option when the electrical components they will be used with have a long product life cycle. Carbon fiber fillers are not without their challenges, to obtain the bulk surface resistance required it typically takes a loading of 15% to 20% carbon fiber by volume. Carbon fiber will cause wear over time in injection molding nozzles and tools due to its abrasive nature. These short-chopped carbon fiber filled materials are also a challenge for trays that contain fine features, whether they are manufactured by injection molding or machining. If a tray has fine features the chopped carbon fibers can cause issues by clumping in those areas or not machining cleanly creating sections of the tray that do not meet the blueprint requirements.

The final method used to adjust the bulk resistance of high temperature thermoplastics is to blend carbon nanotubes into the high-performance thermoplastic. Carbon nanotubes lend themselves better to adjusting the conductivity of the final raw material compared to carbon fiber. This is attributed to the lower density of the carbon nanotubes relative to carbon fiber, $0.28\ {}^{gm}/_{cm^3}$ versus $1.78\ {}^{gm}/_{cm^3}$. This allows the use of less of the carbon nanotubes per volume to create the full network of carbon nanotubes through the cross section of the tray. Carbon nanotubes also improve the mechanical strength of the composite material similar to carbon fiber. These blended materials are usually clean and safe for interaction with humans and electronic components. Carbon nanotubes can be expensive relative to the other filler materials described and there is limited research on the use of these materials when blended with high performance thermoplastics. Their availability and lack consistent mechanical properties can add extra challenges to their use as well.

Additive Manufacturing is a technology that is experiencing tremendous growth in both the industry and personal manufacturing space, but has seen limited use in the electronics industry. Additive Manufacturing is expected to grow from $15.8 billion in 2020 to $35.6 billion in 2024 [6]. This growth has been due to the expiration of key patents and the development of materials that can create end use products instead of prototypes [7]. Early adopters of additive manufacturing used it for prototyping efforts, that has changed in the last few years as more parts are manufactured as end use items. The challenge for the additive manufacturing industry to continue this growth in the marketplace is the continued development of materials and new printing processes to expand the parts created directly from additive manufacturing. The typical perception of the public is that you should be able to just take a CAD model and print a fully functional part is likely decades away. Although there are many researchers working on solving the underlying physics issues to make this a reality, if we are to use current materials, we must consider the additive manufacturing process in addition to the product design to create a successful product directly from additive manufacturing [8].

Additive manufacturing has reached a level of maturity where it is economical to manufacture low rate production parts using various additive manufacturing processes [9] [10]. Some researchers have demonstrated that if the part design is considered with the additive manufacturing process considered to develop the final part design, additive manufacturing can be used for medium production rates of up to 100,000 units annually and will be lower in costs than injection molding [6] [8]. This is primarily because additive manufacturing processes typically do not require the design of an expensive mold to manufacture the part.

The JEDEC tray is typically manufactured using injection molding from pellet raw stock or machining from an extruded raw stock. The tools required for injection molding are expensive, a simple injection molding tool costs at least $5000 and has a lead time of at least 6 weeks. The injection molding tools for a JEDEC tray are complex and likely cost more than $30,000 with a lead time of twelve to sixteen weeks. A typical injection molding tool will go through two revisions before it finally produces a part that is of acceptable quality. The tooling costs associated with injection molding is typically amortized over the total quantity of parts needed to make this process cost effective, this makes injection molding a great choice for high volume production but not an ideal solution for low volume manufacturing. Additive Manufacturing does not need any specialized tooling to manufacture a part, making it an ideal choice for fabrication of a JEDEC tray used for low rate production processes. This is an area where additive manufacturing can be a disruptive technology, lowering the cost and manufacturing cycle time of JEDEC trays [6] [7] [8]. This technology could also be a disruptive technology in the electronics industry for low rate production of other ESD compliant tooling as well.

PEEK, Poly Ether Ether Ketone, polymer is a high-performance thermoplastic with a semi crystalline structure that exhibits high strength and high temperature resistance, this material is used in the manufacture of some JEDEC trays. Researchers have been successful in mixing PEEK with carbon nanotubes (CNTs) as a focus to improve mechanical properties, as a side benefit is it also changes the electrical properties of the PEEK-CNT matrix [11] [12]. The current use of PEEK in a JEDEC tray and the research work to blend CNTs to improve bulk surface resistance shows that it may be possible to develop a Fused Filament Fabrication (FFF) filament that could be used to print a JEDEC tray.

The accuracy of well-tuned open source and commercial grade additive manufacturing machines provide an accuracy of between 50 to 200 microns [13] [14] [15]. The accuracy needed to print a JEDEC tray is approximately 50 microns in order to provide a tray that will meet the necessary blueprint requirements. Several commercial and a few open source additive manufacturing printers can reach the required glass transition temperature of PEEK polymer at the print head, a temperature between 350^{o} and 425^{o} Celsius is required [16].

LITERATURE REVIEW

Carbon nanotubes have been an area of intense research for the last couple of decades. The high level of interest has been due to their incredible strength to weight ratio and their ability to improve the mechanical strength of various materials when properly mixed, creating a composite matrix [11] [17]. To create these PEEK/CNT polymer matrixes most researchers used melt blending with a twin-screw extruder [18]. Researchers have mixed multiwall and single wall CNTs into various polymer matrices with similar reduction in bulk surface resistance results regardless of the polymer used [11] [18]. The researchers noted that the polymer matrix had improved mechanical strength with CNTs added and a reduction in bulk surface resistance. This improvement of mechanical strength and bulk surface resistance improvement tapers off once the CNT content reached the percolation threshold [19]. The percolation threshold level is dependent upon the type of CNT and the method of mixing CNT with the polymer.

Additive manufacturing is a unique process where the design of the part and the additive manufacturing technology used to manufacture the part are closely intertwined, picking the wrong method of additive manufacturing will likely result in failure of the part early in its life cycle. Several researchers have studied and published their results of how to take advantage of the unique characteristics in various additive manufacturing technologies to produce successful production parts [10] [8].

There is also research into the mechanical properties of high performance thermoplastics such as PEEK [20] [11]. It has been noted in this research that PEEK in its raw form and manufactured into a part via additive manufacturing has the strength to weight ratio approaching 6061T6 aluminum. This research allows us to draw the conclusion that the addition of CNTs to the PEEK polymer will not degrade the mechanical properties while simultaneously improving the bulk surface resistance to create an ESD compliant material.

EXPERIMENTAL

Filament Fabrication and Characterization

Fabrication of the 1.75 mm diameter filament would require dispersing the Multi Walled Carbon Nanotubes 20-30 nm (CNTs) with the Victrex PEEK 450G powder prior to extruding in a low-cost filament extruder. The extruder selected was manufactured by Noztek, Figure 3, is not a twin screw Banbury style extruder as described in several research papers [18] [20].

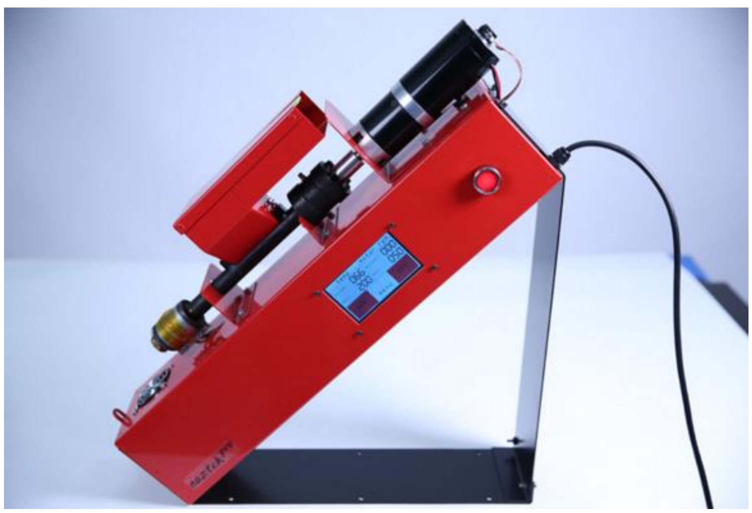
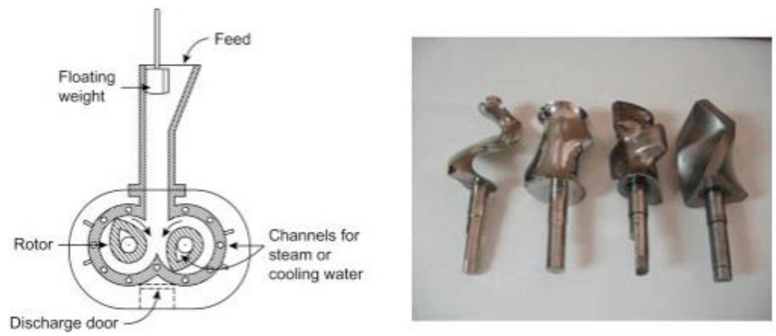
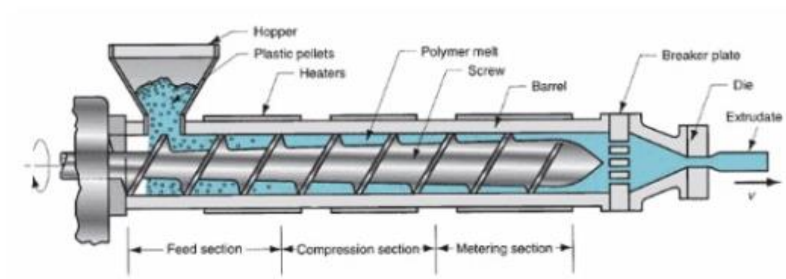


Figure 3 Noztek Extruder for CNT/PEEK Filament Fabrication

The Banbury twin screw style extruder has close tolerances in the twin screw mesh causing a high shear forces on the polymer promoting an even mixture of the CNT/PEEK polymer matrix. The Noztek extruder is a single screw design and the tolerances in the crew assembly are not as close as they are in a Banbury style extruder, this extruder will not provide the high shear forces of the Banbury design, see Figure 4.



Banbury Extruder



Single Screw Extruder

Figure 4 Comparison of Extruder

One advantage of the low cost Noztek extruder is that it is computer controlled which provides the ability to control temperature and speed precisely, nozzle temperature to +/- 5^{o} Celsius and the rpm of the screw is controlled to +/- 1 rpm for repeatable processing of filament. The extruder can reach 600^{0} Celsius which is significantly higher than the glass transition temperature of PEEK, which is approximately 375^{o} Celsius. Since the single extruder selected could not provide the high shear forces on the polymer it was determined that another method of evenly distributing the CNT in the PEEK polymer would need to be found.

The CNTs and the PEEK polymer need to be mixed to create a homogenous mixture that when extruded to a 1.75 mm diameter it will be ESD compliant, approximately $10^6\ \Omega - cm$. This 1.75 mm PEEK/CNT will need to be dimensionally stable enough to print a JEDEC tray that is ESD complaint and meets dimensional tolerances similar to a machined or injection molded tray. *Figure 5* shows the proposed processing steps that will be necessary to print an ESD compliant JDEC tray.

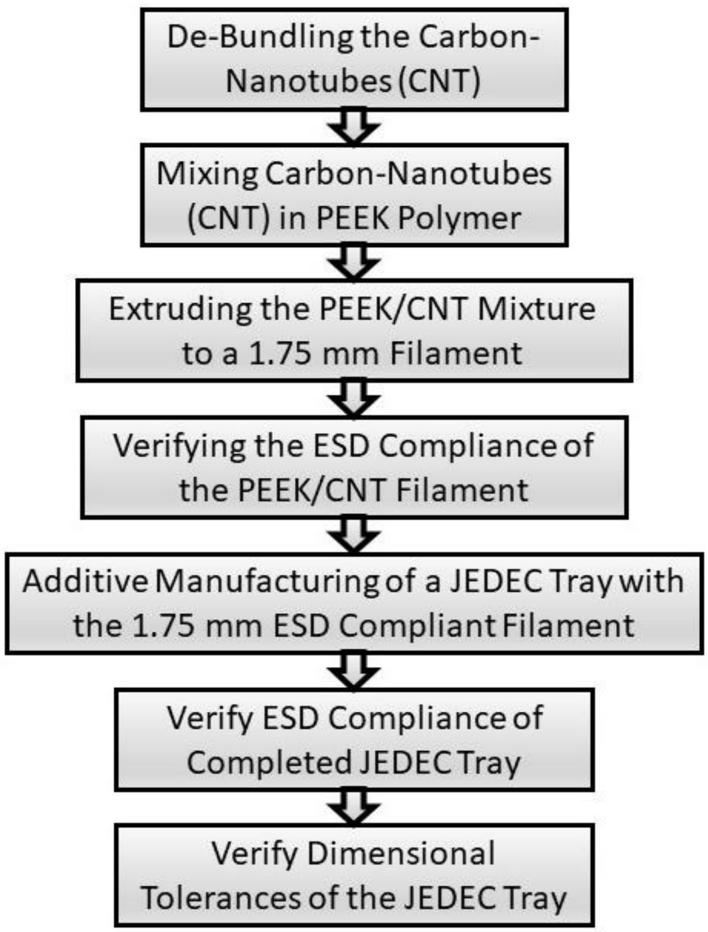


Figure 5 Process to Create an ESD Compliant JEDEC Tray

CNTs exhibit high Van der Walls forces that cause the CNTs to clump together which can make them difficult to disperse evenly in another material to make a homogeneous mixture. There is various research available on methods to disperse CNTs in organic solvents and a decision was made to attempt CNT dispersion using acetone and ultrasonic mixing [18] [21]. The initial mixing trials of the CNTs with acetone produced results representative of the research, the CNTs would stay suspended in the acetone for a few days after the mechanical or ultrasonic mixing was stopped. However once the PEEK polymer was added to the CNT/acetone mixture the CNT/PEEK mixture would begin to precipitate from the acetone as soon as the mechanical energy of the ultrasonic mixing was stopped, Figure 6.

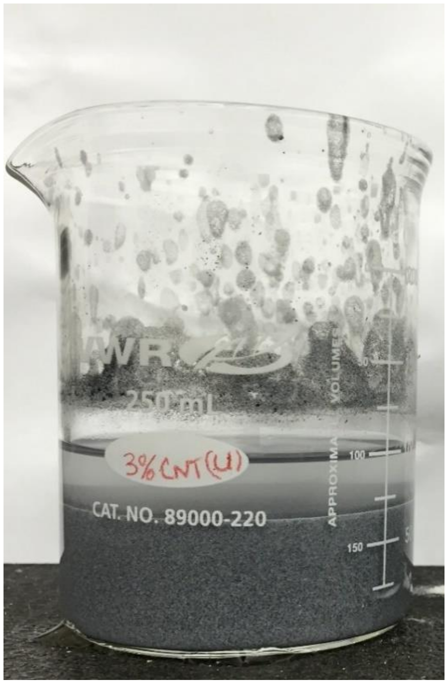


Figure 6 3% CNT/PEEK After Ultrasonic Mixing

After several attempts to disperse the CNTs evenly with acetone a screening experiment was performed to determine if acetone was not the appropriate solvent to use for preparing the CNT/PEEK mixture. The CNTs as received, dispersed and dried in acetone and 99% isopropyl alcohol was conducted and observed with the Scanning Electron Microscope (SEM). As can be noted in Figure 7 there is a significant difference in the de-bundling of the CNTs in the isopropyl alcohol. There appears to be a covalent bond between that the molecular structure of isopropyl alcohol and the CNTs that is stronger than the Van der Waals forces of the CNTs. The de-bundling remained after the isopropyl alcohol had evaporated.

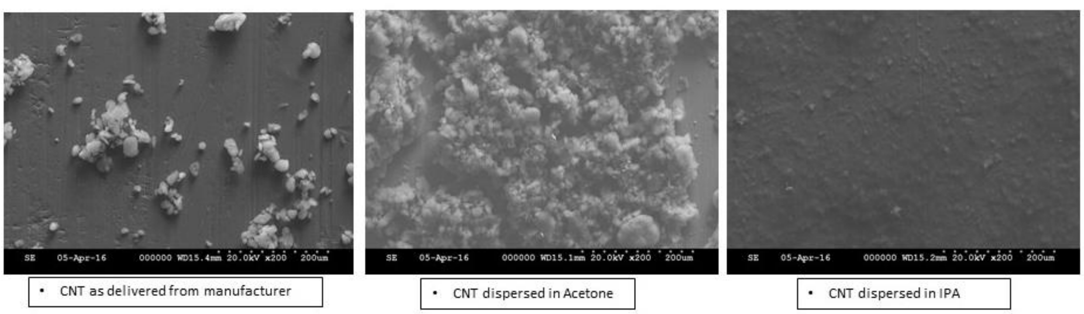


Figure 7 Carbon Nanotube De-bundling

Based upon this screening experiment it was decided to attempt mixing CNT/PEEK mixture using 99% isopropyl alcohol as the solvent. It was noticed immediately that the viscosity of the CNT 99% isopropyl alcohol mixture increased dramatically when the ultrasonic energy was applied. Figure 8 shows how the CNTs seem to form a structure in the isopropyl alcohol and maintain it after the ultrasonic mixing energy was removed. The structure appeared jelly like and would remain in this jelly like state even if an instrument like a spoon was used to scoop some of the material from the beaker. The de-bundling of the CNTs mixed with the 99% isopropyl alcohol allowed the CNTs to create a matrix that expanded to fill the volume of the isopropyl alcohol used.

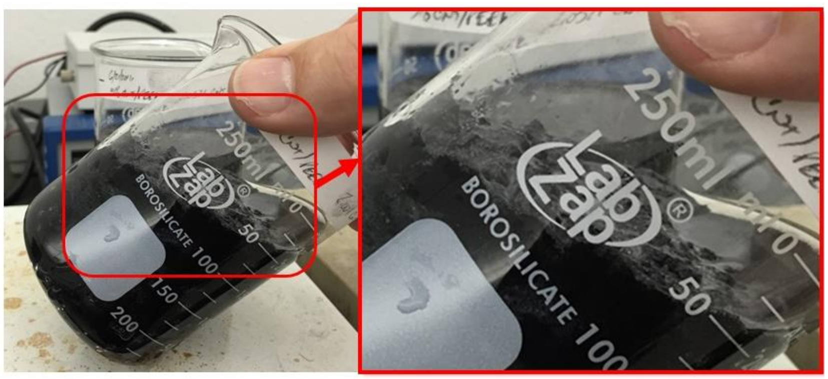


Figure 8 Structure of Ultrasonic Mixed CNT and Isopropyl Alcohol

Based upon this success, a range of CNT/PEEK mixtures were mixed using the same protocol described previously. Mixtures of CNT/PEEK were created, the % CNT was based upon total weight of the CNT/PEEK mixture, a 5% CNT/PEEK contained 95% PEEK and 5% CNT by weight. As can be seen in Figure 9 the CNTs remained de-bundled in the CNT/PEEK mixture with isopropyl alcohol even after being removed from the ultrasonic energy. The CNT/PEEK mixture appears to be homogenous even when the material is removed from the mixing container.

Figure 9 5% CNT/PEEK in Isopropyl Alcohol After Ultrasonic Mixing

Figure 10 shows how well the CNTs stayed de-bundled after drying the isopropyl alcohol from the PEEK/CNT mixture. The mixture visibly appears to be homogeneous when it is dry as well. An interesting observation of the dry PEEK/CNT mixtures in Figure 10 is that the volume of the final mixture when dry varied depending on the content of CNTs in the mixture, even though the total weight of the PEEK/CNT mixture in each mixing container was the same. The mixtures in the beakers of Figure 10 all contain the same total weight of CNT and PEEK. This demonstrates that the CNTs are creating a structure within the isopropyl alcohol when excited by the ultrasonic energy allowing the CNTs to de-bundle and the structure remains after the isopropyl alcohol was removed from mixture.

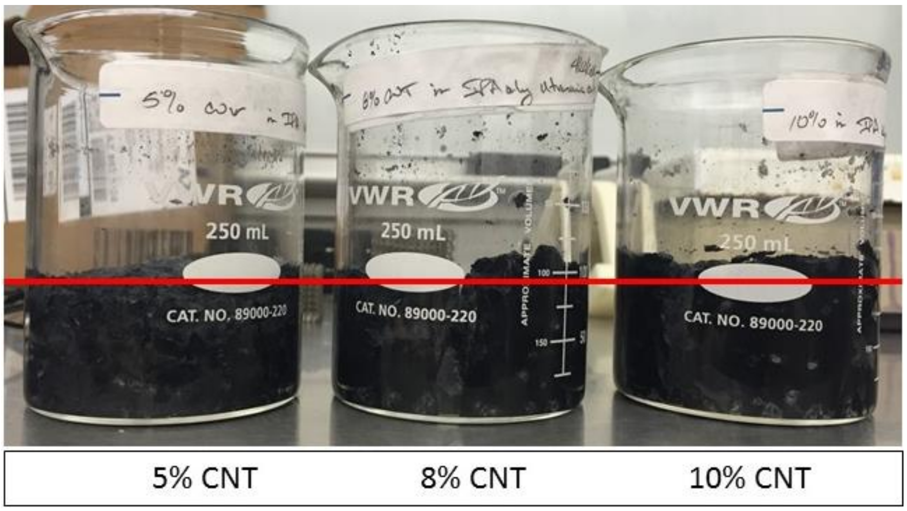


Figure 10 Volume Change in CNT/PEEK at Various Mixture Ratios

Now that there were samples of PEEK/CNT material that appeared to be a homogenous mixture it was time to develop a filament fabrication process. Filament was fabricated from the raw PEEK powder to determine baseline settings of the Noztek extruder for temperature and speed to produce a consistent 1.75 mm diameter filament suitable for printing. The settings on the Noztek extruder was 355^{o} Celsius with a screw speed of 25 rpm. These settings created several hundred feet of baseline PEEK material to test in the printer. When extruding the CNT/PEEK raw stock it was noted that the temperature had to be raised to 365^{o} Celsius to produce filament. This seemed to be due to an improvement in thermal conductivity of the PEEK/CNT mixture and is attributed to the added CNT content, it has been reported in various research papers that thermal conductivity is improved along with electrical conductivity as the CNT content is increased [19]. This improvement in thermal conductivity also affected the ability to create a consistent diameter of 1.75 mm filament. The CNT in the filament allowed the heat to travel down the filament much further after exiting the nozzle of the extruder which caused a larger section of filament to remain above the heat deflection range of the material, which allowed the filament to stretch and thin if not supported. Another challenge occurred during the fabrication process, the lubricating qualities of the CNTs in the mixture did not allow the PEEK/CNT mixture to be drawn into the screw under gravity, a plunger device was used to force the material into the screw as the material was fabricated.

Figure 11 to Figure 13 show the morphology of a selection of filaments fabricated for this project using a SEM. The samples were processed using the same methods for all the images. The samples were prepared using liquid nitrogen to perform a freeze fracture across the diameter of the filament. The samples were then sputtered with gold after being mounted to a stage. The stage was then placed in the SEM to obtain images of the cross section to help determine the distribution of the CNTs in the filament. Figure 11 are images of the raw PEEK filament to provide a baseline for the images in Figure 12 and Figure 13. This sample of PEEK, Figure 11, shows that the specimen underwent a brittle fracture and shows little to no porosity in this cross section.

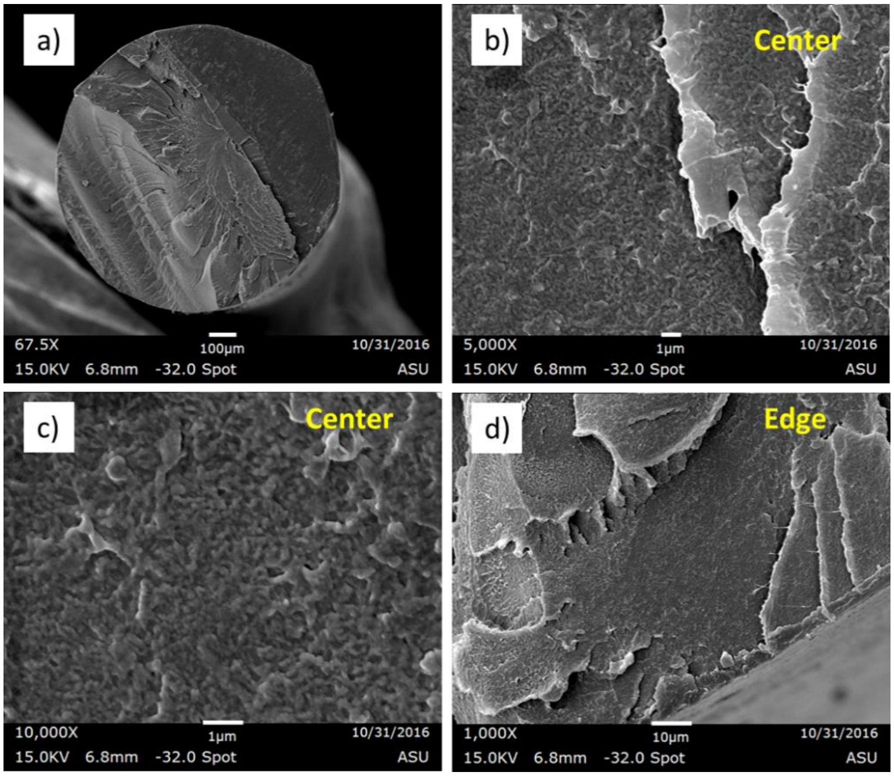


Figure 11 SEM Images of Raw PEEK Filament

Figure 12 are the SEM images from a 2% CNT/Peek filament and the CNTs can be seen clearly on the surface of the break. It is also noted in Figure 12b that the CNTs have formed bundles like those noted in the CNT/PEEK powder mixture when acetone was used as the dispersing agent. There are significantly more CNTs in the center of the filament creating a network of CNTs that should improve the electrical and mechanical properties of this zone of the filament. The edge of the filament shows a much lower density of CNTs than the center demonstrating that there is a lack of CNT network near the surface of the filament. There are also no CNTs in this sample on the exterior surface of the filament, this could be due to the flow dynamics in the extruder. Typically, at the wall of most extruders including the extruder in a Fused Filament Fabrication printer the velocity of the wall is very near zero if not zero. This low velocity at the wall seems to affect the distribution of the CNTs at this low loading of 2% CNT.

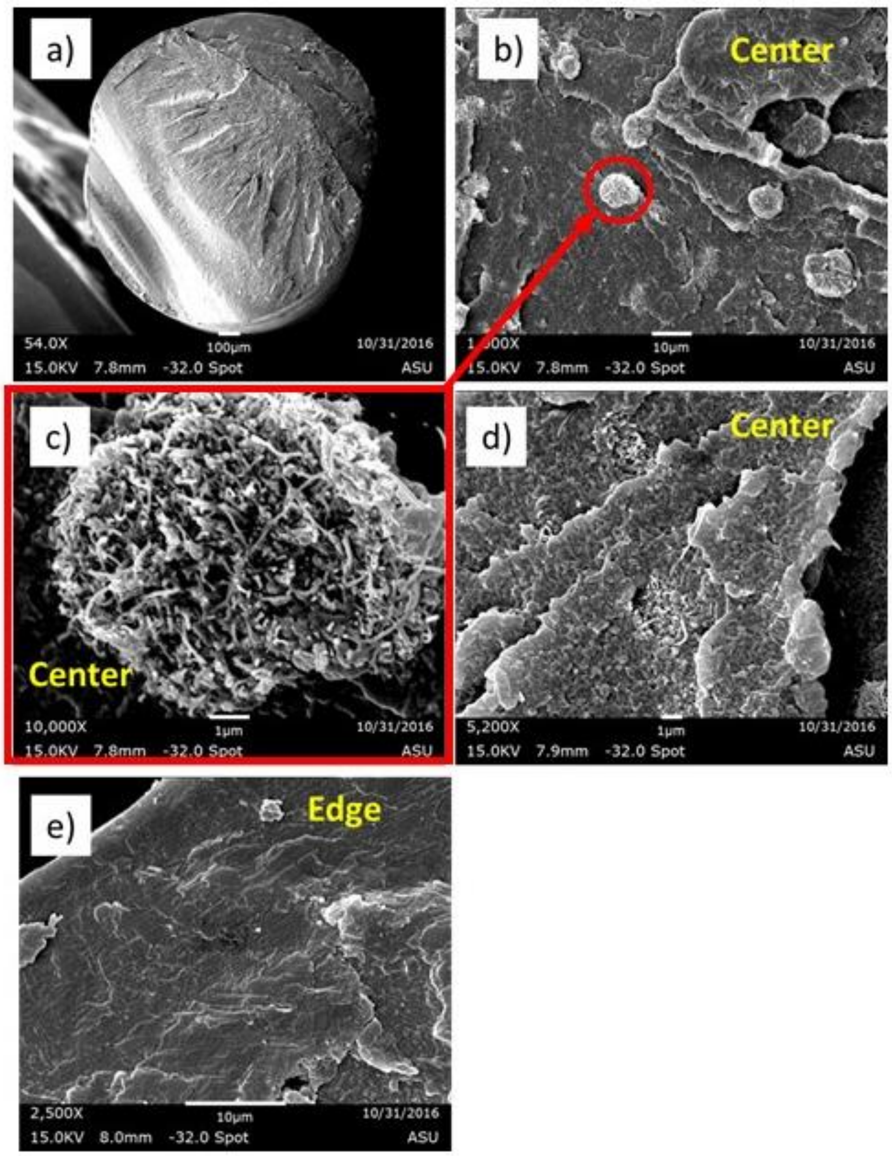


Figure 12 SEM of 2% CNT/PEEK Filament

Figure 13 shows SEM images of 9% CNT/PEEK filament, this sample shows that there is a continuous network of CNTs across the entire surface of the filament. The density of the CNTs is not even across the surface of the but the network appears to be complete and there is also evidence that some of the CNTs were pulled from the PEEK substrate during the fracture of the specimen. The density of the CNTs in this sample shows that it may be possible to lower the % of CNTs in the matrix and still create a complete network of CNTs in the polymer matrix to improve electrical conductivity.

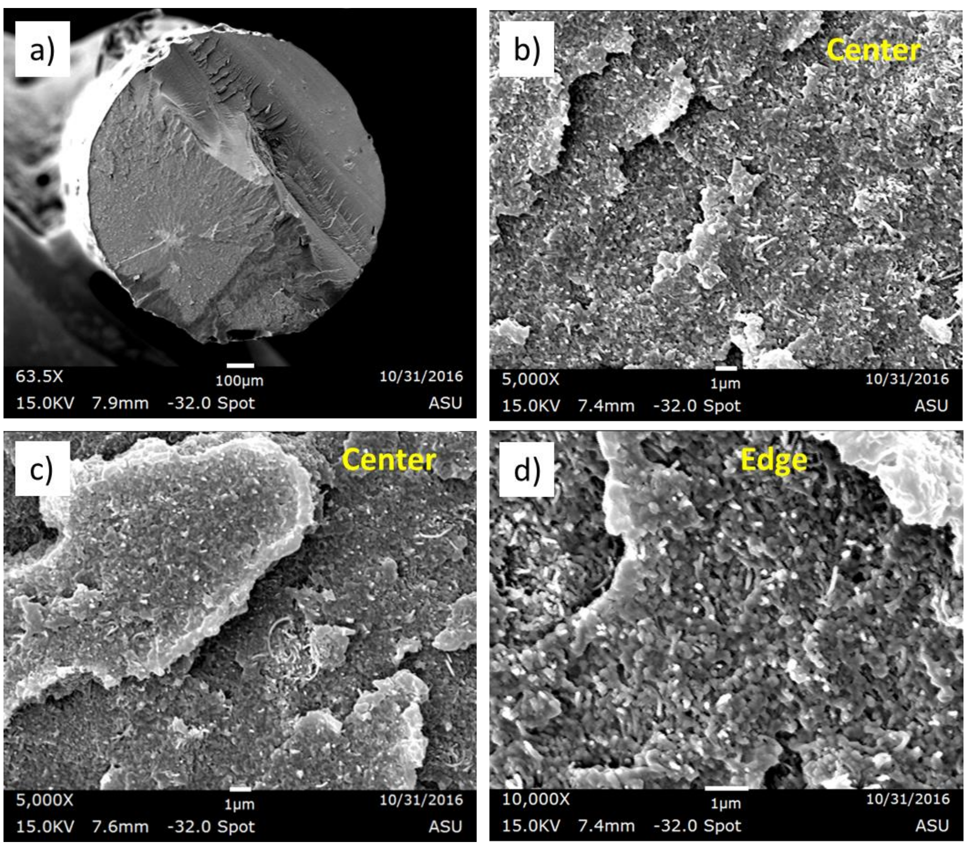


Figure 13 SEM Images of 9% CNT/PEEK Filament

CNC Gantry Selection and Modifications

There are not any open source additive manufacturing printers available on the market with the required accuracy and temperature capabilities to print a PEEK/CNT polymer filament. The printers that are potentially capable are commercially available and are locked to the vendor material, they do not lend themselves to experimentation. The goal is to develop a cartesian coordinate CNC controlled printer capable of printing the PEEK/CNT filament at an accuracy of +/- 50 microns.

The CNC gantry system that was selected is manufactured by Stepcraft, Figure 14, they manufacture CNC gantry systems for use by the hobbyist market. Their systems are multifunctional and can used as a small CNC mill, 3D printer and laser cutter by changing the end effector on the gantry. Their systems tend to have improved accuracy over many other gantry style systems on the market due to the use of balls screws on all axis versus the belt systems used on most other hobbyist level machines, balls screws are used on many industrial CNC machines due to their repeatable accuracy. Their published repeatability for a system that has been tuned to remove backlash is 50 microns. The system was tested prior to any modifications and was found to have a resolution on all axis of approximately 100 microns. It was felt that with software tuning to reduce the backlash from the mechanical system that the repeatability could be reduced to below 50 microns with minimal effort.

Figure 14 Unmodified Stepcraft CNC Gantry System

The CNC gantry system was an excellent platform to begin developing the 3D printer for this project, however some of the features of the printer were not adjustable enough to allow printing of the PEEK/CNT polymer. Specifically, the software was optimized for use with ABS or PLA material and their glass transition temperatures are much lower than PEEK with typical printing temperatures of less than 230^{o} Celsius. The software shipped with the gantry system was capable of 3D printing but had a software restriction of 260^{o} Celsius for the extruder. The software was also not open source so there was not enough information to allow for modification of the electronics or the firmware for the expected extrusion temperature range needed to fabricate quality parts from a PEEK based polymer.

The decision was made to convert the electronics over to an open source system that would allow full control over every aspect of the CNC gantry system. The system selected was a RAMPS 1.4 electronics and associated firmware for a 3D printer, the electronics and firmware were developed by the RepRap community and is an Arduino based microcontroller and firmware system, Figure 15.

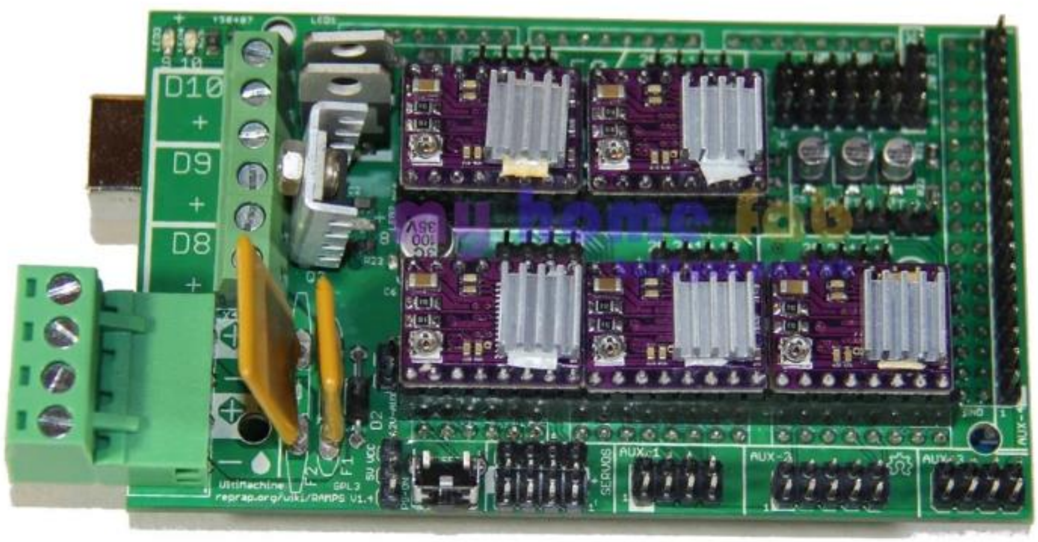


Figure 15 RAMPS 1.4 Microcontroller

The RepRap community was started to create open source hardware and software to allow end users to manufacture 3D printers that can print another 3D printer [22]. The primary advantage for using this electronics and software system is the ability to control all aspects of the CNC gantry system since the source code as well as the hardware is open source. Figure 16 shows the CNC gantry system with the electronics system installed and the control computer in the background during calibration of the system to produce desired results from the G-code. The underlying open source code that is used with this type of controller is Arduino based and allows a person proficient in the language to adjust any parameters desired.

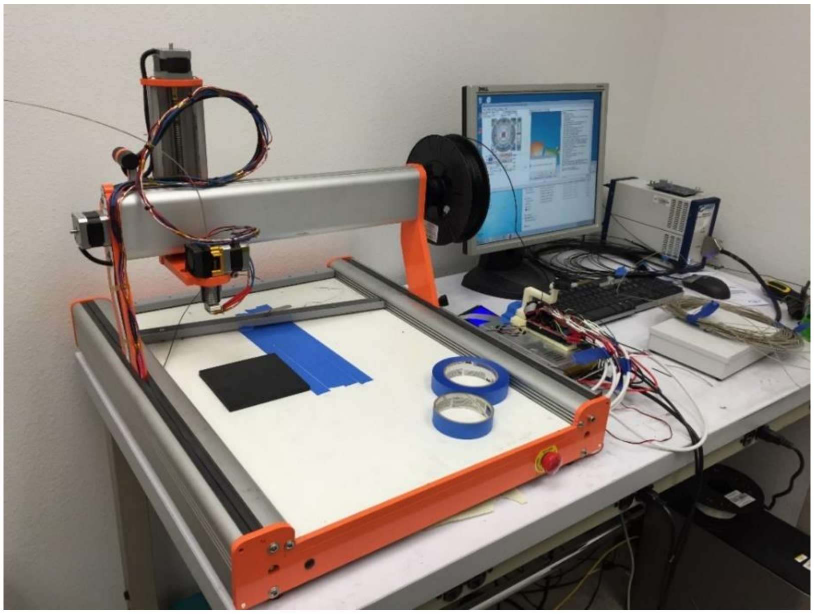


Figure 16 CNC Gantry System with Electronics and Hot End Incorporated

The next challenge that needed to be overcome was to find a solution for the temperature required to extrude the PEEK/CNT material. Published data by the PEEK manufacturer Victrex shows that the melting temperature for PEEK powder is 343^{o} Celsius, previous experience with the Noztek filament extruder demonstrated that the extrusion temperature required to create a reasonable quality PEEK/CNT filament was 365^{o} Celsius. Typical hot ends used in the consumer level printers typically cannot exceed 260^{o} Celsius, this is due to either a low power heater assembly or a material compatibility issue with the high temperatures. A hot end assembly that is available and is designed to be operated at these elevated temperatures was procured from E3D Online, Figure 17, this company has developed several extruders and has an extruder that can reach 400^{0} Celsius with minor modifications, adding a thermocouple instead of a thermistor and editing the Arduino firmware on the controller. E3D Online also manufactures custom nozzle diameters that will allow experimentation to determine the minimum feature size that the printer can achieve.

Figure 17 E3D Online Hot End

PEEK polymers and other high temperature polymers require a heated build environment to create 3D printed parts successfully. Figure 18 shows the gantry system with the heated build environment installed. The gantry system had a heated build platform added using a silicone heater attached to a 0.250-inch-thick MIC6 Aluminum plate to be used as the build platform and can maintain 120^0 Celsius using a PID controller and a thermocouple. An infrared heater was added to increase the temperature in the build zone, the parts to be built on the printer are less than 12 mm tall and the temperature within 15 mm of the build plate was maintained at 120^0 Celsius even without a fully enclosed build chamber. This temperature will be high enough to promote good interlayer adhesion but not too high to cause the CNT/PEEK material to sag during the printing process, per the data sheet the Victrex 450G PEEK has a heat deflection temperature of 152° Celsius as tested per ASTM D648.

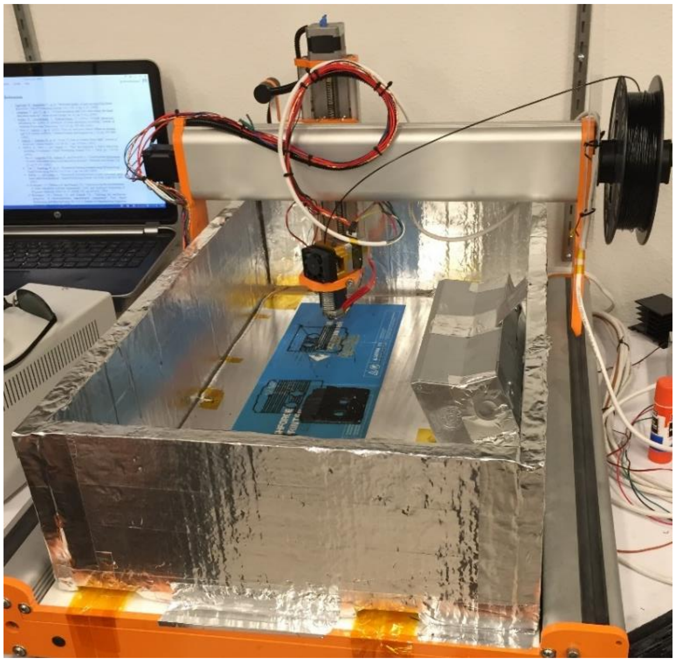


Figure 18 Heated Build Plate, IR Heater Integrated

Several test parts were printed with this modified gantry system to dial in the final firmware settings. After the settings were adjusted the gantry system printed parts well enough to start test prints of PEEK and PEEK/CNT materials.

The development of a method to fabricate a 1.75 mm ESD compliant filament has been completed as well as the building and tuning of an open source printer specifically to print this material.

Testing

Testing of the bulk surface resistance in the CNT/PEEK materials was accomplished using a Gamry Potentiostat instrument, reference Figure 19.

Figure 19 Gamry Reference 600 Potentiostat

The potentiostat can supply a varying voltage while measuring the current between the probes. The bulk surface resistance of the material can be calculated using this data. Figure 20 is the data from a 10 % CNT/PEEK filament of 1.75 mm diameter with the probes placed approximately 10 mm apart on the sample. The resistance can be calculated by either dividing the voltage by the current or using a linear regression to determine the slope of the data. In this data set the resistance of the filament is $2\ x\ 10^7\ \Omega$ which meets the requirements of this project. When conductive paint was applied to the sample to create a larger electrical contact area between the probes and the sample the resistance was reduced by two orders of magnitude, other researchers have used this method of determining the electrical resistance of similar materials [11].

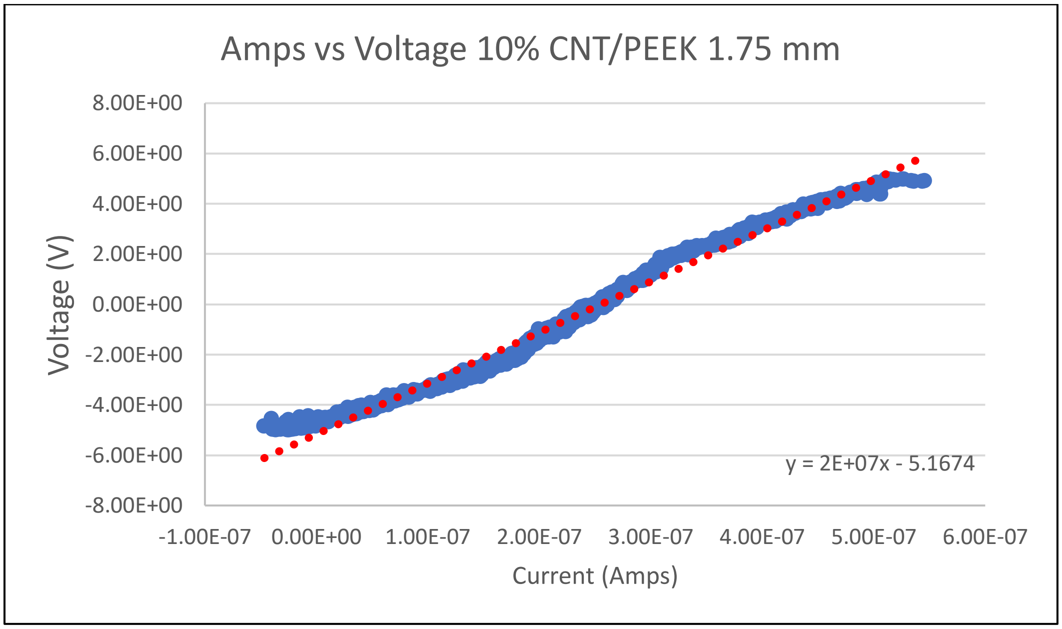


Figure 20 Graph of Data from Gamry Potentiostat

Figure 21 shows the conductivity of various CNT content filaments, this data shows that the filament reaches the required electrical conductivity somewhere between 6% and 7% CNT content by weight. Figure 21 appears to show a step function between 6% and 7% this is due the PEEK/CNT filament reaching the electrical percolation threshold in this region with this particular method of preparing the PEEK/CNT filament. The electrical percolation threshold is the point when an insulator changes to a conductor. This electrical percolation threshold is higher than published in various research papers but is less than the CNT content of other ESD compliant materials on the market [19]. The Stratasys MSDS for their ABS-ESD7 material states the material is approximately 96% ABS implying 4% is CNTs. 3DXtech MSDS for their ESD compliant materials from ABS to Ultem state the base polymer is at least 90% of the content of the material, implying that the CNT material is up to 10% CNT. This shows that the method used for fabricating the filament has a similar CNT content to other ESD compliant materials available in the additive manufacturing community.

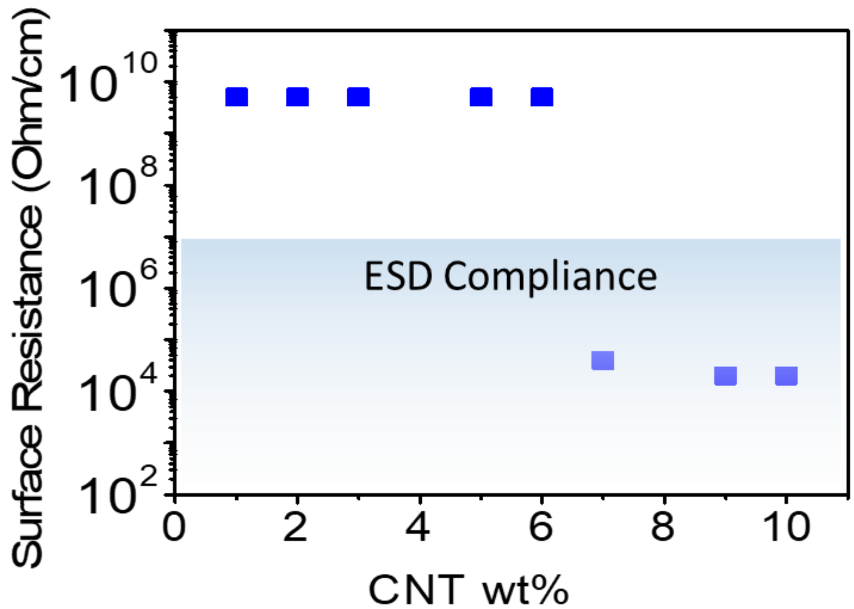


Figure 21 Surface Resistance of Various %CNT/PEEK Filaments

At this point it was time to use some the PEEK/CNT filament to fabricate test parts to verify that the material strength has not been degraded by process of manufacturing the filament or the printing process. There are many causes to the reduction strength that could occur due to the printing process, under-extrusion, interlayer adhesion reduction, raster orientation and extrusion temperature variations. A small tensile dog bone was designed and printed to verify that the CNC gantry system developed and produced parts similar in strength to data developed by other researchers, reference Figure 22 for the dog bone design.

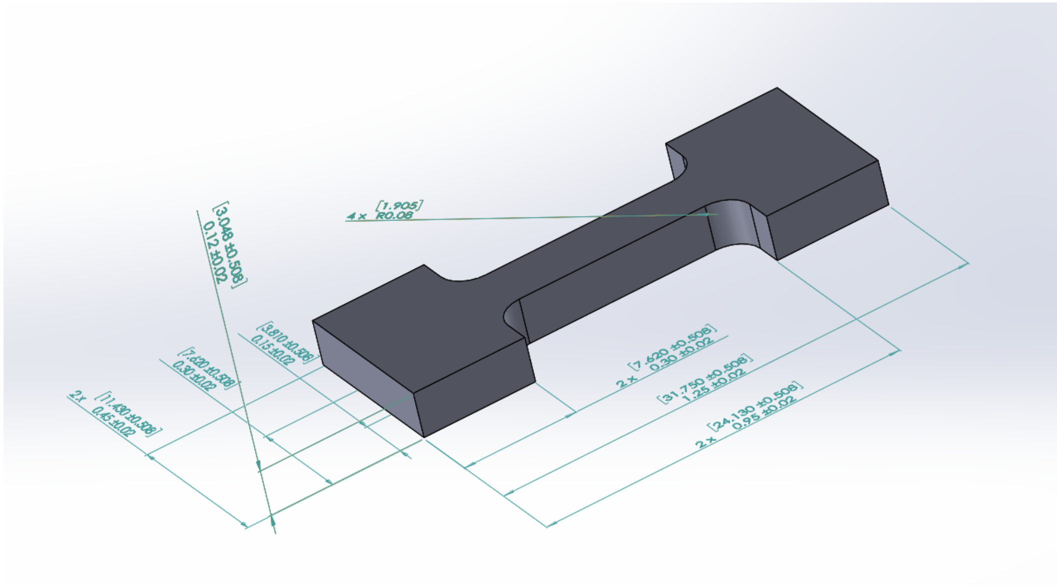


Figure 22 Tensile Dog Bone Dimensions

After printing a selection of dog bones in PEEK and PEEK/CNT they were tested on static tensile tester in the Polytechnic Innovation labs to determine if the printer was producing parts comparable to published data. Figure 23 is the Instron static tester that was used for testing these test specimens for tensile strength and elongation.

Figure 23 Instron 5944 Static Tensile Tester

Figure 24, shows the data collected from the testing and the tensile strength of the PEEK as well as the PEEK/CNT material. The data shown in the figure is from parts that were all printed from the same print profile to minimize variability. The material strengths, approximately 70 MPa, shown below are representative of the strengths for PEEK polymer, that has been printed, and published by various researchers [11] [23]. This suggests that the printing parameters and the CNT added to the PEEK polymer have not degraded the performance of the PEEK itself.

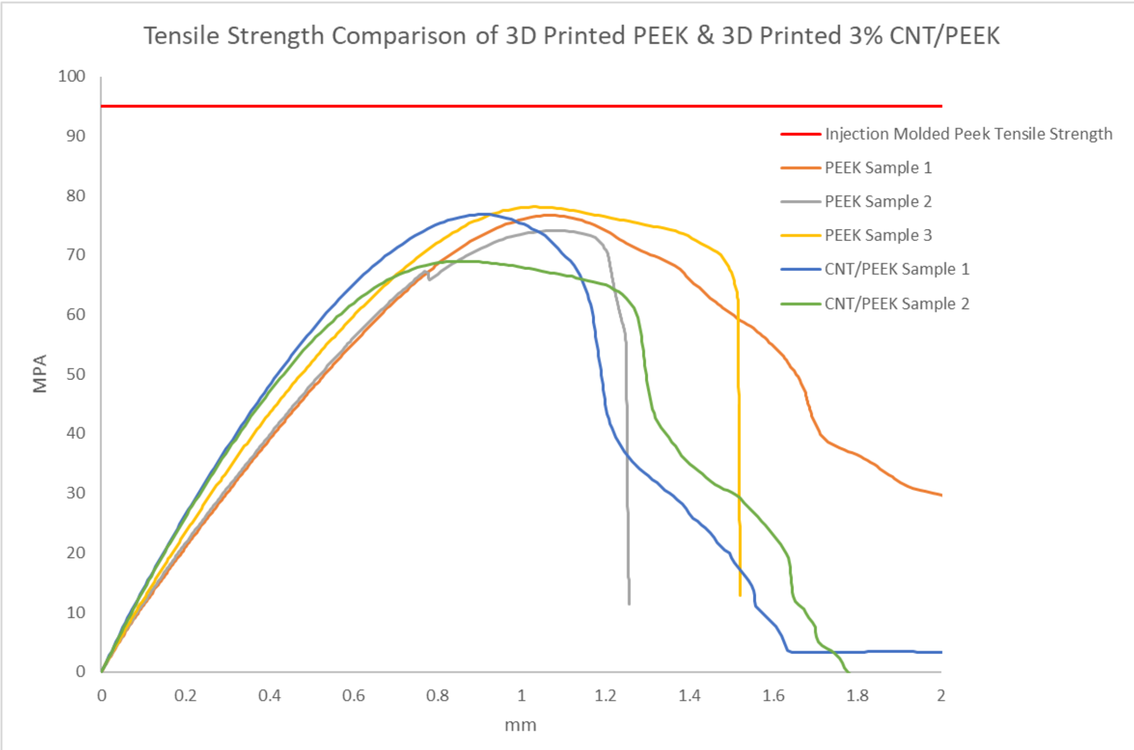


Figure 24 Tensile Strength of Test Dog Bones

The testing has reached the point that it is time to start testing various layer heights to determine how well an FFF printer can manufacture a JDEC tray. A JEDEC tray file was provided by the sponsor of this project and was modified to two rows of the seven-row tray to reduce print time and material usage during these experiments. The nozzle diameter for printing of all these trays was 0.4 mm in diameter, the layer heights were 0.2 mm, 0.1 mm, and 0.05 mm. A CAD model of the modified tray that was printed is shown in Figure 25.

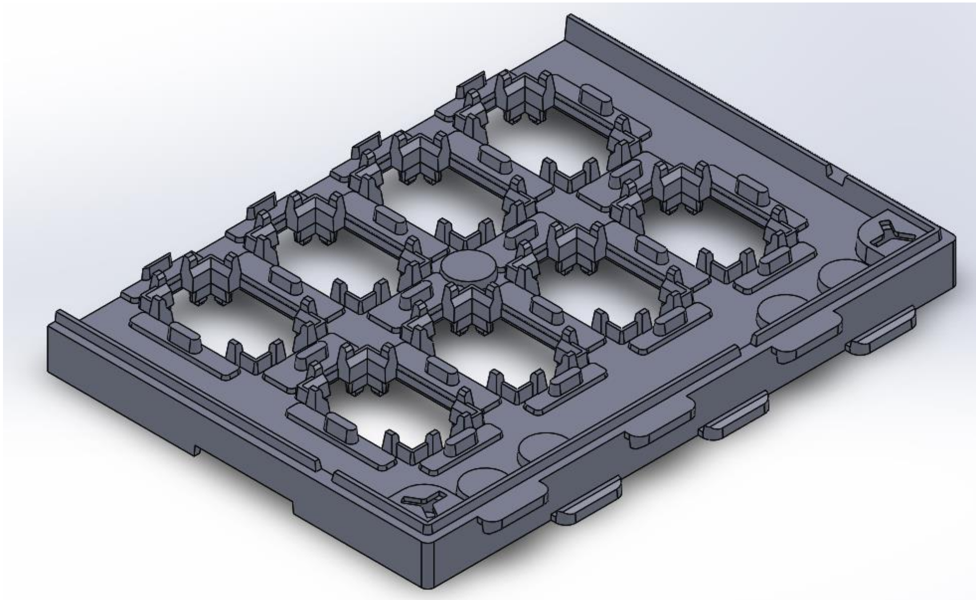


Figure 25 CAD of Modified JEDEC

Shown in Figure 26 are three trays printed at different layer heights to test if the surface finish improves with layer height reduction. Additionally, it is to determine if the printer can achieve a layer height of 0.05 mm, in the Z-axis direction, without a loss in accuracy in the X and Y-axis directions.

Figure 26 Trays Printed at Three Layer Heights

Figure 27 shows magnified images of the critical features for these trays, the images are at approximately 25 times magnification. As can be seen in Figure 27 the surface finish improves significantly as the layer height is reduced, the layers are almost not visible in the 0.05 mm sample even with the 25 times magnification. The prints are not perfect but the areas that show some defects still can be improved by adjusting the print parameters or potentially the CAD file. The small features at the top that do not show crisp edges like the CAD model are likely there to improve the ability of the JDEC tray to be removed from the injection mold dies. These features could be redesigned to be more compatible with additive manufacturing. For FFF an increase in the feature size will improve the dimensional accuracy, FFF printers will struggle with feature sizes under four times the nozzle diameter without some custom editing of the G-code. The features at the top of the taper exhibiting rounded edges measure 1.0 mm by 1.6 mm at the upper surface and cannot dissipate the heat from the filament to maintain its shape.

Figure 27 Closeup of the Test JEDEC Trays

RESULTS AND DISCUSSION

Fabrication of an ESD compliant high temperature polymer was successfully accomplished. The CNT content in the PEEK/CNT polymer filament was higher than other researchers had reported but the resulting filament printed a partial JEDEC tray that met the ESD requirements established per ANSI ESD S20.20 for a dissipative surface. This CNT content level will cause additional wear in nozzles of the filament extruder as well as the printer, a reduction CNT content will improve this as well as reduce costs of the filament.

The project also developed an open source printer capable of printing these JEDEC trays with the ESD complaint PEEK/CNT filament. This project was started in 2016 and at that time there were no open source printers on the market that could print a material like this. To print a PEEK/CNT material would have required purchasing a $250,000 printer and hacking it to allow the use of open source materials. Today however there are at least half a dozen manufacturers that sell a printer capable of these temperatures and the accuracy required to print a JEDEC tray that is ESD compliant while also being open source allowing for experimentation. The raw material, the filament, can be a challenge to obtain and the vendors tend to change the recipe on occasion which could drive variability in the final product.

CONCLUSION

This project has successfully been completed, meeting all the outcomes in the original project plan. Development of a fabrication process that creates a CNT/PEEK polymer composite FFF filament with the required bulk surface resistance. Development, design, and manufacture of a 3D printer capable of manufacturing a JEDEC tray that meets dimensional requirements and bulk surface resistance necessary to be ESD compliant.

In addition to completing this project, which started in the Spring Semester 2016, I have successfully collaborated on the publication of the following. Four conference papers and one journal article, two are focused on the topic of additive manufacturing, two are focused on human compliant robotics and the last conference paper is in the practical application of strain measurements

- Interlayer Thermal History Modification for Interface Strength in Fused Filament Fabricated Parts, 2018.
- The Use of Additive Manufacturing to Fabricate Structural Components for Wearable Robotic Devices, 2015.
- A Passive and Active Joint Torque Augmentation Robot (JTAR) for Hip Gait Assistance, 2014
- A Joint Torque Augmentation Robot (JTAR) for Ankle Gait Assistance, 2014

- The Effects of High Strength Protective Coatings on Strain Measurements, Fall 2020.

I have been active in applications for patents as well in the last four years and they are listed below. I currently have three invention disclosures with my employer that are being evaluated for possible patents, two of the disclosures are in the field of additive manufacturing and the third is a novel control methodology for a multi-actuator test system.

- Joint Torque Augmentation System and Method for Gait Assistance
    - US9662262B2 Awarded May 30, 2017
- Devices and Methods of Applying One or More Testing Forces to a Rotor Blade
    - Patent application 15/886480, US 2019-0234828 A1, Patent Pending
- Methods of Marking Additively Manufactured Parts for Traceability
    - Provisional Patent Application No. 62/845,743, filed May 9, 2019
- Three additional invention disclosures in review with Boeing Intellectual Property

In addition, I have been active in STEM education, Mesa Community College had acquired Additive Manufacturing equipment through a grant from U.S. Department of Labor's Employment and Training Administration. I developed the DFT255 course using the guidance Society of Manufacturing Engineering requirements for Additive Manufacturing certification. I successfully developed the content for the course in the fall of 2016 and taught the course for three years. Two additional Additive Manufacturing technologies were added to the program tripling the hands-on experience by the students. The course started with only hands on experience with Fused Filament Fabrication (FFF) technology. I was able to add Stereolithography (SLA) and Material Jetting (MJ) o the hands-on curriculum. .

FUTURE WORK

Fabrication of the PEEK/CNT filament is currently a time-consuming process and would be difficult to scale with the equipment used during this project. Based on the research performed previously a Banbury extruder with an automated method to feed the PEEK/CNT matrix would allow the filament fabrication to scale. An active cooling and measurement system to adjust the system would produce more consistent diameter filament with less waste.

The project demonstrated that the percolation level for the PEEK/CNT with the methods used occurred somewhere between 6% and 7%. Other researchers have been able to reduce the CNT content to under 3% with the use of functionalized CNTs and ball milling of the PEEK/CNT mixture to improve dispersion [11] [24]. The reduction of CNTs per volume of PEEK would reduce the cost of the filament dramatically. CNTs are the most expensive part of this process.

Research to use Van der Waals forces to improve dispersion of nano-particles with and electric field may be another method to reduce the CNT content required to improve the bulk surface resistance [25]. This technique could potentially be applied at the filament fabrication process when the material is at the glass transition temperature during extrusion.

The final part as built has significant internal stresses due to how the part is manufactured layer by layer. The layer below the layer being added has typically cooled below the glass transition stage of the material, this cooling only allows a percentage of the next layer in contact with the layer below to diffuse across the boundary creating stress risers due to the small voids created. Additional research into a heat treatment process post fabrication would help to determine if the normal use of the components will reduce the internal stresses over time or aggravate them. There has been some research in this area that shows promising results, with improved ductility as well as improved strength of the part [25]. There have been other methods researched to reduce these internal stresses in the part, these methods increase the energy at the interface of the layers through various methods. The results are that the parts have improved strength and ductility [26] [27].

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APPENDIX

A TEST LOG

Methods of PEEK-CNT mixing	CNT composition	Observations/test results at different stages of PEEK-CNT synthesis								
		CNT in solvent by mechanical mixing	CNT in solvent by ultrasound dispersion	CNT+Mixing/dispersion+PEEK	Resistance/cm of PEEK-CNT dry mix	Resistance/cm of PEEK-CNT Extruded Filament	Resistance/cm of PEEK-CNT printed samples	Date of Mixing	Date of Filament Extrusion	Temp & Speed of extrusion
CNT mixed in 100% Acetone	0.50%	Yes (Hand)		Mechanical Mixing (Hand)	∞ Ω/cm	∞ Ω/cm		2-Mar-16	3-Mar-16	365 C / 25RPM
CNT mixed in 100% Acetone	1.00%	Yes (Hand)		Mechanical Mixing (Hand)	∞ Ω/cm	∞ Ω/cm		2-Mar-16	3-Mar-16	365 C / 25RPM
CNT mixed in 100% Acetone	1.50%	Yes (Hand)		Mechanical Mixing (Hand)	∞ Ω/cm	∞ Ω/cm		2-Mar-16	3-Mar-16	365 C / 25RPM
CNT mixed in 100% Acetone	2.00%	Yes (Hand)		Mechanical Mixing (Hand)	∞ Ω/cm	∞ Ω/cm		2-Mar-16	3-Mar-16	365 C / 25RPM
CNT mixed in 100% Acetone	2.50%	Yes (Hand)		Mechanical Mixing (Hand)	∞ Ω/cm	∞ Ω/cm		2-Mar-16	3-Mar-16	365 C / 25RPM
CNT mixed in 100% Acetone	3.00%	Yes (Hand)		Mechanical Mixing (Hand)	∞ Ω/cm	∞ Ω/cm		2-Mar-16	3-Mar-16	365 C / 25RPM
CNT mixed in 100% Acetone	3.00%	Yes (Stir Plate 30 minutes)		Mechanical Mixing (Stir Plate 30 minutes)	∞ Ω/cm	∞ Ω/cm		16-Mar-16	28-Mar-16	365 C / 25RPM
CNT mixed in 100% Acetone	2.00%	Yes (Stir Plate 30 minutes)		Mechanical Mixing (Stir Plate 30 minutes)	∞ Ω/cm	∞ Ω/cm		17-Mar-16	28-Mar-16	365 C / 25RPM
CNT mixed in 100% Acetone	3.00%		Yes (30 Minutes)	Mechanical Mixing (Stir Plate 30 minutes)	∞ Ω/cm	∞ Ω/cm		21-Mar-16	28-Mar-16	365 C / 25RPM
CNT mixed in 100% Acetone	2.00%		Yes (30 Minutes)	Mechanical Mixing (Stir Plate 30 minutes)	∞ Ω/cm	∞ Ω/cm		21-Mar-16	28-Mar-16	365 C / 25RPM
CNT mixed in 91% IPA	2.00%		Yes (30 Minutes)	Mechanical Mixing (Stir Plate 30 minutes)	∞ Ω/cm	∞ Ω/cm		31-Mar-16	8-Apr-16	365 C / 25RPM
CNT mixed in 91% IPA	3.00%		Yes (30 Minutes)	Mechanical Mixing (Stir Plate 30 minutes)	∞ Ω/cm	∞ Ω/cm	∞ Ω/cm	31-Mar-16	8-Apr-16	365 C / 25RPM
CNT in 75% Acetone - 25% IPA (91%)	2.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	> 200MΩ/cm	∞ Ω/cm		8-Apr-16	15-Apr-16	365 C / 25RPM
CNT in 50% Acetone - 50% IPA (91%)	2.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	~1MΩ/cm	∞ Ω/cm		8-Apr-16	15-Apr-16	365 C / 25RPM
CNT in 91% IPA	2.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	~5kΩ/cm	∞ Ω/cm		6-Apr-16	15-Apr-06	365 C / 25RPM
CNT in 91% IPA	3.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	~2kΩ/cm	∞ Ω/cm		6-Apr-16	15-Apr-06	365 C / 25RPM
CNT in 99.5% IPA	5.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	>1kΩ/cm	∞ Ω/cm		18-Apr-16	20-Apr-16	365 C / 25RPM
CNT in 99.5% IPA	10.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	>1.5kΩ/cm	∞ Ω/cm		18-Apr-16	20-Apr-16	365 C / 25RPM

Methods of PEEK-CNT mixing	CNT composition	Observations/test results at different stages of PEEK-CNT synthesis								
		CNT in solvent by mechanical mixing	CNT in solvent by ultrasound dispersion	CNT+Mixing/dispersion+PEEK	Resistance/cm of PEEK-CNT dry mix	Resistance/cm of PEEK-CNT Extruded Filament	Resistance/cm of PEEK-CNT printed samples	Date of Mixing	Date of Filament Extrusion	Temp & Speed of extrusion
CNT in 99.5% IPA	5.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	>5kΩ/cm	∞ Ω/cm		22-Apr-16	3-May-16	365 C / 25RPM
CNT in 99.5% IPA	8.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	5-10kΩ/cm	∞ Ω/cm		22-Apr-16	3-May-16	365 C / 25RPM
CNT in 99.5% IPA	10.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	3-5kΩ/cm	∞ Ω/cm		22-Apr-16	3-May-16	365 C / 25RPM
CNT in 99.5% IPA	10.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	3-5kΩ/cm	∞ Ω/cm & 20 KΩ/cm	∞ Ω/cm	31-May-16	6/15/2016 & 06/06/2016	See Notes
CNT in 99.5% IPA	5.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	3-5kΩ/cm	∞ Ω/cm	∞ Ω/cm	21-Jun-16		
CNT in 99.5% IPA	7.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	3-5kΩ/cm	1MΩ/cm	∞ Ω/cm			
CNT in 99.5% IPA	9.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	3-5kΩ/cm	500 KΩ/cm	∞ Ω/cm			
CNT in 99.5% IPA	3.00%		Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	3-5kΩ/cm	∞ Ω/cm	∞ Ω/cm			
CNT in 99.5% IPA			Yes (15 Minutes)	Ultrasonic Mixing (30 minutes)	3-5kΩ/cm	∞ Ω/cm				