Organic-Inorganic Graphite and Transition Metal Dichalcogenide Based Composites for 3D Printing

Jorge Alfredo Catalan Gonzalez
University of Texas at El Paso, jacatalan@miners.utep.edu

Follow this and additional works at: https://digitalcommons.utep.edu/open_etd

Part of the Electrical and Electronics Commons, Materials Science and Engineering Commons, Mechanical Engineering Commons, and the Mechanics of Materials Commons

Recommended Citation
https://digitalcommons.utep.edu/open_etd/423

This is brought to you for free and open access by DigitalCommons@UTEP. It has been accepted for inclusion in Open Access Theses & Dissertations by an authorized administrator of DigitalCommons@UTEP. For more information, please contact lweber@utep.edu.
ORGANIC-INORGANIC GRAPHITE AND TRANSITION METAL DICHALCOGENIDES BASED COMPOSITES FOR 3D PRINTING

JORGE ALFREDO CATALAN GONZALEZ

MASTER’S PROGRAM IN METALLURGICAL AND MATERIALS ENGINEERING

APPROVED:

________________________________________
Anupama B. Kaul, Ph.D., Chair

________________________________________
Stephen Stafford, Ph.D.

________________________________________
Shailendra K. Varma, Ph.D.

________________________________________
Charles Ambler, Ph.D.
Dean of the Graduate School
Copyright ©

by

Jorge Alfredo Catalan Gonzalez

2017
Dedication

I would like to dedicate this work to my mother, father, brother, cousins, and friends. Also, I would like to make a special mention and dedication to my uncle Fernando González, who passed the way 9 years ago. While he was alive, he was to me: a father, a friend and a teacher… simply the best human being I have met.
Acknowledgements

I wish to specially thank my professor and advisor Dr. Anupama B. Kaul, for being an excellent and patient mentor. Without her excellent mentoring skills and sponsoring a Research Assistant position for me, I would not be able to grow as a graduate student. I will never forget that she helped me to give my first oral presentation at the American Vacuum Society (AVS) international conference held in Nashville, Tennessee in November 2016. This was one of the most fulfilling experiences that I have had in my career. Also, under her guidance I was able to learn a great deal about two-dimensional (2D) materials, a topic that is of much scientific interest. I do not have words to describe how grateful I feel for having this opportunity to work in Dr. Kaul’s research group.

Moreover, I wish to thank Dr. Stephen Stafford and Dr. Shailendra Varma for accepting to be on my thesis committee. It is a great honor for me to have two of the best Professors in the Metallurgy, Materials and Biomedical Engineering department as graduate mentors. Also, I would like to thank Professor Witold Brostow and his students, Nathalie Hnatchuk and I Kang Chen from the University of North Texas who helped with some of the mechanical properties measurements that are discussed in this thesis. They graciously agreed to help with obtaining some of the mechanical property data on our 3D printed composites from UTEP.

Special thanks also goes to Damaris Cortés and Perla Pérez, summer students from the Army Research Apprentice Program provided to the Kaul Group in Summer 2017, for their help during the extrusion and 3D printing process. They helped a great deal throughout the summer which helped accelerate the work. This was a personally enriching experience for me, since it was my first time working as a mentor for two junior students. Also, thanks to Gustavo Saenz, Avra Bandyopadhyay, Ph.D. students in Prof. Kaul’s group, for their guidance and useful discussions that has helped improve the quality of this work. Last but not least, I would like to thank Adriana Ramirez, for her help in the set up of the 3D printing instrumentation, as well as the useful tips she provided during the extrusion and 3D printing process.
Abstract

This project was multipronged to help fuse together topics of additive manufacturing and two-dimensional (2D) layered materials, and studying the mechanical and electrical properties of the composites produced. The composites are made from the thermoplastic polymer acting as a matrix and the graphite and 2D transition metal dichalcogenides (TMDs) serving as the filler or reinforcement. Different concentrations of TMD’s were added to the matrix to study the effect of composition on the mechanical and electrical properties. To shed insights into the mechanical properties, test coupons were produced as “dog bone” structures for tensile testing using the ASTM D638 type 5 standard, which were printed with the aid of a Lulzbot TAZ 6 3D printer. In the same way, two-terminal resistor-like structures were printed to test the electrical properties inherent to the composites.

From the measurements conducted, polyethylene terephthalate glycol (PETG) – graphite composites had a yield strength (YS) ≈ 50 MPa, an ultimate tensile strength (UTS) ≈30 MPa and had a better ductility (strain to rupture ≈ 8%) compared to the acrylonitrile butadiene styrene (ABS) composite counterparts. Also, molybdenum disulfide (MoS$_2$) had a more positive effect than tungsten disulfide (WS$_2$), since the strength was retained while the ductility was increased at low loadings of the material. Strain levels were measured to be 30% - 120% when adding 1 wt% of MoS$_2$ and WS$_2$. On the other hand, with high additions of MoS$_2$ and WS$_2$ (15 and 20 wt%) ductility was completely lost since no plastic deformation occurred during the testing. Moreover, PETG – graphite resistor-like structures were 3-dimensional (3D) printed and tested with the help of a semiconductor parameter analyzer. All samples were tested at different radius of curvatures (0 cm$^{-1}$, 0.072 cm$^{-1}$, 0.087 cm$^{-1}$, 0.112 cm$^{-1}$, 0.157 cm$^{-1}$, and 0.262 cm$^{-1}$) which showed a composite that was strain insensitive. The obtained average conductivity and resistivity were ≈ 5.27 Siemens-m$^{-1}$ and 0.250 Ohm-m, respectively. In the process of forming the composites, some pretreatment of the 2D material may also be necessary. We studied one aspect of this pretreatment by looking at particle size measured using dynamic light scattering. The fragmentation rate ($FR$) of 2D MoS$_2$,
WS₂, and graphite in N-methyl-pyrrolidinone (NMP) was computed in chemical exfoliants, where $FR$ is a measure of the particle size reduction as a function of ultrasonication time. For the 2D layered materials, the highest $FR$ generally occurred for sonication times $t_{\text{sonic}} = 30$ min., after which point $FR$ varied less sensitively with $t_{\text{sonic}}$. The highest $FR$ occurred for graphite, where $FR_{\text{Graphite}}$ was $\sim -1176.4 \mu\text{m-hr}^{-1}$, while $FR_{\text{WS₂}}$ and $FR_{\text{MoS₂}}$ was measured to be $\sim -32.4 \mu\text{m-hr}^{-1}$ and $\sim -3.8 \mu\text{m-hr}^{-1}$, respectively. This pretreatment maybe an important step to further tune the properties of the hybrid organic-inorganic composites of 2D materials with polymeric systems for a number of application platforms.
Table of Contents

Acknowledgements .............................................................................................................. v

Abstract ................................................................................................................................. vi

Table of Contents .................................................................................................................. viii

List of Tables .......................................................................................................................... x

List of Figures ........................................................................................................................ xi

Chapter 1: Background Information ...................................................................................... 1

1.1 - Graphene .......................................................................................................................... 2

1.2 – Transition Metal Dichalcogenides (TMD’s) ................................................................. 4

1.3 – Additive Manufacturing (AM) ........................................................................................ 4

  1.3.1 Stereolithography (SLA) ............................................................................................... 5

  1.3.2 Laminated Object Manufacturing (LOM) ................................................................. 6

  1.3.3 Selective Laser Sintering (SLS) ..................................................................................... 7

  1.3.4 Fuse Deposition Modeling (FDM) ................................................................................. 8

1.4 – Composite Materials ..................................................................................................... 10

Chapter 2: Sample Preparation ............................................................................................... 12

2.1 – Material selection ........................................................................................................... 12

  2.1.1 Polyethylene terephthalate glycol (PETG) .................................................................. 12

  2.1.2 Acrylonitrile butadiene styrene (ABS) ....................................................................... 12

  2.1.3 Reinforcements ............................................................................................................ 13

2.2 – Filament Extrusion ......................................................................................................... 13

2.3 - Printing ............................................................................................................................ 19

  2.3.1 Tensile test sample printing ......................................................................................... 19

  2.3.2 Resistor design for electrical characterization ......................................................... 23

Chapter 3: Mechanical Properties .......................................................................................... 25

3.1 – Results ............................................................................................................................ 26

3.2 – Discussion ....................................................................................................................... 45

Chapter 4: Electrical Properties ............................................................................................. 48

4.1 – Results ............................................................................................................................ 48

  4.1.1 Step Annealing versus Continuous Annealing ..................................................... 49
4.1.2 Substrate vs No Substrate Analysis .................................................................55
4.1.3 I-V Measurements 1st Resistor Design ..........................................................59
4.1.4 Application in Wearable Electronics ...............................................................62
4.2 – Discussion .........................................................................................................65

Chapter 5: Particle Size Analysis ..............................................................................68
  5.1 – Molybdenum Disulfide (MoS$_2$) .................................................................68
  5.2 – Tungsten Disulfide (WS$_2$) .........................................................................71
  5.3 – Graphite ........................................................................................................73
  5.4 – Discussion .....................................................................................................75

Chapter 6: Conclusions and Future Work .................................................................76

References ................................................................................................................78

Appendix: Procedure for 3D Printing .......................................................................83

Vita 85
List of Tables

Table 1: Lulzbot TAZ 6 Printing Parameters. ................................................................. 22
List of Figures

**Figure 1.1** Two different stereolithography schematics. a) Bath stereolithography consists of a laser curing a layer of liquid resin. After on layer is cured, the stage lowers itself allowing for more liquid resin to cover the cured polymer. After that, laser cures the new layer of resin as specified by the design. b) This approach works in reverse process compared to the bath SLA. Here the sage is submerged inside the resin. Then, the stage is pulled up to allow more resin to flow below the cured polymer. A patter can be added so that the laser can cured the whole layer design at the same time. Obtained from Ref[37]................................................................. 5

**Figure 1.2** Schematic of Laminated Object Manufacturing (LOM) process. Obtained from Ref [36].................................................................................................................................................. 6

**Figure 1.3** Schematic of selective laser sintering (SLS) process. Obtained from Ref [36]. ....... 8

**Figure 1.4** Schematic of fused deposition modeling (FDM) process. Obtained from Ref[36].... 9

**Figure 2.1** Side view of Filabot EX2 extruding system................................................................. 14

**Figure 2.2** Filabot spooling system. It is placed in front of the extruder to create spools of the extrude filament. Also, it helps to regulate the filament size............................................................... 15

**Figure 2.3** Silverson L5M-A Laboratory Shear ................................................................. 15

**Figure 2.4** Schematic of the hand mixing process to produce uniform mixtures of solid compounds. This process is similar to the one made by a cement truck mixer ...................... 17

**Figure 2.5** Filament coming out of the Filabot extruder. The 90° angle created by the filament allows the user to know that the extrusion and spooling speed are synchronized. Having this synchronization is crucial in obtaining a certain filament diameter. If the filament is extruding faster than what the spooling can handle, then the filament will be thick (big diameter) and most likely it will knot itself up. On the other hand, if the extrusion speed is to slow and spooling
speed is faster, the filament diameter will be to thin due to the excessive pulling force produced by the spooler. ................................................................. 18

**Figure 2.6** (a) Frontal view of tensile specimen ASTM D638 type 5. (b) Isometric view of the “dog bone” sample. ................................................................. 20

**Figure 2.7** Two different resistors like structures. Left structure (with complicated geometry) has higher resistance due to the overall longer channel length. Right structure is simple but allows faster designs and is easier to handle during electrical characterization. ....................... 24

**Figure 2.8** Small, medium, and large resistor like structures for electrical characterization. ...... 24

**Figure 3.1** (a) & (b) Stress vs strain plots of ABS and ABS – 1wt% graphite. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ......................... 27

**Figure 3.2** (a) & (b) Stress vs strain plots of ABS – 5wt% and ABS – 10wt% graphite. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ......................................................................................... 28

**Figure 3.3** (a) & (b) Stress vs strain plots of ABS – 15wt% and ABS – 20wt% graphite, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ......................................................................................... 29

**Figure 3.4** (a) & (b) Stress vs strain plots of PETG and PETG – 1wt% graphite. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ... 31

**Figure 3.5** (a) & (b) Stress vs strain plots of PETG – 5wt% and PETG – 10wt% graphite, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ......................................................................................... 32
Figure 3.6 (a) & (b) Stress vs strain plots of PETG – 15wt% and PETG – 20wt% graphite, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ................................................................. 33

Figure 3.7 (a) & (b) Stress vs strain plots of PETG and PETG – 1wt% MoS$_2$. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ............ 35

Figure 3.8 (a) & (b) Stress vs strain plots of PETG – 5wt% and PETG – 10wt% MoS$_2$, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ................................................................. 36

Figure 3.9 (a) & (b) Stress vs strain plots of PETG – 15wt% and PETG – 20wt% MoS$_2$, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ................................................................. 37

Figure 3.10 (a) & (b) Stress vs strain plots of PETG and PETG – 1wt% WS$_2$. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ............ 39

Figure 3.11 (a) & (b) Stress vs strain plots of PETG – 5wt% and PETG – 10wt% WS$_2$, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ................................................................. 40

Figure 3.12 (a) & (b) Stress vs strain plots of PETG – 15wt% and PETG – 20wt% WS$_2$, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample. ................................................................. 41

Figure 3.13 Comparison between ABS (a) and PETG (b) stress vs strain curves with graphite. (a) ABS series show a series of lines corresponding to control, 1 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt%. (b) PETG – graphite series lines correspond to the same loadings as in (a)......... 42
Figure 3.14 (a) Young’s modulus of each ABS polymer composite with different graphite loadings. (b) Strain at failure for each ABS – graphite composite. ................................. 43

Figure 3.15 (a) Young’s modulus (YM) of each PETG polymer composite with different graphite loadings. (b) Strain at failure for each PETG – graphite composite. ................................. 43

Figure 3.16 Comparison between PETG MoS$\textsubscript{2}$ (a) and WS$\textsubscript{2}$ (b) stress vs strain curves. (a) MoS$\textsubscript{2}$ series show a series of lines corresponding to control, 1 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt%. (b) WS$\textsubscript{2}$ series lines correspond to the same loadings as in (a). .............................................. 44

Figure 3.17 (a) Young’s modulus (YM) of each PETG polymer composite with different MoS$\textsubscript{2}$ loadings. (b) Strain at failure for each PETG – MoS$\textsubscript{2}$ composite. ................................. 44

Figure 3.18 (a) Young’s modulus (YM) of each PETG polymer composite with different WS$\textsubscript{2}$ loadings. (b) Strain at failure for each PETG – WS$\textsubscript{2}$ composite. ................................. 45

Figure 3.19 (a) SEM picture of as received graphite powder. Average particle size of about 600 $\mu$m. (b) Graphite powder after 4 hours of shear mixing at 6000 rpm. Particle size decreased to average size of around 5 $\mu$m. ......................................................... 47

Figure 3.20 Particle size comparison. (a) As received graphite powder particles. (b) As received MoS$\textsubscript{2}$ powder particle size. (c) WS$\textsubscript{2}$ as received particles. Graphite particle size was the biggest of all three 2D materials. Further treatment to reduce the particle size was needed to prevent 3D printer’s nozzle clogging and at the same time improved matrix – filler uniformity. .................. 47

Figure 4.1 Micromanipulator and semiconductor parameter analyzer (HP 4156A) set up used to measure electrical properties of the conductive printed structures. ........................................... 49

Figure 4.2 Step Annealing of the 3 sets of samples formed by small, medium and large. (a) – (c) Shows data regarding current levels at 20V every 1 hour. Blue, red, and green represent the color small, medium, and large samples, respectively. ......................................................... 51
Figure 4.3 (a) – (c) I-V curves of not annealed small, medium, and large resistor like structures.
....................................................................................................................... 52

Figure 4.4 (a) – (b) Correspond to the I-V curves of small, medium, and large annealed for 4 hours at 80 °C resistor samples, respectively................................................................. 53

Figure 4.5 (a) –(b) Show the Current vs Radius of curvature plots. The three plots contain blue lines (not annealed samples data) and red lines (annealed samples data). From top to bottom (a) correspond to small size structures, (b) to medium size, and (c) to large size......................... 54

Figure 4.6 All five bending structures, with their corresponding radius of curvature values, designed to test the flexibility and sensitivity of printed structures.............................................. 55

Figure 4.7 Two set of three 50 wt% graphite – PETG samples. The first set on the left is composed of three samples (small, medium and large). These three samples were not printed on any surface. On the other hand, the set on the right was printed on top of PET substrate. ........ 56

Figure 4.8 (a) – (c) Correspond to small, medium, and large specimens that were not printed on any type of surface. All samples were tested electrically tested using 5 different bending structures (shown in Figure 4.6). No sensitivity to the bending is detected like in a, however there are some graphs ( (b) & (c) ) showing son discrepancies. These discrepancies are due to contact issues between the probes and the surface of the samples. ............................................ 57

Figure 4.9 (a) – (c) I-V curves of samples (small, medium, and large) printed on PET substrate. All samples were tested electrically tested using 5 different bending structures (shown in Figure 4.6). ..................................................................................................................................................... 58

Figure 4.10 This graph represents the current values at 20 V of small, medium, and large samples from both sets (with no substrate and with PET substrate). Dotted/dashed lines represent data taken from samples printed on top of the PET substrate, while continuous lines are
used to represent data from no substrate samples. The minimum current value was around 5 mA, while the highest was about 23 mA. ................................................................. 59

**Figure 4.11** (a) – (e) I-V graphs with corresponding picture. Each picture is marked with a red line. Extreme ends of red line on each picture represent the place where probes were placed in order to take electrical data. The channel length increases from top to bottom (red line is longer). As channel length increases, current level decreases................................................................. 61

**Figure 4.12** Current values at 20 V for different channel lengths. All lines are almost a straight line, meaning no sensitivity to the radius of curvature. ................................................................. 62

**Figure 4.13** Data gather from a medium size resistor structure mounted on an index finger. (a) – (d) Shows the different finger positions during these measurements. (e) I-V graph of all 4 different finger positions. All lines overlap because resistor like structure is not sensitive to the different movements showed in the pictures. ................................................................. 64

**Figure 5.1** (a) Particle size distribution measured using the MicroTac for $t_{\text{sonic}}$ = 0 min. (control), 30 min., 6 hr, 12 hr and 18 hr.; inset shows the peaks in the MoS$_2$ distribution at lower length scales. (b) Mean particle size $S$ as a function of $t_{\text{sonic}}$ showing the 1$^{\text{st}}$, 2$^{\text{nd}}$ and 3$^{\text{rd}}$ modes in the distribution function. (c) SEM micrographs showing a higher population of smaller particles in the background for samples where $t_{\text{sonic}}$ = 18 hr (iii) compared to the control (i). (d) Raman Spectra .............................................................................................................................. 70

**Figure 5.2** Characterization of treated WS$_2$ in (a) - (d). (a) Particle size distribution showing $S_{\text{WS2}} \approx 18.5 \, \mu\text{m}$ for as received material and the inset shows the WS$_2$ particles over smaller length scales. (b) $S$ as a function of $t_{\text{sonic}}$ showing the 2$^{\text{nd}}$ mode occurring at $t_{\text{sonic}} = 12$ hr. (c) WS$_2$ SEM micrographs showing a higher population of smaller particles in the background for the longer $t_{\text{sonic}} = 18$ hr in (iii) compared to the control (i). (d) Raman Spectra. ................................................................. 72
Figure 5.3 (a) Particle size distribution measured using the MicroTac for graphite; inset shows the peaks in the graphene distribution at lower length scales. (b) S as a function of $t_{\text{sonic}}$ showing the 1$^{\text{st}}$ and 2$^{\text{nd}}$ modes in the distribution. (c) SEM micrographs showing a higher population of smaller particles in the background for the longer $t_{\text{sonic}} = 18$ hr in (iii) compared to the control in (i). (d) Raman spectra.
Chapter 1: Background Information

Two-dimensional layered materials have gained increased popularity since the discovery of graphene in 2004 by Geim and Novoselov. Before 2004, through thermodynamic considerations it was believed that single atom layers of any material would not stable, but this notion was later denounced after these two renowned scientists isolated a single layer of carbon atoms, called graphene on a Silicon substrate. In order to achieve this, they implemented what it is known as the “scotch tape” technique. In this method, a flake of graphite was placed on scotch tape, and then multiple layers were peeled off from the graphite flake, until one single layer of carbon atoms remained glued to the scotch tape. Once transferred onto an oxidized silicon substrate, this layer of material showed remarkable electrical, thermal, mechanical, and optical properties, opening a new door that promised to revolutionize the technology in our electronic devices, to potentially replace silicon. While graphene has played a pivotal role in the 2D layered materials field, it however does not possess an inherent bandgap. Due to the lack of a band gap, scientists worked on trying to induce a band gap in graphene; alternatively, they also considered looking at different materials that showed a similar structure to graphene. The materials that simulated this honeycomb-like structure of graphene happened to be the transition metal dichalcogenides, materials that have been used since the 1960’s as dry lubricants.

In the same way, additive manufacturing increased its popularity after 2009, when patents regarding this technology expired. Due to these two recent episodes, researchers started to develop new materials that could retain some of the 2D materials' properties and to be processed and manufactured using one of the existing additive manufacturing technologies. Polymer composite materials were the selection of choice, since thermoplastic could act as the matrix of the composite, since their relative low melting and low glass transition temperatures make them suitable to be 3D printed using a method known as, fused deposition modeling (FDM). Also, these polymer matrices were already used along with carbon fibers. So, the exchange of carbon fibers with graphite, graphene, and or any other TMD particles, seemed a plausible option to act as the reinforcement
agent in these polymer based composites. In order to have a better understanding of these topics, I will provide background on: graphene, TMDs, additive manufacturing techniques, and composite materials.

1.1 - Graphene

As mentioned above graphene is considered an allotrope of carbon that was first discovered at Manchester University by Geim and Novoselov in 2004. Graphene is said to be the building block for other carbon allotropes since it is a single layer of sp\(^2\) hybridized carbon atoms. If this layer is taken and then rolled as tubes we will end up with was is known as a single-walled carbon nanotube. In the same way, if it is wrapped around like a sphere we will end up with fullerenes (bucky balls). Lastly, if the single layers are re-stacked again, graphite will be the final outcome.

Before this, it was believed that under ambient conditions, single layer materials were not stable enough to remain as a solid. Impressively, graphene showed to the world that a single sheet of carbon atoms could exist without the need of a substrate. Usually, substrates provide enough stability for single layer materials to exist. This led to fascinating studies of graphene, exposing impressive thermal, optical, electrical and mechanical properties for various applications such as: strain sensors, health monitoring sensors, transparent screens, flexible electronics, gas filtering systems, and photovoltaics, among others.\(^{[5-12]}\) Unfortunately, graphene carries its own problems that keep the research community scratching the back of their heads trying to find possible solutions. First, commercial production of graphene is still not possible since most techniques that allow a high yield, high quality and large area are very expensive to be economically efficient for companies. The most important problem with graphene is its lack of a band gap because it limits the possible applications of the material. This is a serious problem specially in electronic devices since it was believed that graphene was going to replace silicon, originating a new era of faster and smaller electronic devices, but because it does not have a band gap this is still not possible.
There are different approaches that scientists have come out with in order to produce high quality, and high yields of graphene. These approaches can be separated into two main topics: top-down approach and bottom-up approach. Top-down approaches, as the names implies, generally consist of starting up with a bulk material (in this case graphite), and then start reducing the number of layers until a single layer is achieved. This top-down approach can be divided into two common sub-categories: mechanical exfoliation[^13-16] and chemical exfoliation.[^17-20] Mechanical exfoliation uses external agents such as scotch tape or solvents to peel off or break off the stacks of bulk material. In fact, “scotch tape” method was the one used in the discovery of graphene. Solvent-based exfoliation techniques[^21-25] are gaining more popularity since they have a high yield of graphene flakes at the expense of size. In this technique, a solvent such as N-methyl-2-pyrrolidone (NMP) is used and with the help of a bath sonicator, horn tip sonicator, and/or shear mixer, energy is transferred so that tactoids of the materials are broken up in to smaller thinner stacks until single layers are completely separated from each other. On the other hand, chemical exfoliation utilizes the help of ions, especially lithium (Li) ions since they are small enough to fill the space between layers of graphene, and with the help of an electric field single layers of carbon are produced.

The other approach is the “bottom-up” approach,[^26-30] and as as the name implies, here we start by forming a single layer of material and keep depositing subsequent layers until the desired thickness is reached. Bottom-up approaches can be divided into epitaxial growth, physical vapor deposition, and chemical vapor deposition. Epitaxial growth consists on the growth of a single layer of carbon on top of a single crystal of silicon carbide. Physical vapor deposition technique consists of the material in use goes to a vapor state and then it is condensed back, until a layer is deposited on top of a substrate. Lastly, in chemical vapor deposition precursor materials are needed, then they are placed inside a heated vacuum chamber, allowing the reaction of this precursor to be deposited on a substrate placed inside the same chamber. Usually, these methods produce high quality single layers, but they are very expensive.
1.2 – Transition Metal Dichalcogenides (TMD’s)

In order to solve problems related to graphene, some researchers try to look for materials that have a similar structure to carbon allotrope. The materials of choice are called transition metal dichalcogenides, which were used in industry as dry lubricants. TMD’s are compounds formed by a transition metal from IV B, V B, or VI B families, and a chalcogen (sulfur, selenium, tellurium). This type of compounds has a honeycomb like structure, where the transition metal (molybdenum, tungsten, niobium, etc) is sandwich in between layers of the chalcogen. Metals are covalently bonded to the chalcogen, while Van der Waal forces weakly bond the layers. Due to these weak interlayer bonding, TMDs can be exfoliated into single layers. One interesting feature of TMDs, is that as the number of layers is decrease their band gap changes from indirect to direct type (for most of them). This characteristic makes them suitable to build transistors, emitters and detectors.[31-34] In fact, some of the most common TMDs are: molybdenum disulfide (MoS$_2$), tungsten diselenide (WSe$_2$), and tungsten disulfide (WS$_2$).

1.3 – Additive Manufacturing (AM)

Additive Manufacturing[18-20, 35-37] can be defined as the process of joining layers of materials until the desired shape and size of a product is achieved. AM is a term, that although interchangeable, exists since the 1980’s. This process gained the attention of the research community because it initially acted as rapid prototyping tool. This means, that scientists were able to provide a sample of what an object or desired part was going to look like. After some years, different technologies of AM started to appear offering the capability of utilizing different materials such as: metals, ceramics, composites, polymers, and organic materials. With further advances, AM changed from a prototyping idea to an actual manufacturing process, since AM allowed to design and process objects with complicated geometries in a small period of time. Moreover, it did not produce nearly as much waste material as a conventional top-down manufacturing approach. In fact, AM keeps growing specially in the aerospace industry since the different available technologies allowed to 3D print components composed of complicated metals,
alloys and super alloys, that by conventional casting and machining methods hard to produce due to their hardness and machinability. Lastly, some of the most common AM technologies are: Stereolithography (SLA), Laminated Object Manufacturing (LOM), Selective Laser Sintering (SLS), and Fused Deposition Modeling (FDM).

1.3.1 Stereolithography (SLA)

This AM technology takes advantage of the photosensitivity concept. The way it works is that a photosensitive polymer resin is selected as the printable material. This material is fed into a container that with the help of rollers or some other type of components will uniformly spread the photosensitive material across a surface. Then, the computer will help a laser to trace the first layer shape on top of the liquid photosensitive resin. When in contact with the laser, the sensitive to light resin will undergo a polymerization process, leaving a solid layer of the material. After that, more resin will be respreads on top of the printed layer, so that the laser can keep building up the desired final component. This technique is rather expensive because of the price of the photosensitive resin, but the final products printed with this method have a smooth surface finish. Figure 1.1 shows a visual representation of SLA technology.\[38-41\]

![Figure 1.1](image)

**Figure 1.1** Two different stereolithography schematics. a) Bath stereolithography consists of a laser curing a layer of liquid resin. After one layer is cured, the stage lowers itself allowing for more liquid resin to cover the cured polymer. After that, laser cures the new layer of resin as specified by the design. b) This approach works in reverse process compared to the bath SLA. Here the stage is submerged inside the resin. Then, the stage is pulled up to allow more resin to flow below the cured polymer. A pattern can be added so that the laser can cured the whole layer design at the same time. Obtained from Ref[37]
1.3.2 Laminated Object Manufacturing (LOM)

Figure 1.2 displays a schematic of the LOM technology. This inexpensive process consists of gluing together sheets of material, with the help of a binding agent. Then, with the help of a laser, cutting of the sheet is needed to give the desired final shape. The laser is calibrated to avoid any dimensional defects of the final product. Different materials (paper, metal, fabrics, polymers, composites, etc) can be 3D printed with this process. As mentioned earlier, it is not an expensive process, but some of the drawbacks of it are the mechanical properties and Z-axis stability. Mechanical properties are affected in the final component since a binding agent was used to glue the layers together, meaning that the final properties will not be exclusively of the sheet material, but of the sheet and the coating holding the layers. Also, the Z-axis dimension can be a problem since it will greatly depend on the amount of binder used on each sheet, plus sometimes localized shrinking caused by heat generated from the laser.

Figure 1.2 Schematic of Laminated Object Manufacturing (LOM) process. Obtained from Ref [36].
1.3.3 Selective Laser Sintering (SLS)

Selective Laser Sintering \cite{41-46} is another AM technology that is very similar to SLA. The main difference between this too is the material used to print. The selected material for SLA is a photosensitive monomer resin, while the preferred material on SLS is a powder. This powder can be of metal, ceramic, or polymer, but it does not mean that it is restricted to only those since any material that can be pulverized into powder can be used in this type of set up. SLS uses a high power laser to provide enough heat to fuse powder particles together. Another feature of this technology is that the printing surface (bed) has the capability to raise the temperature. This is to heat the bed close to the melting temperature of the printed material, so that dimensional defects related to temperature difference can be neglected or minimized as much as possible. The laser follows the printing pattern of each layer provided by the computer aid design (CAD) file. Each sintered layer is recover so that the laser can keep building the final component. Although it is a relatively fast printing mechanism, there are some downsides to it. The first one is the final surface of the component, since it does not have a smooth surface finish as in SLA. Another negative side of it, is the difficulty on changing of material, since all the powder has to be removed from the printer before feeding the new material. This equipment is expensive as well, and many variables have to be taken into account during the printing process. Figure 1.3 shows with the help of an illustration the main parts on the SLS process.
1.3.4 Fuse Deposition Modeling (FDM)

The last technique introduced in this document is the fuse deposition modeling (FDM)\textsuperscript{[47,48]}, commonly known as 3D printing because these printers are accessible to a vast amount of people.\textsuperscript{[49-51]} Figure 1.4 provides a visual representation of the FDM process. The cost of this equipment is around the two thousand up to six to seven thousand U.S. dollars, making it more common for a family to have one, especially if they are interested on science and engineering. As in the other methods, a computer-aided design (CAD) of the component is needed. These CAD file is then uploaded into software that is commonly called “slicer,” which is the one that will
divide the designed piece into layers/slices so that the head of the printer can follow and print the desired pattern. Usually, the head of the printer is free to move in all 3 directions (x, y, and z) to deposit thin layers (few hundred microns) on top of bed. Polymers are very common materials printed through this technique since polymers, more specifically thermoplastics, tend to have relatively low melting points (few hundred °C) and an even lower glass transition temperature (Tg). As it can be inquired from this information, printers using this approach will not reach temperatures higher that 400 °C, although the user can modify them to increase their temperature working range. Depending on the settings selected, the quality of the final product can vary. Printing very fast will not provide a smooth surface, dense, high quality piece; while printing slow might help to improve those traits, but might take a few hours or even days (depending on the size of the final product).

![Figure 1.4](image)

**Figure 1.4** Schematic of fused deposition modeling (FDM) process. Obtained from Ref[36].
1.4 – Composite Materials

Composites can be defined as a combination of two or more materials. They are divided into two main parts: matrix and reinforcement material. The matrix of a composite is the material that will hold together particles; fibers or other shapes of reinforce materials. A matrix can be classified into three different categories: metal matrix, polymer matrix and ceramic matrix composites. From these three categories, polymer matrix composites are the most common ones in our daily lives. For example, tires are a polymer matrix composite reinforced with metal fibers. Metal matrix and ceramic matrix composites are mostly used in research facilities or aerospace industries, where very specific sets of properties are required. The other components of the composites are the reinforcement materials. Reinforcements can be present in different forms. Continuous fibers, discontinues fibers, whiskers, sheets, and particles are some of the more common geometries and shapes selected to reinforce a matrix. Continuous fibers directionally improve the properties of the composites. In other words, depending on the direction of the fibers inside the matrix, the properties will be improved or weaken. Also, the length of the fibers plays a crucial role in improving properties. Alternating layers of either fibers or sheets in different ways (0˚, 45˚, and 90˚) is a common solution to anisotropic composite materials. Some of the more common fibers commercially available are carbon fibers and glass fibers.

Fibers are a common reinforcement in commercially available composites since their production has been master to have a cost effective outcome. However, now a days particles or flakes are becoming more popular as reinforcements (laboratories and research facilities). This is because the processing of some novel materials, such as graphene and TMDs, will not produce fibers or big sheets. Perhaps, these flakes or particles reinforcements might not have the same impact on mechanical properties, but this does not matter since the focus is a little bit changed. In these cases electrical, thermal, optical properties can be improved.

The purpose of this study is to investigate the effect that some van der Waals materials, such as (MoS2, WS2), and graphite particles, might have on a polymer matrix. Two different polymer matrices are choose based on different factors that will be explained in short.
Acrylonitrile butadiene styrene (ABS) is the first matrix material of choice. This is because ABS has a relatively low glass transition and melting temperature, making it a very common material in the 3D printing (FDM) industry. Polyethylene terephthalate glycol (PETG) is the other material of choice. Although it has a higher melting and glass transition point than ABS, PETG is a biocompatible material. In fact, water, soda, and other type of bottles are made out of this material. Particles of graphite, MoS$_2$, and WS$_2$ were selected as reinforce material to observe the changes in mechanical and electrical properties on the composite.
Chapter 2: Sample Preparation

2.1 – Material selection

Selecting the materials is the first step when preparing different samples for mechanical and electrical testing. PETG and ABS were selected among other thermoplastics, to be the matrix of the composites. While three different compounds were selected as reinforcement materials for both matrices. First, a brief background on the materials will be provided so that readers can understand the reasoning behind selecting these materials. Also, readers will be able to find some properties of the different materials, so that they could easily think of purposes and application other than the ones proposed in this document.

2.1.1 Polyethylene terephthalate glycol (PETG)

This material is classified as a copolymer because it is produced by copolymerizing polyethylene terephthalate (PET) and ethylene glycol. C10H8O4 is the general formula of this copolymer. The glycol addition to the PET carbon chain provided additional stability during printing procedures. Therefore, PETG is a polymer designed thinking on 3D printing purposes specifically. It has a melting and glass transition temperature of around 210°C and 80 °C, respectively. PETG starts degrading at a temperature of about 265 °C. It has a density of 1.27 g-cm⁻³, while at same time it has a hardness of 108 (Rockwell Hardness “R” scale). In addition to these general properties, PETG has some attributes such as chemical resistance, impact resistance, optical clarity (transparent), and biocompatibility, among others that make it more interesting. These attributes allow the use of PETG in the food industry, health-care field, and electronics. Besides having these properties, the lack of information on composites with PETG as matrix was a strong deciding factor to select it as one of two matrices.

2.1.2 Acrylonitrile butadiene styrene (ABS)

ABS is the second thermoplastic selected to function as the main substance in the other set of composite materials. ABS is a well-known polymer in the 3D printing industry since it is one
of the most commercially available materials to print with. Almost all people working polymers additive manufacturing has worked or known something about ABS printed parts. This polymer is easy to extrude, making filament formation a simple task. It is also used because of its ability to absorb energy during an impact. ABS has a density of around 1.04 g/cm$^3$, and a glass transition temperature of about 105 °C. It is considered an amorphous polymer; therefore a melting point cannot be defined. In short, this material was selected because it will serve as a point of comparison to PETG composites, since ABS has been significantly more studied than the other thermoplastic in this manuscript.

2.1.3 Reinforcements

As mentioned earlier graphite, MoS$_2$, and WS$_2$ will be the selected materials to reinforce the different matrices. These were chosen because they can be easily exfoliated using different solvents such as isopropanol (IPA), methanol, water or NMP (if particle size is big it can be easily reduced). The reason why they can be exfoliated is because their layers are weakly bonded by van der Waal forces. Graphite will be use with the purpose of getting conductive composites, while MoS$_2$ and WS$_2$ are meant to produce composites with semiconductor behavior. Also, from previous experiments I have found both TMDs tend to produce an exothermic reaction when mixed with different polymers, such as poly-methyl methacrylate (PMMA). In fact, WS$_2$ tend to create more flexible PMMA composites.

2.2 – Filament Extrusion

To fabricate the different polymer base composite filaments a Filabot EX2 extruder (Figure 2.1) and a Filabot Spooler (Figure 2.2) were used. Twenty-two different filaments were extruded with the help of the before mention equipment. Two spools correspond to control material, meaning that one is made of pure PETG, and the other of pure ABS. The twenty spools of filament that are left can be divided into 4 different sets of 5 spools. The first set of spools will correspond to 1 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt% graphite powder (Alfa Aesar, 99.9%,
metals basis, LOT: M30A052). The as-received graphite powder had an average particle size of about 500 µm. This represented a problem since the printer’s nozzle size is 300 µm. In order to solve this problem, the graphite powder was comminuted with the help of a shear mixer (Figure 2.3). The solvent used to exfoliate the graphite particles was isopropyl alcohol (IPA). IPA is a suitable solvent to exfoliate graphite and TMDs due to the fact that the surface tension of IPA is somewhat similar to the surface energy of exfoliated particles. N-methyl-2-pyrrolidone (NMP) is, according to literature, the most effective solvent to exfoliate van de Waals materials. But our main purpose was not to completely exfoliate the van der Waals materials, but to reduce the particle size to a point where it is lower than the size of the printer’s nozzle. Another reason why IPA was a better option for this experiment is due to the fact that the resultant particles had to be dried, and this solvent has a lower boiling point than NMP, and it is much less hazardous to human health.

Figure 2.1 Side view of Filabot EX2 extruding system.
Figure 2.2 Filabot spooling system. It is placed in front of the extruder to create spools of the extrude filament. Also, it helps to regulate the filament size.

Graphite powder was treated with the shear mixer for 4 hrs. at 6000 RPM. After the 4 hrs., the graphite particle size got reduced from an average of 500 µm to an average of about 40 µm.
The resultant powder was left inside a preheated oven at 90˚C for 1 day, with the only purpose of completely drying the exfoliated particles. At the same time, PETG pellets were left on another preheated oven at 65˚C for 4 hrs. This was done with the intention of removing all the moisture that could have been trapped inside the polymer pellets. Once the drying process was done, graphite and pellets were weighted in different ratios. 1 g of graphite was mixed inside a plastic container with 99 g of PETG pellets (resulting in 1 wt% graphite – PETG composite). The plastic container was then rotated, for 5 min., along its axis while at the same time it was displaced along the same axis in a circular manner (like if two different conical figures joined by a vertex were drawn) as shown in Figure 2.4. This rotation process, patented by Halliburton, is used to produce uniform mixtures of different solid compounds (powders and pellets). The same procedure was followed with different ratios of treated graphite powder and PETG pellets (5 g of graphite and 95 g of PETG pellets, 10 g of graphite and 90 g of PETG pellets, 15 g graphite and 85 g PETG pellets, 20 g graphite and 80 g PETG pellets). The second set of 5 spools was made using the ABS and shear mixed graphite powder. 1 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt% graphite – ABS composite filaments were extruded. The exact same procedure as with PETG spools was used for this set of spools. The only difference was the drying step of the ABS pellets. ABS pellets were dry in a preheated oven at 80˚C for 4 hrs. The third and fourth sets of 5 spools (total of 10 spools) were made of PETG with 1 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt% of MoS$_2$ (Alfa Aesar, 98%, LOT: P12B015), and WS$_2$ (Alfa Aesar, 99.8%, metals basis, LOT: N01C036). At the end one set of spools correspond to PET - graphite (with different concentrations), ABS – graphite, PETG – MoS$_2$, and PETG – WS$_2$. 
Figure 2.4 Schematic of the hand mixing process to produce uniform mixtures of solid compounds. This process is similar to the one made by a cement truck mixer.

To extrude the PETG-graphite composites, each solid mixture of the powder and the pellets were fed individually into the extruder. For 1 wt\% graphite - PETG mixture the temperature of the extruder was set at 205 °C. During the extrusion the extrusion and spooling speed can be control. Filabot extruder and spooler do not have digital controllers regulating their respective speeds. Therefore, it is hard to state the exact velocity values. This part has to be regulated by the user relying on visual observation. The desired filament diameter was around 2.80 mm. To obtain this approximate value, the velocities were set once the filament coming out form the extruder’s
nozzle formed a 90° angle with the bench surface, as shown in Figure 2.5. This was found to be a desired feature during the extrusion process in order to obtain the before mentioned diameter size. For 5 wt% graphite – PETG the extrusion temperature used was 205 °C. For 10 wt%, 15 wt%, and 20 wt% the extrusion temperatures used were 210 °C, 210 °C, and 215 °C respectively. For 1 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt% graphite – ABS composites, the extrusion temperatures used were 195 °C, 195 °C, 200 °C, 200 °C, and 210 °C respectively. For 1 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt% MoS$_2$ – PETG composites, the extrusion temperature used was 215 °C for all of them. Finally, for 1 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt% WS$_2$ – PETG composites, the extrusion temperatures used were 190 °C, 190 °C, 180 °C, 165 °C, and 160 °C respectively.

**Figure 2.5** Filament coming out of the Filabot extruder. The 90° angle created by the filament allows the user to know that the extrusion and spooling speed are synchronized. Having this synchronization is crucial in obtaining a certain filament diameter. If the filament is extruding faster than what the spooling can handle, then the filament will be thick (big diameter) and most likely it will knot itself up. On the other hand, if the extrusion speed is to slow and spooling speed is faster, the filament diameter will be to thin due to the excessive pulling force produced by the spooler.
2.3 - Printing

After finishing extruding, printing is the following step during this experimental procedure. Three different samples are will be printed in order to test mechanical and electrical properties. From those 3 samples, the first one will be used specifically to measure mechanical characteristics of all the composites. Then, the other two types of samples will be used during the electrical characterization of the material.

2.3.1 Tensile test sample printing

Figure 2.6 shows the CAD file of a “dog bone” tensile specimen (ASTM D638 Type V). Figure 2.6 (a) is a frontal view of the sample. The total length of the sample is 63.50 mm, while the width of the head is 10 mm. The neck of the sample has a width of 3.18 mm. Figure 2.6 (b) is the isometric view of the specimen. From here it is easier to visualize what the whole sample will look like. This American Society for Testing and Materials (ASTM) standard size is convenient when testing these polymer composites, because not a lot of material is required to print out each sample. In order to have the best possible data, 10 tensile specimens of each composite filament were printed. This made a total of two hundred and twenty “dog bone” specimens.

19
Nozzle temperature, bed temperature, and Z-offset were some of the most important parameters during the 3D printing of the samples. Nozzle temperature is the temperature at which the tip of the printing head will be, at all time, until the specimen is finished. This temperature will vary specially when changing from set to set. For example, changing from PETG composites to ABS composites. Also, changing the filler material will have an impact on the printing temperature set up, but not as big of an impact as changing the matrix material. The concentration of the filler will not do much of a difference on the nozzle temperature, unless the difference in concentration is very high. Then, bed temperature is the temperature of the surface onto which the layers are going to be deposited. This setting will manly depend on the matrix material. In some
composites with TMDs fillers, like WS$_2$ – PETG material, when varying the concentration of the filler the bed temperature might be an issue to take into account. This is because according to personal experience WS$_2$ tend to interact with polymers causing some change in the material properties. When 15 wt% or more of WS$_2$ is added to PETG, PETG tend to loose viscosity. This then requires a reduction in temperature; otherwise the final print out will have dimensional defects. Lastly, the Z – Offset is another important parameter that need to be taken into account when printing different materials. This setting refers to the distance between the tip of the nozzle and the surface of the bed. This setting can change from print to print since nozzles can expand during printing. PETG is a material that can be air printed. This means the distance between the nozzle and the bed can be of a few millimeters, because of the good adhesion of the material to the bed. On the other hand, other materials might need a much smaller distance since adhesion between layers and surface is not very good. **Table 1.1** shows different parameters (nozzle temperature, bed temperature, and Z – Offset) used to print the tensile specimens. **FIGURE** displays an actual 3D printed “dog bone” sample.
Table 1: Lulzbot TAZ 6 Printing Parameters.

<table>
<thead>
<tr>
<th>Material</th>
<th>Nozzle Temp. °C</th>
<th>Bed Temp. °C</th>
<th>Z-Offset (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>245</td>
<td>100</td>
<td>0.1</td>
</tr>
<tr>
<td>1 wt%G – ABS</td>
<td>245</td>
<td>110</td>
<td>0.1</td>
</tr>
<tr>
<td>5 wt%G – ABS</td>
<td>245</td>
<td>115</td>
<td>0.1</td>
</tr>
<tr>
<td>10 wt%G – ABS</td>
<td>245</td>
<td>115</td>
<td>0.1</td>
</tr>
<tr>
<td>15 wt%G – ABS</td>
<td>245</td>
<td>115</td>
<td>0.1</td>
</tr>
<tr>
<td>20 wt%G – ABS</td>
<td>230</td>
<td>115</td>
<td>0.15</td>
</tr>
<tr>
<td>PETG</td>
<td>220</td>
<td>100</td>
<td>-0.7</td>
</tr>
<tr>
<td>1 wt%G – PETG</td>
<td>235</td>
<td>100</td>
<td>-1.185</td>
</tr>
<tr>
<td>5 wt%G – PETG</td>
<td>225</td>
<td>100</td>
<td>-1.185</td>
</tr>
<tr>
<td>10 wt%G – PETG</td>
<td>220</td>
<td>100</td>
<td>-1.185</td>
</tr>
<tr>
<td>15 wt%G – PETG</td>
<td>218</td>
<td>100</td>
<td>-1.215</td>
</tr>
<tr>
<td>20 wt%G – PETG</td>
<td>215</td>
<td>100</td>
<td>-1.315</td>
</tr>
<tr>
<td>1 wt%MoS2 – PETG</td>
<td>230</td>
<td>100</td>
<td>-0.85</td>
</tr>
<tr>
<td>5 wt%MoS2 – PETG</td>
<td>230</td>
<td>100</td>
<td>-0.85</td>
</tr>
<tr>
<td>10 wt%MoS2 – PETG</td>
<td>235</td>
<td>100</td>
<td>-0.85</td>
</tr>
<tr>
<td>15 wt%MoS2 – PETG</td>
<td>235</td>
<td>100</td>
<td>-0.85</td>
</tr>
<tr>
<td>20 wt%MoS2 – PETG</td>
<td>245</td>
<td>100</td>
<td>-0.85</td>
</tr>
<tr>
<td>1 wt%WS2 – PETG</td>
<td>240</td>
<td>70</td>
<td>-1</td>
</tr>
<tr>
<td>5 wt%WS2 – PETG</td>
<td>240</td>
<td>70</td>
<td>-1</td>
</tr>
<tr>
<td>10 wt%WS2 – PETG</td>
<td>240</td>
<td>70</td>
<td>-1</td>
</tr>
<tr>
<td>15 wt%WS2 – PETG</td>
<td>240</td>
<td>70</td>
<td>-1</td>
</tr>
<tr>
<td>20 wt%WS2 – PETG</td>
<td>240</td>
<td>70</td>
<td>-1</td>
</tr>
</tbody>
</table>
2.3.2 Resistor design for electrical characterization

New filaments were made through the same process used before. This time the concentrations used were much higher (30 wt%, 40 wt%, and 50 wt%). The best candidate to print some conductive samples was 50 wt% graphite – PETG material. The decision was taken based on the fact that 50 wt% graphite – PETG was the material showing electrical conductivity all over the filament, and not only on localized areas, like the other materials. In addition, high filler PETG materials are much easier to print with the TAZ 6 printer than high filler ABS materials. The nozzle got clogged when trying to print with 50 wt% graphite – ABS filament. Taking all this into account, 50 wt% graphite – PETG was the selected composite to 3D print the resistor structures. The temperature used to extrude such a material was 220°C.

Figure 2.7 allows us to see both resistor designs. The first one has a more complex designed since the intentions were to test the printing capabilities to the limit. The channel width of this type of resistor is around 1 mm, while the thickness of the whole sample was 300 µm. This designed demonstrated that complicated geometries could be printed with the TAZ 6. Unfortunately, this designed was difficult to work with since the square contact pads were bigger and heavier than the channel itself, creating stress concentrator zones. This led to rupture of the channel connecting both pads. This designed was used to make some electrical measurements to prove that complicated shapes are printable and functional. Then, a redesigned of the resistor structure was needed to improve the handling of the samples making them more convenient for multiple testing. Figure 2.8 shows 3 different graphite – PETG printed lines. The contact pads are much smaller so the ratio contact pad to channel is much smaller. This produced less fragile structures. Then only difference between the 3 new resistor designs is the channel length. Small, medium, and large are the labels selected to refer to the different length resistors.
**Figure 2.7** Two different resistors like structures. Left structure (with complicated geometry) has higher resistance due to the overall longer channel length. Right structure is simple but allows faster designs and is easier to handle during electrical characterization.

**Figure 2.8** Small, medium, and large resistor like structures for electrical characterization.
Chapter 3: Mechanical Properties

In this chapter, we will talk about the mechanical properties of the different composites. Tensile test is one of the most popular methods to explore the mechanical properties of a material. It measures the resistance of a material to a slowly applied force. The result of a tensile test is what is commonly known as stress-strain diagram. From the stress strain diagram, different parameter can be obtained, such as: Young’s modulus (YM), yield strength (YS), and ultimate tensile strength (UTS). Hooke’s law, also known as Young’s modulus (Eq. 1), is the relationship between the stress and the strain in the elastic region of the stress-strain diagram. Yield strength is the point at which plastic deformation start to happen. In metals, the yield strength is the stress required to promote dislocation motion, while on polymers it correspond to the stress required to promote disentanglement of the carbon chains. Ultimate tensile test is the highest applied force on metals. At this point, it is noticeable the change in dimensions on the tensile sample (necking). However, on polymers UTS is the stress to rupture. In other words, in polymers the yield point/yield strength corresponds to the highest applied force, and the ultimate tensile test is the stress at the moment of rupture. In order to measure all these parameters, ASTM D638 Type V samples where printed with the help of the Lulzbot TAZ 6.

Young’s modulus ($E$) is defined as stress ($\sigma$) divided by strain ($\varepsilon$). At the same time, stress is given by the ratio of force ($F$) and area where the force is applied ($A$). Lastly, strain is defined as the change in length ($\Delta l$) divided by the original length ($l$).

\[
E = \frac{\sigma}{\varepsilon} \quad \text{Eq. 1}
\]
\[
\sigma = \frac{F}{A} \quad \text{Eq. 2}
\]
\[
\varepsilon = \frac{\Delta l}{l} \quad \text{Eq. 3}
\]

If combined Eq. 2 and Eq. 3 with Eq. 1, we can redefine the YM to the following expression:

\[
E = \frac{F \cdot l}{A \cdot \Delta l} \quad \text{Eq. 4}
\]
3.1 – Results

More than 200 “doge bone” samples (ASTM D638 Type V) were printed using a Lulzbot TAZ 6. The different printed specimens can be conveniently divided into four main categories: ABS – graphite, PETG – graphite, PETG – MoS$_2$, and PETG – WS$_2$. At the same time, each category has five filler loadings (1 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt% filler particles). Ten samples of each different loading were printed to obtain reliable results. In order to compare the results of each different composite, 10 tensile samples of pure ABS and PETG were printed as well, giving a total of 220 tensile specimens.

ABS – graphite composites showed some interesting results. Printed ABS with no filler additions was the one, among all other ABS loadings composites, showing the highest yield strength (≈ 43 MPa). Also, this category showed the highest tensile strength at around 37 MPa. From Figure 3.1 – 3.3, more information can be extracted, such as the ductility of the material. Each line in the graph represents the stress-strain curve obtained from one sample. Since 10 samples from each category were tested, 10 different stress-strain curves will be seen on each graph.

The strain values were sensitive to filler loadings. Even though ABS results depict a wide range of different strain levels, this set of samples showed the best ductility among the ABS composites. Pure abs had a maximum strain value of ≈ 11%, while the lowest one was ≈ 4%. It is true that these values do not sound very exciting because polymers tend to have better ductility, exhibiting values over 100%. However, other properties (electrical conductivity and optical absorbance) could be improved with additions of graphite particles as a trade off. In these types of composites the addition of graphite reduced the strength and toughness. As more graphite was added, more strength and ductility was lost. At the highest graphite loading the strength and strain was reduce to ≈ 25 MPa and 2%, respectively.
Figure 3.1 (a) & (b) Stress vs strain plots of ABS and ABS – 1wt% graphite. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Figure 3.2 (a) & (b) Stress vs strain plots of ABS – 5wt% and ABS – 10wt% graphite. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Figure 3.3 (a) & (b) Stress vs strain plots of ABS – 15wt% and ABS – 20wt% graphite, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Six different graphs corresponding to PETG – graphite composites can be observed from Figure 3.4 (a) – (b) to Figure 3.6 (a) – (b). In the same way as ABS – graphite composites, these materials showed highest strength when no additions or at small loadings (1 wt% and 5 wt%). The highest YS value was ≈ 50 MPa, while the ultimate tensile strength UTS was around 30 MPa. On the contrary to ABS – graphite composites, PETG – graphite showed slightly less sensitivity to the graphite loadings. In other words, adding graphite powder did not harm the mechanical properties (strength and ductility) as much as when added to ABS. This is especially true at lower loadings (1 wt%, 5 wt%, and 10 wt% graphite) since the YS, UTS, and strain to fracture (50 MPa, 30 MPa, and 10%) remain almost the same.
Figure 3.4 (a) & (b) Stress vs strain plots of PETG and PETG – 1wt% graphite. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Figure 3.5 (a) & (b) Stress vs strain plots of PETG – 5wt% and PETG – 10wt% graphite, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Figure 3.6 (a) & (b) Stress vs strain plots of PETG – 15wt% and PETG – 20wt% graphite, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Figure 3.7 (a) – (b) to Figure 3.9 (a) – (b) correspond to PETG and MoS$_2$ composite series. Compared to previous graphs, it can be immediately noticed that MoS$_2$ additions to PETG do not detriment the mechanical properties of the material. According to the results, PETG retains most of its yield strength ($\approx$50 MPa), while the ultimate tensile strength is gradually decrease from 30 MPa after more than 5 wt% MoS$_2$ is added to the PETG matrix. In this group of materials, it can be noticed that MoS$_2$ helps the ductility of the polymer matrix. With no filler material addition are present into this polymer, the strain to fracture is at a value near 10 %. However, when 1 wt% MoS$_2$ is added to the matrix, it increases the ductility from 10 % strain up to a minimum value of around 20 %, and a maximum of 120 %. Adding this van de Waals material does not affect the YS at all, while it aids the ductility even at very high loadings (15 wt% and 20 wt% MoS$_2$).
Figure 3.7 (a) & (b) Stress vs strain plots of PETG and PETG – 1 wt% MoS₂. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Figure 3.8 (a) & (b) Stress vs strain plots of PETG – 5wt% and PETG – 10wt% MoS$_2$, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Figure 3.9 (a) & (b) Stress vs strain plots of PETG – 15wt% and PETG – 20wt% MoS$_2$, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Then, Figure 3.10 (a) – (b) to Figure 3.12 (a) – (b) show the data obtained from PETG – WS\textsubscript{2} composites. At first glance, WS\textsubscript{2} is a material that can greatly affect the behavior of the polymer matrix. For loadings higher or equal to 5 wt\%, the composite reduces its ductility becoming incredibly brittle. For small loadings (0 wt\%, 1 wt\%, and 5 wt\%), the YS is retained at around 50 MPa, and a UTS of around 30 MPa. Also, the ductility is increased (up to 65\%), particularly, at 1 wt\% WS\textsubscript{2} samples. Adding more than 5 wt\% filler 2D material will harshly harm the mechanical properties of the composite. In fact, the ductility got reduced to a value close to 1 \% strain. This van de Waal material can benefit the ductility as shown in the graphs when only small amounts (max 1 wt\%) are added. Otherwise, this material will only affect the performance of the composite by making it lose its ductility.
Figure 3.10 (a) & (b) Stress vs strain plots of PETG and PETG – 1wt% WS$_2$. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Figure 3.11 (a) & (b) Stress vs strain plots of PETG – 5wt% and PETG – 10wt% WS$_2$, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
**Figure 3.12** (a) & (b) Stress vs strain plots of PETG – 15wt% and PETG – 20wt% WS$_2$, respectively. Each graph shows 10 different measurements. Each measurement corresponds to 1 “dog bone” sample.
Based on the results obtained from the tensile test experiment, it can be said that PETG – graphite composites have better mechanical properties than ABS – graphite ones. From Figure 3.13, we can observe two stress vs strain curves of the ABS and PETG series. These stress vs strain graphs averaged all the data from the ten samples of each loading. Max YS and max strain to failure of ABS series correspond to pure ABS material, with value of 43 MPa and 8 % strain. Adding graphite to ABS considerably reduced the overall toughness of the material. PETG composites retained its YS of around 48 MPa while keeping a better ductility when compared to ABS. Also, the Young’s modulus (YM) of ABS composites was around 1.85 GPa as showed in Figure 3.14 (a). Average strain to fracture of ABS series can be observed from Figure 3.14 (b). Moreover, PETG series has an average YM of about 2 GPa. Addition of graphite did help to improve a little bit the YM of PETG composites (Figure 3.15 (a)). Figure 3.15 (b) represent the strain to fracture of PETG – graphite series.

![Figure 3.13 Comparison between ABS (a) and PETG (b) stress vs strain curves with graphite. (a) ABS series show a series of lines corresponding to control, 1 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt%. (b) PETG – graphite series lines correspond to the same loadings as in (a).](image-url)
Likewise, **Figure 3.16 (a) - (b)** compares PETG – MoS$_2$ and PETG – WS$_2$ series. PETG – MoS$_2$ series showed better mechanical properties than its WS$_2$ counterpart. This can be said since for MoS$_2$ series the YS was mostly retained at all loadings, while the UTS and ductility gradually decreased. On the other side, WS$_2$ series lost became incredibly fragile for 5 wt% or higher loadings of filler powder. This can be seen from the stress vs strain graph (**Figure 3.16 (b)**) since there is no plastic deformation when WS$_2$ is added in high quantities. Also, from **Figure 3.17** and **Figure 3.18** it can be seen that the YM of MoS$_2$ and WS$_2$ composite series are around 1.7 GPa and 2 GPa, respectively. However, if analyzed in depth it can also be perceived that additions of WS$_2$ to PETG did increase the YM of the material (stiffer material), but it decreased the ductility as well.
Figure 3.16 Comparison between PETG MoS$_2$ (a) and WS$_2$ (b) stress vs strain curves. (a) MoS$_2$ series show a series of lines corresponding to control, 1 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt%. (b) WS$_2$ series lines correspond to the same loadings as in (a).

Figure 3.17 (a) Young’s modulus (YM) of each PETG polymer composite with different MoS$_2$ loadings. (b) Strain at failure for each PETG – MoS$_2$ composite.
3.2 – Discussion

From this mechanical testing experiment it can be said that in general the additions of theses type of fillers materials decreased the toughness of the material. In other words, the area under the stress – strain curves of the composites was small, therefore less energy is absorbed by the material, when compared to the stress – strain curves of the pure matrix material (ABS and PETG). This can be mainly attributed to the fact that graphite is a much stiffer material than both the thermoplastics used during these experiments. After a certain loading, the matrix properties will be overcome by the fillers properties. However, adding small amounts of filler material can improve the physical properties of the composite as observed in previous results. The usage of both van de Waals materials as fillers in the composites produced some interesting results. MoS$_2$ additions did improve the toughness of the material by keeping the YM, and YS of the matrix (PETG), but improving the ductility. This enhancement in ductility can be observed specially at small additions of MoS$_2$ and WS$_2$. PETG seemed to be more sensitive to the addition of WS$_2$ than MoS$_2$. This can be said since WS$_2$ composites showed interesting mechanical behavior for loadings lower than 5 wt%. After 5 wt%, a very brittle material that did not plastically deform
was produced. In the same way MoS$_2$ composites show their best performance at 1 wt% concentrations. However, even though the overall toughness of the composite did decrease when more than 1 wt% filler material was added, it did not decrease as drastically as in PETG – WS$_2$ series. To explain this behavior, we would like to point out the pellets and powder interaction during the mixing process. MoS$_2$ powder mixed much better with the polymer than WS$_2$. In the first case, all the van de Waal powder covered all the surface area of the polymer pellets, while the WS$_2$ powder did cover the PETG pellets but to a lesser extent. It could be seen that the MoS$_2$ had a better affinity for the polymer than the WS$_2$. Therefore, PETG – MoS$_2$ series showed better toughness at all points when compared to WS$_2$. PETG – WS$_2$ series showed interesting properties but at small amounts of filler added because the affinity between PETG and WS$_2$ was not as much as with MoS$_2$. Also, particle size is something that might affect these pellets and particles interactions. For example, as received graphite powder had a very large size (Figure 3.19). When trying to mix this powder with PETG or ABS pellets it could be observed that graphite particles did not wanted to combine with polymer pellets. Nonetheless, after the graphite particle reduction with the shear mixer the pellet particle interaction was improved to something similar to the PETG – MoS$_2$ series. As shown in Figure 3.20 it can be seen that MoS$_2$ flake size is smaller than that of WS$_2$. This can be a reason why there was a better interaction with MoS$_2$ than with WS$_2$. Reducing the flake size is somewhat easy for these van der Waals materials, however it is not easy to keep a small size since few layers size particles tend to re-aggregate. It is possible to retain an exfoliated state with the addition of surfactants or solvents with surface tension similar to the surface energy of the van de Waals materials, but it is not easy to implement solvents or surfactants during the mixing of these composite materials. If the smallest possible layer thickness can be achieved (single atom layer thickness) to reinforce composites it is more than likely that amazing properties can be achieved with only small additions.
Figure 3.19 (a) SEM picture of as received graphite powder. Average particle size of about 600 µm. (b) Graphite powder after 4 hours of shear mixing at 6000 rpm. Particle size decreased to average size of around 5 µm.

Figure 3.20 Particle size comparison. (a) As received graphite powder particles. (b) As received MoS$_2$ powder particle size. (c) WS$_2$ as received particles. Graphite particle size was the biggest of all three 2D materials. Further treatment to reduce the particle size was needed to prevent 3D printer’s nozzle clogging and at the same time improved matrix – filler uniformity.
Chapter 4: Electrical Properties

This chapter consists on the electrical characterization of two different 3D printed structures as shown in Figure 2.7. With the help of the set up shown in Figure 4.1, which consists on a micromanipulator and a semiconductor parameter analyzer (HP 4156A), current vs voltage graphs where obtained. In total, three different experiments where done in order to understand better the electrical traits of our composite material. The first experiment consists on a step annealing process, where each sample was annealed at 80 °C in intervals of one hour for a total of four hours. Then, small, medium, and large structures where electrically analyzed when printed on a PET substrate. This was a comparison between data collected between samples printed on PET substrate versus samples that were not printed on a PET surface. The third experiment consists on electrically characterizing more complex 3D printed structures (as shown in Figure 2.7 left) while mounted on structures with different radius of curvature (Figure 4.6). Lastly, with the purpose of showing some possible applications, a medium size sample was analyzed while mounted on a human index finger. This shows a possible application as a wearable sensor.

4.1 – Results

As mentioned before, different designs were produced to test electrical properties of the 50 wt% graphite – PETG. In Figure 2.8 you can see three different samples. These are simple line structures with contact pads on the end. All samples (small, medium, and large) have the same thickness, which is set to be around 0.6 mm. The channel width is the same for all three structures, as well. However, channel length will differ from object to object. Small, medium and large resistor like structures will have a channel length of 9.90 mm, 12.20 mm, and 20.00 mm, respectively. With this information and the data gather from the semiconductor parameter analyzer and micromanipulator (Figure 4.1), conductivity and resistivity of the material will be calculated. In order to learn more about the electrical traits of this polymer based composite material, 3 different experiments were planned. The first experiment is set to understand how annealing benefits or harms the electrical performance of the composite. Second experiment, is designed in
order to understand the material’s behavior when printed on a PET substrate. Then, a different resistor structure will be subjected to different radius of curvature to prove that more complex geometries can be printed with these composites using a TAZ 6 3D printer. Lastly, one of the structures will be taped to a finger to check the electrical characteristics while the sample is subjected to different strain levels produce by the normal movement of an index finger.

Figure 4.1 Micromanipulator and semiconductor parameter analyzer (HP 4156A) set up used to measure electrical properties of the conductive printed structures.

4.1.1 Step Annealing versus Continuous Annealing

In this experiment 3 different sets of samples were used; 1 small, 1 medium, and 1 large resistor like structures compose each set of samples. Before any treatment is done to the samples, I-V curves are taken with the help of the Micromanipulator and semiconductor parameter analyzer set up. From Figure 4.2 (a) – (c) it can be seen that for all three sets of samples the current values are very low. The sets have a current (I) range of 5 – 250 µA. Once the initial measurements were taken, a step annealing experiment was conducted. This step annealing process consists on
warming the samples at a temperature of around 80˚C for four hours, but checking IV curves every hour. In other words, the samples were taken out of the oven every 1 hour for data gathering purposes, the samples were placed back again into the oven for another hour in order to repeat the process until the 4 annealing hours were completed. From Figure 4.2, it can be observed that the current values greatly differ from step to step. Current values were as low as 1 µA to as high as 1mA. Ideally, it was expected to see an overall increase on current values. However, that increasing trend was not noticeable. Theoretically speaking, small resistor structures should have shown the highest current values since the channel length is the smallest in these specimens, therefore having a lower resistance. This is not true in our experiment since for some sets, larger specimens showed less resistance than small samples.

After getting some inconsistencies with the step annealing process, it was decided to change the annealing from steps to just one 4 hours heating process. The resistor like structures showed a better performance when annealed for 4 straight hours than by annealing in 1-hour intervals. This can be seen from information presented in Figure 4.3 & Figure 4.4 since they show much higher current values a every voltage from 0 V to 20 V. One set of samples was test without annealing while the other set was annealed, and then tested. Also, each set (annealed and not annealed) was characterized with the help of some bending structures, shown in Figure 4.6. From the graphs it can be said that both annealed (Figure 4.3 (a) – (c) ) and not annealed (Figure 4.4 (a) – (c) ) have similar results. Small resistor structures (annealed and not annealed) showed a maximum current level of around 2 mA. Medium size specimens showed values closed to 1 mA, while large designs showed values higher than 2 mA. From this data it can be said that annealing did not improve the electrical performance of the material. Also, bending the different samples did not produce an effect on the current levels, meaning that this composite is not sensitive to different stresses and strains values. Based on this this material can be utilized as a device that supplies the same amount of power independently of the amount of stress or strain applied of the material. Figure 4.5 (a) – (b) shows the current value when 20 volts were supplied at different
radius of curvatures. The resistors were flexible enough to stand the highest radius of curvature, while not changing significantly the current values.

**Figure 4.2** Step Annealing of the 3 sets of samples formed by small, medium and large. (a) – (c) Shows data regarding current levels at 20V every 1 hour. Blue, red, and green represent the color small, medium, and large samples, respectively.
Figure 4.3 (a) – (c) I-V curves of not annealed small, medium, and large resistor like structures.
Figure 4.4 (a) – (b) Correspond to the I-V curves of small, medium, and large annealed for 4 hours at 80 °C resistor samples, respectively.
Figure 4.5 (a) – (b) Show the Current vs Radius of curvature plots. The three plots contain blue lines (not annealed samples data) and red lines (annealed samples data). From top to bottom (a) correspond to small size structures, (b) to medium size, and (c) to large size.
Figure 4.6 All five bending structures, with their corresponding radius of curvature values, designed to test the flexibility and sensitivity of printed structures.

4.1.2 Substrate vs No Substrate Analysis

After noticing that annealing does not benefit the performance of the material, a different characteristic was tested. This time, one set of samples was printed on top of a PET sheet. Adhesion of the structures to the PET substrate was good, meaning that it was very hard to unstick the PETG specimen from the PET film. In Figure 4.7 both set of samples can be seen. Samples on the left are not printed on PET substrate, while the samples shown on the right are printed on a PET surface. Both set were electrically characterized using the same fixtures as in the previous experiment. Before any measurement was made, the surface of all samples was slightly polished with the help of sand paper to ensure a good contact with the probes. Polishing did improve the contact made with the probes and the surface of the composite. Small resistor structures showed current values as high as 20 mA at 20 V, and as low as around 5 mA that is in fact higher than samples used in previous experiment. In the same way, it can be observed that bending the resistor did not change current values keeping the same no stress sensitive behavior. Figure 4.8 (a) – (c) & Figure 4.9 (a) – (b) show this performance. Figure 4.10 corresponds to current vs radius of curvature for small, medium, and large resistors. The range of current values goes from about 5 mA to around 23 mA. On thing that has to be notice from this experiment is that PET substrate samples where not as flexible as the structures with no PET substrate. All samples (small, medium, and large) failed when mounted on last bending (fifth bending, Figure 4.6) structure.
Figure 4.7 Two set of three 50 wt% graphite – PETG samples. The first set on the left is composed of three samples (small, medium and large). These three samples were not printed on any surface. On the other hand, the set on the right was printed on top of PET substrate.
Figure 4.8 (a) – (c) Correspond to small, medium, and large specimens that were not printed on any type of surface. All samples were tested electrically tested using 5 different bending structures (shown in Figure 4.6). No sensitivity to the bending is detected like in a, however there are some graphs ( (b) & (c) ) showing son discrepancies. These discrepancies are due to contact issues between the probes and the surface of the samples.
Figure 4.9  (a) – (c) I-V curves of samples (small, medium, and large) printed on PET substrate. All samples were tested electrically tested using 5 different bending structures (shown in Figure 4.6).
Figure 4.10 This graph represents the current values at 20 V of small, medium, and large samples from both sets (with no substrate and with PET substrate). Dotted/dashed lines represent data taken from samples printed on top of the PET substrate, while continuous lines are used to represent data from no substrate samples. The minimum current value was around 5 mA, while the highest was about 23 mA.

4.1.3 I-V Measurements 1st Resistor Design

During this experiment, no annealing was performed since we have found that annealing did not improve the performance of the material. The designs were not printed onto PET substrate because according to the results from the past experiment PET substrate does harm the flexibility of the material. However, the polishing step was included to this design since polishing allows a better contact of the probes with the composite’s surface. Once again, printing this design
corroborates the fact that 3D printing brings more complicated geometries to the table. Structure thickness is 0.3 mm, channel width in this design is 1 mm, and the channel total length is around 45 mm. The neck length was divided into 5 different sections as shown by the picture in Figure 4.11 (a) – (e). Since bending does not affect the electrical outcome, the samples were only tested at 3 different radius or curvatures (0 cm$^{-1}$, 0.072 cm$^{-1}$, and 0.262 cm$^{-1}$). As expected, the first length has the highest current value because the length is the lowest, introducing less resistance. 0.86 mA, 0.42 mA, 0.25 mA, 0.18 mA, and 0.13 mA are the currents values at 20 V for the 1st, 2nd, 3rd, 4th, and 5th segment, respectively. Once again, almost horizontal lines can be observed in Figure 4.12, due to the fact that the material is not sensitive to the stress produce at different radius of curvature. Also, it can be seen that as the channel/neck length increases, the current decreases due to the increase in resistance. Also, the current values are much lower than in previous experiment because the thickness of the resistor has been cut in half (from 0.6 mm to 0.3 mm). This decreases the cross-sectional area of the specimen, limiting the amount of electrons flowing through.
Figure 4.11 (a) – (e) I-V graphs with corresponding picture. Each picture is marked with a red line. Extreme ends of red line on each picture represent the place where probes were placed in order to take electrical data. The channel length increases from top to bottom (red line is longer). As channel length increases, current level decreases.
4.1.4 Application in Wearable Electronics

Last portion of this project involves a physical tryout of one of the resistors made out of 50 wt% graphite and PETG thermoplastic. A medium size resistor was selected to be placed on top of the middle and proximal phalange of an index finger. In this region, the resistor will be tested for flexibility and no sensitivity. In other words, the current levels should remain the same when index finger is bent into different positions. Figure 4.13 (a) – (d) depicts the different positions made with the index finger. The first position is without any bending of the phalanges. Then, the finger was gradually bent until reaching the final state shown in Figure 4.13 (d). After the final bending, the medium resistor went back to its original position. However, it was notice that
bending the finger a little more than the amount shown by the picture will cause a fracture at the middle portion of the sample’s neck. As shown in the graph from Figure 4.13 (e), all bending positions have a similar current value that is around 3.75 mA. In short, this experiment shows the capability of this material to be implemented on applications where independently of the input provided by environment or human hand it will send back the same output when needed. Also, it can be implemented as a non-invasive sensor that could be place on skin since PETG is a biocompatible material and it is even use in the food industry. It did not produce any immediate allergic reaction when placed on the finger. However, more long term testing had to be done before thinking on implementing this material on applications related to human beings.
Figure 4.13 Data gather from a medium size resistor structure mounted on an index finger. (a) – (d) Shows the different finger positions during these measurements. (e) I-V graph of all 4 different finger positions. All lines overlap because resistor like structure is not sensitive to the different movements showed in the pictures.
4.2 – Discussion

In this section, more explanation upon the results and findings from previous chapters will be provided. During the first step annealing and one time annealing experiment many inconsistencies can be found. These irregularities are more visible in the step annealing process. The reason why this happened was found to be a probe contact issue. In other words, the probes used for electrical characterization were not physically touching an even surface of the composite. Since the material is made of 50 wt% thermoplastic (insulator) it had poor results when not a good contact was made. To solve this issue a scratch was made along the specimens’ necks so that the probes could be placed at the extremes of the scratch. This helped a little on getting better data, however, when the samples were placed back to the oven for more annealing time, the scratch made on the surface was self-heal. This “self-healing” was produced due to the fact that the temperature was close to the range of PETG glass transition temperatures. Also, because of the recovery of the materials it was determined to change from a step annealing process to a one time annealing for 4 hours. Later, it was found that annealing the material did not help to improve the electrical performance of the material, but the uniform scratching of the surface was indeed improving the current levels showed by the material.

Another characteristic that was found of this composite material is that the thickness of the 3D printed sample affected the flexibility of the material itself. In other words, the higher the thickness of the specimen the lower flexibility or ability to bend. This was taught during the second experiment, where samples were printed on PET substrate and electrically tested under different bending degrees (radius of curvature). The results in this experiment showed that resistor structures printed on PET sheets were not able to withstand the final bending fixture with a radius of curvature of 0.262 cm$^{-1}$. In fact, small, medium, and large designs broke during testing at this curvature. The only reason found was that the additional layer (PET sheet) decreased the flexibility of the composite specimen. This additional thickness and the interface between both materials (PET and 50 wt% graphite- PETG composite) limited the material’s ability to bend.
Taking into account, all the previous findings, a different designed was made in order to prove that 3D printing allows users to fabricate products with complicated shapes and relatively small features in a short period of time. These resistor like structures (Figure 2.8) where printed in about 3 minutes each. These new designs were tested in the same way as previous designs. In fact, they show more flexibility than small, medium, and large samples, but they also had some designing problems. The main problem with these designs was the size of the contact area and size of the channel/neck. The size difference between both features led to a fragile contact-channel interface. This interface made difficult to handle each sample since it acted like a stress concentrator. Nonetheless, reducing this contact-channel ratio will possibly improve the design by making it less fragile and easier to handle. Due to this design flaws, these resistor structure was not selected for the following test. The last experiment uses a medium size 3D printed resistor specimen in order to see and characterized the behavior of the composite when in touch with skin and exposed to a daily environment (finger movement). These designs were able to retain electrical properties without bending at various degrees. But they did not were able to resist a complete bending of the finger, making it a little less suitable for full motion joints sensors. If compared to other materials with possible sensor applications,\cite{52-59} this one does not have great strain properties since it cannot be aggressively stretch as some other polyisoprene or polydimethylsiloxane\cite{60} composite materials that can elongate at least 1.5 times its original size. However, those materials did have strain sensitivity while this one does not, so it could be implemented in applications where no sensitivity is needed. This was a surprising finding since a poly-methyl methacrylate based composite show strain sensitivity.\cite{61,62}

Lastly, a lot of current level variability was observed in this experiment. This was mainly because of three main reasons: dimensions, surface contact, and uniformity. Current levels will vary depending on specimen’s dimensions, since resistance is not an intrinsic property. Calculating resistivity and conductivity instead of reading resistance values can solve uncertainty. Contact problems were solved by evenly scratching the surface with the help of silicon carbide sand paper. Lastly, uniformity of the composites is a great problem since it is possible that more
graphite powder (conducting material) can be present in some zones of the samples than in others. The main reason why this can happen is because the hand-mixing step used in this experiment. Although a good hand-mixing process it is not the best for scientific purposes since it has the human factor involved. Not having the necessary equipment to uniformly mix the material was the driving factor for taking this decision. In order to try to avoid this uniformity issues, an average of the conductivity and resistivity was calculated. Conductivity and resistivity of all samples used in this experiment was calculated using two simple equations:

\[
\rho = \frac{RA}{L} \quad \text{Eq. 1}
\]

\[
\sigma = \frac{1}{\rho} \quad \text{Eq. 2}
\]

Resistivity (\(\rho\)) is defined as the resistance (\(R\)) times the cross sectional area (\(A\)), divided by the length (\(L\)). Conductivity (\(\sigma\)) is the reciprocal of the resistivity.

The average resulting from all these calculations are 0.250 Ohm-m (resistivity) and 5.27 Siemens-m\(^{-1}\). If compared to metals, this material is around 7 orders of magnitude less conductive. However, the conductivity is good enough to be used in sensing applications. In other words, a material with conductivity lower than metals, but at least 20 orders of magnitude better than more polymers were developed. The results described in the previous two chapters will be put together as a peer-reviewed manuscript to be submitted in Spring 2018.\[^{63}\]
Chapter 5: Particle Size Analysis

The mechanical properties of the PETG – MoS$_2$ and WS$_2$, revealed an interesting trending. When reinforcing this matrix with the TMDs, ductility of the composite can be increased from $\approx 15\%$ strain to about $120\%$. Meaning that TMDs can improve up to 10 times the ductility of some materials when finding the right parameters. Particle size is an important parameter when talking about 2D materials. Depending on the particle size of the van de Waal material, some properties can be improved. For example, graphene that is a single layer of atoms improves their conductivity in such a way that can be consider a semi-metal. Therefore, a particle size experiment is proposed in order to find how different sonication times affect the particle size of our reinforcement materials.

Particle size measurements were conducted using the MicroTrac S3500 (Bluewave Model). The treated powder is dispersed in IPA for measurements to be conducted in the MicroTrac, where three lasers (two blue and one red laser) are focused onto the sample and a light scattering technique is used to compute the particulate size in the range of 0.02 to 2800 $\mu$m. The red laser scatters light from 0 to $60^\circ$ to acquire the scattered signal from the larger particles, while the blue lasers are responsive to smaller sized particulates in the sub-micron and nm-scale regime.

5.1 – Molybdenum Disulfide (MoS$_2$)

After subjecting the MoS$_2$ to ultrasonication, the particle size of MoS$_2$ ($S_{MoS2}$) shifted to the left as the sonication time $t_{sonic}$ increased, as shown by the data in Figure 5.1 (a), where $S_{MoS2}$ ($t_{sonic} = 30$ min.) $\sim 4.5$ $\mu$m. As sonication proceeded, multi-modal distributions were observed, such as bi-modal (2$^{nd}$ mode) and tri-modal (3$^{rd}$ mode) that are illustrated in the magnified plot in the inset of Figure 5.1 (a). Figure 5.1 (b) provides a quantitative measure of the 1$^{st}$, 2$^{nd}$, and 3$^{rd}$ modes as they appear for MoS$_2$ with increasing $t_{sonic}$. In the case of MoS$_2$, a bimodal distribution was observed for all $t_{sonic}$ considered up to 18 hours, while a trimodal distribution was evident at $t_{sonic} = 6$ hours, that later evolved into a bimodal for $t_{sonic} = 12$ hours. This suggests that as the powder is ultra-sonicated for a longer duration at the same power level, the tri-modal population
evolves toward a bi-modal distribution with a net reduction in $S_{MoS_2}$. The origin for the higher-order modes comes about due to a transition from the “coarse” regime toward the “fine” particle regime. Once the fragmentation proceeds to completion as a function of time, migration toward a single mode distribution may arise, unless other sonication parameters, such as power, or frequency are varied, which may provide an additional driving force for the propagation toward a lower $S$.

While $S$ was measured quantitatively using the dynamic optical light scattering technique, we also conducted direct physical characterization of the dispersions using SEM, as shown by the images in Figure 5.1 (c) i - iii. Here, we clearly see smaller particulates in the background on the Si substrate that were sonicated for 18 hours (Figure 5.1 (c) iii) when compared to the control sample, where $t_{sonic} = 0$ hr (Figure 5.1 (c) i) that depicts just a few large particles. Consequently, Raman Spectra (Spatial resolution of the Raman system was ~ 1µm) obtained for MoS$_2$ shown in Figure 5.1 (d) indicates a Raman Shift, $\Delta k = A_{1g} - E_{2g} = 22.85$ cm$^{-1}$ for samples where $t_{sonic} = 18$ hours, which is lower when compared to $\Delta k \sim 25 - 26$ cm$^{-1}$ for bulk MoS$_2$ or the control. This $\Delta k$ shift of ~ 22.85 cm$^{-1}$ is indicative of 2-3 layer thick platelets of MoS$_2$ for samples where $t_{sonic} = 18$ hours.
Figure 5.1 (a) Particle size distribution measured using the MicroTac for $t_{\text{sonic}} = 0$ min. (control), 30 min., 6 hr, 12 hr and 18 hr.; inset shows the peaks in the MoS$_2$ distribution at lower length scales. (b) Mean particle size $S_{\text{as}}$ as a function of $t_{\text{sonic}}$ showing the 1$^{\text{st}}$, 2$^{\text{nd}}$ and 3$^{\text{rd}}$ modes in the distribution function. (c) SEM micrographs showing a higher population of smaller particles in the background for samples where $t_{\text{sonic}} = 18$ hr (iii) compared to the control (i). (d) Raman Spectra.
5.2 – Tungsten Disulfide (WS₂)

Another sulfide TMDC, specifically WS₂, was analyzed to understand the impact of sonication on its structural and morphological character. The as-received WS₂ bulk powder exhibited $S_{WS₂} \sim 18.5$ µm, as shown by the data in Figure 5.2 (a). As sonication proceeded, the peak in the distribution shifted toward the left. For example, $1.0$ µm < $S_{WS₂}$ ($t_{sonic} = 30$ min.) < $2.3$ µm < $3.0$ µm but for $t_{sonic} > 30$ min. no further reduction in $S_{WS₂}$ was noted up to $t_{sonic} = 18$ hours, as observed in Figure 5.2 (b). A biomodal distribution for WS₂ was evident at $t_{sonic} = 12$ hours, as seen in Figure 5.2 (a) (inset) and Figure 5.2 (b). The separation between the 1st and 2nd modes was small ~ 2 µm, and this 2nd mode vanished after $t_{sonic} = 18$ hours. This suggests that even though $t_{sonic}$ increased, $S_{WS₂}$ remained within the same range even for $t_{sonic} = 12$ hours given the proximity of both modes at this sonication time.

The structural characteristics of WS₂ after sonication were analyzed using SEM, just as for MoS₂, and the data are shown in Figure 5.2 (c). Here, even after $t_{sonic} = 18$ hours, the characteristic 120-degree vortices of the hexagonal crystalline platelets were surprisingly still evident (Figure 5.2 (c) iii), as is the high density of finer particles in the background, as compared to the control in Figure 5.2 (c) i. The Raman shift for $t_{sonic} = 18$ hours was computed to be $\Delta k_{18hr} = 68.63$ cm⁻¹ as shown in Figure 5.2 (d), which was comparable to the Raman shift $\Delta k$ of the control, suggesting that the number of layers in the sonicated samples is still within the bulk regime (i.e. > 10 layers).
Figure 5.2 Characterization of treated WS\textsubscript{2} in (a) - (d). (a) Particle size distribution showing $S_{WS2} \sim 18.5$ $\mu$m for as received material and the inset shows the WS\textsubscript{2} particles over smaller length scales. (b) $S$ as a function of $t_{\text{sonic}}$ showing the 2nd mode occurring at $t_{\text{sonic}} = 12$ hr. (c) WS\textsubscript{2} SEM micrographs showing a higher population of smaller particles in the background for the longer $t_{\text{sonic}} = 18$ hr in (iii) compared to the control (i). (d) Raman Spectra.
5.3 – Graphite

For the as received graphite powder, $S_{\text{Graphite}}$ was measured to be $\sim 837 \, \mu\text{m}$, and the Extreme Value probability distribution function provided a good fit to the data. Despite the fact that the particulates in the graphite powder were considerably coarser than the TMDs, nonetheless, a shift to the left was seen in $S_{\text{Graphite}}$ as sonication time increased, where a reduction in particle size by $\sim 73\%$ was noted, i.e. $S_{\text{Graphite}}(t_{\text{sonic}} = 30 \, \text{min}) \sim 296 \, \mu\text{m}$, as seen in Figure 5.3 (a). From Figure 5.3 (b) and inset of Figure 5.3 (a), a bimodal distribution is also evident for $t_{\text{sonic}} = 30 \, \text{min}$ and 6 hours, and after $t_{\text{sonic}} > 12 \, \text{hours}$, a single mode distribution arises where $S_{\text{Graphite}} (t_{\text{sonic}} > 12 \, \text{hours}) \sim 5.5 \, \mu\text{m}$. In Figure 5.3 (c), SEM micrographs show the reduction in particle size with increasing sonication time (Figure 5.3 (c) ii - iii) when compared to the bulk (Figure 5.3 (c) i). The samples with $t_{\text{sonic}} = 18 \, \text{hours}$ exhibited an $S_{\text{Graphite}} \sim 3.89 \, \mu\text{m}$. Shown in Figure 5.3 (d) is the Raman spectra for graphite, where the well-defined D, G and 2D peaks occur at 1350 cm$^{-1}$, 1580 cm$^{-1}$ and 2700 cm$^{-1}$, respectively. The D band is attributed to the in-plane $A_{1g}$ zone-edge mode and can be used to monitor the defect distribution of graphite films by computing the D/G ratio.$^{[64]}$ The D/G ratio showed 0.987 for samples where $t_{\text{sonic}} = 18 \, \text{hours}$, compared to the bulk, as received material where the ratio was 0.870, which suggests that the defect distribution in the sonicated graphene dispersions has increased as expected by the exposed to sonication. Figure 5.3 (d) also reveals that the Raman intensity ratio $I_{2D}/I_G$ was $< 2$ which suggests that our dispersions comprise of multilayer graphene nanomembranes.
Figure 5.3 (a) Particle size distribution measured using the MicroTac for graphite; inset shows the peaks in the graphene distribution at lower length scales. (b) $S$ as a function of $t_{\text{sonic}}$ showing the 1st and 2nd modes in the distribution. (c) SEM micrographs showing a higher population of smaller particles in the background for the longer $t_{\text{sonic}} = 18$ hr in (iii) compared to the control in (i). (d) Raman spectra.
5.4 – Discussion

We now compare the quantitative outcomes of the fragmentation rate \( FR \), which is a measure of the particle size reduction with sonication time for all of the materials analyzed here, and the data are shown in Figure 2h. For the 2DLMs, the greatest particle size reduction or the highest \( FR \) generally occurred within the initial 30 min., after which point the \( FR \) varied less sensitively with time. The highest \( FR \) occurred for graphite powder where \( FR_{\text{Graphite}} \) was \( \sim -1176.4 \, \mu\text{m-hr}^{-1} \), and the \( FR_{\text{WS2}} \) and \( FR_{\text{MoS2}} \) were determined to be \( \sim -32.4 \, \mu\text{m-hr}^{-1} \) and \( -3.8 \, \mu\text{m-hr}^{-1} \), respectively. Despite the fact that the \( FR_{\text{MoS2}} \) was the lowest, the Raman analysis however clearly indicated that the ensuing platelets were 2-3 layers thick, and suggested that the sonication conditions used were effective in shearing the bulk material into few layer crystallites.
Chapter 6: Conclusions and Future Work

There is no doubt that van de Waals materials are currently in the spotlight. They have been used in gas filters membranes, in solar cells, flexible electronics, piezoelectric sensors, and transparent displays, among others. However, they have not been extensively used as reinforcement material in composites. Different allotropes of carbon, such as carbon nanotubes and carbon black have been used as reinforcement material in thermoplastic matrices. On the other hand, TMDs have not been taking into account in this regard, not even in their bulk state. Knowing that there is not much research on 3D printing polymer composites reinforced by 2D materials, this study gains significance because is one of the first ones, if not the first one, to combine MoS$_2$ and WS$_2$ with printable thermoplastics such as ABS and PETG. Interesting conclusions can be drawn from the different mechanical an electrical testing performed on the different composites.

From the mechanical characterization, it can be said that PETG – graphite series demonstrate better properties than ABS – graphite. PETG – graphite series had YS ($\approx 50$ MPa), UTS ($\approx 30$ MPa) and better ductility (strain to rupture $\approx 8\%$) than ABS counterparts. Also, MoS$_2$ had a more positive effect than WS$_2$ since the strength was retained while the ductility was increased at low loadings of the material. Even at high loadings (15 wt% and 20 wt%) the ductility was not lost as with additions of graphite powder or WS$_2$. On the other hand, with high additions of WS$_2$ (15 and 20 wt%) YM was increase, however ductility was completely lost since no plastic deformation occurred during the testing.

Moreover, filaments with graphite powder as reinforcement showed electrical conductivity making it possible to plan some experiments and provide information for new applications were this composite could be used. First, it was found that electrical properties of 50 wt% graphite – PETG composites were unaffected by annealing. Annealed and not annealed samples showed about the same electrical performance. Printing on top of PET substrate reduces the flexibility of the final product. During this experiment, resistors like structures were printed on top of PET sheets and they were not able to bend to a degree where the radius of curvature was 0.262 cm$^{-1}$.  

76
This might be because thickness is an important parameter when printing flexible electronics. The thicker the final outcome, the less flexible it becomes. The extra PET layer contributes to the overall thickness of the material. While at the same time the interface created with the composite and the PET substrate contributes to the flexibility of the material. Also, 3D printed complex resistor geometries showed better performances in terms of electrical conductivity and flexibility. In fact, this electrically conductive composite material shows a behavior known as no strain sensitivity. In other words, the current flowing through the material does not change during bending. Furthermore, due to all these features, this material can be used as some sort of biocompatible device that has to produce the same output independently of the degree of bending/movement. These findings provide new possible application for van der Waals materials in composites. More research is still needed since there is a lot more to find on this type of composites that can be implemented by the additive manufacturing industries. This is just a study that opens up the field were these composites could be used, since it shows some biocompatibility while exhibiting electrical conductivity and flexibility.

Lastly, a clear trend was seen with the 2DLMs, which showed the greatest FR within the first 30 min. of sonication. For the 2DLMs, the $F_{R_{\text{Graphite}}}$ was $\sim -1176.4 \, \mu m\, hr^{-1}$, and the $F_{R_{\text{WS2}}}$ and $F_{R_{\text{MoS2}}}$ were determined to be $\sim -32.4 \, \mu m\cdot hr^{-1}$ and $-3.8 \, \mu m\cdot hr^{-1}$ respectively. Despite the fact that the $F_{R_{\text{MoS2}}}$ was the lowest, the Raman analysis however clearly indicated that the ensuing platelets were 2-3 layers thick, and suggested that the sonication conditions used were effective in shearing the bulk material into few layer crystallites.

The following is proposed for future work which include: (a) Mechanical testing of ABS – MoS$_2$ and WS$_2$ series, (b) Printing capacitor like structures and perform capacitance measurements, (c) Differential Scanning Calorimetry on dog bon samples, (d) Nano indentation on fractured tensile samples, (e) SEM of tensile fracture surfaces, (f) Print composite samples with recycled plastic bottles (PET), and (g) Reduce particle size of MoS$_2$ and WS$_2$. 

77
References


Appendix: Procedure for 3D Printing

1.0 Setting up printer: Follow manufacturer instructions for assembling machine

2.0 Setting up software on computer: Go to the Lulzbot website and download the appropriate CURA software for computer.

3.0 Make or obtain the .STL or .OBJ file of the piece(s) to be 3D printed.

4.0 Plug in printer and turn on. Also turn on computer.

5.0 Open the CURA software on the computer and change settings by clicking the ‘Expert’ tab on the header bar and click on ‘Switch to full settings’.

6.0 Click the ‘Load Model’ button and select the .STL/.OBJ file. Make sure printer is connected by computer through USB cable.

7.0 Select the ‘Control’ button and input printing temperature of cleaning filament of choice in the Pronterface window opened. Make sure the temperature is ‘set’.

8.0 Wait until input temperature is reached then load the filament into printer head. Click the Extrude 10 button until the extruded material coming out form the nozzle matches the color of the cleaning filament.

9.0 Remove extruded material with tweezers and remove cleaning filament from the head. Close Pronterface window.

10.0 Move the piece around the printing bed plate in the software as desired. Make any changes (rotation, orientation, etc.) ensuring that the piece will print based on its orientation.

11.0 Measure the diameter of filament to be used for printing using a caliper. Input diameter (mm) under the ‘Basic’ settings. Define the Printing temperature (°C) as well as Bed temperature (°C) for the chosen material under the same ‘Basic’ settings.

12.0 Check the other settings and make any changes as needed.desired. Make sure to set the ‘Skirt’ line number under Expert Settings and set it at least equal to 4.

13.0 Prep the bed (if needed) based on the chosen filament.

14.0 Reopen Pronterface window and click the ‘Print’ button.

15.0 See the initial nozzle cleaning/bed leveling sequence and wait until the printer finishes sequence and reaches desired temperatures so it starts printing.

16.0 Once the printer starts, make sure the piece starts printing properly. Any changes (such as nozzle or bed temperature, flow, etc.) can be adjusted through LCD.
17.0 If print starts printing properly, let it run its course. Otherwise, press the ‘Cancel’ button located in Pronterface and ‘Print’ again.

18.0 When the piece finishes printing, wait for the cooling sequence to happen. The bed will move to the back of the printer.

19.0 Once the cooling sequence is complete, the plate will come forward. The piece is ready to be removed.

20.0 Using the knife that came with the printer, carefully remove the skirt printed around the object.

21.0 Utilizing the same knife, carefully start lifting the corners of the printed piece until it becomes lose and is removed.

22.0 Clean the bed with a tissue and water or with a wipe of isopropyl alcohol.

23.0 Print again, or turn off all equipment.
Vita

Jorge Alfredo Catalan Gonzalez was born and raised in Ciudad Juarez, Chihuahua, Mexico. He attended to Instituto Tecnologico de Estudios Superiores de Monterrey (ITESM) high school, where he graduated with a 99 out of 100 GPA. After that, he enrolled in University of Texas at El Paso (UTEP) in Fall 2010 to pursue a Bachelor of Science in Metallurgical and Materials Engineering. At UTEP, many doors were open to him when Dr. John McClure recommended him to work in Dr. Zubia’s NanoMIL Lab. In summer of 2013, he was accepted at UC Berkeley to work during the summer under Dr. Tsu Jae King Liu’s Lab. There he had the opportunity to learn about Metal Oxide Resistive Switching Memory. In summer 2014, he got accepted at Stanford University for another summer research experience. This time, he joined Dr. Robert Sinclair’s Lab, which specializes on Transmission Electron Microscopy (TEM). There he learned different TEM sample preparation methods (tripod polishing and FIB methods).

In Spring 2016, he enrolled for a master of science (M.S.) in metallurgy and materials engineering at UTEP. Now, under Dr. Kaul’s tutelage he has contributed significantly to advancing research in composites of 2D materials, this has resulted in his work being showcased at various international conferences. These include: American Vacuum Society Conference at Nashville, Tennessee, and Materials Research Society Conference held at Phoenix, Arizona. Also, two manuscripts will be submitted for peer review shortly.

Contact Information: jacatalan18@gmail.com