ELECTRICAL AND MECHANCIAL PROPERTIES OF FUSED FILAMENT FABRICATION OF POLYAMIDE 6 / NANOGRAPHENE FILAMENTS AT DIFFERENT ANNEALING TEMPERATURES

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Abstract

Polyamide 6 (PA 6) nanographene composites are viable engineered nanocomposite materials with high potential for electrostatic discharge applications. This can be attributed to the ability of the nanographene particles in reducing the electrical resistivity of the parent polyamide 6 and in turn creating a conductive network for a controllable discharge of static electricity. In addition, PA 6 nanographene composites can also exploit the good mechanical properties of the parent polyamide 6, a structural thermoplastic ideal for 3D printing via fused filament fabrication (FFF). Hence, 3, 5, and 7 wt.% of NGP were blended with PA6 using co-rotating twin screw extruder to produce 1.75mm diameter for FFF using Lulzbot TAZ 6 3D printer. Scanning Electron Microscopy (SEM) was used to evaluate the degree of exfoliation of the nanographene and tensile and electrical resistivity test samples were manufactured via fused filament fabrication. The polyamide 6 nanographene composites were further subjected to annealing treatment at 80ºC, 140ºC, 200ºC and a comparison study was carried out on the observed tensile properties and electrical resistivity values of both annealed and not annealed treated.

1. Introduction

1.1 Motivation

The scope of this research is to evaluate the effects on electrostatic charge dissipation at different annealing temperatures of nanographene platelets (NGP) added in polyamide 6 (PA6) filaments. Previous research of polymers filled with NGP suggests that the improved electrical conductivity properties are ideal for the parts manufactured by fused deposition modeling (FDM) also known as fused filament fabrication (FFF) that require electrostatic discharge protection. The size of the NGP platelets is 50 nm in diameter and the size of the filaments are 1.75mm in diameter. In this study, NGP were blended into PA6 using co-rotating twin screw extruder to compare electrical and mechanical properties and exfoliation of the nanoparticles. Scanning Electron Microscopy (SEM) was used to determine the degree of dispersion. Loadings of 3, 5, and 7wt% of NGP were evaluated in filaments that were not annealed and annealed at 80ºC, 140°C, and 200°C. Tensile and electrical resistivity test coupons were prepared using FFF on a Lulzbot TAZ 6 3D printer and subsequently tested.

1.2 Literature Review

There is a problem with the emission of electromagnetic waves that can interfere with sensitive electronic devices. Nonconductive plastics do not provide Electromagnetic Interference (EMI) shielding. A solution is to use conductive plastics where the material absorbs the electromagnetic waves by increasing the volume resistivity of the plastic. Conductive plastics are dependent on the material thickness, dispersion of the additive, and the conductivity of the additive. An advantage of using a conductive plastic instead of a coating is that the EMI shielding is integral to the part and cannot be removed by abrasion [1].

Another problem with nonconductive polymers is electrostatic discharge (ESD). ESD is the flow of an electrical charge that is stored in the nonconductive polymer to a material with a different electrical potential. Semiconductor and medical device industries need protection from ESD. Sensitive electronics manufacturers therefore establish electrostatic protective areas free of static electricity, using measures to prevent charging, such as avoiding highly charging materials by increasing the electrical conductivity of the polymer to that between an insulator and a conductor the material can provide ESD shielding [2].

The packaging of these electrically sensitive devices can be fabricated with a conductive polymer to meet the ESD requirements. The ESD requirements of materials need to be antistatic (prevent a triboelectric charge), be able to dissipate an electrical charge with low surface or volume resistivity, or shield from electrostatic fields. If the material is expected to have surfaces that will rub against each other it needs to have antistatic properties to not generate a static charge. If the material has a low enough electrical resistance it can dissipate the charge by grounding the electrical charge away from the sensitive electronics. To be categorized as a static dissipative the material needs a resistivity of greater than a conductor (1×10^4 Ohms) or less than an insulator (1×10^{11} Ohms). To have shielding characteristics the surface resistance needs to be less than 1×10^3 Ohms [3].

FDM filaments with Polylactic Acid (PLA) polymer and reduced grapheme oxide (r-GO) have been used to make printed flexible circuits that can replace copper wire because of its high conductivity. 6wt% r-GO has shown a conductivity of the filament of 4.76 S/cm (0.21 Ohm*cm) [4]. Black Magic is producing PLA with r-GO with a volume resistivity of 0.6 Ohm*cm to 3D print electrically conductive components [5].

Various nanomaterials (e.g, Carbon Nanotubes (CNT), carbon black etc.) have been used to make nanocomposites for the purpose of electrostatic charge dissipation. S. Athreya in 2009 made 4 wt% PA12/carbon black nanocomposites using Selective Laser Sintering (SLS) and showed that electrical conductivity and flexural modulus of the samples were higher than the samples made by injection molding [6]. Monica Calin in 2015 studied the electrical conductivity of PA6/MWCNT samples obtained by electrospinning and showed that volume resistivity decreased and surface resistivity remained unchanged with the applying load [7]. Joseph G. Smith in 2004 prepared nanocomposites with space durable polyamides, SWCNT, and conductive additive (CuSO4 salt) that met the electrostatic charge dissipation requirements at space environment [8].

Graphene Nanoplatelets (GNP) are flat nanosheets of carbon that is a high-quality cost-effective alternative to CNT. The lateral size is a few hundred nanometers to several micrometers and the thickness is 10 – 20 nm. With good dispersion the GNP will form a percolation network to form an ESD protection. Nylon is an engineered plastic and is a member of the polyamide group. It is a light weight, strong, flexible material and stable in chemicals, heat, UV light. The minimum quantity of filler required to form a conductive path within a polymer is defined as the Percolation Threshold (PT). A PT can be achieved with the addition of GNP of 5 wt% loading and above [9].

In situ polymerization, solvent mixing, or melt mixing can be used to disperse GNP into PA11. However, these dispersion methods have low yield and high production costs due to the energy required for dispersion and the large amounts of solvent that would be required in mass production. Melt Compounding in twin screw extruder is a dispersion method that is scalable, cost effective, fast, and would be a continuous mass production process. Filaments have been fabricated by Rashmi et. al. with PA11 with 0.5, 1, 3, 5 wt% GNP. They have reported filament volume resistivity of PA11 / 0.5 wt% GNP (4.54×10^7 Ohm * cm), PA11 / 1 wt% GNP (3.12×10^7 Ohm * cm), PA11 / 3 wt% GNP (2.27×10^7 Ohm * cm), and PA11 / 5 wt% GNP (1.92×10^7 Ohm * cm). If the properties of the filament can be transferred over to a FDM printed part ESD protection is possible [10].

Polyamide 11 (PA11) / GNP have been studied by Tate, et al. for ESD dissipation by using the additive manufacturing method of SLS. GNP at 1, 3, and 5 wt% showed improvement in mechanical, thermal, and electrical properties. The GNP was dispersed using sonication in Isopropyl Alcohol (IPA). This sonication method produced a high degree of uniform dispersion and moderate exfoliation. Thin sheets of material were fabricated using compression molding. Scanning Electron Microscopy (SEM) was used to measure the quality of dispersion of the GNP. It was determined that less than 3 wt% GNP was needed to achieve low enough electrical resistivity for ESD applications. The PT for ESD applications is a surface resistance of 10^6 to 10^{10} Ohms/cm^2 or an Electrical Resistivity of 10^4 to 10^8 Ohms*cm. PA 11 / 5 wt% GNP had an electrical resistivity of 2.46×10^6 Ohms*cm [11].

Tate, et al. has researched the dispersion of 1, 3, 5, and 7 wt% NGP in PA11 by using a co-rotating twin-screw extrusion to be used in SLS. NGP has been shown increase electrical and thermal properties without degradation in the mechanical properties using SLS. The PT was increased to 7 wt% NGP to achieve an electrical resistivity on the order of 2.3×10^9 Ohms*cm with the injection molding process. The PT for volume resistivity is 10^{10} to 10^{11} Ohms*cm. The PT was increased to 5wt% NGP to achieve a volume resistivity 1.18×10^9 Ohm*cm with the compression molding process. It is believed that the twin screw extrusion process affected electrical resistivity from the high shear breaking down the NGP and decreasing the aspect ratio of the platelet. The sonication process had a better lower PT but will have limitations to scaling up for mass production [12].

The drawback of the SLS process is that the machine cost is five times higher than a Fused Deposition Modeling (FDM) machine. PA11 / 3wt% NGP filaments were FDM 3D printed using a Lulzbot 4 3D printer. The electrical resistivity was measured using a Hioki Megaohmmeter at 500V with 30s of electric charge with a sample size 88 mm diameter 2.5 mm

thick. The neat PA11 FDM printed polymer had a volume resistivity of 3.46 x 10^{13} Ohm*cm and an ultimate tensile strength of 4.59 MPa. The PA11 / 3wt% NGP that was FDM printed had a volume resistivity of 3.26 x 10^{13} Ohm*cm and an ultimate tensile strength of 11.73 MPa. It was stated that the print quality was poor with interlaminar separation after printing. This study only looked at 3 wt% NGP which was not enough to reach the PT in the previously research using injection molding or compression molding. It was stated in the SAMPE conference proceeding that the electrical resistivity values of injection molded PA11 and 3wt% PA11/NGP nanocomposites were lower than 3D printed samples [13]. However if the data is reported correctly this statement is not true. The injection molded PA 11 / 3wt% NGP had a volume resistivity of 3.0 x 10^{14} Ohm*cm, the compression molded PA 11 / 3wt% NGP had a volume resistivity of 1.64 x 10^{14} Ohm*cm, and the FDM printed PA 11 / 3wt% NGP had a volume resistivity of 3.26 x 10^{13} Ohm*cm. The FDM printed sample has ten times lower volume resistivity [12].

In subsequent research the polymer was switched from PA11 to PA6 because of the availability. PA6 / GNP were FDM printed using a Lulzbot TAZ 6 3D printer at 3, 5, 7 wt% GNP. SEM showed that the GNP structure was uniformly dispersed in the PA6. The tensile strength decreases with addition of GNP, tensile modulus increases at 3% wt but decreased at 5 and 7 wt%, and the % elongation increase with loading of GNP. All 3D printed parts showed interlaminar separation after printing. The volume resistivity of the FDM printed neat PA6 was 10.68 x 10^{13} Ohm*cm, PA6 / 3 wt% GNP was 11.62 x 10^{14} Ohm*cm, PA6 / 5 wt% GNP was 12.28 x 10^{14} Ohm*cm, and PA6 / 7 wt% GNP was 5.62 x 10^{14} Ohm*cm. The poor print quality created interlaminar separation which caused air pockets that increased electrical resistivity. This study suggested using an IR light mounted ahead of the extruder for localized heating to fuse the layers together [14].

1.3 Applications

The GNP has shown to have promise to make an ESD protected polymer material in PA6 and PA11 at a PT of 5 to 7 wt%. However, the FDM printing process of this material has produced parts that would not be acceptable for ESD protection. It was reported that the parts had poor interlaminar adhesion. Research needs to be conducted to improve the FDM printing process with these materials. It has been suggested that using Infrared Heating Lamps on the printed part could raise the temperature to eliminate the delaminations. If electrical resistivity can be decreased more, then we can use the nanocomposite for EMI shielding. Since GNP is available at a broad range of platelet lengths, future research can be done to develop nanocomposites using GNP of various sizes.

2. Experimentation

2.1 Material System

The material systems used were polyamide 6 (PA6) in an extrusion grade homopolymer obtained from Advansix and nanographene platelets (NGP) M grade platelets obtained from XG sciences.

2.2 Manufacturing Methods

The NGP was dispersed in the PA6 using melt compounding in a Werner Pfliederer co-rotating twin screw extruder. The screw diameter is 30 mm with a length to diameter (L/D) ration of 1:27. This dispersion method is scalable, cost effective, fast, and would be a continuous mass production process. 1.75 mm filaments were extruded for 3D printing using the fused filament fabrication (FFF) method. Filaments were made with 3, 5, and 7 weight percent NGP using a volumetric feeder. The PA6 was dried in a desiccant drier before compounding. A Lulzbot Taz 6 was used to 3D print tensile samples that are shown in Figure 1.

Figure 1. Lulzbot TAZ 6 Printer and Printed Tensile Samples

2.3 Characterization Methods

The mechanical and electrical property characterization method of PA6/NGP was tensile (ASTM D638) and electrical resistance (ASTM D257). Samples were printed of the neat PA6 and 3, 5, and 7 wt% NGP. The tensile testing compared the tensile strength, tensile modulus, and percent elongation. Figure 2 shows the tensile testing setup and tested specimens. An extensometer was used to measure the strain in the tensile samples. Three specimens were testing for each material condition.

Figure 2. Tensile Testing Setup and Tested Specimens.

3. Results

3.1 Mechanical Properties

Tensile tests were performed on the neat, 3 wt.%, 5 wt.%, 7 wt.% NGP non-annealed samples, three samples were tested form each category. The annealing treatment at 80º and 140ºC does not lead to significant improvement in the tensile properties of the nanocomposites. However, it could be observed that annealing at 80ºC exhibits significant increase in the percentage elongation at loading levels 3 and 5 wt%. This is an indication of high ductility and could be attributed to the stress mitigation of highly heat affected areas, thereby distributing this out more evenly through the entire print, eliminating the possibility of fracture at specific region.

Annealing at 200ºC led to degeneration of the ultimate strength and elongation values and minor improvement in the modulus of elasticity. This could be as a result of the high temperature employed which is well above the glass transition of the parent PA 6 matrix. The glass transition of polyamide 6 ranges between 47- 50ºC and the 200ºC annealing temperature is approaching the melting temperature of the PA6 which ranges between 223-250 ºC. There could have been certain thermal degradation occurring which in turn degrade the interfacial strength between the PA6 and NGP.

Table 1 shows the summary of the tensile testing samples. The ultimate tensile strength and modulus of elasticity was found to decrease with the addition of NGP. The percent elongation increased with the addition of NGP. The electrical resistivity decreased for the 80°C annealed specimens but increased for the 140°C and 200°C specimens. Figure 3 shows the ultimate tensile strength comparison. The highest ultimate tensile strength was found at the neat sample (33.44 MPa). Figure 4 shows the comparison of the modulus of elasticity. The modulus of elasticity decreased with the addition of NGP. Figure 5 shows the percent elongation comparison. The percent elongation increased with the addition of NGP. .

Table 1. Tensile Testing Summary of Not Annealed and Annealed at 80°C, 140°C, and 200°C FFF 3D Printed PA6/NGP.

	Ultimate Strength (MPa)	Modulus of Elasticity (GPa)	Elongation (%)
Neat	33.44	1.90	1.77%
3 wt%	32.53	1.78	3.30%
5 wt%	27.09	1.38	3.47%
7 wt%	27.52	1.44	3.11%
Neat 80°C	39.60	1.72	4.22%
3 wt% 80°C	31.07	1.68	6.01%
5 wt% 80°C	20.92	1.13	11.34%
7 wt% 80°C	33.39	1.70	3.34%
3 wt% 140°C	33.31	1.55	2.62%
5 wt% 140°C	30.74	1.27	3.64%
7 wt% 140°C	19.73	0.89	2.13%
3 wt% 200°C	8.16	1.67	0.49%
5 wt% 200°C	13.54	2.07	0.61%
7 wt% 200°C	14.29	2.13	0.61%

Table 2 shows the summary of the electrical resistivity testing. Electrostatic Discharge (ESD) percolation threshold for ESD applications is a volume electrical resistivity of 10^{10} to 10^{11} Ohms*cm. The percolation threshold is the minimum quantity of the nanoparticles required to form a conductive path within the PA 6 matrix. The annealing of the specimens at 80°C decreased the electrical resistance but did not achieve the percolation threshold for ESD applications. Annealing the samples at 80ºC qualified the specimens for ESD applications.

Table 2. Electrical Resistivity Testing Summary of Not Annealed and Annealed at 80°C, 140°C, and 200°C FFF 3D Printed PA6/NGP.

Loading Levels	Not Annealed (Ω*cm)	80°C (Ω*cm)	140°C (Ω*cm)	200°C (Ω*cm)
3 wt.%	1.17E+12	6.48E+11	5.93E+13	7.33E+13
5 wt.%	1.36E+12	4.83E+11	1.07E+13	7.54E+13
7 wt.%	3.24E+12	5.58E+11	9.91E+13	1.87E+14

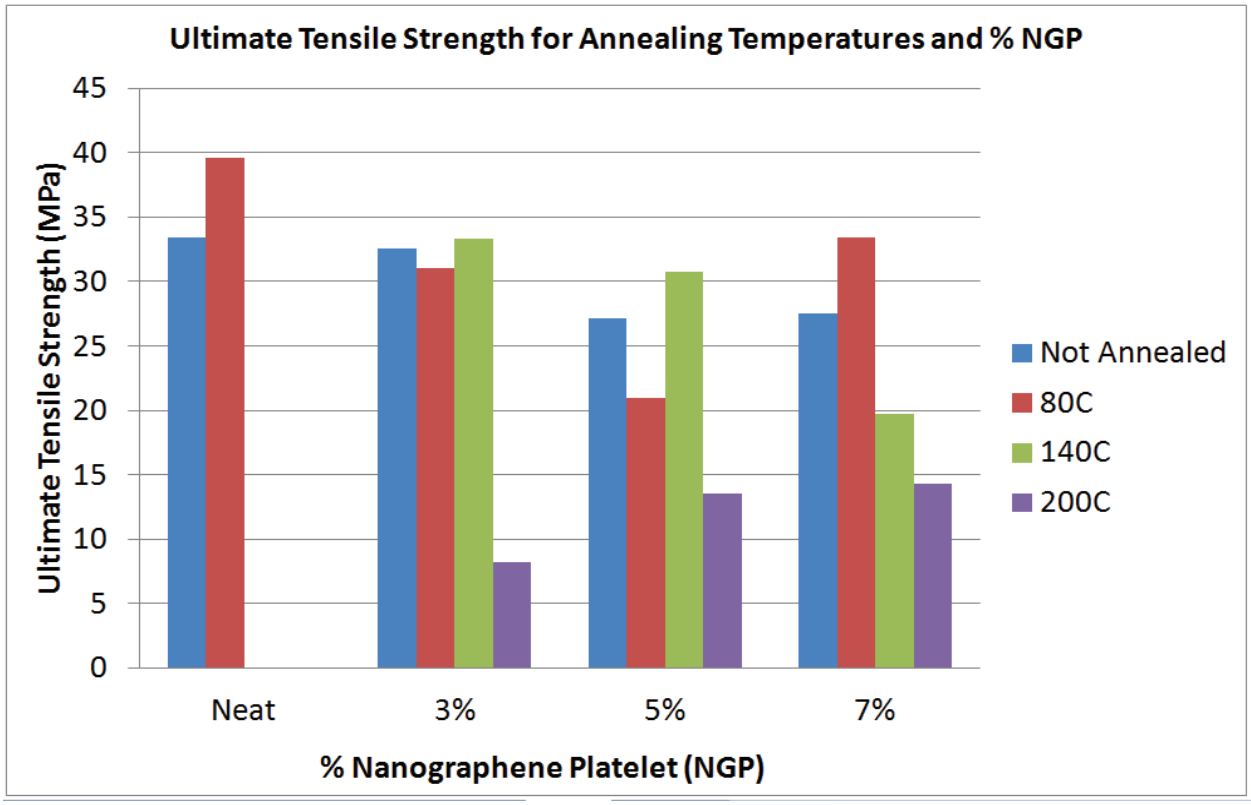

Figure 3. Ultimate Tensile Strength for Annealing Temperatures and Wt.% NGP.

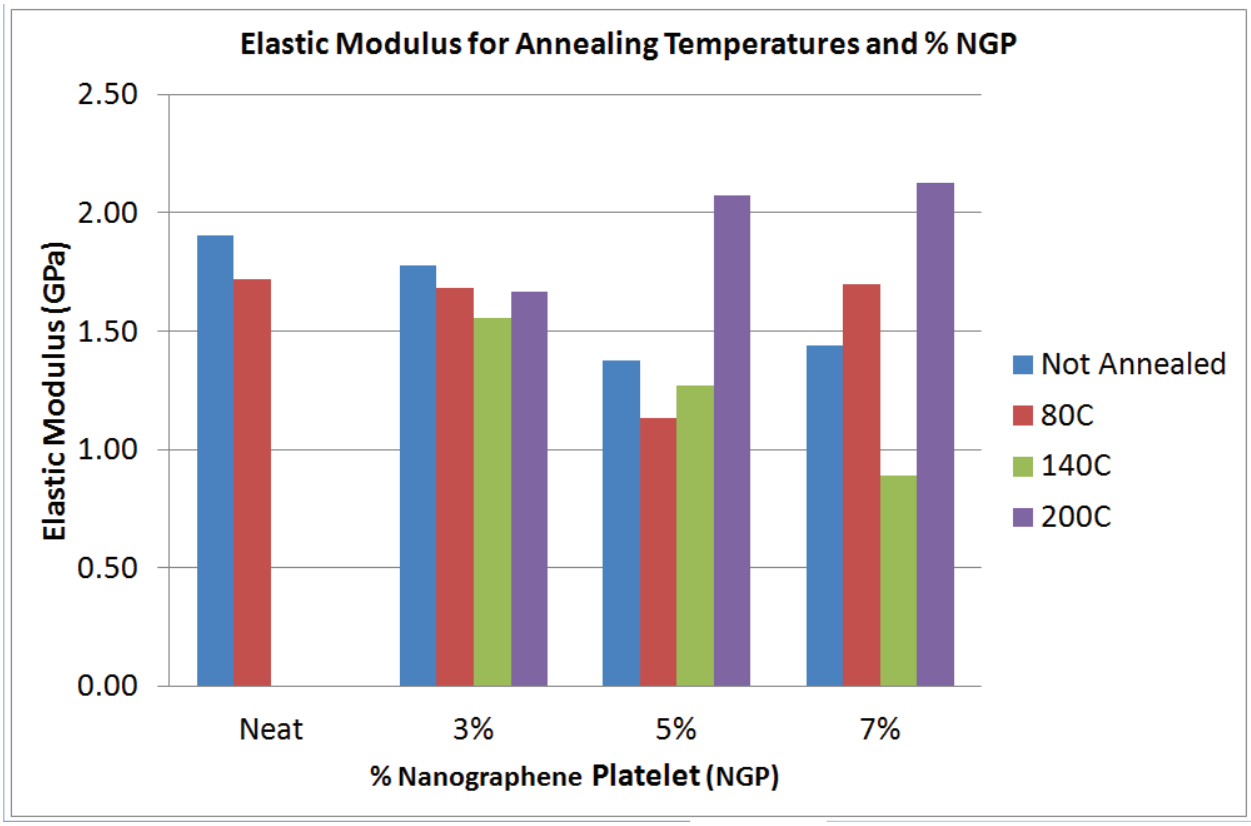

Figure 4. Elastic Modulus for Annealing Temperatures and Wt.% NGP.

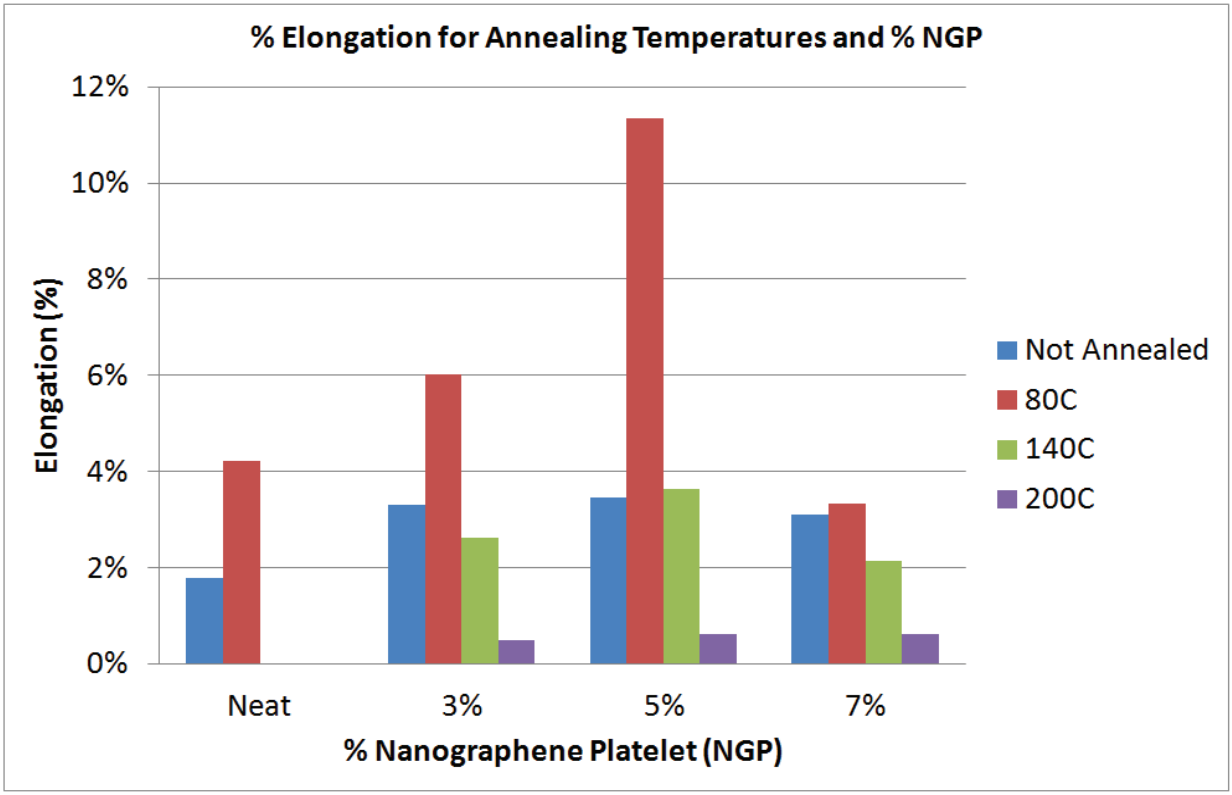

Figure 5. % Elongation for Annealing Temperatures and Wt.% NGP.

The dispersion of the NGP in the PA6 and the morphologies of the not annealed and annealed at 80°C samples of the filaments were evaluated using scanning electron microscopy (SEM). The samples were sputter coated with three nanometers of gold. The filament samples were cut at a 45 degree angle before coating. The SEM images are taken on the cut surface. The representative micrographs are shown in Figures 6 to 11. All samples showed a good dispersion of the NGP in the PA6. The NGP are believed to be the rough looking areas and the smoother areas are the PA6. There was not a visible difference in the morphology between the annealed and not annealed samples.

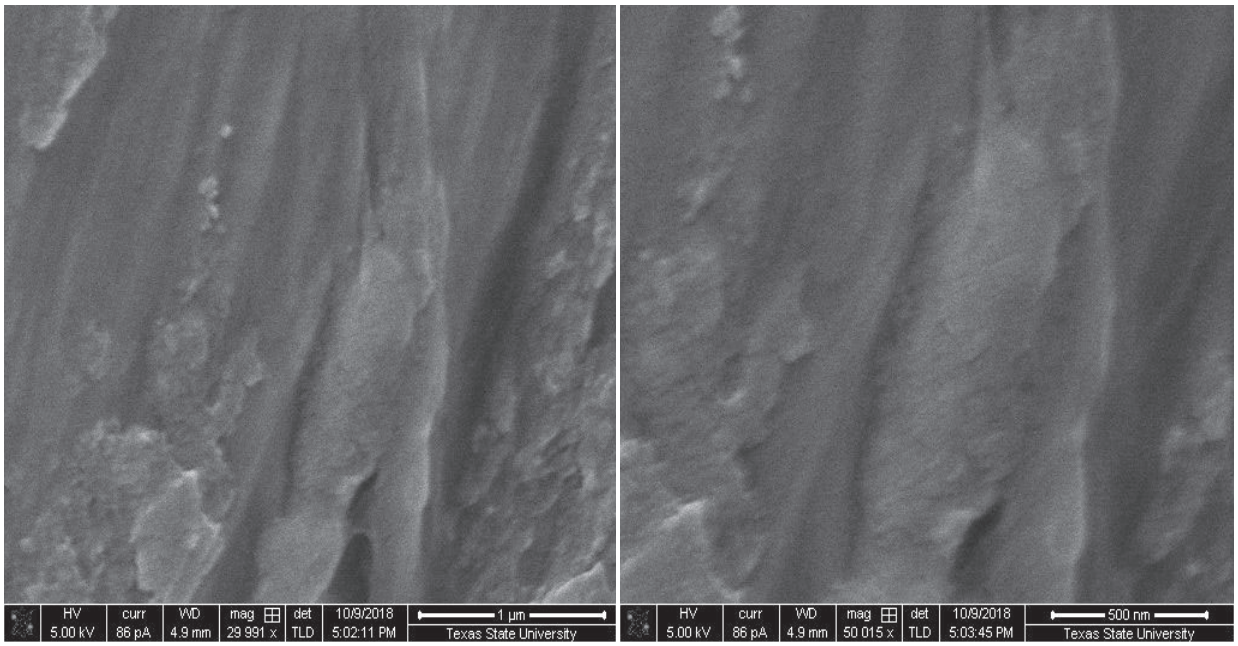

Figure 6. SEM – 3% Annealed at 80°C

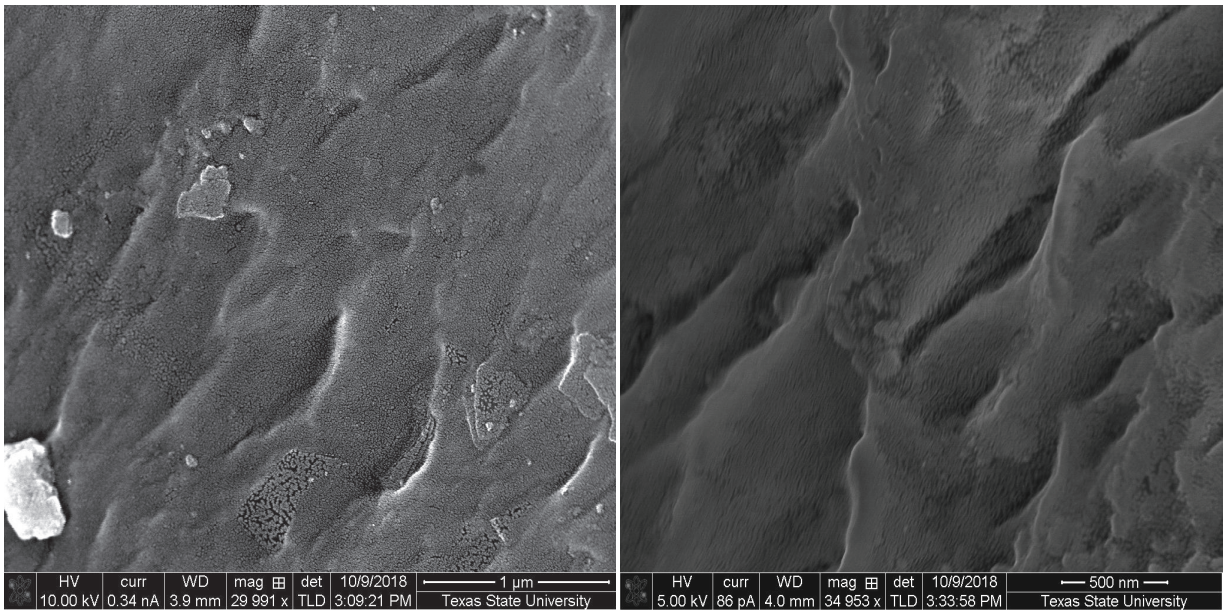

Figure 7. SEM – 3% Not Annealed

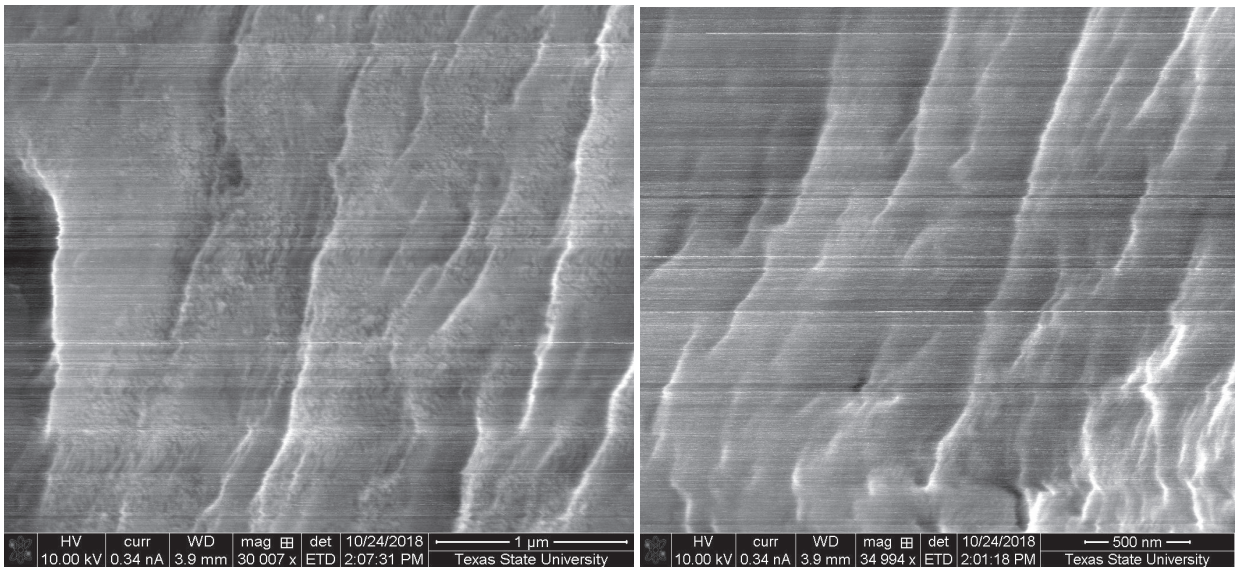

Figure 8. SEM – 5% Annealed at 80°C

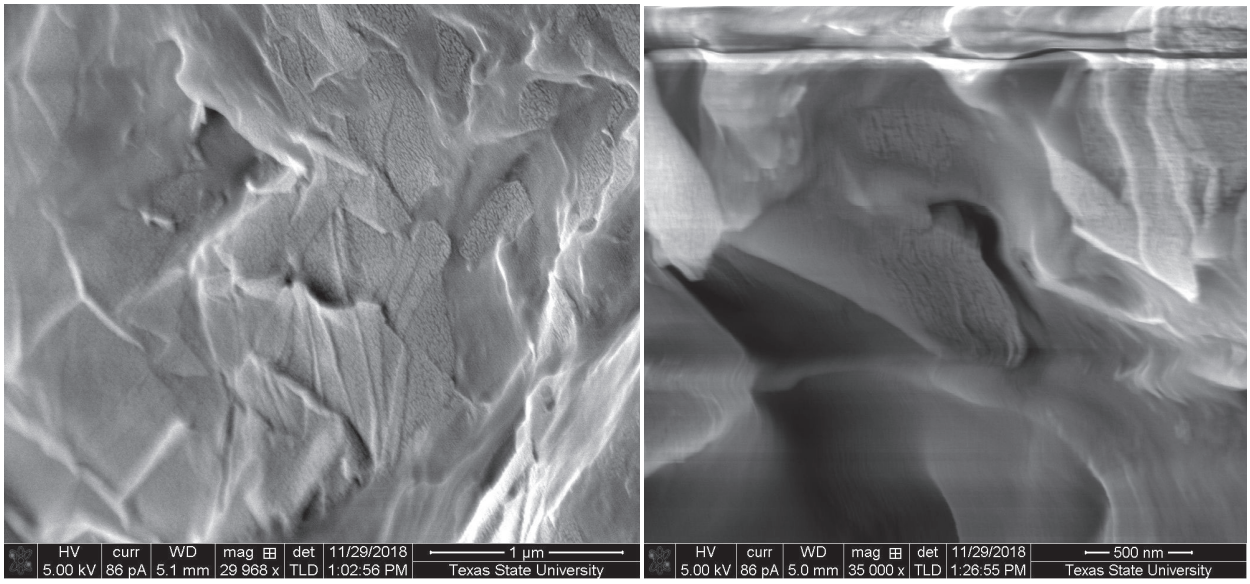

Figure 9. SEM – 5% Not Annealed

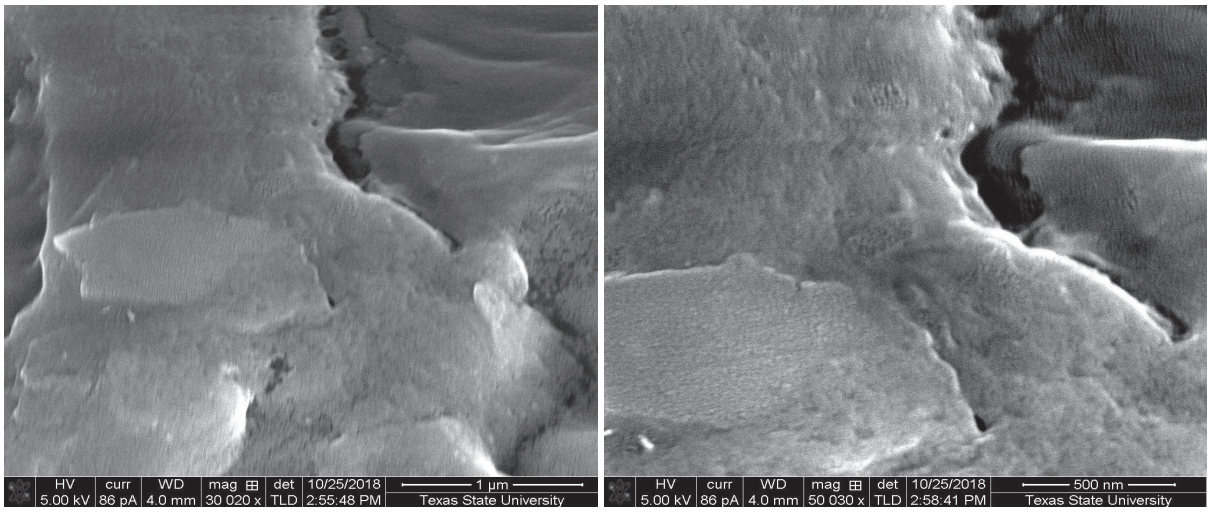

Figure 10. SEM – 7% Annealed at 80°C

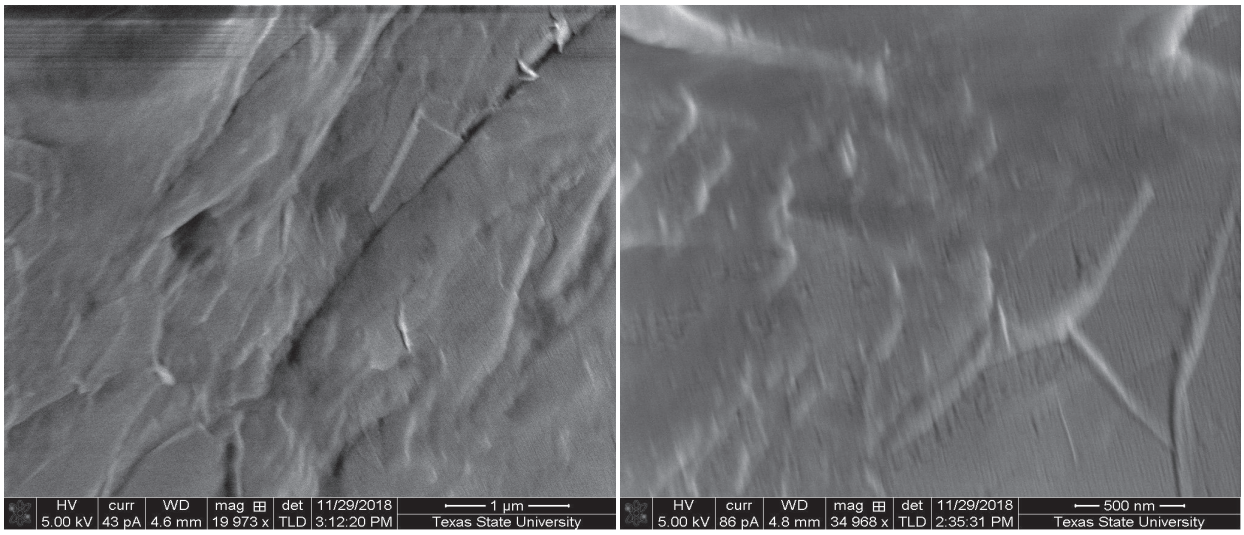

Figure 11. SEM – 7% Not Annealed

4. Conclusions

Tensile test specimens were 3D printed using the FFF method for the neat PA6, and with 3 wt%, 5wt%, and 7 wt% NGP and annealed at 80°C, 140°C, and 200°C. In conclusion the tensile strength and modulus of elasticity decreased with the addition of NGP in PA6 3D printed using the FFF method except for the 200° annealed specimens. The percent elongation decreased with the addition of NGP except for the 80°C Annealed increased up to 5% NGP. Addition of NGP in PA6 for FFF printing will increase the % elongation at the expense of decreased tensile strength and modulus. Electrical resistivity decreased for the 80°C annealed specimens to reach ESD percolation threshold. Electrical resistivity increased for the 140°C and 200°C annealed specimens. SEM was used to verify the dispersion and morphology of filament samples that were annealed at 80°C and not annealed. The filaments showed good dispersion on all samples by using twin screw extrusion. It is unknown if annealing changed morphology as it was not a change observed in the SEM images. Some specimens were not flat. Heating profiles could be investigated to decrease warpage.

5. References

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