# FEASIBILITY STUDY OF THERMOPLASTIC NANOCOMPOSITE FOR ESD APPLICATION USING ADDITIVE MANUFACTURING

by

Sagar Vijay Navale, B.S.

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Committee Members:

Jitendra S. Tate, Chair

Bahram Asiabanpour, Co – Chair

Jesus Jimenez

## FAIR USE AND AUTHOR'S PERMISSION STATEMENT

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## ABSTRACT

Nanocomposite materials are the multiphase solid materials where one of the phases has one, two or three dimensions less than 100 nanometers (nm). Nanocomposite materials play a vital role in a wide range of applications in aerospace, automotive, sports, and biomedical industry because of their adaptability to different situations and desirable properties. The major goal of this study is to produce and characterize polyamide 6/nanographene platelets (NGP) nanocomposites that have improved electrical resistivity for electrostatic charge dissipation applications with minimal reduction in mechanical properties. Polyamide 6 and nanographene platelets were melt blended using industry size co-rotating twin-screw extrusion. Tension and electrical resistivity test samples for neat PA6, PA6/NGP with 3wt. %, 5wt. % and 7wt. % loadings were produced using fused deposition modeling (FDM) on commercially available open source 3D printer. Electrical resistivity was measured using Keithley Megohmmeter Instrument. Mechanical characterization includes tensile test of the samples. The recommended electrical resistivity range of nanocomposite material system for the ESD applications is $10^6$ – $10^{12}$ Ω-cm. Stress release annealing helped in improving both mechanical and electrical properties of the material system. Mechanical test results of neat PA6 and 7 wt % loading of NGP into PA6 showed improved properties while annealed 3 and 5 wt % loading showed droppage. % elongation of 7 wt % Pa6/NGP dropped after annealing, as recrystallization takes place in annealing and increases the ductility of the material. Electrical resistivity was improved by annealing and all nanomodified PA6 material system showed resistivity in the range of

$10^{11}$ ohm-cm, all qualifying for ESD applications. Out of all nanomodified PA6 material 7 wt % PA6/NGP was preferred as its showed both improved mechanical and electrical properties.

**Key Words:** Additive manufacturing, 3D printing, Fused deposition modelling (FDM), Twin screw extrusion, Electro Static charge dissipation, Annealing.

# 1. INTRODUCTION

Composite materials are the combination of two or more materials at a microscopic scale, which results in improved properties than that of the constituent materials. The major elements of the composite materials are reinforcement and matrix. Polymer nanocomposites consists polymer as matrix material and nanoparticles as reinforcement or, filler. Polymer nanocomposites may or may not have additional fiber reinforcement such as glass and carbon. In recent years, polymer matrix nanocomposites have attracted a remarkable interest due to significant improvements in properties such as tensile strength and modulus, elastic modulus [1], thermal stability and fire resistance [1] compared with those of neat polymers. Neat polymers have no nanoparticles or fiber reinforcement added to it. The conventional polymers offer significant resistance to electrical conduction and several methods has been explored to increase their electrical conductivity values. One of the most important methods is to add conductive fillers such as carbon black, nanographene platelets, carbon nanotubes (CNT), or metal particles to polymer matrices. At certain concentration, the conductive path is observed in the polymer matrix formed by the conductive filler particles. In addition, these materials could be used in the applications where electrostatic charge dissipation (ESD) is crucial.

The additive manufacturing (AM) technology is the technology, which builds the object in layer-by-layer form based on computer-aided design (CAD). There is renewed interest in producing functional parts using AM technology that produces the complex objects with minimal use of harmful chemicals. Among all AM methods, fused deposition modeling (FDM) is the most affordable that could be used for prototyping, molds, functional parts, and personal 3D printing.

## 1.1 Background:

The combination of nanoparticles and polymer resin, known as polymer matrix composite, are used widely in automotive and aerospace industries due to their unique properties, and processing techniques. Studies have shown the addition of nanoparticles into polymer matrix exhibit multi-functional, high performance polymer characteristics, as compared to neat polymeric materials. Blending of nanoparticles, nanofibers, or nanoplatelets into polymer matrices have shown improved mechanical, thermal, electrical, rheological, chemical, optical, and gas barrier properties.

Gaikwad et. al in 2013 studied the electrical and mechanical properties of PA11 blended with Nanographene platelets using an industrial size, twin-screw extruder for SLS. The study concluded there was significant improvement in both tensile and flexure modulus, with the increase in 1 wt.% NGP within PA11 matrix. UTS and flexure strength of PA11 nanocomposites were reduced as compared to the base material. Researchers used TGA analysis to determine the effect on compositional analysis of nanocomposites. They found thermal stability increased with the increase in wt.% of NGP. They also found improved mechanical, electrical and thermal properties of PA11/NGP nanocomposite, due to more thorough dispersion of nanoparticles into the polymer matrix. Percolation thresholds for ESD applications were achieved at 7 wt.% of Nanographene platelets. [2]

Paggy RA et. al in 2009 also studied the mechanical and electrical behavior of PA12/MWCNT nanocomposite samples fabricated via SLS. This study was also successful in achieving the goal of developing a material system suitable for ESD applications. Many researchers use polyamide polymer resin combined with nanoparticles for SLS. In 2006, Koo et al conducted a study on polyamide nanocomposite for SLS, and Chen et. al conducted a study on powder processing and property characterization of polyamide 11-graphene nanocomposites for SLS. [3]

Monica et. al. in 2014, conducted a study measuring electrical properties of MWCNT/PA6. In the study, three different techniques were applied to the CNT's i.e. chemical, mechanical, and a combination of both chemical and mechanical treatments to the samples. They measured the electrical volume and surface resistance via a homemade plate electrode. Those results were compared with the neat PA6 sample. Scanning electron microscope (SEM) and Atomic force microscope (AFM) analysis were also conducted in their study. The study concluded, by increasing pressure on samples, the volume resistivity decreased, while surface resistance showed no significant changes, independently of the CNT content. The overall study proved a great potential of MWCNT/PA6 nanocomposites in sensor application. [4]

Kamaljit et. al. in 2015, conducted a study on tribological behavior of PA6/AlAl2O3 and ABS parts fabricated using FDM. The study investigated different loads of 5, 10, 15 and 20 Al and Al2O3. The study concluded all FDM built PA6/AlAl2O3 components displayed improved wear resistance compared to their ABS built counterparts. It was also found the composite material prepared with different proportions were more wear resistant, having less frictional coefficient and friction force compared to commercially used ABS material for FDM components. [5]

After considering previous studies of material systems used in additive manufacturing, and due to desirable mechanical, electrical, thermal, and wear resistant properties of PA6 and NGP, PA6 (as a polymer matrix) and NGP (as a conductive filler) were selected as the material system for our research. The preferred quality filaments were manufactured using an industrial size, co-rotating twin-screw extruder, to ensure cohesive compounding of the material, and uniform dispersion of Nanographene (NGP) platelets into polyamide-6 (PA6) pellets. In this research, mechanical and electrical characterizations were conducted. Morphological study will be performed consisting of scanning electron microscopy (SEM).

### 1.1.1 Material:

Hybrid materials known as Polymer Matrix Composites are widely used in the aerospace and high-end automotive industry due to their high strength to weight ratio and ease of processing. They are typically made up of a liquid polymer resin and a reinforcement material. Engineers can tailor the material performance by selecting various resin and reinforcement material combinations. Further engineering modifications of the raw materials include the addition of nanoscale fillers. Polymer Nanocomposite materials exhibit multi-functional, high performance polymer characteristics beyond what traditional filled polymeric materials possess. Blending of nanoparticles, nanofibers, or nanoplatelets into polymer matrices have proven benefits in: mechanical, thermal, electrical, rheological, chemical, optical, and gas barrier properties. [6]

**Polymer resins used in AM:**

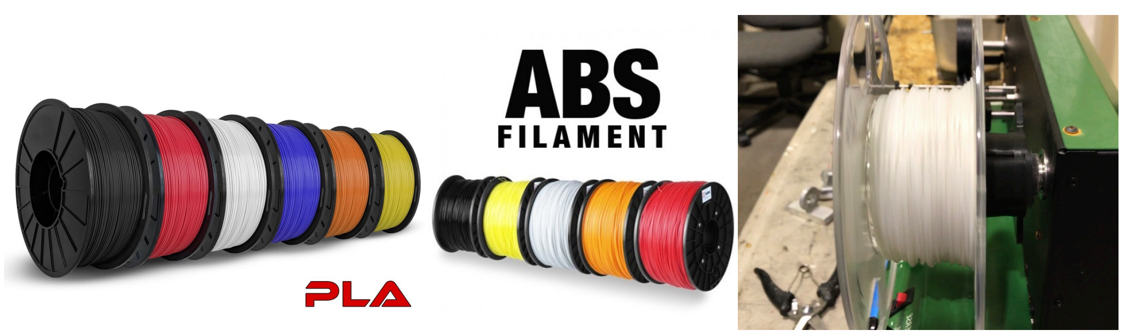



**Figure 1: Different 3D printing filaments like PLA, ABS, and PA6**

**Acrylonitrile butadiene styrene (ABS):** ABS is the most commonly used 3D printed thermoplastics. It is used in most of the real-world applications like car bodyworks, cell phone cases, appliances, etc. It is a polybutadiene-based thermoplastic which makes the ABS more flexible and resistant to shocks. The recommended extruder temperature for ABS in 3D printing is between 230 ºC – 250 ºC. ABS shrink when comes in contact with air. For prevention of wrapping the bed should be heated between 70 ºC- 85 ºC. ABS is amorphous thermoplastics. [7]

**Polylactic acid (PLA):** PLA is manufactured using renewable raw material corn starch. The major advantage of PLA over ABS is, it is biodegradable. It is one of the easiest processable materials to 3D print which doesn't require heated bed. Moreover, it requires a lower extruder temperature between 180 ºC – 200 ºC as compared to ABS' 230 ºC – 250 ºC. The high cooling and solidification speed make PLA difficult to manipulate. PLA comes in different colors. PLA is amorphous thermoplastics. [7]

**Polyamide 6 (Nylon 6 or PA6):** PA6 is available in fine, white granular powder and also in pellets form. Powder form PA6 can be used in laser sintering and multi-jet fusion type 3D printers. PA6 constitutes of semi crystalline structures which has a good balance of chemical and mechanical characteristics. PA6 offers good thermal and dimensional stability, rigidity, and shock resistance. PA6 is widely used plastics in engineering industry. It's used in manufacturing of gears, parts for aerospace sector, automotive sector, robotics, medical sector like protheses, and injection molding. PA6 is semi crystalline which creates challenges in 3D printing. [8]

**Table 1: Comparison of material properties of different polymer resins [9]**

| Material Properties | PA6 | PA11 | PA12 | PLA | ABS |
|---|---|---|---|---|---|
| Density, g/cc | 1.13 | 1.02 | 1.04 | 1.21 | 1.02 |
| Tensile Strength, MPa | 48 | 47 | 35 | 42 | 36.4 |
| Tensile Modulus, GPa | 2.5 | 3.2 | 2.23 | 2.7 | 2.03 |
| % elongation at Yield | 20.0 | 25.0 | 32.0 | 36.0 | 34.2 |
| Coefficient of friction | 0.806 | 0.347 | 0.452 | - | 0.35 |
| Coefficient of thermal expansion, $10^{-6}$ $K^{-1}$ | 83 | 110 | 100 | - | 88.6 |
| Electrical resistivity, Ohm-cm | 2.16E+12 | 1.96E+15 | 1.55E+15 | - | 9.42E+15 |
| Thermal conductivity, W/m-k | 0.273 | 0.253 | 0.248 | 0.195 | 0.172 |
| Heat deflection temperature, (HDT) at 0.46 MPa | 130 C | 180 C | 160 | 52 | 92.2 |
| Glass transition temperature, C | 50 | 46 | 45 | 65 | 108 |
| Melting Temperature, C | 220 | 200 | 200 | 180 | 200 |

PA 6 is easily available plastics. It was selected in this research because of its good mechanical properties and resistance to chemicals, wear and abrasion. PA6 also have low permeability to gases. However, high moisture absorptivity can negatively affect electrical and mechanical properties.

### 1.1.1.2 Nanoparticles:

Nanoparticles are particles between size 1 and 100 nanometers (nm). They have very high surface to volume ratios which makes them ideal for use in polymeric materials. Nanoparticles when used as fillers improves different material properties like mechanical, electrical, thermal, barrier properties also multi-functional properties. [10] Different nanoparticles like carbon nanotubes, graphene, etc are mostly used in polymer matrix.

**Multi wall carbon nanotubes (MWCNT):** MWCNT consists of multiple rolled layers (concentric form) of graphene. The number of these concentric walls may vary from 6 – 25 or more. The diameter of MWCNT typically is around 30 nm. They are used as reinforcement due to their high aspect ratio. They have high electrical conductivity. MWCNT have wide range of applications including wafer processing fabrication, antistatic elastomeric and plastic components for automobile fuel line components, RFI shieling materials etc. [11]

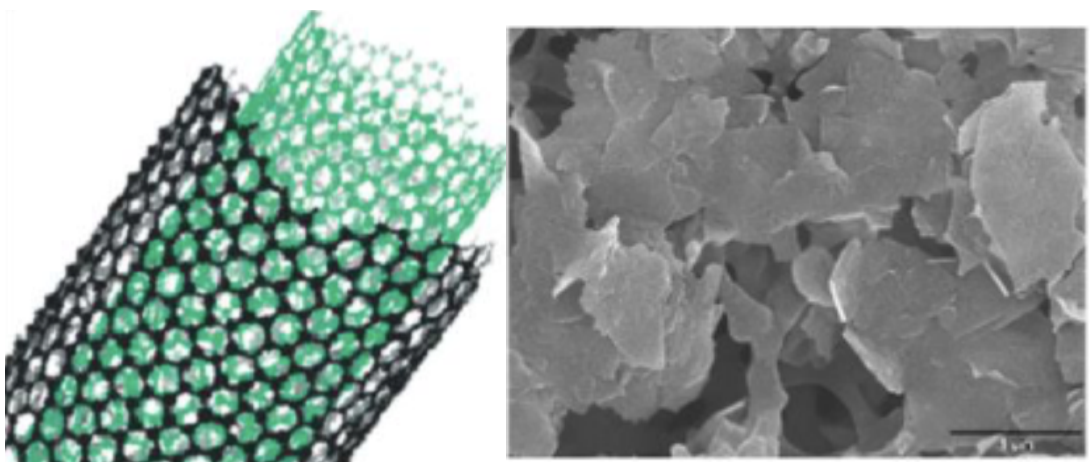


**Figure 2: a) MWCNT structure b) NGP structure**

**Nanographene platelets (NGP):** NGP are the 2D platelets of carbon atoms exfoliated from graphite, their thickness is in the range 0.34 – 100 nm [12]. They are used as nanofillers into polymer matrices to increase the material properties [12]. They are layered natural minerals and the layers can be intercalated with alkalis, acids, salts etc. and can be exfoliated into nanosized platelets with high aspect ratio. The hydrogen and covalent bonds with the polymer matrix can be achieved due to the existence of functional groups at the edges of the NGP platelets. When used as the nanofillers NGP can improve the mechanical, electrical, thermal and barrier properties of the material. Platelet like structure of NGP helps in making a proper conductivity path in the material system and also after doing the analysis from the table below and because of superior properties of NGP we decided to go with it in this research. Table 2 exhibit properties of different nanoparticles used.

**Table 2: Comparison of different properties of nanoparticles. [10] [13]**

| | Carbon Nanotube | Nanographene platelets | Carbon Black | Graphite flakes |
|---|---|---|---|---|
| Density | 1.2 – 2.1 g/cc | ~2.0 g/cc | 1.7 g/ml | 1.3-1.95 g/cc |
| Tensile strength | 3 – 7 GPa | ~ 10 – 20 GPa | 4.8 GPa | 20-50 GPa |
| Tensile modulus | 0.25 – 1.7 TPa | ~ 1.0 TPa | 4.1 GPa | 8-15 GPa |
| Electrical resistivity | $10^{-3}$ – $10^{-6}$ Ohm-cm | ~ 1 Ohm-cm | ~$10^{-8}$ Ohm-m | ~$10^{-6}$ Ohm-m |
| Thermal conductivity | 20 – 3000 W/m K | 3000 W/m K | 114 W/m.k | 25-470 W/m.K |
| Coef. Thermal Exp | -1 x $10^{-6}$ | ~ 1 x $10^{-6}$ | ~0.6 x $10^{-6}$ | 1.2-8.2 x $10^{-6}$ |

### 1.1.2 Material Properties:

#### 1.1.2.1 Mechanical:

Tate et al. (2013) used NGP modified PA11. It is observed that 3-5wt% improved electrical and thermal properties without decrease in the mechanical properties. The size of NGP particles and processing method directly affect the mechanical properties. The high shear action involved in the extrusion process leads to improvement in the mechanical properties. The screw size and angle of the extrusion machine also helps in good shearing action. [14]

#### 1.1.2.2 Electrical:

Gaikwad et. al (2012) used NGP modified PA11 where they observed that electrical resistivity reduces with the increase in percentage loading of NGP into PA11. Different processing techniques and parameters, types of conductive fillers used, and their properties are the important factors affecting electrical resistivity of the components. Higher concentration of nanoparticles in the polymer matrix helps in creating a conductive path through the polymer matrix which leads to achieve expected electrical resistivity of the material. [15]

#### 1.1.2.3 Thermal:

Coefficient of thermal expansion (CTE) of polymers is much higher compared to NGPs and other carbon-based nanomaterials. Mancic's et. al (2015) studied the thermal and mechanical properties of PA11/titanium nanotubes in which they found that the addition of 1% wt. MWCNT increases the thermal stability of PA11 by a significant amount, whereas an addition of 5% wt CNF has little to no effect. The addition of fire retardants with CNF is a better combination for heat deflection. [16]

## 1.2 Material System:

### 1.2.1 Polyamide 6 (PA6 or Nylon 6):

**Figure 3: AdvanSix PA6 pellets**

The polymer resin used in this research is Polyamide 6 resin produced by AdvanSix. The resin provided is a semi-crystalline PA6 homopolymer resin. It is medium viscosity extrusion grade for high strength mono and multifilament applications [19]. AdvanSix's PA6 exhibits excellent extrusion characteristics which makes its applicable for variety of plastic applications from automotive parts to electronics. It exhibits good strength, stiffness, and toughness as well as excellent heat, chemical and abrasion resistance.

**Table 3: Common properties of PA6 [17]**

| Property | Values |
|---|---|
| Density | 1.13 g/cc |
| Melting temperature | 220 C |
| % Elongation at yield | 20.0 |
| Tensile modulus | 2.5 GPa |
| Volume resistivity | 2.16E+12 Ohm-cm |
| Coefficient of thermal expansion | **1** x $10^{-6}$ $K^{-1}$ |

### 1.2.2 Nanographene platelets:

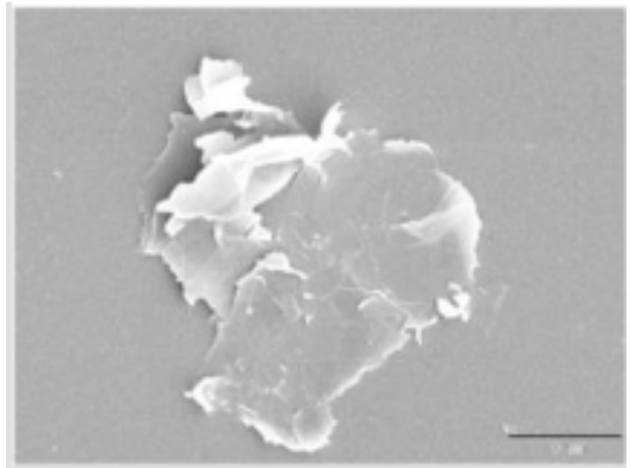


**Figure 4: SEM image of Grade M graphene nanoparticles by XG Sciences**

The nanoparticles used in this research was nanographene platelets (NGP) produced by XG Sciences. It was grade M unique nanoparticle consisting of short stacks of graphene sheets having a platelet shape. Each particle of NGP has a typical surface area of 120 to 150 $m^2/g$ and a particle diameter of 50 nm. The physical properties of NGP are listed in the figure below.

**Table 4: Typical properties of NGP by XG Sciences [18]**

| Property | Value - Parallel to surface | Value – perpendicular to the surface | Unit of measure |
|---|---|---|---|
| Density | 2.2 | 2.2 | g/cc |
| Carbon content | >99.5 | >99.5 | % |
| Thermal conductivity | 3000 | 6 | W/m K |
| Thermal expansion | $4\text{-}6 \times 10^{-6}$ | $0.5 – 1.0 \times 10^{-6}$ | m/m/deg -K |
| Tensile strength | 1000 | Na | GPa |
| Tensile modulus | 5 | Na | GPa |
| Electrical conductivity | $10^7$ | $10^2$ | Siemens/m |

### 1.3. Manufacturing:

### 1.3.1 Selective Laser Sintering (SLS):

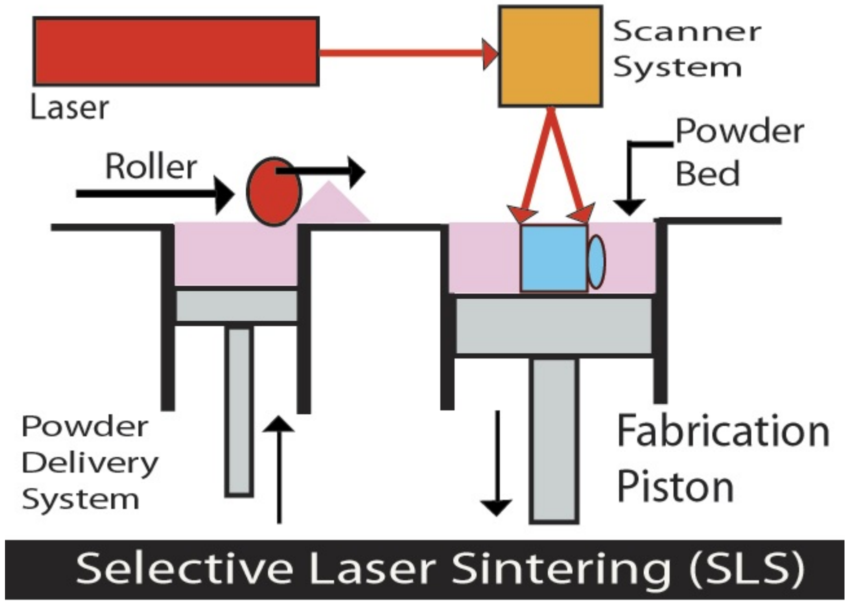



**Figure 5: Schematic diagram of SLS**

3-D printing is an additive manufacturing process that builds an object by adding material layer by layer. This technology was mostly used in rapid prototyping, but the increase in 3-D printing technology has found more use in manufacturing ready to use parts. Features that set 3-D printing apart from traditional subtractive manufacturing methods include parts made free of form, with internal mechanisms, over hanging dome shapes, and with low lead time. Selective Laser Sintering (SLS) is a 3-D printing technology first invented by Dr. Carl Deckard at the University of Texas in 1987 [19]. Powder material is spread flat in a bed and a laser source is aimed precisely to sinter the material, plastic or metal [23]. This process is repeated over and over until the desired part is achieved from the CAD drawing.

### 1.3.2 Fused Deposition Modeling (FDM):

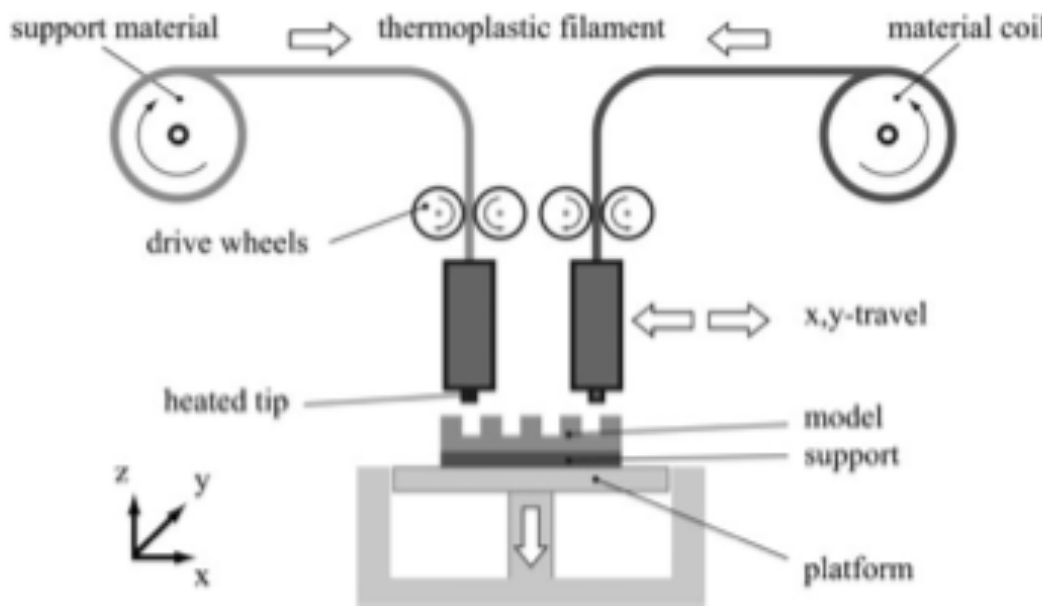



**Figure 6: Procedure of fused deposition modeling**

Fused deposition modeling (FDM) can be defined as an additive manufacturing technology based on the definition of each layer by the extrusion of filaments of thermoplastic material [20]. The process starts off with an STL file used to communicate the machine how the structure should be generated. The 3D printer dispenses the molten and support material to create the part. Finally, the part is put into a solution to dissolve off the support material. Advantages of the FDM printers include lower layer thickness, the speed of production, affordable equipment, and ease of operation and maintenance. However, FDM printers use limited types of plastics and restricts the size of the part.

**Table 5: Comparison between FDM and SLS**

| | FDM | SLS |
|---|---|---|
| **Feed Stock** | Plastic filament | Metal and polymer powder |
| **Materials** | ABS, PLA, Nylon, PC, PVA | ABS, Nylon, Alumide, Stainless steel, Titanium |
| **Function** | Extrudes the plastic filament layer by layer | Requires high power laser to fuse small particles of plastic powder into desired shape |
| **Precision** | 25-75 microns | 150 microns |
| **Part strength** | Medium | High |
| **Part Size (mm)** | 600x500x600 | 700x380x550 |
| **Material availability** | Easily available and cheap. | Not easily available and is expensive. |
| **Price** | USD 2,000 onwards. | USD 400,000 onwards |

Lulzbot Taz 6 FDM printer was used in this research because of its affordability. It is open source printer where different materials including self-developed materials can be used and can be easily modified.

### 1.4 ESD Applications:

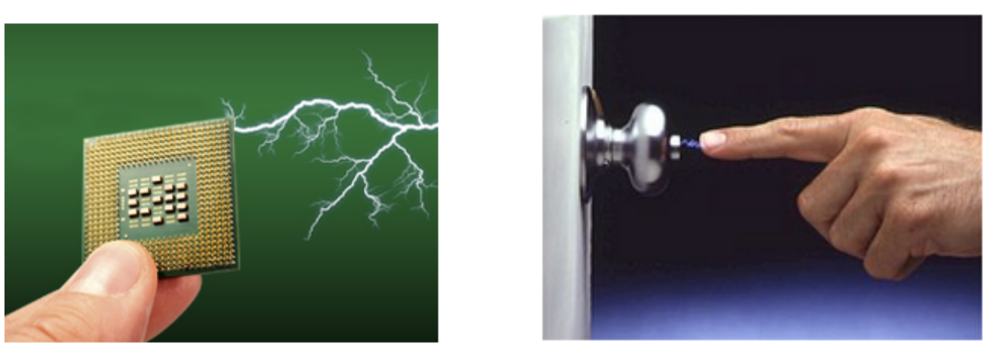


**Figure 7: ESD**

Electrostatic charge dissipation (ESD) occurs when a non-conducting surface is rubbed against each another causing development of charge and the ability to dissipate that charge is called ESD. Basically, ESD allows the electric charge to flow through the material. Each year, an estimated $40 Billion losses are occurred in the electronic industry alone due to ESD damage. So, protection from ESD damage can be resolved by using material made from conductive thermoplastic compounds which does not allow the static charge to develop to high level and dissipate that charge before it accumulates to dangerous level [21]. Electrostatic charge dissipation (ESD) is an unfavorable consequence of excess electric charge finding a path to an object at a different electrical potential. This phenomenon has devastating consequences and accounts for a significant amount of failures in the electronics industry. In the case of adding NGPs to PA6, the goal is to reduce the electrical resistivity so that PA6 qualifies for ESD applications. A couple techniques for reducing ESD include grounding points for charge dissipation and lowering electrical resistivity of the product either by coating or embedding nanomaterials. A material is said to have ESD prevention when its surface or volume resistance is less than 1 x 10E11 Ohms. Currently, carbon black, conductive graphite flakes, Multiwall Carbon Nanotubes (MWCNT), Carbon Nanofibers (CNF), and nickel are added in plastics for ESD and EMI applications.

## 1.5 Broader Goal and Objectives of Research:

The motivation for the present research was to develop a material system which will protect from ESD damage. So, the primary goal was to produce Fused Deposition Modeling (FDM) nanocomposite parts that meet the electrical requirements for Electrostatic charge dissipation (ESD) applications. While other applications wish to improve mechanical properties in composites, the goal of this study is to increase the electrical properties while still maintaining the initial mechanical properties. Previous research has focused on processing the nanocomposite samples using compression molding, injection molding, and Selective Laser Sintering (SLS). Sample made using SLS have shown considerable reduction in electrical resistivity. The major drawback of SLS is the high cost of the machinery. Comparing the pricing of other 3D printing methods, a Fused Deposition Modeling (FDM) machine would help the cost predicament by a 1 to 5 ratio. Since FDM is still an emerging technology, this study will show if this process will meet the electrical requirements needed for ESD applications.

The specific objectives of this research are:

a) Uniformly blend the NGP's into PA6 pellets using co-rotating twin screw extrusion.
b) Produce filament of 1.7mm diameter which will be used 3D printing test samples.
c) 3D print test samples using commercially available open source 3D printer after producing filaments.
e) Determine mechanical and electrical properties of neat PA6 and nanomodified PA6 material system.
f) Determine the effect of annealing on the properties of the material system.

# 2. EXPERIMENTATION

## 2.1 Dispersion of NGP in PA6:

## 2.2 Conical twin-screw extrusion:

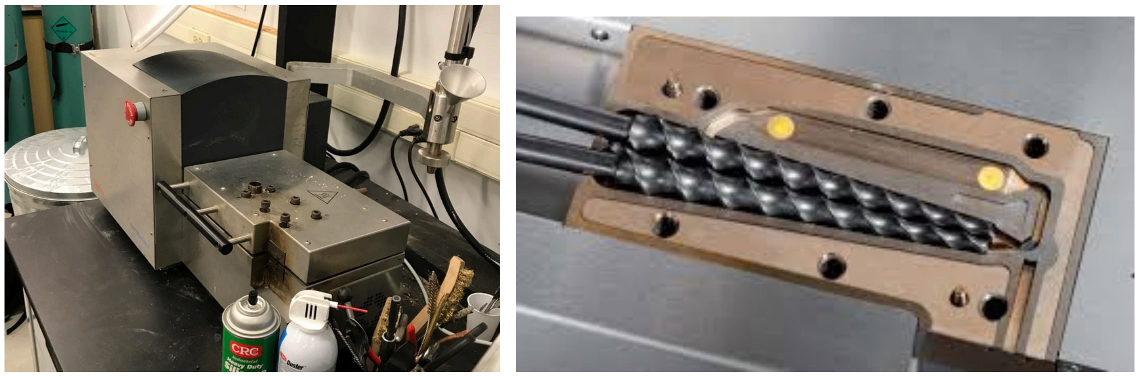



**Figure 8: Haake mini-lab 2 conical twin screw extruder**

Uniform dispersion of nanoparticles into polymer resins is challenging. High shear extruders are used for dispersion of nanoparticles. As compare to the single screw extruder, co-rotating or counter-rotating twin screw extruder is highly preferred because of the higher shearing forces and quality dispersion of nanoparticles into polymer matrix. In this research, Haake Mini-lab 2 conical twin screw extruder was used for fine tuning the process parameters for producing 1.75 mm filaments before using industrial size co -rotating twin screw extruder. The batch size of this extruder is only about 5 grams. It uses a heater coupled with twin conical co-rotating screws as shown in Figure 8. The extruder also features a computer-controlled bypass valve that allows for control the time that the batch circulates within the screw of the extruder. The PA6 pellets were conditioned in the CONAIR slimline resin dryer at 76 ºC. for 10-12 hours before extruding.


**Figure 9: PA6 pellets dried in the CONAIR slimline resin dryer**

PA6 is hydrophilic in nature and has a tendency of absorbing moisture from the air. If the pellets are not dried, then it will cause bubbles in the extruded material due to creation of steam. The pellets were fed into the conical twin screw extruder with temperature set to 200 ºC with a screw speed of 40 rpm for 5 minutes. After mixing the bypass valve was opened and the material was extruded out, then the extruded material was chopped into small pellets with scissors.

**2.3 Injection machine:**

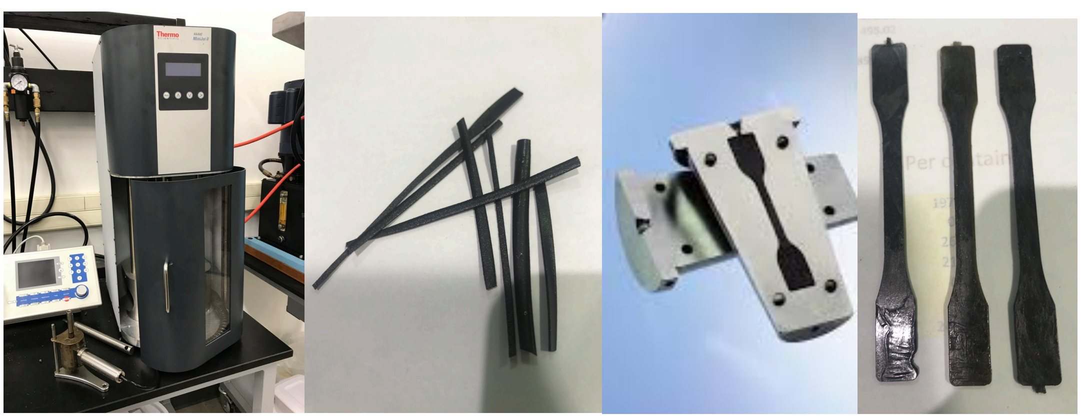


**Figure 10: Haake Minijet 2 injection molding machine and molding dies**

Haake-MiniJet 2 injection molding machine was used to produce tensile test specimens. The mold can produce a single specimen at a time with minimal material waste.

The heat temperature was set to 230 ºC, pressure to 68 MPa, post pressure to 27 MPa and the mold temperature to 40 ºC. Once the process parameters were optimized industrial size co – rotating twin screw extruder was used to for produce 1.75 mm diameter filaments of neat PA6 and PA6 with different percentage loading of nanographene platelets like 3,5 and 7 wt%.

**2.4 Industrial size co – rotating twin screw extrusion:**

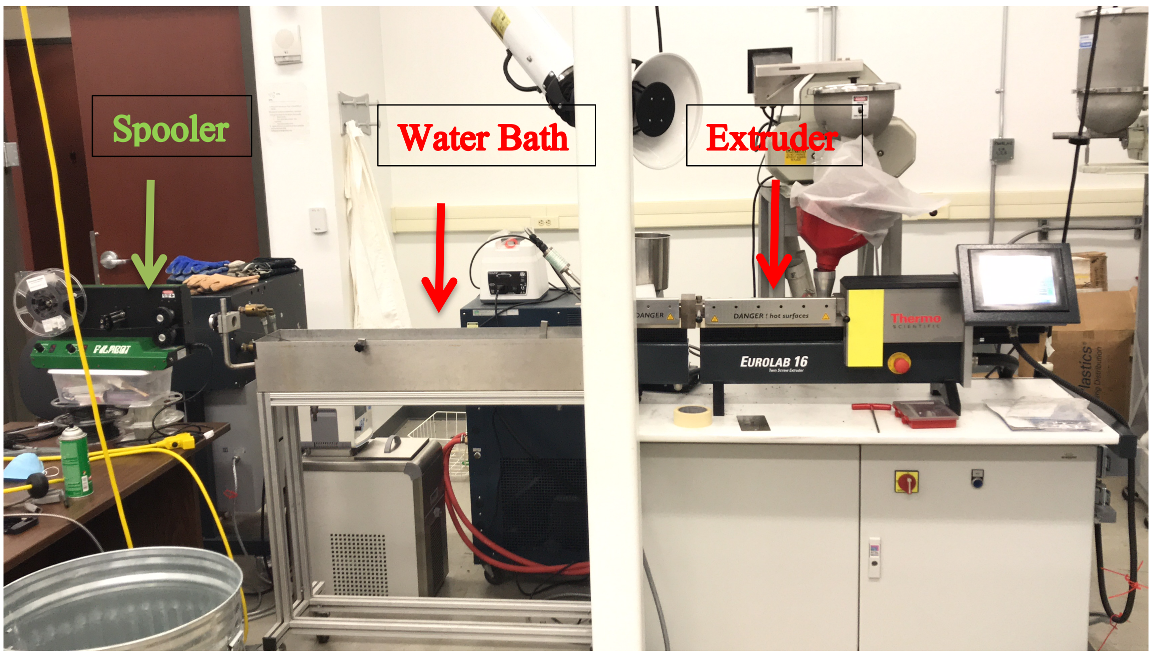



**Figure 11: Set up of co-rotating twin screw extruder for producing filaments**

The Thermo Scientific Eurolab 16 co-rotating twin screw extruder was used for melt-blending nanographene platelets into PA6 pellets to obtain master batch. PA6/NGP filaments were produced using three different NGP loadings: 3, 5 ang 7 wt %. The diameter of the screw was 15.6 mm and the length to diameter (L/D) ratio was 25:1, with maximum screw speed of 500 rpm. There were 10 different temperature zones (barrels). Out of 10 temperature zones, the 6 temperature zones were maintained at 245 ºC, and other 4 zones were maintained at 220 ºC. The speed of the screw was set to 145 rpm. A conventional method was used to mix the different loadings of NGP's into PA6. The filaments were produced in a single pass. PA6 pellets were completely dried in a desiccant dryer before compounding. Approximately 1.5 kg of material were produced in each category.  Figure 12 shows the extruded 1.75 mm diameter filaments spools PA6/NGP.

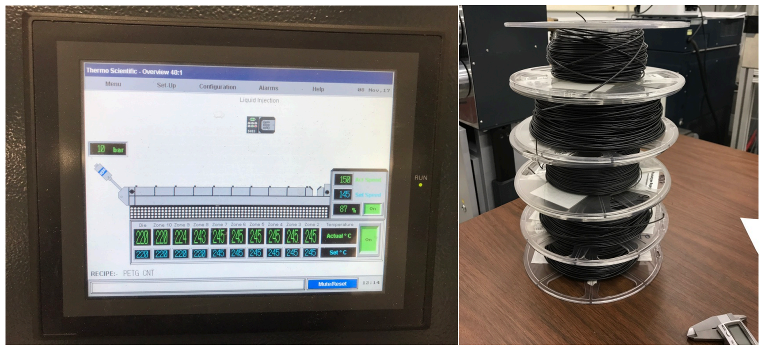


**Figure 12: Temperature zones and Extruded filaments**

**2.5 3D printing test samples:**

After producing the good quality filaments from the co – rotating twin screw extrusion next goal was to produce 3D printed test samples. Commercial off-the-shelf (COTS) Lulzbot Taz 6 3D printer was used for producing mechanical and electrical test samples. Extensive experiments were conducted to fine tune printer process parameters.

**Exp. 1** - 3D printer without enclosure with good quality PLA samples

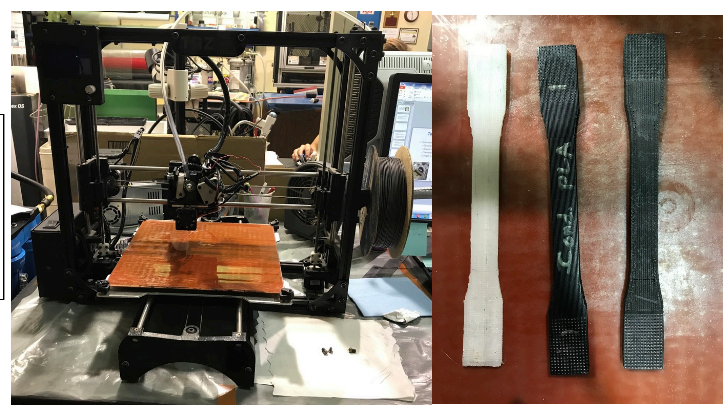


**Figure 13: Initial practice of 3D printing different metal filled PLA's**

Initially, 3 different metal filled PLA samples were printed. The machine's extruding temperature was set to 200 ºC as per the materials melting point, bed temperature was set to 65 ºC as the PLA doesn't require high bed temperature. Layer height and first layer height was set to 0.35 mm with no solid layers (horizontal shells), 100% infill with rectilinear pattern, the travel speed set was 80 mm/s. All the samples were printed in XY orientation. For printing PA6 sample the machine's extruding temperature was set to 260 ºC with the bed temperature 100 ºC as PA6 requires higher temperature then PLA and ABS, layer height and first layer height was set to 0.28 mm with no horizontal shells, 100 % infill with rectilinear pattern, 30 mm/s as travel speed and XY printing orientation was used for printing samples.

**Exp. 2** - 3D printer without enclosure. The sample is peeling up from the bed and is unable to stick to the bed because of the atmospheric temperature

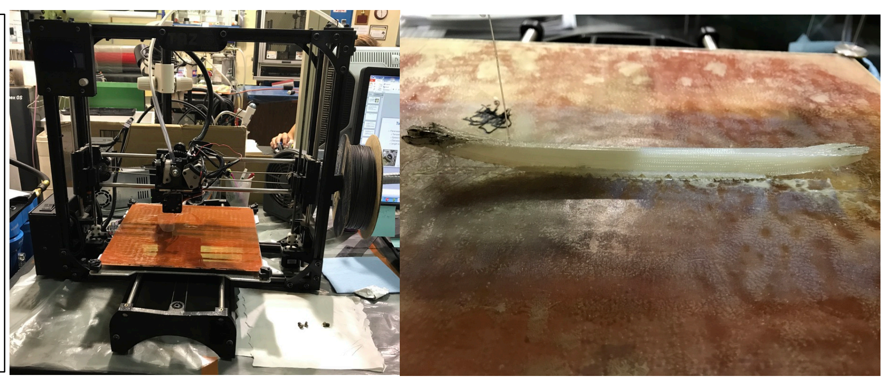


**Figure 14: Primary experiment of 3D printing neat PA6 samples**

The PA6 is semi crystalline in nature and it crystallizes very quickly if it didn't get enough heat. As shown in the Figure 14 the sample's bottom layer is not sticking the bed and peeling up. This warping led to poor quality specimens. The neat PA6 samples were printed without an enclosure as shown in Figure 14. As the surrounding temperature was not maintained, the PA6 was not getting enough heat to bond the layers to each other.

**Exp. 3** - 3D printer with cardboard enclosure. Good quality neat PA6 sample.

**Figure 15: 3D printer with cardboard enclosure and good quality neat PA6 sample**

In the next experiment a cardboard enclosure as shown in Figure 15 was used for maintaining the surrounding temperature inside the 3D printer. Cardboard enclosure worked well to maintain surrounding temperature and good quality neat PA6 and PA6/NGP samples were printed. One each of neat PA6 and 7 wt% NGP/PA6 electrical resistivity samples were printed. Electrical resistivity measurements were 2.36E+13 ohm-cm and 1.54E+13 ohm-cm for neat PA6 and 7wt% NGP/PA6, respectively. Increase in electrical resistivity indicated that printing parameters were not fined tuned.

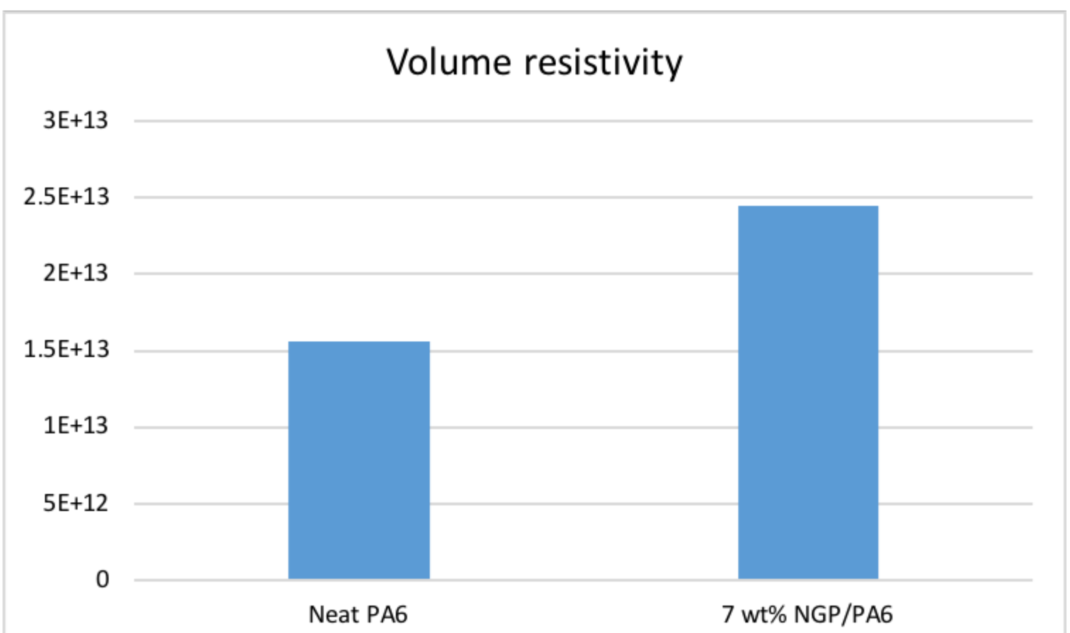



**Figure 16: Volume resistivity of neat PA6 and 7 wt% NGP/PA6**

Several studies were conducted for understanding the problem of material property deterioration. Theoretical density of nanocomposite was measured by the following equation.

$$Density\ of\ nanocomposite = \frac{1}{\left[\frac{0.93}{\rho PA6}\right] + \left[\frac{0.07}{\rho NGP}\right]}$$

where, $\rho_{PA6}$ = 1.08 g/cc and $\rho_{NGP}$ = 2.00 g/cc

therefore, theoretical density of nanocomposite is 1.15 g/cc which is more than water. Experimental density can be computed by measuring weight in the air and weight in the water.

$$Density\ of\ nanocomposite = \frac{W\ in\ the\ air}{(W\ in\ the\ air - W\ in\ the\ water)}\ x\ Density\ of\ water$$

The density of printed samples 0.91 g/cc (using density method) which is less than water, which means the sample was not solid and the layers were not bonded properly and there might be air gaps between them. Figure 17 shows the 3D printed 7 wt % PA6/NGP sample floating in water and showing failure in fined tuning parameters.

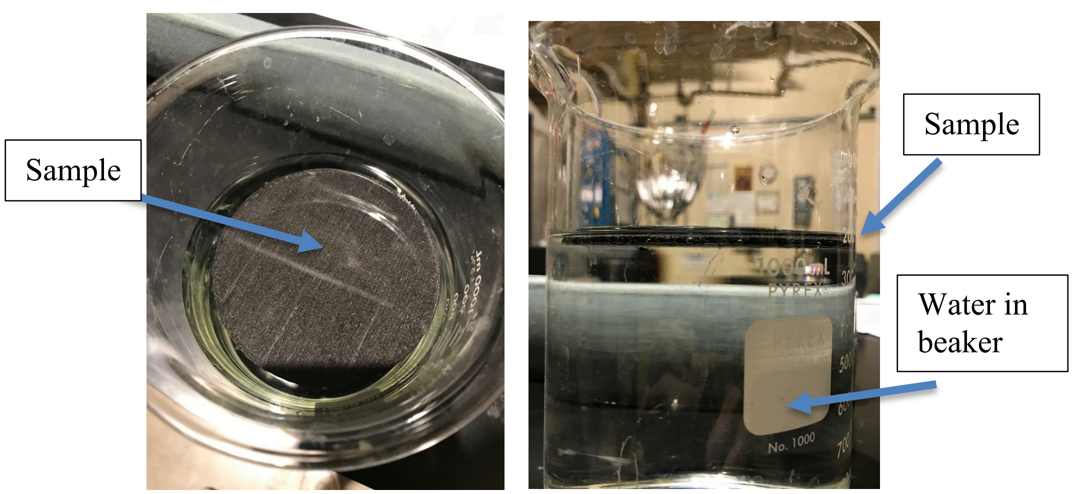



**Figure 17: 3D printed 7 wt% NGP/PA6 sample floating in the water**

Further a wooden enclosure shown in Figure 18 was used and higher temperature were tried to see if the layers bond properly. A good quality 7 wt % PA6/NGP sample was printed as shown in Figure 18. Properties were not improved.

**Exp. 4** - 3D printer with wooden enclosure. Good quality neat NGP/PA6 sample.

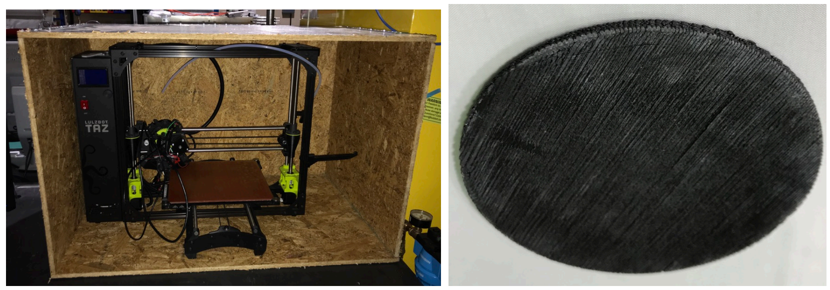


**Figure 18: 3D printer with wooden enclosure and 7 wt% NGP/PA6 sample**

Figure 19 shows Lulzbot TAZ6 with commercially available enclosure by Printed Solid made of 3 mm thick extruded acrylic material. Using that enclosure and changing some parameter like nozzle temperature set to 265 ºC, bed temperature set to 100 ºC, layer height set to 0.28 mm and speed to 30 mm/sec helped in printing good quality test sample.

**Exp. 5** - 3D printer with Lulzbot TAZ 6 enclosure by printed solid and good quality 7 wt% NGP/PA6 sample.

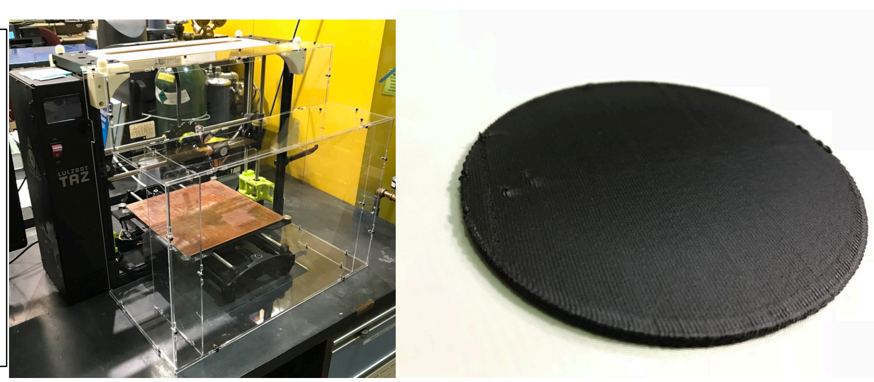


**Figure 19: 3D printer with Lulzbot TAZ 6 enclosure and 7 wt % NGP/PA6**

After achieving success in getting good quality 3D printed samples, 1 sample each of neat PA6 and 7 wt % PA6/NGP was planned to be produced for mechanical and electrical characterization. For initial screening ultimate tensile strength, tensile modulus and percentage elongation were measured to compare the mechanical properties of neat PA6 and 7 wt % PA6/NGP sample. All samples were stored in the desiccant dryer after printing to avoid absorbing moisture content from the atmosphere. Figure 20 shows samples stored in desiccant dryer.

**Figure 20: 3D printed samples stored in desiccant dryer**

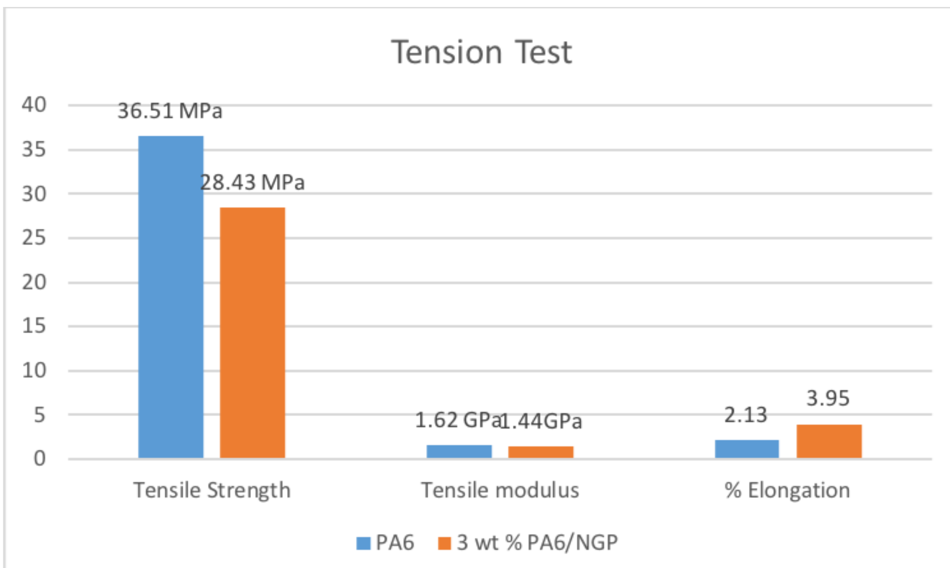



**Figure 21: Tensile strength, tensile modulus and % elongation of neat PA6.**

Figure 21 shows the results of the mechanical test. The neat PA6 showed tensile strength 36. 51 MPa higher then tensile strength 28.43 MPa of 7 wt % PA6/NGP. Tensile modulus of 7 wt % PA6/NGP dropped as compared to neat PA6. % elongation increased with nanomodification of PA6. The results were not as expected. Literature showed stress relief annealing process helps in improving material properties, so stress relief annealing was conducted on the 3D printed samples. Annealing is the heat treatment process which is used to increase the strength of the metal [22]. It is the process which is used to change the physical properties of the metal part without changing its shape. Same annealing process has been adapted for plastics for increasing the strength and stiffness of the 3D printed plastic, the process helps in reducing the stresses in highly effected areas and dissipating it out more evenly through the print, making it less likely to fracture at any specific point [23]. Annealing of plastics is different than the metals, the FDM process involves extrusion of material to form a part in layered construction. Plastics being poor conductor of heat causes uneven cooling of the part which develops stress in the 3D printed part followed by shrinkage of polymers in different ways. Annealing of plastics involve heating the part to the temperature equal to glass transition or above but below its melting temperature and then slowly allowing it to cool down. Different annealing temperature and duration depends on the type of material [24]. Researchers have also conducted a study on effect of different annealing temperatures on the mechanical properties of PA6/MWCNTs were they found improved mechanical properties after annealing at 80 ºC for 6-10 hours [24]. Similar annealing temperature and duration were carried out in this research. Annealing was done by placing the samples on the metal plate and the metal plate was kept in the regular oven as shown in the Figure 23.

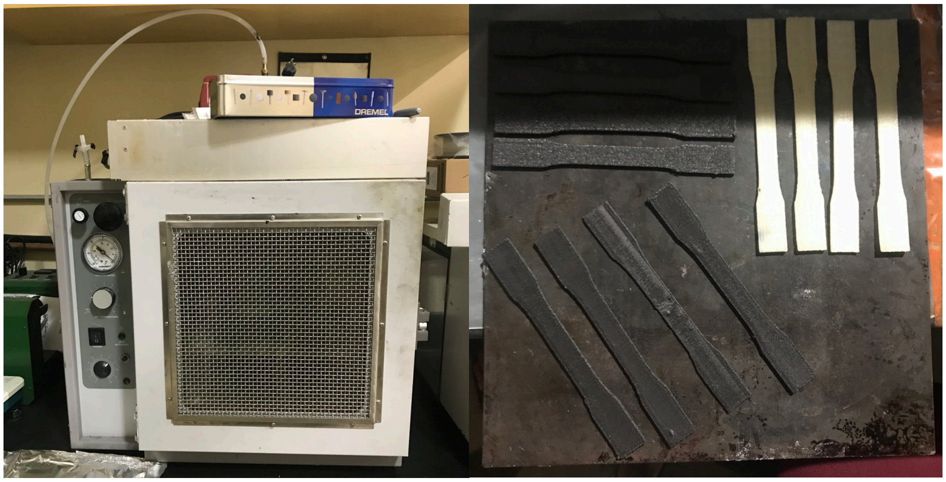



**Figure 22: Oven and mechanical test samples on the metal plate.**

# 3. PERFORMANCE EVALUATION

## 3.1 Mechanical Testing:

Tensile strength, tensile modulus and percentage elongation were measured to compare the mechanical properties between the neat PA6 sample and 3, 5 and 7 wt% of PA6/NGP samples. All the printed samples were stored in the desiccant dryer. Tension test samples were prepared using commercially available 3D printer. Six samples each of neat PA6 and 3, 5 and 7 wt% PA6/NGP in which 3 samples non-annealed and 3 samples annealed at 80 C for 10 hours were tested, averaging 3.28 in thickness and 165 mm in width with the gauge length of 57 mm. All tension samples were tested as per the ASTM D638 with a test rate of 2 mm/min, extensometer gauge length of 25.4 mm and data acquisition rate of 1 Hz. Testing was conducted on MTS 810 Servo hydraulic Test System.


**Figure 23: Tension testing.**

Figure 23 shows the tension sample mounted on the MTS machine with two sliver crossheads, fixed top crosshead and pulling bottom crosshead. An extensometer is mounted on the sample with a gauge length of 24.5 mm to measure the axial strain.

### 3.2 Electrical Testing:

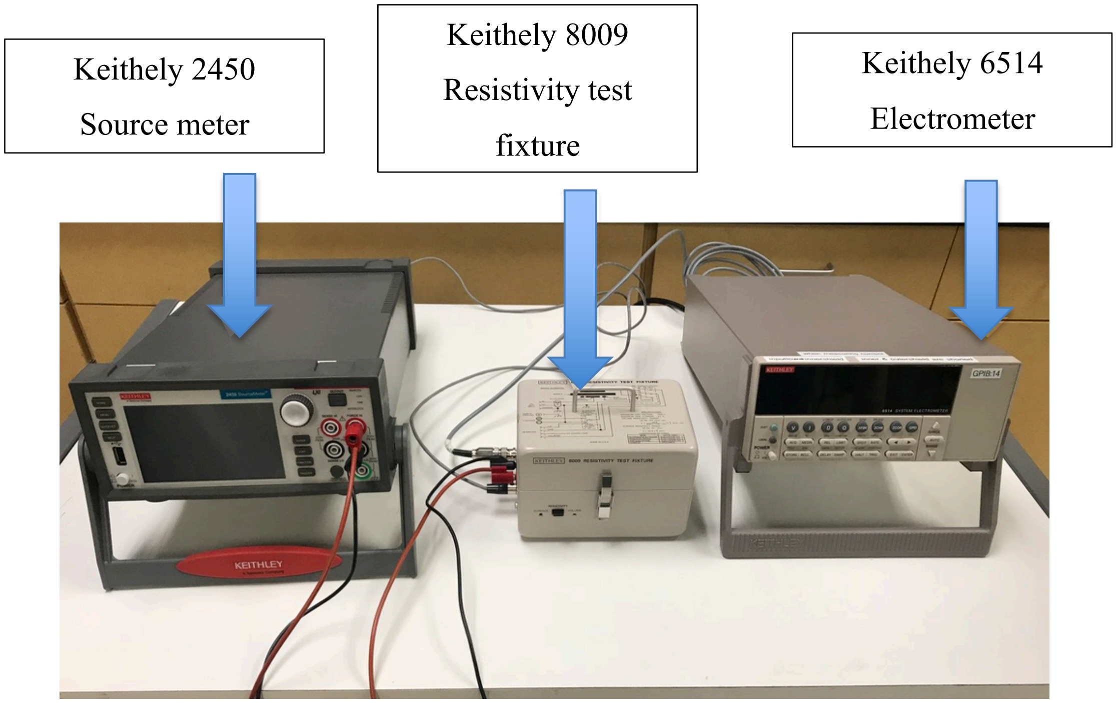



**Figure 24: Keithely Megohmmeter Instrument for electrical testing.**

Volume resistivity was determined using the Keithely Megohmmeter Instrument following the ASTM D257 standards. Six samples each of neat PA6 and 3, 5 and 7 wt% PA6/NGP in which 3 samples non-annealed and 3 samples annealed at 80 C for 10 hours were tested. Each sample had an average thickness of 2.23 mm and 3.5 inches in diameter. Testing was conducted on the Keithely Megohmmeter Instrument, which includes Keithely 2450 source meter which connects to the resistivity test fixture followed by connecting it to the Keithely 6514 electrometer. The voltage applied to every sample was 5V for 60 sec using the source meter and the amount of current flowed through the material in the test fixture was recorded by the electrometer. The volume resistivity of the sample was calculated using the following formula:

$$\rho = \frac{22.9}{Material\ thickness,\ \ cm} \times \frac{V}{I}\ Ohm - cm$$

### 3.3 Scanning Electron Microscopy (SEM):

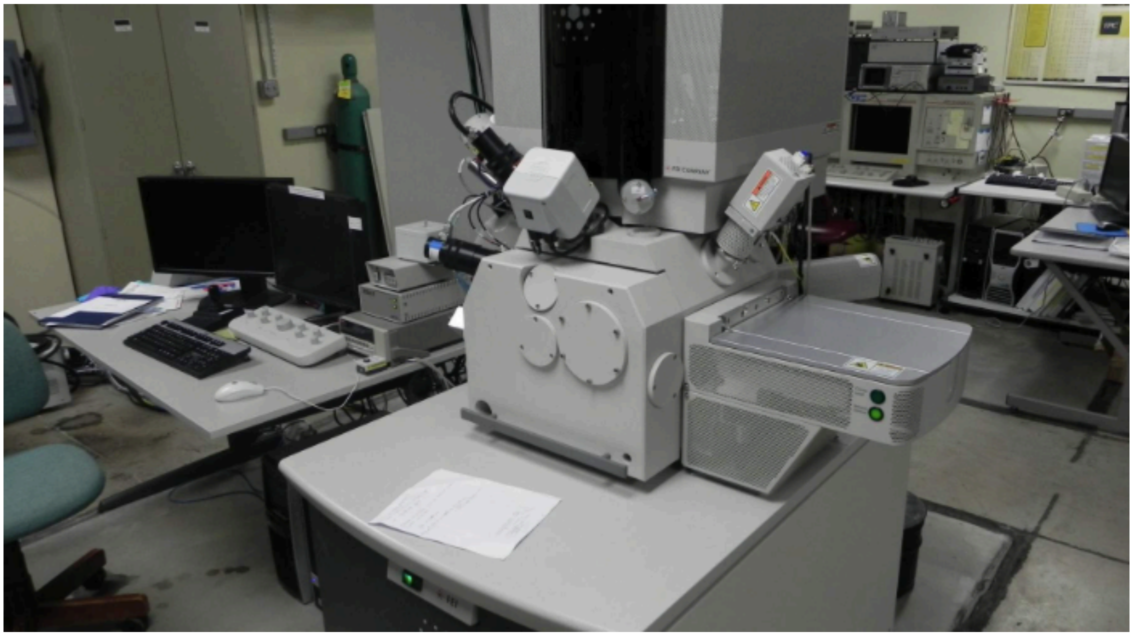


**Figure 25: FEI Helios Nano Lab Dual beam system**

SEM was conducted on the FEI Helios Nano Lab Dual beam system machine as shown in the Figure 25. The system's ultra-high-resolution electron optics are capable of 0.9 nm at optimal working distance of 15 kV and 1.0 nm at the Dual beam coincident point with 350 V – 30 kV beam voltage range. SEM was carried on the neat PA6 and 3, 5 and 7 wt% PA6/NGP filaments, each averaging 4mm in length. SEM was conducted to understand the uniform dispersion of NGP platelets into PA6 pellets. Uniform dispersion of NGP's into PA6 helps the NGP to create a proper conductive path in the material system.

# 4. RESULTS AND DISCUSSION

## 4.1 Mechanical Properties Testing:

### 4.1.1 Tension test:

Tension testing was done on both not annealed and annealed samples, also results of tensile strength, modulus and % elongation of annealed and not annealed samples is shown in Figure 26, Figure 27 and Figure 28.

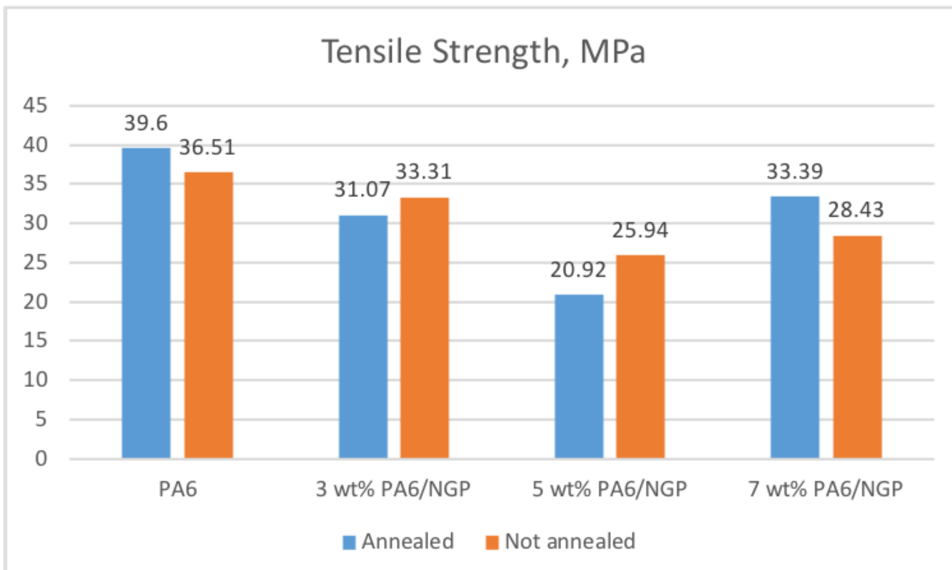



**Figure 26: Tensile strength results of annealed and not annealed samples.**

Annealed neat PA6 and 7 wt % PA6/NGP samples showed improved mechanical properties as compared to that of not annealed samples. Similar trend of properties was seen in both annealed and not annealed material system. Annealed neat PA6 (39.6 MPa) and 7 wt % PA6/NGP (33.39 MPa) sample showed improved tensile strength as compared to not annealed neat PA6 (36.51 MPa) and 7 wt % PA6/NGP (28.43 MPa). Annealed 3 (31.07 MPa) and 5 wt % PA6/NGP (20.92 MPa) samples showed decreased tensile strength as compared to not annealed 3 (33.31 MPa) and 5 wt % PA6/NGP (25.94 MPa).

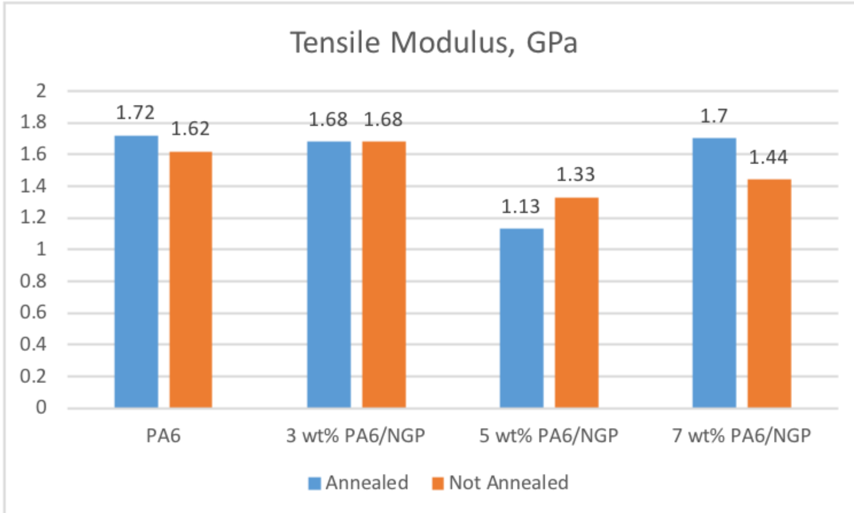



**Figure 27: Tensile modulus results of annealed and not annealed samples.**

Annealed neat PA6 (1.72 GPa) and 7 wt % PA6/NGP (1.7 GPa) showed improved tensile modulus as compared to not annealed neat PA6 (1.62 GPa) and 7 wt % PA6/NGP (1.44 GPa). There was no significant difference in tensile modulus of 3 wt % PA6/NGP (1.68 GPa). Tensile modulus of annealed 5 wt % PA6/NGP (1.13 GPa) decreased as compared to not annealed 5 wt % PA6/NGP (1.33 GPa).

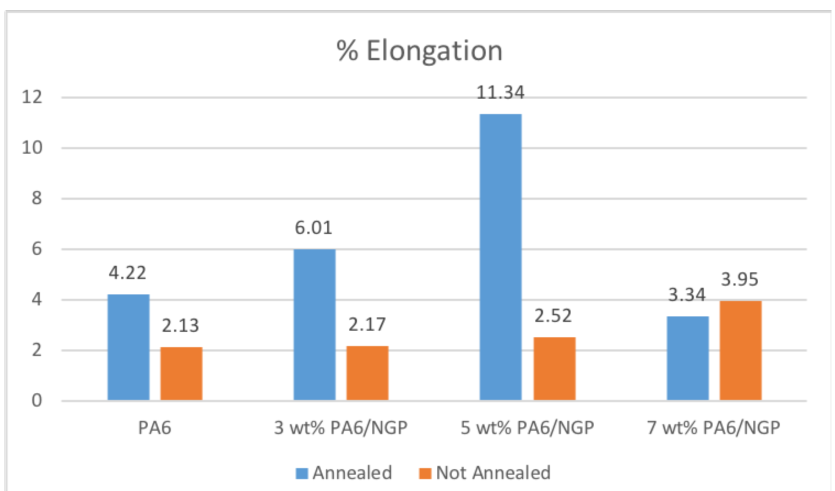



**Figure 28: % Elongation results of annealed and not annealed samples.**

Percentage elongation increased with the increase in % loading of NGP's into PA6 for not annealed samples. Annealed neat PA6 (4.22), 3 (6.01) and 5 wt % PA6/NGP (11.34) showed improved % elongation as compared to not annealed neat PA6 (2.13), 3 (2.17) and 5 wt % PA6/NGP (2.52). % Elongation of annealed 7 wt % PA6/NGP (3.34) decreased as compared to not annealed 7 wt % PA6/NGP (3.95) because recrystallization takes place in stress relief annealing process where it makes the material ductile. Table 6 shows the comparison between tension test properties of annealed and not annealed test samples.

**Table 6: Comparison table of not annealed and annealed samples**

| | Not Annealed tension results | | | | Annealed tension results | | | |
|---|---|---|---|---|---|---|---|---|
| | PA6 | 3 wt % NGP/PA6 | 5 wt % NGP/PA6 | 7 wt % NGP/PA6 | PA6 | 3 wt % NGP/PA6 | 5 wt % NGP/PA6 | 7 wt % NGP/PA6 |
| Tensile strength, MPa | 36.51 | 33.31 | 25.94 | 28.43 | 39.6 | 31.07 | 20.92 | 33.39 |
| Tensile modulus, GPa | 1.62 | 1.68 | 1.33 | 1.44 | 1.72 | 1.68 | 1.13 | 1.70 |
| % Elongation | 2.13 | 2.17 | 2.52 | 3.95 | 4.22 | 6.01 | 11.34 | 3.34 |

### 4.2 Electrical properties testing:

#### 4.2.1 Volume Resistivity:

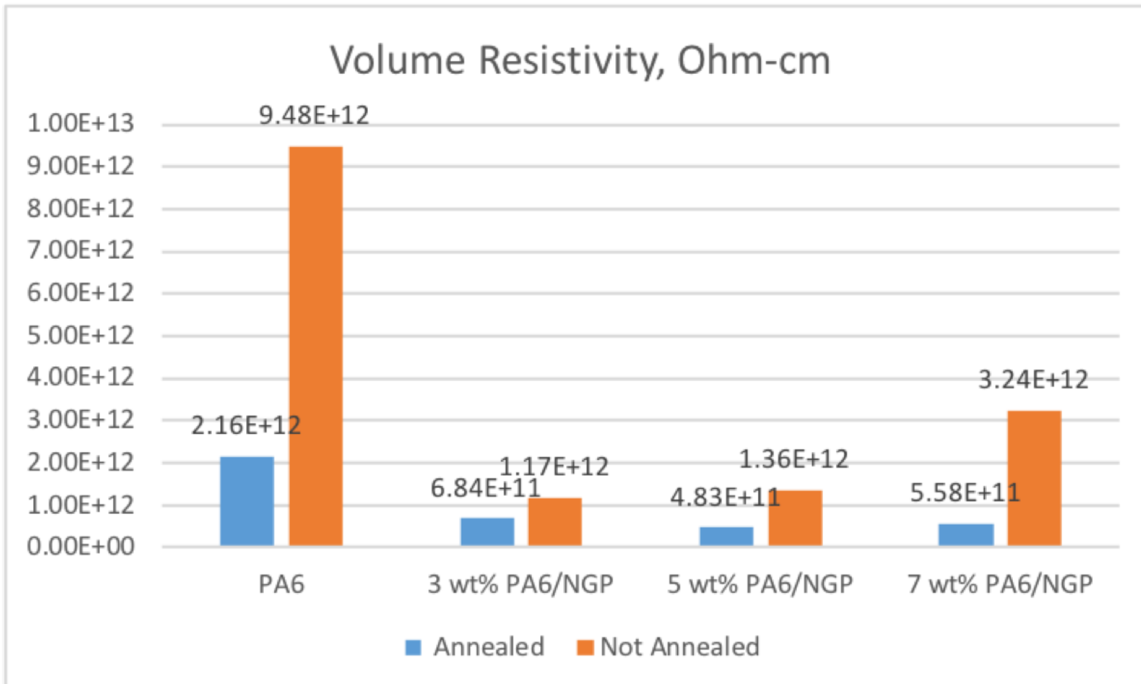



**Figure 29: Volume resistivity results of annealed and not annealed samples.**

Volume resistivity results of annealed and not annealed neat PA6 and 3, 5 and 7 wt % PA6/NGP samples are as shown in Figure 29. Nanomodification of not annealed PA6 showed reduced volume resistivity but not in the expected range. Resistivity of not annealed 3 wt % PA6/NGP (1.17E+12 ohm-cm) showed reduction as compared to neat PA6's resistivity (9.47E+12), resistivity of not annealed 5 (1.36E+12 ohm-cm) and 7 wt % PA6/NGP (3.24E+12 ohm-cm) showed rise as compared to 3 wt % PA6/NGP sample but less than neat PA6 sample. None of the not annealed samples qualified for ESD application. Annealing helped in improving electrical properties as compared to that of not annealed samples. Annealed 3 wt % PA6/NGP showed volume resistivity of 6.85E+11 ohm-cm less as compared to neat PA6 sample (2.15E+12 ohm-cm), but higher than 5 wt % PA6/NGP

(4.82E+11 ohm-cm) and 7 wt % PA6/NGP (5.58E+11 ohm-cm). All annealed nanomodified PA6 samples qualified for ESD application.

### 4.3 Scanning Electron Microscopy (SEM) test:

In order to study the dispersion and exfoliation of NGP's into PA6 polymer matrix, SEM test was performed with sputter coating on neat PA6 and nanomodified filaments. In Figure 33. a, b and c show the SEM images of 3, 5 and 7 wt % PA6/NGP filaments respectively.

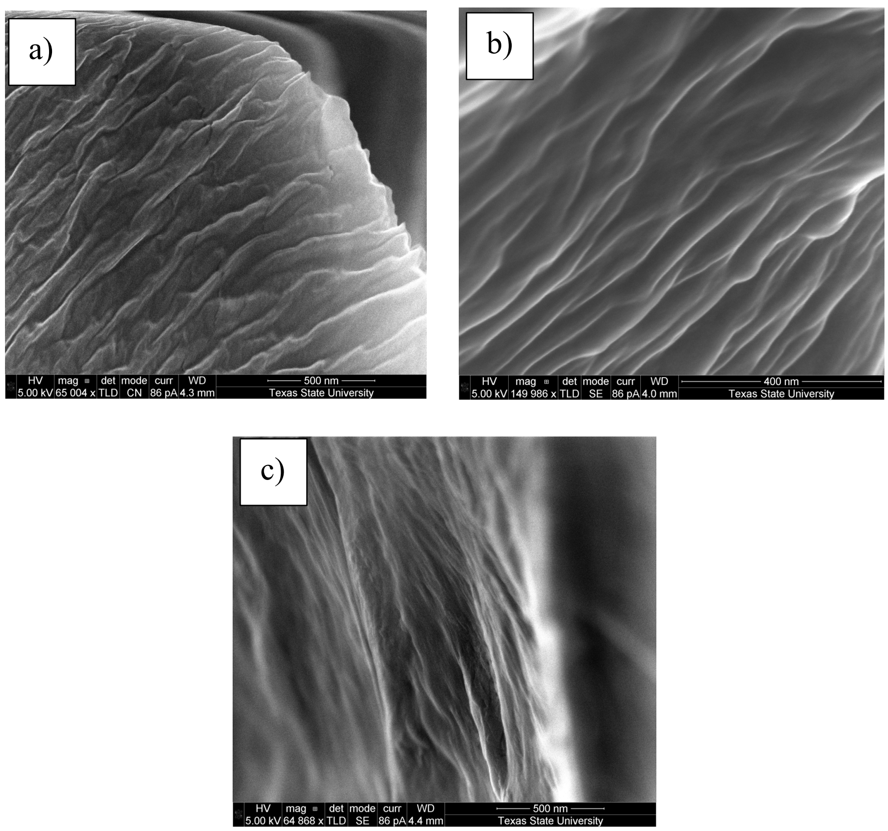



**Figure 30: SEM of a) 3 wt% PA6/NGP, b) 5 wt % PA6/NGP, c) 7 wt% PA6/NGP**

SEM image of 3 wt % PA6/NGP and 7 wt % PA6/NGP was taken at 500 nm magnification while that of 5 wt % PA6/NGP was taken at 400 nm magnification. In 3 and 5 wt % PA6/NGP image the clean flake-like and plate-like appearance of NGP's can be seen within the PA6. Whereas 7 wt % PA6/NGP there was agglomeration in some areas and NGP's with clean flake like structure in remaining areas. From all these observations the plate and flake like appearances of NGP in the material system indicates the uniform dispersion and exfoliation of NGP's within the PA6 matrix.

# 5. CONCLUSION

PA6 pellets and nanographene platelets were successfully blended using co-rotating twin screw extruder to produce 1.75 mm diameter filaments to be used for 3D printing. These extruded filaments were than used for producing the neat PA6 and nanomodified samples using the commercially available desktop 3D printer for electrical and mechanical property measurements. SEM testing with different magnification showed NGP's were well dispersed into PA6 matrix. Initially there was no significant improvements in the mechanical properties and electrical resistivity of the nanomodified samples also reduced as compared to the neat PA6 samples, which was against the hypothesis of the research. Study of density measurement solved the problem of reason behind properties droppage. Further good quality samples were produced with better arrangement and techniques using same commercially available 3D printer.

The neat PA6 and nanomodified PA6 samples showed average tensile strength of 33 MPa and modulus of 1.62 GPa with average percentage elongation of 2.32. Tensile strength and modulus dropped for 3 and 5 wt % PA6/NGP as compared to neat PA6. While 7 wt % PA6/NGP showed increased strength and modulus compared to 3 and 5 wt % PA6/NGP but less then neat PA6 creating a possibility of further study of adding more percentage of NGP's into PA6 for improved properties. Volume resistivity of both neat PA6 and nanomodified PA6 samples were in the range of $10^{12}$ Ohm-cm, where none of them qualified for ESD applications.

Literature showed the reason behind low properties were the developed stresses in the samples while printing. Stress relief annealing samples at 80 C for 10 hours before test was the solution for getting rid of the developed stresses. Annealed neat PA6 and 7 wt %

PA6/NGP showed improved mechanical properties as compared to that of not annealed. Tensile strength and modulus of annealed samples increased with decrease in percentage elongation. Annealing also helped in improving electrical properties. Annealed electrical nanomodified PA6 samples showed reduced resistivity as compared to that of annealed neat PA6 samples. 3, 5 and 7 wt % PA6/NGP showed volume resistivity in the range of $10^{11}$ ohm-cm, all qualifying for ESD applications with 5 wt % PA6/NGP being with the lowest resistivity amongst all. Because of improved mechanical and electrical property of 7 wt % PA6/NGP, it was been selected for ESD application.

## APPENDIX SECTION

Technical data sheets:

AdvanSix

NYLON SOLUTIONS

# Aegis® H95ZI Nylon 6 Extrusion Grade Homopolymer

## Description

**Aegis® H95ZI** is a medium viscosity, nylon 6 extrusion grade homopolymer for high-strength monofilament and multifilament applications (typical filament tenacities 5.0-9.0 gpd).

| Typical Properties | Test Method | Unit | Value |
|---|---|---|---|
| **Parameter** | | | |
| Viscosity, FAV | D-789 | | 86-98 |
| 96% SAV | | | 3.28 |
| Moisture Content | ASTM D-6869 | % | Max. 0.06 |
| Extractable Content | SOP-702-307 | % | Max. 0.8 |
| **Thermal** | | | |
| Melting Point | ASTM D-3418 | ºC (ºF) | 220 (428ºF) |
| Density (Typical) | ASTM D-1505 | $g/cm^3$ | 1.13 |
| Forms | | | Pellets |

## Processing Guidelines

### Material Handling

Aegis® H95ZI homopolymer is supplied in sealed containers and drying prior to processing is not required. However, high moisture is the primary cause of processing problems. If drying becomes necessary, a dehumidifying or desiccant dryer operating at 80°C (176°F) is recommended. Drying time is dependent on moisture level. Further information concerning safe handling procedures can be obtained from the Safety Data Sheet. Alternatively, please contact your AdvanSix representative.

*The values presented in this data sheet are typical values and are not to be interpreted as product specifications.*

**Contact AdvanSix**
To learn more about the benefits of of Aegis® Nylon Resins, visit **AdvanSix.com/NylonSolutions** or call:
**1-844-890-8949** (toll free, U.S./Can.)
**+1-973-526-1800** (international)

**AdvanSix**
300 Kimball Drive, Suite 101
Parsippany, NJ 07054



AdvanSix

**Figure 31: AdvanSix PA6 technical data sheet**

# Technical Data Sheet

## xGnP® Graphene Nanoplatelets - Grade M

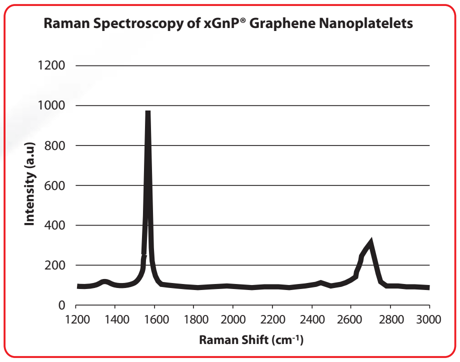
***xGnP® Graphene Nanoplatelets*** are unique nanoparticles consisting of short stacks of graphene sheets having a platelet shape. Each grade contains particles with a similar average thickness and surface area.

**Grade M** particles have an average thickness of approximately ***6 - 8 nanometers*** and a typical surface area of ***120 to 150 m²/g***. Grade M is available with average particle diameters of ***5***, ***15*** or ***25*** microns.

### Characteristics of Bulk Powder

| *Property* | *Typical Value* |
|---|---|
| Appearance | Black granules |
| Bulk Density | 0.03 to 0.1 g/cc |
| Oxygen Content* | < 1 percent |
| Residual Acid Content* | < 0.5 wt% |

**Note: nanoplatelets have naturally occurring functional groups like ethers, carboxyls, or hydroxyls that can react with atmospheric humidity to form acids or other compounds.*




### Typical Properties of xGnP® Graphene Nanoplatelets

| *Property* | *Typical Value - Parallel to Surface* | *Typical Value - Perpendicular to Surface* | *Unit of Measure* |
|---|---|---|---|
| Density | 2.2 | 2.2 | grams/cc |
| Carbon Content | >99.5 | >99.5 | percent |
| Thermal Conductivity | 3,000 | 6 | watts/meter-K |
| Thermal Expansion (CTE) | $4\text{-}6 \times 10^{-6}$ | $0.5 – 1.0 \times 10^{-6}$ | m/m/deg.-K |
| Tensile Modulus | 1,000 | na | GPa |
| Tensile Strength | 5 | na | GPa |
| Electrical Conductivity | $10^7$ | $10^2$ | siemens/meter |



5020 Northwind Drive, Suite 212, East Lansing, MI 48823
517.203.1110 517.203.4140 (f) www.xgsciences.com

XG sciences

**Figure 32: XG Sciences Nanographene Platelets technical data sheet**

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