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Synthesis of Electrically Conductive Polylactic Acid Composites for 3D Printing

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Synthesis of Electrically Conductive Polylactic Acid Composites for 3D Printing

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Synthesis of Electrically Conductive Polylactic Acid Composites for 3D Printing

Abstract

3D printing technology is a process of synthesizing an object by slicing a three-dimensional object into two-dimensional layers. It is making its mark as it reshapes product development and manufacturing industry in which everyone can participate in the process of 3D printing.The demand for various types of materials is increasing as customers become more innovative with designs. The overarching goal of this project was to create innovative 3D printing materials for a conventional 3D printer. Conductive filaments allow us to 3D print electrically conductive components using almost any commercially available desktop 3D printer. The electrically conductive filament for this research was made with carbon black and clear polylactic acid (PLA) pellets. Two different experimental methods were carried out to produce electrically conductive filaments. The first method involved a heating treatment of PLA pellets whereas the second method included a plasticizer to ease the process. Resistance measurements were taken for samples produced with both methods. The resistance increased as the length of the sample increased while the width was held constant. The resistance measurements were inconsistent which may be due to the non-uniform surface. The surface and cross sections of a 3wt% sample were studied under scanning electron microscope (SEM) machine. Certain features of the composite as well as the thermoplastic were observed with the SEM images.

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Introduction

1.1 Introduction to 3D Printing Technology

Additive manufacturing technology, more widely known as 3D printing technology, is a method of creating an object by slicing a three-dimensional object into two-dimensional layers. Objects are fabricated in a bottom-up, additive fashion directly from digital designs. The material is deposited in successive, thin layers on top of each other to build up a solid

3D object[1], similar to building a house by putting bricks onto each other. As 3D printing technology become more accessible, a wider range of materials can be printed on a desktop 3D printer.

The demand for various types of materials is increasing as customers become more innovative with designs. This uptake in usage has been coupled with a demand for printing technology and materials able to print functional elements. This senior project focused on the formulation of electrically conductive polylactic acid (PLA) composite. The conductive thermoplastic composite can be used to produce custom sensing devices and user interface devices along with printed object with embedded sensing capability. Compare to other conductive materials such as metals, this composite is lightweight and easy to manufacture. It has resistance to corrosion, and the ability to be readily adapted to the needs of a specific application. With engineers, designers and artists wishing to create ever more complex and high-tech products using 3D printing technology, this research can help develop low-cost and functional materials.

1.2 Project Objectives

The overarching goal of this research project is to create innovative composites for a conventional 3D printer and observe the properties of the composite. Since the demand for conductive resins is still growing, further research is needed to keep pace and to meet the needs of new, high-tech applications. By combining electrically conductive carbon with light weight plastics, composites can be formed to provide the electrical properties necessary for various electronic components. Conductive PLA filaments allow us to 3D print electrically conductive components using almost any commercially available desktop 3D printers

such as Makerbot. This type of machine works on the simple principle of extruding a thin filament of molten thermoplastic from a feedstock of larger filament through a heated nozzle onto a room temperature or heated build platform. The printed filament network cools and adheres to the previously deposited layers to build up a solid 3D object. In the process, external supports may be printed for overhanging features and can be mechanically removed upon completion of the parts[2]. Polymers such as PLA are typically electrical insulators whereas carbon particles are electrical conductors. The electrical conductivity of polymers can be increased by adding carbon fillers such as carbon fibers, carbon black or graphite[3].

1.3 Literature Research

1.3.1 Fabrication and Characterization of Poly(lactic acid)/ Acetyl Tributyl Citrate/ Carbon Black as Conductive Polymer Composites[4]

A paper by students in Tianjin University utilized acetyl tributyl citrate (ATBC) as a plasticizer of PLA and carbon black. As stated in the paper, with the increasing of carbon black content, the glass transition temperature increases but the elongation at break decreased. The results demonstrated the mechanical properties, dynamic mechanical thermal analysis and most importantly, the electrical conductivity of the composite. The plasticizer can improve the interaction between the PLA matrix and carbon black particles based on the mechanical response. The strong interaction and the low processing viscosity are propitious to decrease the size of carbon black agglomerates when the plasticizer is added. The appropriate carbon black agglomerates are developed to contact together and form random networks. Therefore, the plasticizer can decrease the percolation threshold of carbon black.

The introduction of carbon black can improve the glass transition temperature of the composites, but the reverse for the plastic.

1.3.2 Multiple Melting Behavior of Polylactic Acid Filled with Modified Carbon Black[5]

Modified carbon black composites were compared to carbon black composites in a paper[5]. A new technique was developed to modify the surface of CB with a low molecular weight compound by in situ reaction[6]. Results indicate that organic small molecules were grafted onto the surface of carbon black. As a result, the size of the modified carbon black particles was much smaller than nontreated ones. Moreover, the modified carbon black could be dispersed in polymers or organic solvents in a stable and uniform manner. Both modified carbon black and carbon black could significantly accelerate crystallization rate of semicrystalline polymers. Compared with carbon black, modified carbon black was dispersed in PLA more uniformly and with smaller particle size. Carbon black and modified carbon black not only affected the crystal behavior of PLA in a significant manner but also have a strong effect on melting behavior.

1.4 Project Materials

1.4.1 Polylactic Acid

For this project, PLA is used since it is produced via polymerization of renewable products and deserves particular attention in the area of environmentally degradable polymer materials. The worldwide capacity of bio-based plastics, according to company announcements, is increasing dramatically[7]. One of the outstanding achievements in the realm of polymers

from renewable resources is undoubtedly the rapid progress related to the research and development activities for the production of PLA. The molecular structure of PLA is displayed in figure 1.

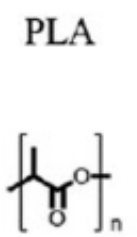

Figure 1.1: Molecular structure of PLA

1.4.2 Carbon Black

Electrically conductivity measures the ability of a material to conduct an electric current. Conductive ink can be made using graphite. Graphite is easy to obtain and mix well with paint[8]. Electrically conductive ink and paint are widely available on the market. It is relatively easy to make inexpensive electrical conductive ink. Conductive polymer composites can be obtained by filling a polymer matrix with electrically conductive particles such as carbon black, carbon nanotubes, graphite and metal powder. Conductive carbon black can be used to produce the electrically conductive filament with thermoplastics. This filament can be used to create capacitive sensors and electrically conductive circuitry.

In general, conductive carbon black products are composed of elongated aggregates which have a particle size of about 30nm. Traditionally, carbon black has been used as a pigment in black ink, as well as for toners in copy machines and printers. The carbon black

used in this project is provided by Cabot Corporation[9] since the recommended use of this material is additive or filler for plastic and rubber.

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Experimental Procedure

Safety concerns were especially considered regarding the level of hazardous of carbon black. The material, carbon black, should not be heated to above 300°C. Otherwise, it may release hazardous products of combustion which include carbon monoxide, carbon dioxide, oxides of sulfur, and organic products. The substance may also cause mechanical irritation with eye or skin contact. Therefore, a small fraction of the carbon black sample received was

transferred from the plastic container to a sealed glass container which was placed in the fume hood. PLA pellets were kept dry in a separate plastic container.

Two experimental methods were carried out to produce electrically conductive filaments. The first method was a physics procedure that involved heating up the PLA pellets, adding carbon black and then stirring thoroughly until two substances were well mixed. The other method was a chemistry method which included a plasticizer, dichloromethane, to dissolve the PLA pellets.

2.1 Method 1

With the heating method, 1 gram of PLA pellets (figure 2.1) was measured with a balance and heated until the pellets were visually melted. The temperature reached the glass transition temperature, at around 80°C for the thermoplastic to change from a hard and stiff glass-like solid to a soft and flexible elastomeric rubber. Then 1wt%, 2wt%, 3wt% and 4wt% of carbon black (figure 2.2) were added to the matrix separately. The mix was then stirred thoroughly with a mechanical Teflon stir provided by Prof. Hagerman until the two substances were uniformly mixed. Lastly, the sample was set aside and cooled down to room temperature before further use. The thermoplastic should be prevented from overheating. Otherwise, carbon black fillers would no longer mix with PLA.

The following containers were used in sequence during the experiments to contain the PLA pellets: glass beaker (figure 2.3), silicone gel container (figure 2.4) and Teflon beaker.

Using a regular glass beaker with or without tape, thermoplastic adhered to the bottom of glass after cooling. The beaker was broken with a hammer in order to take out the sample. A silicone container seemed to work well with thermoplastic but had a low thermal

Figure 2.1: 1 gram of PLA pellets was measured with a balance

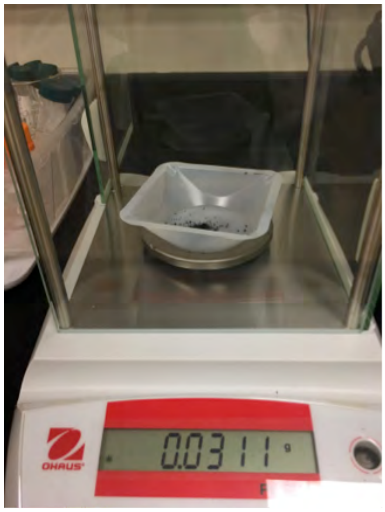

Figure 2.2: 3wt% of carbon black was measured with a balance

conductivity. As a result, the PLA pellets took a longer time to heat up. A few samples were successfully synthesized using the silicone container. A Teflon beaker with carbon base was purchased with Student Research Grant (SRG). A fraction of the synthesized sample was adhered to the bottom of the Teflon beaker after cooling. Therefore, silicone containers were the optimized material for keeping PLA separated from the bottom of the container after the heat treatment.

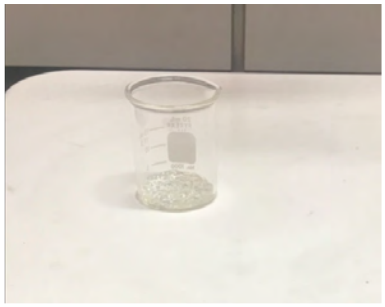

Figure 2.3: 1 gram of PLA pellets was being heated up in a glass beaker

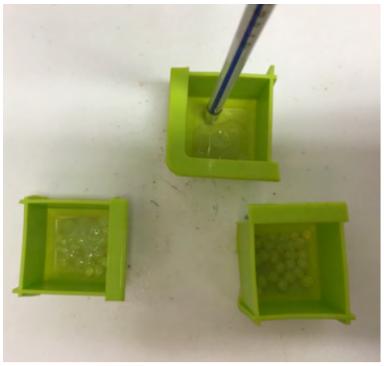

Figure 2.4: 3 separate samples of 1 gram of PLA pellets were being heated up with silicone containers. A thermometer was placed to measure the temperature of the pellets

2.2 Method 2

The second synthesis involved a plasticizer, dichloromethane, to promote mixing of PLA and carbon black. Dichloromethane is usually used as a solvent due to its volatility and ability to dissolve a wide range of organic compounds[10]. The purpose of the plasticizer was to break the bond between the matrix and the filler, and trigger the formation of the composite. 3g of the thermoplastic was added to a stirred suspension of conductive carbon black in 40ml of dichloromethane. Stirring was continued for one hour as shown in figure 2.5. After stirring the suspension was poured onto a watch glass and dichloromethane was allowed to evaporate in a fume hood for 1 hour as shown in figure 2.6. The resultant composite film was placed in a water bath at 80°C for 1 minute then removed. The filament was then left to cool for 2 hours before further use[2].

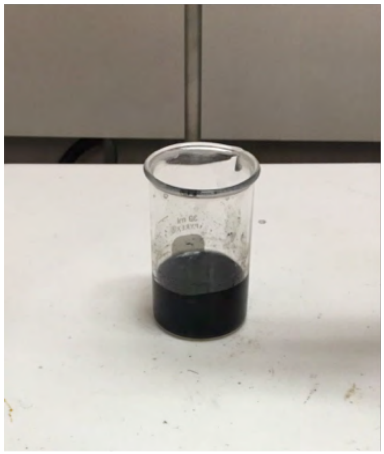

Figure 2.5: 1 gram of PLA pellets and 3wt% of carbon black were mixed in a glass beaker with dichloromethane

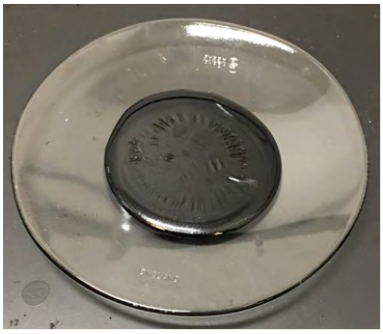

Figure 2.6: The mixed sample was then placed onto a glass watch to let dichloromethane evaporate

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Results and Discussion

3.1 Synthesized Samples

An increasing amount of carbon black was added to the PLA matrix with the first method from owt% to 4wt%. 3wt% and 4wt% of carbon black were added to the PLA matrix using the second method. Resistivity was then measured for each sample with a multi-meter (figure 3.1).

Figure 3.1: Resistivity measured with a multi-meter

Figure 3.1 to figure 3.10 are the composite samples of PLA synthesized using the first method with 0wt% carbon black (figure 3.1 and 3.2), 1wt% carbon black (figure 3.3 and 3.4), 2wt% carbon black (figure 3.5 and 3.6) and 3wt% carbon black (figure 3.7, 3.8, 3.9, 3.10). Each sample size was around 1.8cm. The sample in figure 5a experienced a lower temperature change than that in figure 5b. As shown in figure 3.1 and 3.2, a higher temperature resulted in a better mix. With 1wt% of carbon black, as shown in figure 3.3 and 3.4, some clear PLA were still visible on the bottom of the sample. This indicates that more an uneven mix and that more carbon black could be added. Figure 3.5 and 3.6 demonstrates an even mix of carbon black and PLA when 2wt% of carbon black was added. More carbon black was added to increase the conductivity of the sample. In figure 3.7 and 3.8, the 3wt% carbon black sam-

ple shows a uniform mix. However, the resulted composite broke into two pieces. This could possibly be the result of a decrease in ductility. This speculation could be proved with the 4wt% sample, as shown in figure 3.9 and 3.10, which broke into three pieces when it was removed from the container.

Since a very small fraction of carbon black particles was left on the bottom of the silicone container and did not mix with the thermoplastic matrix when 4wt% of carbon black was added, it was assumed that the matrix was saturated with carbon black filler. Therefore, the maximum amount of carbon black filler added for this research project was 4wt%. Note that due to this phenomenon, the actual amount of carbon black filler mixed with PLA was between 3wt% and 4wt%.

The bottom of all samples synthesized with method one seemed to have a dull but smooth surface whereas the top tended to be glossy and bumpy. This indicates that more carbon black particles set on the bottom of the container during synthesis.

Figure 3.2: Top of a 1g clear PLA sample after heat treatment

Figure 3.3: Top of a 1g clear PLA sample with a higher temperature heat treatment comparing to sample 1

Figure 3.4: Top of a 1g PLA sample with 1wt% carbon black, synthesized with method 1

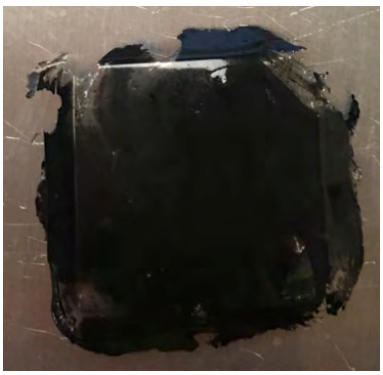

Figure 3.5: Bottom of a 1g PLA sample with 1wt% carbon black, synthesized with method 1

Figure 3.6: Top of a 1g PLA sample with 2wt% carbon black, synthesized with method 1

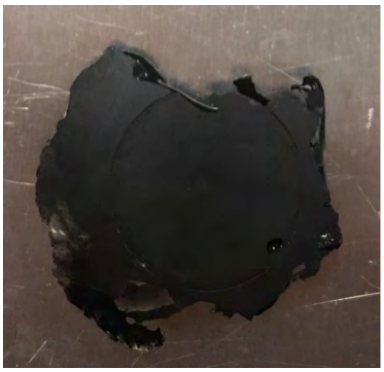

Figure 3.7: Bottom of a 1g PLA sample with 2wt% carbon black, synthesized with method 1

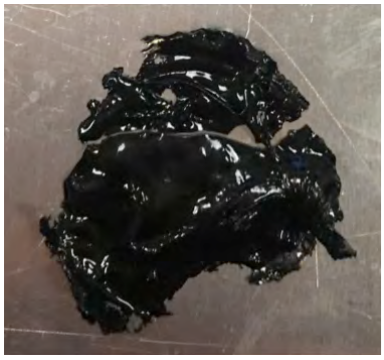

Figure 3.8: Top of a 1g PLA sample with 3wt% carbon black, synthesized with method 1

Figure 3.9: Bottom of a 1g PLA sample with 3wt% carbon black, synthesized with method 1

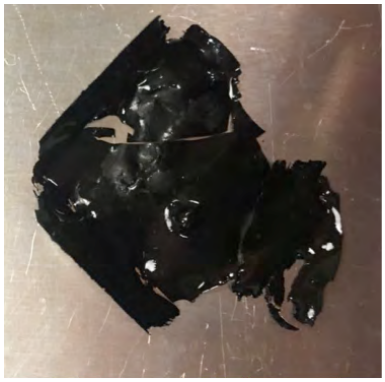

Figure 3.10: Top of a 1g PLA sample with 4wt% carbon black, synthesized with method 1

Figure 3.11: Bottom of a 1g PLA sample with 4wt% carbon black, synthesized with method 1

3.2 Resistance Measurements

Electrical resistivity measures how strongly a given material opposes the flow of electric current whereas electrical conductivity is the reciprocal of electrical resistivity and measures a material's ability to conduct an electric current[11]. Resistance was measured to observe the resistivity of the composite using the following. The resistivity can be predicted by using measured resistance multiplied by the cross-sectional area of the sample divided by the length of the sample.

$$\varrho = R \times \frac{A}{L}$$

where ϱ is the resistivity of a material, R is the resistance, A is the cross-sectional area and L is the length of the measured sample.

Resistivity was measured for all samples synthesized using both methods mentioned in section 2.1 and 2.2.

3.2.1 Method 1

As shown in figure 3.13. the resistance increases with an increase of length of the fragment of a 4wt% carbon black sample. The range of the resistance is from 15 kΩ to 194.5 kΩ.

Conductivity models account for filler volume fraction, constituent conductivity, compatibility of the filler and matrix, filler aspect ratio and properties of the composite structure such as filler orientation. 1wt% and 2wt% samples did not show resistivity measurements. According to the PH.D. thesis by Clingerman[3], at lower filler loadings, the conductivity of the composite is still very close to that of pure polymer matrix. When enough filler was added to the polymer matrix where the percolation threshold was reached, the filler

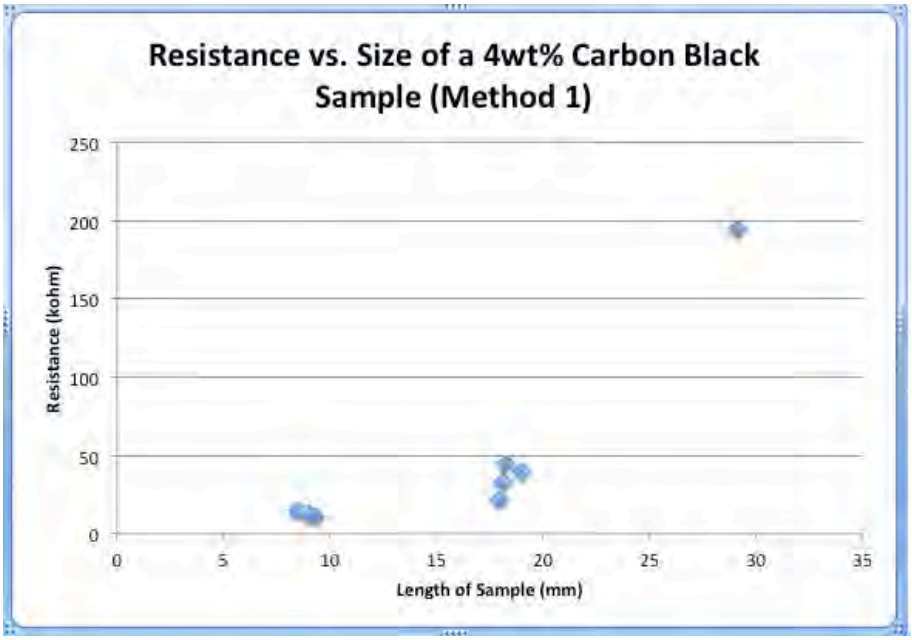

Figure 3.12: The resistivity measurements of a 4wt% carbon black sample, synthesized using method 1

began to form a continuous path through the matrix. Once the volume fraction reaches a certain point, the conductivity begins to increase much slower until the material is saturated with filler.

3.2.2 Method 2

The resistance of a 3wt% carbon black sample was 2634 kΩ and that of a 4wt% carbon black sample was 1987 kΩ. The resistance measurements of the samples with method two were larger than those with method one by one magnitude. Therefore, the first method resulted a better conductivity of the composites due to the samples' lower conductivity.

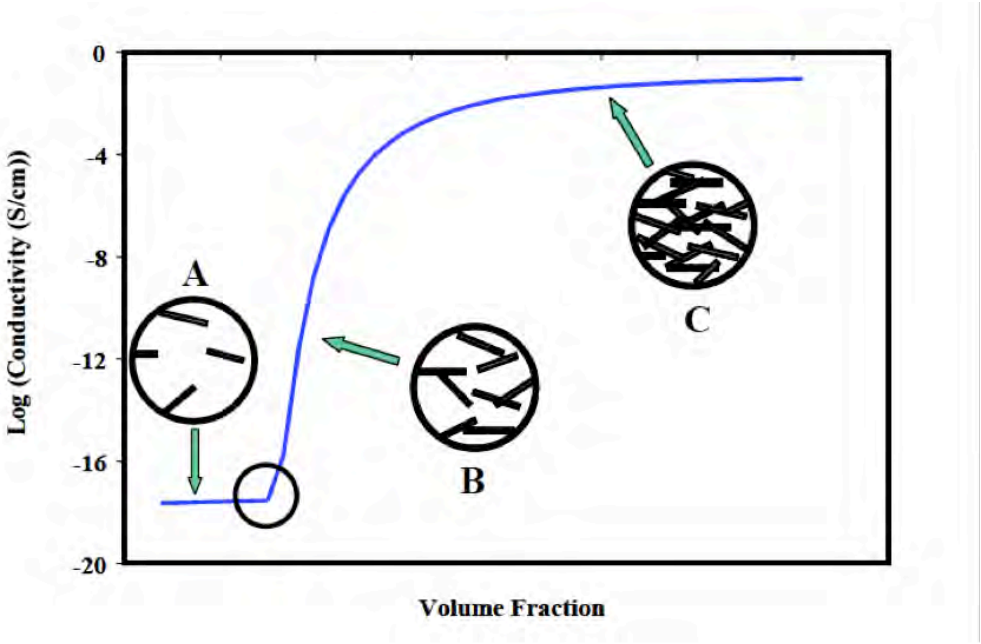

Figure 3.13: Dependence of Electrical Conductivity on Filler Volume Fraction [3]

3.3 Scanning Electron Microscope Imaging

Figure 3.13 shows an SEM image of two pieces of a 3wt% carbon black sample with a crack. The image suggest a uniformly mixed region on the top left side in which carbon black particles are well-embedded in the thermoplastic matrix. This conclusion could be confirmed by the SEM images published by Su, shown in figure 3.14. The other regions with a unsmooth surface in figure possibly suggests the crystallization of PLA.

PLA appears to form in layers during the heat treatment. As shown in figure 3.16, the cross sections of the two broken pieces demonstrate layer characteristics of the composite. In figure 3.17, a layer formation can be found in the left side. Figure 3.18 shows the strand caused by the shear stress of the breaking action. This reflects the feature that PLA is linear polymers which are one-dimensional chains.

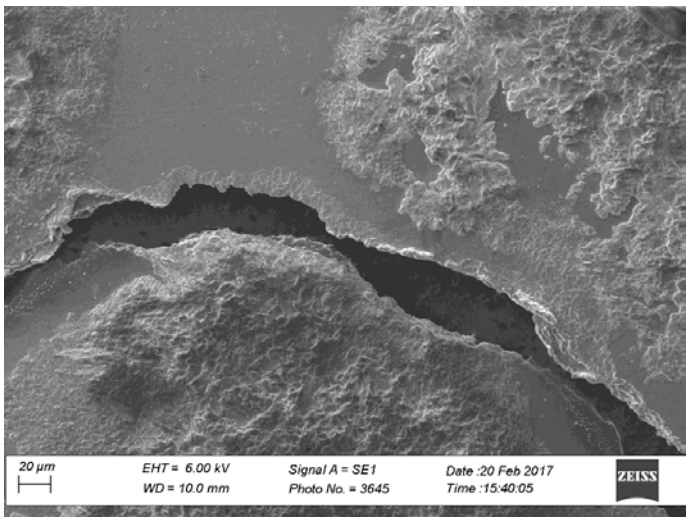

Figure 3.14: an SEM image of the bottom surface and cracks of two broken pieces of a 3wt% carbon black sample

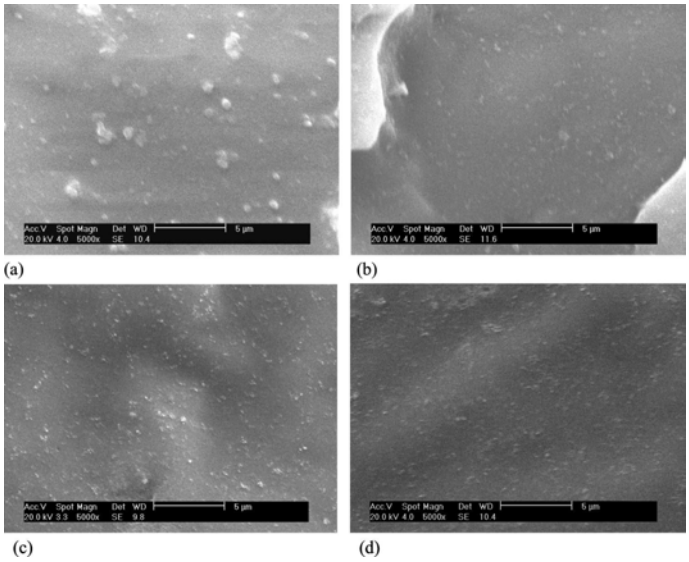

Figure 3.15: SEM micrographs of cryofractured PLA/ATBC/CB composites: (a) PLA/ATBC (100/0) with 1.39 vol % CB, (b) PLA/ATBC (100/10) with 2.46 vol % CB, (c) PLA/ATBC (100/20) with 1.2 vol % CB, and (d) PLA/ATBC (100/30) with 2.03 vol % CB.[12]

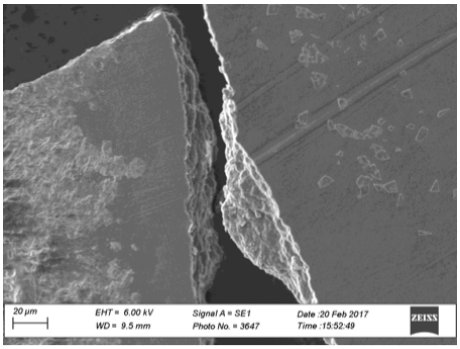

Figure 3.16: an SEM image of the cross sections of two broken pieces of a 3wt% carbon black sample

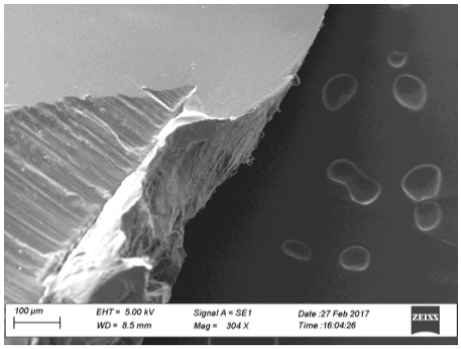

Figure 3.17: an SEM image of the cross section of a broken piece indicating the layer feature of PLA

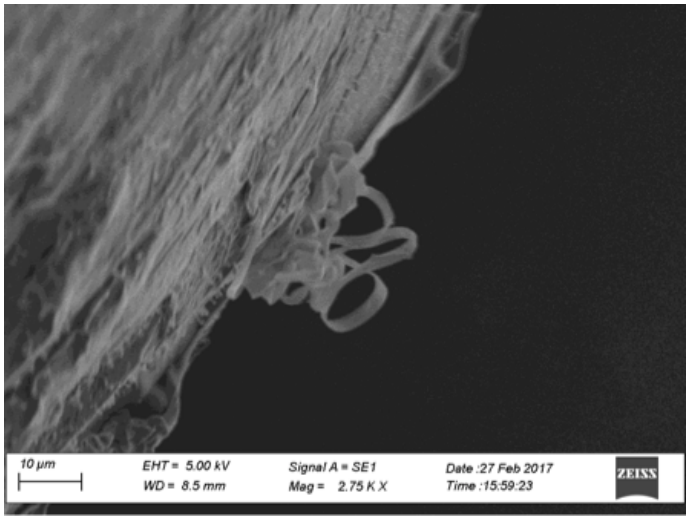

Figure 3.18: an SEM image of the cross section of the 3wt% carbon black sample indicating the chain characteristics of PLA

4

Project Timeline

4.1 Fall Term Review

In the fall term of 2016, during week one and two, two ideas were proposed for this project. The first one was to explore multicolor 3D printing for different materials. This idea focused on the possibilities of integrating color into various printing materials such as PLA and resin. The capability of printing gradients consisting of both different materials and

colors would be investigated. Then the mechanical properties affected by adding pigments would be identified. The characteristics of the polymers at a nano-scale would be analyzed and applications of the materials would be studied. The other idea was to explore innovative filaments with diverse functions. Multiple types of possible filaments were proposed such as thermochromic filaments, electrically conductive filament, flexible filament and liquid-based filament. The types of filament were then reduced to thermochromic filament and electrically conductive filament.

The idea was then decided in the third week to be creating electrically conductive and thermochromic PLA filaments. Background research was conducted from week 3 to around week 7. A number of meetings were held with Amanda Ervin in the 3D printing lab at Union College to discuss the types of filaments that were present on the market. The 3D printing lab currently owns a roll of electrically conductive PLA filament that was purchased with a price of around 65 dollars.

Meetings were held weekly with Professor Hagerman in the chemistry department to discuss research findings and possible methods of performing the procedure for creating electrically conductive filament. Various resources of vendors were found for purchasing the chemicals and materials based on the information provided by published papers. A detailed budget was proposed indicating the companies, price and the amount needed for the chemicals and materials. In order to be familiar with the lab equipment, assistance was given to a student who performed the synthesis of conductive carbon black aerogel in the chemistry lab. A 2 lbs of carbon black sample was received at the end of the fall term. An oral presentation was carried out and a Student Research Grant proposal was written.

4.2 Winter Term Review

The synthesis of conductive filaments was carried out in Professor Cortez's lab throughout the term in the winter term of 2017 to optimize the electrical conductivity of the conductive filament.

The resistance of the composite was tested using a voltmeter with current running through after each sample was successfully synthesized. According to the resistance measurements of the tests, modifications on the portion of the additives was adjusted. SEM images were taken by professor Hagerman in the imaging lab at Union College later in the term. The synthesis of thermochromic filament was postponed since the dye found on Sigma-Aldrich was relatively expensive. The amount of dye required for the synthesis process would result in an expensive cost that reaches the budget limit for this research.

An elevator pitch presentation was carried out and a formal report was written at the end of the term.

Note that this project was advised by Professor Cortez in the mechanical engineering department and co-advised by Professor Hagerman in the chemistry department.

5

Conclusion

Conductive polymer composites can be obtained by filling polymer matrices with electrically conductive particles. This composite has a wide variety of potential applications as biodegradable polymer becomes more widely used in the 3D printing industry and innovative filaments are needed for designers and engineers. The overarching goal of this project was to create innovative 3D printing materials for a conventional 3D printer. The electri-

cally conductive filament was made with carbon black and clear polylactic acid (PLA) pellets.

Literature research was done to prepare necessary materials for experiments and design methods for synthesis. Experiments were carried out later to synthesize conductive PLA filament.

Two experimental methods were carried out to produce electrically conductive filaments. The first method was to heat up PLA until the pellets become fluid-like. Then varying weight percent of carbon black was added a certain weight percent of carbon black to the matrix and then stir until the two substances were uniformly mixed. The second synthesis involved a plasticizer, dichloromethane, to promote mixing of PLA and carbon black. The plasticizer's purpose is to break the bond between the matrix and the filler, and triggers the formation of the composite. The sample was stirred for an hour then set on a watch glass for an additional hour to allow dichloromethane to evaporate. The sample was then placed in a water bath for one minute in order to separate the mixed filament from the watch glass.

The resistivity of each sample was measured with a multi-meter. For the first method, no resistivity reading was measured with 1wt% and 2wt% of carbon black. Resistivity varies depending on the distance between two probes and the location of probes. The samples from both methods were observed using the scanning electron microscope. The images indicated interesting features of the conductive composite.

In the future, more accurate conductivity or resistivity of the samples can be measured using a better machine or device. Graphite can potentially be used as the filler due to its higher conductivity comparing to carbon black.

References

[1] 3d printing, Mar 2017.

[2] Simon J. Leigh, Robert J. Bradley, Christopher P. Purssell, Duncan R. Billson, and David A. Hutchins. A simple, low-cost conductive composite material for 3d printing of electronic sensors. *PLOS ONE*, 7(11):1–6, 11 2012.

[3] Matthew Lee Clingerman. *Development and modelling of electrically conductive composite materials*. PhD thesis, Michigan Technological University, 2001.

[4] Jiugao Yu, Ning Wang, and Xiaofei Ma. Fabrication and characterization of poly(lactic acid)/acetyl tributyl citrate/carbon black as conductive polymer composites. *Biomacromolecules*, 9(3):1050–1057, 2008. PMID: 18290627.

[5] Zhizhong Su, Qiuying Li, Yongjun Liu, Guo-Hua Hu, and Chifei Wu. Multiple melting behavior of poly(lactic acid) filled with modified carbon black. *Journal of Polymer Science Part B: Polymer Physics*, 47(20):1971–1980, 2009.

[6] Jing Chen, Xianhui Li, and Chifei Wu. Crystallization behavior of polypropylene filled with modified carbon black. *Polymer journal*, 39(7):722, 2007.

[7] Serge Bourbigot, Gaëlle Fontaine, Antoine Gallos, and Severine Bellayer. Reactive extrusion of pla and of pla/carbon nanotubes nanocomposite: processing, characterization and flame retardancy. *Polymers for Advanced Technologies*, 22(1):30–37, 2011.

[8] Icecats. Paper electronics: Conductive paints, inks, and more, May 2016.

[9] SDS This. Safety data sheet. *Magnesium*, 102783:51–7, 2015.

[10] Dichloromethane, Mar 2017.

[11] Electrical resistivity and conductivity, Mar 2017.

[12] Jiugao Yu, Ning Wang, and Xiaofei Ma. Fabrication and characterization of poly (lactic acid)/acetyl tributyl citrate/carbon black as conductive polymer composites. *Biomacromolecules*, 9(3):1050–1057, 2008.

A
Additional SEM Images

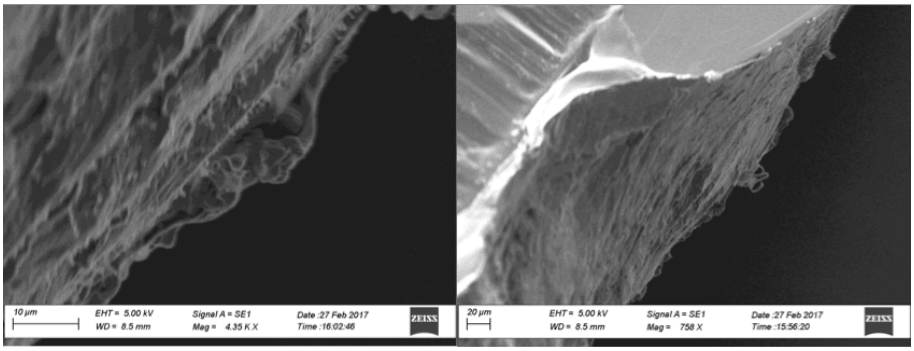

Figure A.1: Additional SEM Images

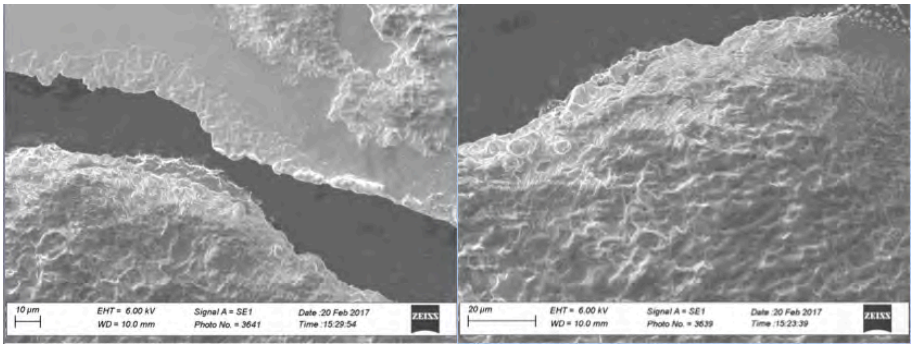

Figure A.2: Additional SEM Images

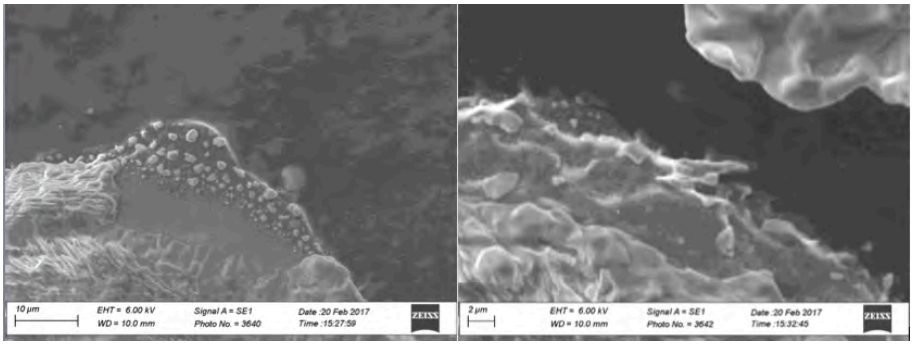

Figure A.3: Additional SEM Images

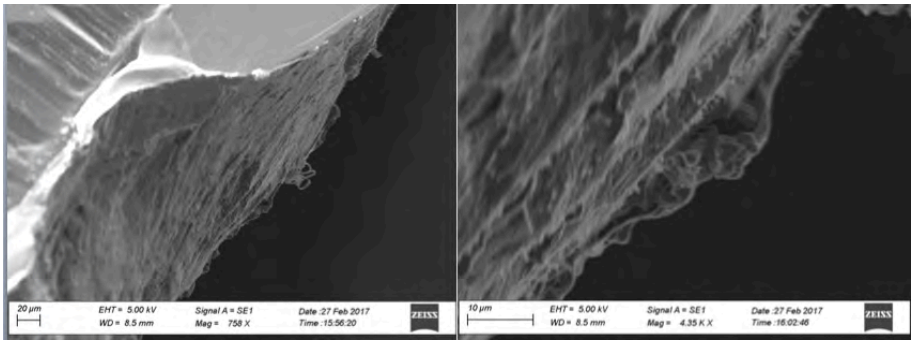

Figure A.4: Additional SEM Images