ADDITIVE MANUFACTURING OF POLYSULFONE AND POLYANILINE COMPOSITES
BY SOLVENT-CAST 3D PRINTING

ZIYI MIAO
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Reviewed and approved* by the following:

Michael Hickner
Associate Professor of Materials Science and Engineering, Chemical Engineering
Thesis Supervisor

Joan Redwing
Professor of Materials Science and Engineering, Chemical Engineering and Electrical Engineering
Honors Adviser

* Signatures are on file in the Schreyer Honors College.
ABSTRACT

3D printing or additive manufacturing is a technique used to synthesize a shape by adding layers of material on top of each other in a sequential manner. This process is most popularly accomplished with thermoplastics, which can be melted and extruded. The melting of a thin bead of polymer is commonly called fused deposition. There are some limitations to fused deposition however, such as high melting point of the desired material and thus the high temperatures needed during extrusion, or thermal degradation of the material during high temperature processing. In this case, melt processing is not the best choice, requiring a lot more energy or changing the properties of the polymer all together. One way around this problem is to use solvents instead of heat to turn the polymer into a liquid or ink, and extrude this ink in layers to create a 3D object. This way, no heating is applied, and after the solvent evaporates, the object hardens. Udel Polysulfone (PSU) is a thermoplastic that is tough and stable, but has a high glass transition temperature of 185-190 °C [1], and even higher processing temperature. Using the solvent-cast 3D printing technique, this polymer was 3D printed at room temperature. Polyaniline (PANI) is an intrinsically conductive polymer that has different oxidation states depending on the pH, but thermally degrades before melting. This polymer was also 3D printed as a composite material with polysulfone.
# TABLE OF CONTENTS

LIST OF FIGURES .................................................................................. iii

LIST OF TABLES .................................................................................... iv

Chapter 1 ............................................................................................... 1

1.1 Introduction ..................................................................................... 1
1.2 Hildebrand and Hansen Solubility ..................................................... 2
  1.2.1 Hildebrand Solubility Parameters .............................................. 3
  1.2.2 Hansen Solubility Parameters ................................................... 5
1.3 Considerations ................................................................................... 9
  1.3.1 Economic .................................................................................... 9
  1.3.2 Environmental .......................................................................... 9
  1.3.3 Sustainability ........................................................................... 10
  1.3.4 Health and Safety .................................................................... 10

Chapter 2 Experimental Procedures ....................................................... 11

2.1 Preparation of Polysulfone Inks ......................................................... 11
2.2 Preparation of Polyaniline Inks ......................................................... 13
2.3 Evaluation of Inks ........................................................................... 14
2.4 3D Printing Objects ......................................................................... 16
2.5 SEM Imaging of Samples ................................................................. 18

Chapter 3 Results and Discussion ........................................................ 19

3.1 Polysulfone Ink Formulations ......................................................... 19
  3.1.1 Using Dichloromethane as Solvent ............................................ 19
  3.1.2 Using Dimethylformamide as Solvent ....................................... 22
  3.1.3 Using an Acetone Bath ............................................................. 23
  3.1.4 Using a Mixture of DCM and DMF as Solvent ......................... 25
3.2 Polyaniline Ink Formulations .......................................................... 29
  3.2.1 Using N-methylpyrrolidone ....................................................... 29
  3.2.2 Using a Mixture of NMP and Acetone as Solvent ..................... 29
  3.2.3 Mixture with PSU Solution in DCM ......................................... 30
  3.2.4: Mixture With PSU Solution in DMF and DCM ....................... 31
  3.2.5 Mixture with PSU Solution in DMF ......................................... 33
  3.2.6 Mixture With PSU Solution in Dichloroethane ....................... 33

Chapter 4 Conclusions .......................................................................... 36

BIBLIOGRAPHY .................................................................................... 37
LIST OF FIGURES

Figure 1: Visualization of the Hansen space, with the Hansen sphere defined by its radius [2].

Figure 2: A 2D representation of the 3D Hansen space. Plotted are the parameters and circles for PVA, PVB, and PVD, along with a variety of solvents [2].

Figure 3: 45 wt% Udel polysulfone in DCM.

Figure 4: Objects extruded by hand. The objects need to hold its shape, and not sag. A) printed using polysulfone ink. B) printed using PANI/PSU composite ink.

Figure 5: Components of the 3D printer. A) Rep-Rap printer. B) modified syringe mount. C) Adapter to attach the syringe to the printer. D) Pressure booster used when high pressure is required.

Figure 6: The 3D model used for printing the majority of samples. The print settings were modified instead of the model to make square wall and square lattice geometries.

Figure 7: An example of printing parameters set for 3D printing. Parameters that pertain to fused deposition such as printing temperature and filament diameter did not matter.

Figure 8: Square wall 3D printed using 35 wt% PSU in DCM. It is printed using 40 psi, at 2 mm/sec.

Figure 9: Flow analysis of 35 wt% PSU in DCM. The relationship seems to be linear, and becomes more inaccurate as needle size decreased due to human error.

Figure 10: Comparison of flow rate with boosted and unboosted pressures.

Figure 11: Flow analysis of 35 wt% PSU in DMF extruded in acetone bath.

Figure 12: Square walls printed with 35 wt% PSU in DMF printed in acetone bath. The pressure was 40 psi, and speed was 2.4 mm/s.

Figure 13: SEM images of the cross section of 35 wt% PSU in DMF printed in acetone bath. The microstructure shows high porosity in the middle. A) View of the entire cross section B) Boundary between inside and surface. C) Pore structure in the center. D) Close-up view of individual pores.

Figure 14: Objects printed using a 5:1 mixture of DCM:DMF as the solvent. A) 30 wt% PSU. The concentration is too low, and the print sags. B) 40 wt% PSU. The higher concentration produced an ink that can hold its shape.

Figure 15: Square wall with 30% infill printed with 35 wt% PSU in 5:1 mixture of DCM:DMF. Printed at 20 psi, 1.67 mm/s.
Figure 16: SEM images of 35 wt% PSU in 5:1 mixture of DCM:DMF. A) View of whole cross section. B) outside boundary. C) boundary at the large pore D) Close-up view of single pore and surrounding area. ..........................................................28

Figure 17: SEM images of 30 wt% PANI in 20 wt% PSU dissolved in 5:1 ratio of DCM:DMF. A) View of the whole cross section. B) View of the outside boundary. C) Close-up view of the interior. D) Close view of the texture on the inside granules. ...............................................32

Figure 18: 3D printed structures using 30 wt% PANI in 20 wt% PSU dissolved in DCE. Left: printing speed at 13.3 mm/s. Right: printing speed at 8.3 mm/s ........................................34

Figure 19: SEM images of 30 wt% PANI in 20 wt% PSU dissolved in DCE. A) View of the whole cross section. B) View of the outside boundary. C) Close-up view of the interior. D) Close view of the texture on the inside granules. ..................................................35
LIST OF TABLES

Table 1. Solubility of polysulfone in List of Solvents ......................................................... 11
Chapter 1

Background

1.1 Introduction

3D printing or additive manufacturing is a way of building an object by depositing material layer-by-layer to create a specific shape. It comes in many forms, including fused deposition, stereolithography, or selective powder sintering. Metals, ceramics, and polymers can be 3D printed, although polymer 3D printing is the most common, and also the most accessible. The most common polymer 3D printing technique currently is fused deposition. In this technique, a spool of thermoplastic filament, commonly acrylonitrile butadiene styrene (ABS) or poly(lactic acid) (PLA) is fed to a heating element, which melts the plastic, and forces it out of a nozzle onto a build surface. With the aid of a machine, the plastic is deposited in thin strands that slowly builds up into a 3-dimensional shape.

There are limitations to what material is printable using fused deposition. First, the polymer must be melt-processable. Polymers that have high melting temperature or high melt viscosity are more difficult to print with. It is not necessarily that high temperature polymers cannot be printed using fused deposition, rather that it requires much higher temperatures, and specialized equipment for printing. The other common limitation of fused deposition is thermal degradation of the melt processed polymer. Some polymers are sensitive to temperature, and tend to thermally degrade before melting. If these polymers are used in fused deposition, the
degradation will alter the properties of the polymer, usually in a detrimental way. Polysulfone (PSU) and polyaniline (PANI) are the two materials investigated in this thesis that represent these limitations. PSU has a high processing temperature while PANI thermally degrades before melting. If these polymers can be 3D printed at room temperature, all of the problems associated with heating and subsequent degradation can be avoided.

The alternative method of making a polymer into a liquid is to dissolve it in a solvent. Whereas heat separates the polymer chains as the material expands and increases chain mobility to allow flow, solvents are molecules that physically separate polymer chains, and acts as lubrication to allow the chains to slide past each other. The resulting solution can then be extruded and allowed to dry, which hardens the polymer. This method of using solvents to create inks and extruding the ink with the aid of a computer is called solvent-cast 3D printing.

1.2 Hildebrand and Hansen Solubility

As the name suggests, solvent-cast 3D printing relies heavily on the right solvents to facilitate processing of the polymer. The appropriate solvents need to be used to make a viable ink formula that holds its shape when cast and dries quickly. There are many different factors in choosing a solvent, including evaporation rate, viscosity, and toxicity, but the solvent needs to dissolve the target polymer first and foremost. Therefore, it is important to understand how solvents interact with polymers and have a method for predicting solubility of a polymer in any solvent. The tool used in this case is Hansen solubility parameters, which is an extension of the Hildebrand solubility parameters.
To determine if a solvent can dissolve a particular polymer, the most definite way would be to test it, and see if it works – an empirical approach. However guessing at solvent-polymer combinations and running lots of experiments can quickly become costly and time consuming. Theoretical predictions can narrow down the choices very easily, and make the process a lot more efficient. Solubility parameters are one way of making that prediction.

1.2.1 Hildebrand Solubility Parameters

Hildebrand solubility parameters are based on the cohesive energy density of a material. It is a measure of the total energy of interactions between molecules of a substance. The solubility of a material with a solvent is directly related to this interaction energy because if two substances have the same interaction energies, then they should be able to mix together without changing their interactions. If one substance has stronger interactions than another, then the molecules of one would have a hard time infiltrating the other. This phenomenon can be observed easily in an example such as oil and water. The water molecules have much stronger interactions to each other that the oil molecules cannot penetrate the water phase. The idea of “like dissolves like” is derived from a solubility parameter analysis.

The method of finding the Hildebrand solubility parameter of a solvent is simple. The cohesive energy density can be calculated by measuring the energy required to evaporate a unit volume of solvent. Heating provides the energy required to break all the interactions, and turns the liquid into a gas. Cohesive energy density can be expressed as:

\[ C = \frac{\Delta E^v}{V}, \text{ where } \Delta E^v \text{ is the energy of vaporization of a volume } V \text{ of the solvent.} \]
The Hildebrand solubility parameter is defined as the square root of the cohesive energy density[2]. Therefore it is defined as:

\[ \delta = C^{1/2} = \left( \frac{\Delta E^p}{V} \right)^{1/2} \]

Finding the Hildebrand parameter is easy for a liquid, but is much more difficult for a polymer because a polymer cannot be evaporated. In the case of a polymer, the group contribution method is used [3]. Each backbone and side group is given a molar constant \( V^* \) and a molar attraction constant \( F^* \). Dividing the sum of the \( F^* \) terms by the sum of the \( V^* \) terms results in the solubility parameter.

To determine if a solvent can dissolve a polymer, a rule of thumb can be used. If the difference between the solubility parameter of a polymer and solvent is less than 1, then the solvent can dissolve the polymer. This rule of thumb can be derived from Flory-Huggins theory. In order for two substances to be miscible, their Gibb's free energy of mixing must be negative.

For a polymer-solvent system the free energy of mixing can be expressed as:

\[ \frac{\Delta G_m}{RT} = n_s \ln \Phi_s + n_p \ln \Phi_p + n_s \Phi_p X \]

Where \( n_s \) and \( n_p \) are the number of moles of solvent and polymer, respectively, \( \Phi \) is the volume fraction, \( R \) is the ideal gas constant, and \( T \) is absolute temperature.

The variable \( X \) is defined as \( X_{sp} = 0.34 + \frac{V_r}{RT} (\delta_s - \delta_p)^2 \), where \( V_r \) is a reference volume defined by the hydrostatic volume of a solvent molecule.

There is a critical value for \( X \), under which the Gibb's free energy of mixing becomes negative. It is also where the second derivative of free energy with respect to composition is positive. The derivation yields:
Here $M_A$ and $M_B$ are the number of segments of polymer A and B, if all the segments are the same volume, assuming a two-polymer mixture. If one of the polymers is instead a solvent, and a segment has the volume of a single solvent molecule, then the $M$ value for that solvent would be 1, and the polymer would have a very high $M$ value. Applying this approximation results in this equation:

$$X_c = \frac{1}{2} \left( \frac{1}{M_A^{1/2}} + \frac{1}{M_B^{1/2}} \right)^2 \approx \frac{1}{2}$$

Now the range of solubility parameters can be calculated for when $X<1/2$.

$$0.34 + \frac{V_r}{RT} (\delta_s - \delta_p)^2 < \frac{1}{2}$$

Solving this inequality results in roughly $(\delta_s - \delta_p)^2 < 1$. The conclusion from this is that a solvent is likely to dissolve a polymer if their Hildebrand solubility parameters are roughly less than 1 unit apart.

### 1.2.2 Hansen Solubility Parameters

As stated above, Hansen solubility parameters are an expansion of the Hildebrand solubility parameters. Instead of using one parameter to describe all the interactions, Hansen solubility parameters attempt to separate the interaction into 3 main types: dispersion (D), polar (P), and hydrogen bonding (H). This analysis assumes that the cohesive energy density of the 3 types of interactions add up to the total cohesive energy. Since the Hildebrand parameter is the
square root of the cohesive energy density, the squares of the Hansen parameters should add up to the square of the Hildebrand parameters.

\[ \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \]

Dispersion forces are the weak attractive forces acting on all molecules. It is the result of random movements of the electron cloud causing induced-induced interactions. If a solvent is non-polar, then all of its interactions can be attributed to dispersion. In this case, the Hildebrand and the dispersion parameters are the same. If the solvent is polar, the homomorph method is used \[2\]. A homomorph of a polar molecule is a non-polar molecule closest to its structure. For example, methane is the homomorph of methanol. The dispersion parameter of the polar solvent is assumed to be the same as the Hildebrand parameter of its non-polar homomorph.

The polar parameter can be found as a function of dipole moment (DM) and molar volume (V) \[4\].

\[ \delta_p = 37.4(DM)/V^{1/2} \]

If the dipole moment information is not available, other methods including group contributions, similarity to other compounds, and experimental data can be used. Once the dispersion and polar parameters are determined, the hydrogen parameter can be found by subtracting the cohesive energy densities from dispersion and polar interactions from the total cohesive energy.

Hansen solubility parameters are best visualized as a sphere in 3D space, since there are three parameters. If each parameter is defined on their own axis, then each solvent and polymer occupies a point in that 3D space. For a polymer, there is a space around its parameters, within which a solvent can dissolve the polymer. This space is visualized as a spheroidal volume, with
the Hansen solubility parameters of the polymer at the center. If the dispersion parameter is doubled, the spheroid shape becomes closer to a sphere [4]. This is convenient because now the sphere can simply be defined by a radius around the Hansen parameters, as can be seen in Figure 1. This radius can be defined experimentally for each polymer by using various solvents and mixtures of solvents.

![Figure 1: Visualization of the Hansen space, with the Hansen sphere defined by its radius [2].](image)

To avoid graphing in 3 dimensions in order to determine if a solvent is viable, an equation can be used to describe the distance between the polymer and the solvent in Hansen space [4].

\[
(Ra)^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2
\]

This is basically the square of the distance formula in 3 dimensions. The relative energy difference (RED) with a polymer describes how similar the parameters of the solvent are to the polymer, and is calculated using the following equation:

\[
RED = \frac{\sqrt{4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2}}{R_0}
\]

\(R_0\) is the soluble radius of the polymer. RED is a ratio of the distance between the polymer and the solvent, and the soluble radius of the polymer. If the RED is less than 1, then the
solvent can theoretically dissolve the polymer. If it is greater than 1, then the system is not compatible.

A 2D graph can also be used to visualize two of the three parameters at a time, which is much more convenient and simple to visualize, such as in Figure 2. However, this representation is not always reliable, since the third parameter is not shown, and the solvent may or may not actually lie in the sphere, even though it is inside the circle.

![Figure 2: A 2D representation of the 3D Hansen space. Plotted are the parameters and circles for PVA, PVB, and PVD, along with a variety of solvents [2].](image)

Although the Hildebrand solubility parameters are much simpler to use, Hansen parameters are used in this case because three parameters describe intermolecular interactions better and more specifically than one parameter. There are some situations where Hansen parameters are not sufficient. For example, the Hildebrand parameters of ethanol and nitromethane are 26.1 and 25.1 Mpa$^{1/2}$ respectively, yet only ethanol is miscible with water [4]. With Hansen parameters, this behavior could be justified as a difference in the distribution of the three parameters.
1.3 Considerations

1.3.1 Economic

Fused deposition is the most accessible form of 3D printing. It does not require any special equipment, and consumer versions are simple to use, and is basically a set of motors moving a nozzle and a platform. Free software exist for the entire process including designing the 3D model, conversion to 3D printing format, and controlling the printers. Converting from fused deposition to solvent-casing is also relatively simple, requiring only a few new parts that could be 3D printed, and some way of controlling the extrusion of viscous solutions. This makes solvent-cast 3D printing relatively cheap to implement. Polysulfone and polyaniline are both commercially available polymers that are not extremely expensive. The solvents used are also commonly used solvents, and only small amounts are required.

1.3.2 Environmental

Ultimately, there is a tradeoff between using heat and using solvents. Using high temperatures consumes more electricity, whereas solvent-casting can be done at room temperature. However, the use of solvents requires the 3D printing to be done inside a fume hood, and solvents need to be disposed of properly. All of these factors indirectly bring the energy expenditure of this method up. However, using solvent-cast 3D printing to print with materials that are difficult or impossible for fused deposition to print can justify these needs. At the current stage, only small amounts of solvent is needed to perform the experiments. However, if the process is to be scaled up, then the environmental impact of using large amounts of solvents should be considered.
1.3.3 Sustainability

3D printing is a quickly growing field that still has potential areas of improvement. Solvent-cast 3D printing is a versatile method that is not limited to the two polymers used here. A similar process could be used to develop inks for a variety of materials, and fulfill various applications where specific, personalized geometries are necessary. 3D printing is already being used in industry for rapid prototyping and design purposes. Increasing the repertoire of materials printable helps move 3D printing towards fabricating end products.

1.3.4 Health and Safety

Since some harmful solvents were used, all experiments were performed within a fume hood. Rubber gloves and goggles were always worn when handling these chemicals. All other safety regulations were followed to ensure safety of myself and other lab members.
Chapter 2

Experimental Procedures

2.1 Preparation of Polysulfone Inks

In order to make a viable Udel polysulfone ink for 3D printing, the polymer must be dissolved in a solvent. To find suitable solvents, Hansen solubility parameters were used. A variety of solvents were investigated, and the results are shown in Table 1.

Table 1. Solubility of polysulfone in List of Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_d$ (Mpa$^{1/2}$)</th>
<th>$\delta_p$ (Mpa$^{1/2}$)</th>
<th>$\delta_h$ (Mpa$^{1/2}$)</th>
<th>RED with PSU</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>17.8</td>
<td>3.1</td>
<td>5.7</td>
<td>0.87</td>
<td>61.15</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>18.2</td>
<td>6.3</td>
<td>6.1</td>
<td>0.53</td>
<td>39.6</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>16.8</td>
<td>5.7</td>
<td>8</td>
<td>0.80</td>
<td>66</td>
</tr>
<tr>
<td>Dimethylformamide</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
<td>0.96</td>
<td>152</td>
</tr>
<tr>
<td>Acetone</td>
<td>15.5</td>
<td>10.4</td>
<td>7</td>
<td>1.09</td>
<td>56</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>19.02</td>
<td>7.362</td>
<td>4.09</td>
<td>0.57</td>
<td>84</td>
</tr>
<tr>
<td>Nitroethane</td>
<td>16</td>
<td>15.5</td>
<td>4.5</td>
<td>1.38</td>
<td>112</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>20</td>
<td>8.6</td>
<td>4.1</td>
<td>0.53</td>
<td>210.9</td>
</tr>
<tr>
<td>Aniline</td>
<td>19.4</td>
<td>5.1</td>
<td>10</td>
<td>0.46</td>
<td>184.13</td>
</tr>
<tr>
<td>N-Methyl-2-pyrrolidone</td>
<td>18</td>
<td>12.3</td>
<td>7.2</td>
<td>0.67</td>
<td>202</td>
</tr>
<tr>
<td>Quinoline</td>
<td>19.4</td>
<td>7</td>
<td>7.6</td>
<td>0.20</td>
<td>237</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>18.4</td>
<td>6.3</td>
<td>13.7</td>
<td>0.79</td>
<td>205.3</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>15.1</td>
<td>5.7</td>
<td>16</td>
<td>1.53</td>
<td>107.89</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>17.4</td>
<td>4.1</td>
<td>13.5</td>
<td>1.01</td>
<td>161.84</td>
</tr>
<tr>
<td>M-cresol</td>
<td>18</td>
<td>5.1</td>
<td>12.9</td>
<td>0.82</td>
<td>202.8</td>
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<tr>
<td>Dioxane</td>
<td>19</td>
<td>1.8</td>
<td>7.4</td>
<td>0.84</td>
<td>101.1</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>14.5</td>
<td>2.9</td>
<td>5.1</td>
<td>1.52</td>
<td>34.6</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>16.6</td>
<td>8.8</td>
<td>17</td>
<td>1.34</td>
<td>116</td>
</tr>
<tr>
<td>Toluene</td>
<td>18</td>
<td>1.4</td>
<td>2</td>
<td>1.24</td>
<td>111</td>
</tr>
<tr>
<td>Dimethyl Sulfoxide</td>
<td>18.4</td>
<td>16.4</td>
<td>10.2</td>
<td>1.09</td>
<td>189</td>
</tr>
<tr>
<td>Pyridine</td>
<td>19</td>
<td>8.8</td>
<td>5.9</td>
<td>0.35</td>
<td>115.2</td>
</tr>
<tr>
<td>1,1,2,2-tetrachloroethane</td>
<td>18.8</td>
<td>5.1</td>
<td>5.3</td>
<td>0.59</td>
<td>146.5</td>
</tr>
</tbody>
</table>
Polysulfone (PSU) has a solubility parameters of $19.7 \text{ Mpa}^{1/2}$ for $\delta_d$, $8.3 \text{ Mpa}^{1/2}$ for $\delta_p$, and $8.3 \text{ Mpa}^{1/2}$ for $\delta_h$, and has a soluble radius, $R_0$, of 8\cite{4}. The solvent in Table 1 were solvents that had relatively similar parameters to PSU. Refer to section 1.2.2 for calculations.

Dichloromethane (DCM) was chosen because it has the smallest RED, which makes it a very good solvent for polysulfone, and a low boiling point that makes it evaporate quickly. Dimethylformamide (DMF) was also used because it can also dissolve polysulfone, but has a much higher boiling point which could be used to lengthen the hardening time. In making an ink, the evaporation of the solvent is an important factor. The ability for both DCM and DMF to dissolve PSU was confirmed by experiments. By choosing DCM, which evaporates quickly, and DMF, which evaporates slowly, a mixture of the two would allow the evaporation rate to be controlled.

Polysulfone solutions were made by first mixing DCM and DMF to the desired volume ratio, and then adding the desired weight into a capped vial. Then, polysulfone pellets were weighed and added to the vial. The vial was capped, and left for about 24 hours to allow the polymer to completely dissolve. At high concentrations, the solutions were highly viscous, so a magnetic stirrer could not be used. By letting the solution dissolve by itself, and then stirring it manually, a uniform solution was obtained at a range of 20-45 wt\% polymer in solvent. A sample of such a solution can be seen in Figure 3.
2.2. Preparation of Polyaniline Inks

Polyaniline was obtained in the form of a fine powder, which is convenient for fast dissolution. However, because the powder is black, and the solution obtained is a very dark blue, it is more difficult to determine if the solution is completely dissolved. It is known from previous literature that PANI is soluble in N-methylpyrrolidone (NMP)[5].

A number of different mixtures were made at various concentrations and various solvents and solvent systems. Acetone, NMP, acetone/NMP mixes were used to make pure PANI inks. These solvents were chosen because acetone does not dissolve PANI, while NMP does. These solvents were added into the powder, and stirred with a stirring rod until well mixed. In the case of NMP, the mixture is left for a period of time - up to two days - to allow the PANI to dissolve.

Composite inks with PSU were also made. PSU solutions were made as described in section 2.1. They were then added to the PANI powder and stirred until well mixed. Solvents used for the PSU solutions include DCM, DMF, DCM/DMF mixture, and 1,2-dichloroethane.
(DCE). Because DMF was found to also dissolve PANI, some of the inks made using DMF were left for 24 hr to allow PANI to dissolve.

2.3 Evaluation of Inks

The inks produced were preliminarily evaluated before being used for 3D printing. One of the major concerns in using a polymer solution to 3D print is the ability of the extruded objects to hold its shape. A small amount of ink was added into a syringe, and was extruded manually through a needle. An air pressure extruder (Nordson EFD Ultimus V) was also used to extrude the ink by hand. The air pressure extruder is the same system that powers the extrusion in the 3D printer. If the pressure required is greater than 50 psi, a pressure booster (see Figure 5D) is used, which transforms the air pressure applied to a piston that applies a greater physical pressure to the syringe.

Test 3D shapes were made by hand using this method, which can be seen in Figure 4. If the ink was able to be extruded and holds its shape after being layered, then it should work on a 3D printer. If the layers sag down or loses their shape, then the formula is rejected. By going through this screening process, any issues with clogging in the needle or problems with flow also became apparent.
Figure 4: Objects extruded by hand. The objects needs to hold its shape, and not sag. A) printed using polysulfone ink. B) printed using PANI/PSU composite ink.

In addition, the extruder was used to find the extrusion speeds that were used to calibrate the printer and analyze the flow rate. A specific pressure was set, and inks were extruded in a straight line by hand. Effort was taken to keep the line straight, and not to stretch the extruded filament or let it bunch together. The time taken to extrude a specific distance was measured, and the speed was calculated. The pressure is adjusted up or down to change the extrusion speed to the desired value. This procedure was used to define the printing speed of the 3D printer. By using different needle sizes and different pressures, the relationship between pressure and extrusion speed can be observed. This process was performed for some earlier ink formulations, but because all the 3D printing was done using a 20G needle, later inks were optimized in real time. During the printing setup, a single working combination of pressure and speed was determined empirically. From test printing by hand, a certain pressure was used so that the ink was extruded at a speed that was comfortable to the person holding it, and was also able to hold its shape. Once that pressure was found, the speed was calculated, which then became the speed setting in the printer.
2.4 3D Printing Objects

The inks that performed well during manual extrusion were used with a 3D printer that positioned the syringe in x-y-z space according to the printing protocol. The 3D printer is a self-constructed Rep-Rap, which was then modified to incorporate the air-pressure extruder, Figure 5.

![Figure 5: Components of the 3D printer. A) Rep-Rap printer. B) modified syringe mount. C) Adapter to attach the syringe to the printer. D) Pressure booster used when high pressure is required.](image1)

First, a 3D computer model of the desired object was composed. For the purpose of this experiment, the 3D model was kept very simple, mostly as a 2 cm x 2 cm x 2 cm cube. The 3D model can be seen in Figure 6. The goal in this part of the work was to show that the ink can be printed into a 3D shape. Cura was the software used to convert a 3D file to printing format. The parameters can be modified to make different prints. An example of a set of parameters can be seen in Figure 7. To print a square wall, the fill density was simply set to 0%. To print a square lattice, a fill density of typically 30% was set. The inner diameter of the extrusion tip was set as
the extrusion width, and the layer thickness is set slightly less than the inner diameter of the needle. These settings were performed to improve layer adhesion. Based on the ink being printed, the speed of the printer was set accordingly. The ink was loaded into the syringe, and a 20G needle tip was attached. As the print was started, the extruder was turned on simultaneously, and the ink was extruded at a constant rate while the printer moved the extruder head. The extruded ink was deposited on a glass build plate with a large sheet of scotch tape to make it easier to clean and remove the object. After the print was complete, the object was left until it has solidified enough to be safely removed.

Figure 6: The 3D model used for printing the majority of samples. The print settings were modified instead of the model to make square wall and square lattice geometries.
Figure 7: An example of printing parameters set for 3D printing. Parameters that pertain to fused deposition such as printing temperature and filament diameter did not matter.

2.5 SEM Imaging of Samples

SEM images are taken with a Nova NanoSEM 630. The samples were sputter coated with gold for 40 seconds to mitigate charging of the polymer samples. The samples were images to visualize the porosity and microstructure of the composites.
Chapter 3

Results and Discussion

3.1 Polysulfone Ink Formulations

Polysulfone can be dissolved by various solvents such as dichloromethane (DCM) and dimethylformamide (DMF), but depending on what solvent or solvent system was used, the printing results were drastically different. Throughout the different experiments, many inks were formulated that simply could not be 3D printed. Some other inks were usable, but have some inconveniences or difficulties. Described below are the various formulas attempted and the results. One issue persisted in all of the formulations, which was polymer concentration. Inks that did not have enough polymer content could not harden fast enough, and as a consequence the structures formed from these inks collapsed from their own weight. On the other hand, inks that had a high concentration of polymer can be printed, but required high pressures from the syringe extruder.

3.1.1 Using Dichloromethane as Solvent

Dichloromethane (DCM) is a good solvent for PSU, and has a low boiling point of 39.6 °C, making it evaporate fairly quickly. The intent of solution 3D printing was to allow the extruded ink to harden quickly, and retain its shape. Many different concentrations were tested, including 20, 30, 35, and 40 wt% PSU concentrations. The same problem persisted across all concentrations, which is due to the fast evaporation. Because the DCM evaporates so quickly, as soon as the ink is extruded out, a thin layer of solid polymer formed on the outside while the
inside was still liquid. While printing, this "tail" disrupted the ink previously put down, and disrupted the flow of the solution. At 35 and 40 wt%, this clumping could be overcome by manually wiping off the clump, and allowing new ink to come out, which sometimes established a stable, consistent flow. However, any small disturbance can break that flow, and clumping started again, such as when the needle touches previously laid down ink. The concentration of the ink also changed over time. DCM slowly evaporated even while the ink was sealed and stored away. This caused the viscosity to slowly increase over time. Even transferring the ink from the container to the syringe caused a significant amount of evaporation.

Figure 8: Square wall 3D printed using 35 wt% PSU in DCM. It is printed using 40 psi, at 2 mm/sec.

Nevertheless, this ink was successfully 3D printed, and a square wall was printed as can be seen in Figure 8. The wall was 2cm x 2cm, but a skirt was added to the base to keep it from warping and allow the structure to adhere to the build plate. The above sample was printed using 40 psi at 2 mm/sec. Clumping still tended to happen, which rendered this ink less than satisfactory.

Flow analysis was performed with the 35 wt% PSU in DCM ink, and the results are shown in Figure 9. The speed of extrusion seems to increase linearly with pressure. As needle size decreased, the speed also decreased for the same pressure applied. This is behavior was
expected, and made logical sense. A smaller needle should require more pressure to extrude the same speed. As the speed approached 0, the pressure approached 0 psi. This is also logical because there should be no extrusion when no pressure is applied. As smaller needles were used, the error became much greater. This is due to the human error of trying to make a perfectly straight line, which is more difficult with a small needle. As a consequence, the linear fit for 25G is very scattered, and the intercept was forced to be 0.

![Flow analysis graph](image)

**Figure 9**: Flow analysis of 35 wt% PSU in DCM. The relationship seems to be linear, and becomes more inaccurate as needle size decreased due to human error.

While making these flow rate measurements, higher pressures were required to extrude the ink at a reasonable speed. To measure how much the pressure increased when the booster was used, a simple comparison was made between unboosted and boosted extrusions. 10 seconds of extrusion was done for different pressures while boosted and unboosted using an 18G needle. Then their slopes were compared. The results can be seen in Figure 10.
Both these lines again appear linear, and have intercepts near 0. The ratio between the slopes is 3.12, which would indicate that the pressure booster increased the pressure by 3.12 times. Knowing this boosting factor allows the boosted pressures to be represented as theoretical unboosted pressures, such as some data plotted in Figure 9.

### 3.1.2 Using Dimethyformamide as Solvent

Because DCM evaporates so quickly that it created clumping at the needle, a solvent with a much higher boiling point was chosen. Dimethylformamide (DMF) has a boiling point of 152 °C, so it will stay in the ink long after it is extruded. Inks using only DMF had the opposite effect of DCM, in that it could not hold its shape. Concentrations of 20, 30, and 35 wt% were tested, and in all cases, after the ink was extruded, it lost its shape, and becomes more like a puddle.
3.1.3 Using an Acetone Bath

The idea of using DMF alone was explored farther by relying on precipitation. PSU is not soluble in acetone, so when extruded directly into excess acetone, PSU will precipitate, and harden. A thin layer of 5 wt% PSU in DMF solution was coated onto the bottom of a deep Petri dish, which helped the ink adhere to the base. The Petri dish was placed onto the build plate, and acetone was poured into it. Then, 35 wt% PSU in DMF was extruded into the acetone bath. As the extruded sample left the needle, the ink turned white, indicating that PSU had precipitated. This precipitation allowed the ink to harden, and preserve its shape. After the print finished, water was added to the bath, which induces further precipitation and further hardened the print.

Flow analysis was performed with this setup, and the results are shown in Figure 11. Interestingly, the trend was clearly not linear, but has a slight curve that is best fitted with a squared relationship. This presents the possibility that the relationship for the ink using only DCM was also slightly curved, but it just was not as obvious. Further analysis of the printing dynamics under flow conditions is warranted.

![Figure 11: Flow analysis of 35 wt% PSU in DMF extruded in acetone bath.](image-url)
Using this method, square walls were printed, as seen in Figure 12. During printing, the build plate would move back and forth, which disturbed the acetone bath. This sometimes caused the ink that was already extruded to move around slightly. The resulting printing was less precise, and the walls did not line up neatly. The settings for the print was 40 psi pressure, and 2.4 mm/s.

![Image of printed walls]

**Figure 12**: Square walls printed with 35 wt% PSU in DMF printed in acetone bath. The pressure was 40 psi, and speed was 2.4 mm/s.

The cross section of the extrusion was imaged using SEM, Figure 13. The internal structure of the extruded material was highly porous. The pores were on the order of 5 µm, and were uniform throughout the cross-section. However, the outside surface was solid, with little or no pores. The pores also seemed to be elongated in a particular direction, as can be observed in Figure 13C. This elongation could be caused by the flow of ink induced by extrusion. This high level of porosity is unique among all the other inks tested, and could be useful for applications where porosity is important. It could also be hypothesized that different concentrations of ink could produce different degrees of porosity in the print.

The major disadvantage of this method is the need for large amounts of acetone, the turbulence in the acetone produced by the movement of the printer, and the difficulty in adhering
the print to the build plate. If these problems could be addressed, this is a potentially significant way of 3D printing porous structures.

![Figure 13: SEM images of the cross section of 35 wt% PSU in DMF printed in acetone bath. The microstructure shows high porosity in the middle. A) View of the entire cross section B) Boundary between inside and surface. C) Pore structure in the center. D) Close-up view of individual pores.]

3.1.4 Using a Mixture of DCM and DMF as Solvent

Because DCM evaporated too quickly and causes clumping at the needle tip, and DMF evaporated too slowly and causes the print to collapse, a mixture of the two solvents were used to
optimize the evaporation rate. The DCM should evaporate first and harden the ink quickly, but the slower-evaporating DMF left in the structure will keep the ink slightly liquid, preventing clump formation.

30 wt% PSU solutions were made with different ratios by volume of the two solvents. They were 1:1, 3:1, 5:1, and 10:1 ratios of DCM:DMF. At all of these ratios, the ink still collapsed after extruding, and clumping still occurred at the needle tip. An example of a print using a 5:1 mixture can be seen in Figure 14A. The pressure was 40 psi, and speed was 3.4 mm/s. This indicates that the ink was simply not concentrated enough at 30 wt%. The concentration was increased to 40 wt% with a 5:1 DCM:DMF mixture. This time, the extrusion was very consistent and uniform. A square wall with 30% infill was printed, which can be seen in Figure 14B. The pressure was set at 50 psi, and the speed was 3 mm/s.

![Figure 14](image)

Figure 14: Objects printed using a 5:1 mixture of DCM:DMF as the solvent. A) 30 wt% PSU. The concentration is too low, and the print sags. B) 40 wt% PSU. The higher concentration produced an ink that can hold its shape.

Lastly, a 35 wt% PSU solution in 5:1 DCM:DMF was tested. This ink is also viable, being printable either with 20 psi at 1.67 mm/s, or with 50 psi at 3 mm/s. The result is shown in Figure 15. This ink formulation was the best one for printing PSU in terms of print quality, consistency, and ease in handling. The ink before printing can be easily transferred to the
syringe, and printing rarely produced errors or problems. The cross section of this printed object was also imaged with SEM. The results are shown in Figure 16. The microstructure of the interior consisted of solid polymer with a few small enclosed bubbles about 5 µm in diameter. Around the outside, the pores were much smaller, and there were a few large pores where the ink contacted the build plate. There are banding across the images, possibly due to inadequate sputter coating, which caused charging at the sample.

![Figure 15: Square wall with 30% infill printed with 35 wt% PSU in 5:1 mixture of DCM: DMF. Printed at 20 psi, 1.67 mm/s.](image)
Figure 16: SEM images of 35 wt% PSU in 5:1 mixture of DCM:DMF. A) View of whole cross section. B) outside boundary. C) boundary at the large pore D) Close-up view of single pore and surrounding area.

This ink could be potentially useful in structural applications. The printed object was mostly solid, which gives it better mechanical properties than the porous object printed in an acetone bath.
3.2 Polyaniline Ink Formulations

Polyaniline (PANI) comes in the form of black powder. PANI is not as soluble as PSU, and making inks with it is overall more difficult. Even a small amount of PANI will make the entire ink so dark that the quality of the ink cannot be evaluated visually. Since the PANI is in powder form, it was tested both as a solution and as a colloid.

3.2.1 Using N-methylpyrrolidone

From literature, it is known that N-methylpyrrolidone (NMP) can dissolve PANI [5]. PANI powder was added to NMP at 10, 20, 30, 35, and 40 wt% concentrations. When the PANI powder was mixed with NMP and stirred, clumps formed inside the mixture, and after some time the mixture thickened and a rubber-like or jello-like consistency was obtained. The time at which the mixture solidifies decreased from days at 10 wt% PANI, to within minutes at 40 wt% PANIs. Before solidifying, extruding by hand was attempted, and the clumps present in the solution clogged the extruder and prevented a consistent flow of material. It is concluded that polyaniline does not make a solution similar to polysulfone, and had to be treated differently.

3.2.2 Using a Mixture of NMP and Acetone as Solvent

Since the powder clumps together in just NMP, acetone was used to attempt at obtaining a more homogenous mixture. Acetone was mixed with PANI powder, and it was found that the powder dispersed very well, but acetone by itself cannot be used because when extruded, all the acetone came out first, leaving a packed body of PANI powder.
A mixture of acetone and NMP was used to see if the addition of acetone would allow for better dispersion and also prevent the solution from becoming rubbery. A two-state process was used. PANI powder was first dispersed in acetone, and then NMP was added and stirred. The PANI concentrations tested were 15, 20, 25, 30, and 40 wt%. The acetone:NMP mixtures used were 1:4, 1:3, 1:1, 3:7, and 3:1. When too little acetone was used, it did not saturate PANI completely, and the resulting ink tended to clog. If too much acetone was used, PANI powder separated when extruded. The best combination was 15 wt% PANI in a 1:4 mixture of acetone:NMP. Even with this slurry, the extrusion tip still clogged often. Another problem arose because of NMP, which changed the consistency of the ink to be more viscous over time, which made it hard to extrude at a consistent and predictable rate. The addition of acetone was not enough to create an ink that can extrude without clogging the needle.

3.2.3 Mixture with PSU Solution in DCM

From the previous two sections, it can be concluded that using PANI alone, it is difficult to make a viable ink. It would be much easier to use PANI if the solvent does not dissolve it at all. Dichoromethane (DCM) was tested by mixing it with PANI. The liquid stayed clear, indicating that DCM cannot dissolve PANI. From Table 1, and previous tests, it was known that DCM is a good solvent for polysulfone (PSU). PSU solutions in DCM were mixed with PANI to make composite inks. PSU solutions were made first, then PANI powder was added in. 5, 10, and 20 wt% PSU in DCM solutions were made, and then PANI was added until the total PANI concentration was 33.3 wt%. Using the 5 and 10 wt% PSU solutions, the same phenomenon occurred as with formulations using acetone in section 3.2.2. The PSU solution along with some
PANI extruded out first, leaving packed PANI powder behind. Using 20 wt% PSU solution, the viscosity of the solution allowed the ink to be extruded consistently. However, using DCM caused the same issue as PSU inks with only DCM (section 3.1.2). The solvent evaporated so quickly that it caused a film to form on the tip of the needle, which drags on the printing surface and made the ink clump up at the tip.

3.2.4: Mixture With PSU Solution in DMF and DCM

To address the clumping of ink at the needle tip problem in section 3.2.3, mixtures of DMF and DCM were used instead of DCM alone to make the PSU solution. This is the same change made for printing with PSU in section 3.1.4. The high boiling point of DMF kept the ink liquid for longer, preventing clumping. Unfortunately, when DMF was tested with PANI, the liquid turned dark blue, indicating that DMF can dissolve PANI, which was unwanted. Nonetheless, this formulation was attempted because the solution would be primarily DCM.

Following the good result in section 3.1.4, the DCM:DMF ratios used was 5:1 by volume. This solvent mixture was used to make a 20 wt% PSU solution. Then, PANI was added in concentrations of 25, 30, and 33.3 wt%. After these inks were made, they were immediately extruded. The 25 wt% PANI ink was not viscous enough, and collapses. The 33.3 wt% PANI ink was very viscous, and was difficult to handle. The 30 wt% PANI ink worked well, and was used to 3D print a squared lattice at 30 psi with the pressure booster, which is approximately 93.6 psi without the booster. The speed was 7.5 mm/s. The problem with using DMF as part of the solvent is that it still dissolves the PANI, causing the viscosity to increase over time. The settings
used to print ink that was freshly made would become progressively worse over time, until the extrusion was no longer continuous, but was stuttered and broken.

Figure 17: SEM images of 30 wt% PANI in 20 wt% PSU dissolved in 5:1 ratio of DCM:DMF. A) View of the whole cross section. B) View of the outside boundary. C) Close-up view of the interior. D) Close view of the texture on the inside granules.

SEM images were also taken of the cross section of this 3D printed ink, as seen in Figure 17. The interior appears granular, and porous, while the outside is non-porous, yet rough. The granules are likely particles of PANI stuck together with PSU. The 3D printed structure was brittle, and will break easily with applied pressure.
3.2.5 Mixture with PSU Solution in DMF

To verify that the viscosity change was due to DMF, inks using PSU dissolved in only DMF were made. 20 wt% PSU in DMF was made, then used to make 20 and 30 wt% PANI mixtures. After 1 day, the 20 wt% PANI ink became visibly more viscous, and the 30 wt% PANI ink became a rubbery solid and broke into pieces when stirred. This confirms that the change in viscosity was at least in a significant part due to the presence of DMF.

3.2.6 Mixture With PSU Solution in Dichloroethane

To avoid the problem of increasing viscosity over time, the solutions used must be one that cannot dissolve PANI, but will dissolve PSU, and at the same time does not evaporate quickly. A new solvent is required. 1,2-Dichloroethane (DCE) was found to dissolve PSU (see Table 1), and yet does not dissolve PANI. This makes sense because DCM cannot dissolve PANI, and DCE has a very similar molecular structure. In addition, DCE has a boiling point of 84 °C, so it evaporates a lot slower than DCM.

A 20 wt% PSU solution in DCE was made, then 30 wt% PANI was added. After the addition of PANI, the ink was left for 24 hours to equilibrate, and allow for any PANI dissolution to occur, even though it should not.

This ink was printed by two different settings. Using 40 psi with the pressure booster, the ideal speed was 13.3 mm/s. Using 30 psi with the pressure booster, the ideal speed was 8.3 mm/s. Square lattices were printed with both settings, and can be seen in Figure 18.
As can be seen in the figure, when the ink was extruded at the faster speed, the extruded structure collapsed slightly, especially in the center, but it still kept its overall shape. When printed at 8.3 mm/s, the lattice was able to hold its shape a lot better. This is because the slower speed allowed more time for DCE to evaporate. SEM images were taken of the cross section, which can be seen in Figure 19. The microstructure appeared similar to the structure of 30 wt% PANI in 20 wt% PSU dissolved in 5:1 DCM:DMF. The only obvious difference was that the outside surface was a lot smoother. This is possibly due to the slower evaporation of DCE, which gave the surface time to smooth out as it hardened. Even though this ink extruded very consistently, its evaporation rate can likely be optimized by using a mixture of DCE and DCM as the solvent for PSU.
Figure 19: SEM images of 30 wt% PANI in 20 wt% PSU dissolved in DCE. A) View of the whole cross section. B) View of the outside boundary. C) Close-up view of the interior. D) Close view of the texture on the inside granules.
Chapter 4

Conclusions

Polysulfone (PSU) and polyaniline (PANI) were used to formulate inks that were used in solvent-cast 3D printing. Numerous factors influenced the quality of 3D printing, including the polymer concentration, choice of solvents, and printing speed. For polysulfone, the most successful ink was 35 wt% PSU dissolved in a 5:1 ratio of DCM:DMF. The ink was extruded consistently without clumping, and hardened fast enough to retain its shape after being deposited. Polyaniline could not be printed by itself because the dissolution of PANI turns the solution into a rubbery consistency, and produced clumps that clogged the needle. Composite inks were formulated using PANI powder and PSU solution as a binder. The best ink was composed of 30 wt% PANI in 20 wt% PSU dissolved in dichloroethane (DCE). DCE has a slower evaporation rate than DCM and did not interfere with PANI.

In the future, some experiments could be done to further characterize the materials. For PSU, the printed objects could be tested for their mechanical properties to see how it compares to the bulk material. For PANI, the composite material can be acid doped and tested for its conductive properties. Additionally, PANI and PSU in the composite material was indistinguishable in the SEM image. Light microscopy or energy-dispersive x-ray spectroscopy could be used to see how the two materials are distributed. The technique of solvent-cast 3D printing is a versatile one. In addition to printing PSU and PANI, the scope could be widened to print other polymers, and even metallic or ceramic powders.
BIBLIOGRAPHY

ACADEMIC VITA
Ziyi Miao
Email: kliff0116@gmail.com

EDUCATION
B.S. in Materials Science and Engineering June 2012 - May 2016
Minor in Biomedical Engineering
The Pennsylvania State University, University Park

RESEARCH & WORK EXPERIENCE
Undergraduate Research June 2014 - Present
- At Penn State, Material Science & Engineering Department
- Worked under Dr. Michael Hickner
- Produced polysulfone fibers by electrospinning
- Utilized solvent cast method to 3D print with polysulfone

Summer Internship With Autodesk June 2015 - July 2015
- At Pier 9, San Francisco
- Worked on Ember, Autodesk's STL 3D printer
- Experimented with methods of reducing clouding in the PDMS windows

PPG Research Fellowship June 2013 - June 2014
- At the Penn State, Material Science & Engineering Department
- Worked under Dr. Jim Adair
- Synthesized fluorescent calcium phosphate nanoparticles (CPNP), and studied its use with Teslin for cancer detection

Receptionist for the Multicultural Resource Center July 2012 - Aug 2012
- At Penn State
- Answered phone calls and set appointments
- Guided visitors to the appropriate staff

HONORS & AWARDS
Schreyer Honors College Aug 2013 - Present
- Honors program of Penn State exclusive to the most excellent scholars
- About 5% of all PSU undergraduate students are in the program

Dean's List Aug 2012 - Present
- Awarded every fall and spring semester to students with GPA of 3.5 or higher

SCHOLARSHIPS 2015-2016
- Bryce and Jonelle Jordan Renaissance Scholarship
- Henderson Scholarship
Norris B. McFarlane Scholarship Fund - Materials Science and Engineering
Teas Scholarship - Earth and Mineral Sciences

2014-2015
- Bryce and Jonelle Jordan Renaissance Scholarship
- William and Estelle Turney Scholarship in Ceramic Science and Engineering
- Class of 1922 Memorial Scholarship
- Richard P. and John N. Davis Scholarship

2013-2014
- Bryce and Jonelle Jordan Renaissance Scholarship
- Matthew J. Wilson Honors Scholarship
- Sam Zerfos Memorial Scholarship
- Philip C. Cook Jr. Memorial Scholarship

2012-2013
- Bryce and Jonelle Jordan Renaissance Scholarship
- Matthew J. Wilson Honors Scholarship
- Bryce Dorothy Pate Enright Endowed Scholarship

RELEVANT EXPERIENCE

Secretary of Material Advantage June 2015 - Present
- Assisted in organizing the Penn State Material Advantage student body
- Managed attendance, membership, and room reservations

Academic Chair of Irvin Hall Jan 2013 - Jan 2015
- Oversaw academic-related events in Irvin Hall, the special living option for the College of Earth and Mineral Sciences at Penn State
- Organized larger academic events

PUBLICATIONS
- Describes the process of making a PDMS window used in the Ember 3D printer in the lab
- Part of the product of the Autodesk internship summer 2015