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# DESIGN AND PERFORMANCE OF STRETCHABLE THERMOELECTRIC NANOWIRE COMPOSITES

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**DESIGN AND PERFORMANCE OF STRETCHABLE  
THERMOELECTRIC NANOWIRE COMPOSITES**

An Honors Thesis Presented

By

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## ABSTRACT

Thermoelectric materials efficiently and directly convert waste heat into electricity, enabling new engineering applications ranging from micro scale solid-state cooling in computers to clean energy harvesting and conversion. For example, thermoelectric alloys have been useful for past NASA missions in deep-space exploration outside the solar system, where traditional solar cells cannot function properly due to the lack of light. NASA uses radioisotope thermoelectric generators on satellites, taking the hot particles from the decay of a radioactive isotope, to heat thermoelectric alloy coatings that generate electricity. The problem with these alloy coating materials, however, stems from their poor mechanical strength. They are generally brittle and break under very small elastic deformation, which makes their integration to curved surfaces or soft fabrics impossible. This study presents optimal conditions to control the growth and harvesting of the nanowires to achieve longer lengths in order to increase conductivity, a substrate that is flexible and stretchable enough, but also strong enough to be considered for wearable electronics, and the mechanical performance of newly-developed flexible polymer composites containing a dense network of thermoelectric alloy nanowires with a diameter less than 200 nm. Further research on such elastically-compliant nanowire-based composite materials could lead to significant technological breakthroughs such as enabling computers to be integrated into clothing, powered by body heat, or cutting down on waste energy from excess heat by wrapping them around hot exhausts and engines to power electrical devices.

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## CHAPTER 1: INTRODUCTION

### 1.1 Literature Background

It has been shown in recent literature that nanowire networks have highly increased elasticity, allowing for extensive stretching and folding without failure. Indium-antimonide (InSb) is a semiconductor with one of the highest thermoelectric power in both bulk form and nano-scale. InSb nanowires, in particular, could be used as a more durable gage because of their ability to handle large elastic strain. Creating a network array of these nanowires in a flexible substrate that maintains its electrical properties under strain could open the door to many possibilities in the field of wearable electronics.

Lohn, Coleman, Tompa, & Kobayashi (2012) have assessed the thermoelectric power factor in silicon nanowire networks. They created a thermal gradient through the network and measured the current and voltage across it. The relation between the thermal gradient and the voltage created across the network is denoted the Seebeck coefficient, which is one of the variables in the calculation for the figure of merit of thermoelectric materials. They found that with certain types of nanowire networks, the Seebeck coefficient is nearly independent of temperature in the range they tested. Even more importantly they discovered that the electrical contact resistance between the nanowires in the network is the largest roadblock for nanowire network technology to thrive. By annealing the network or putting it under strain, it was observed that the nanowires in the network “weld” together or align in such a way to reduce this electrical contact

resistance. This leads to the idea that a nanowire network may hold its electrical conductivity when placed under strain.

Also, Xu and Zhu (2012) have tested highly conductive and stretchable silver nanowire networks. They performed fatigue testing and measured the change in electrical resistance as a function of the number of cycles. When the first strain was applied, the resistance increased linearly relative to the strain, but after each successive loading and unloading cycles up through five, the change in resistance decreased until it was almost constant. After forty cycles the resistance curve demonstrated the same characteristics as the fifth cycle. This supports the hypothesis that after fatigue cyclic loading, the nanowires change position into an optimum orientation. This also supports the hypothesis that putting the network under strain will not completely stop conductivity.

Furthermore, Langley, Giusti, Mayousse, Celle, Bellet, & Simonato (2013) explored the possibilities of flexible conductive materials based on nanowire networks, mainly silver. They stated that due to the great electrical, optical and thermal properties, nanowire networks have the possibilities of enabling flexible screens and transparent heaters, emphasizing the importance of these materials and their potential. Flexible devices must be able to withstand strain, especially the networks that are on them.

## **1.2 Hypotheses**

The method for creating the InSb nanowire networks has been developed and characterized by Daniel Merkel, a MS student in the Sansoz group, over the past two years. It is important to note that the methods for growing the nanowires and transferring

them to a PET substrate were done based on Merkel's findings. This thesis focuses on precisely tweaking his methods to determine optimal parameters for long nanowires by controlling the variables, i.e. deposition time, sonication time, of template-assisted electrodeposited InSb nanowires. Merkel's nanowires tended to be around 3-4 microns long. This is not long enough for good conduction. The deposition time, originally set by Merkel, was 40 minutes, however this study looks at four different deposition times (10, 20, 30, and 40 minutes) in an attempt to combat overgrowth, which results in clumps where nanowires have grown together outside of the template. The amount of time the wires are sonicated also has an impact on length. If they are not sonicated enough, clusters remain. Good conduction requires the nanowires be well dispersed and if they are clustered, there is not enough dispersion. Longer sonication eliminates the clusters, but also makes the nanowires short. This is also problematic in forming networks where the nanowires would touch each other. **The first hypothesis of this thesis is that longer nanowires can be achieved using the electrodeposition method by adjusting the deposition and sonication times.**

Throughout the literature, the common choice of substrate for nanowire networks is polyurethane terephthalate (PET) film due to its flexibility, but for stretchable electronics, PET's elastic properties fall short. It can only undergo minimal strain before fracture whereas an elastomer such as rubber, latex or polydimethylsiloxane (PDMS) has a much better chance to survive under high strain and bending. For wearable energy harvesters and devices, this property is very desirable. The transfer of nanowires to the substrate is also very important in selecting a substrate. But transferring nanowires to

PET is a difficult process with variable yield. Transferring nanowires to PDMS or latex, however, is simpler with high nanowire recovery as shown later. **The second hypothesis is that a soft polymer composite made of a network of indium-antimonide nanowires will maintain electrical performance when placed under large strains.**

### 1.3 Objectives of the Thesis

The specific goals of this thesis are as follows:

- (1) To determine an optimum setting of deposition time and sonication time to achieve maximum length of the nanowires in the composite. In order to achieve this objective, five sonication times will be tested: 3, 6, 9, 12, and 15 seconds with each of the deposition times mentioned earlier. The average length of the nanowires in each batch will be examined by using a scanning electron microscope and the image analysis program ImageJ.
- (2) To determine the ideal polymer for the substrate material of the composite based on ability to withstand strain and nanowire transfer process;
- (3) To study the effects of elastic strain on the electrical current passing through InSb nanowire-based polymer composites using tensile mechanical testing. The elastic performance of the soft polymer substrates will be studied by analysis of tensile stress-strain curves. The electrical performance of the nanowire network embedded in a soft polymer substrate while under strain will also be addressed.

## **CHAPTER 2: EXPERIMENTAL METHODS**

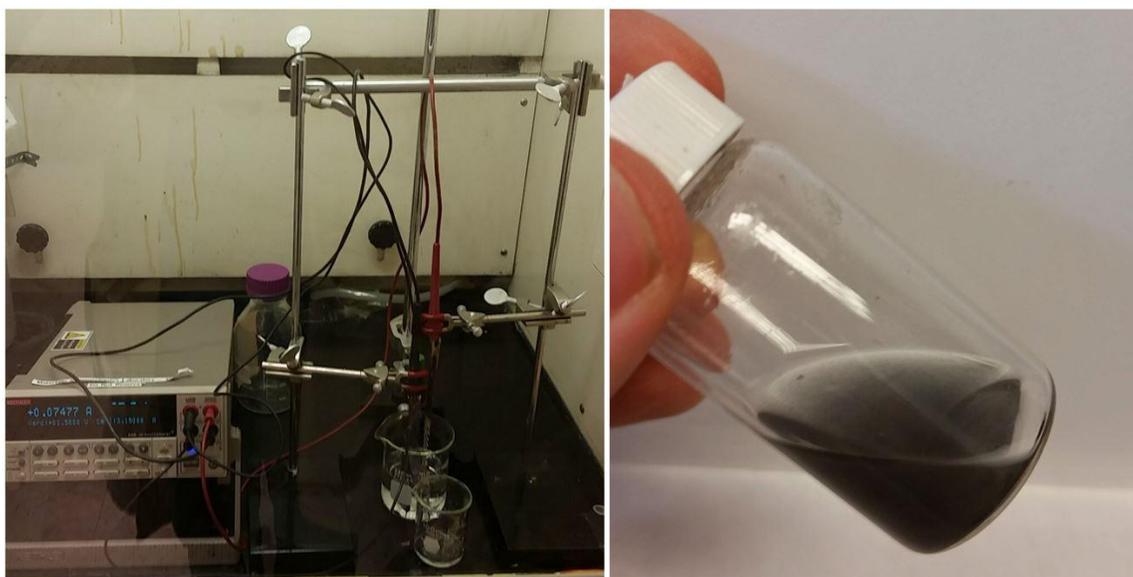
### **2.1 Substrate Testing**

Four possible substrates were tested: latex, PDMS, PET, and rubber. The main basis for determining the substrate was elastic properties, but the transfer success of nanowires was also a contributing factor. To measure elastic properties, a simple tensile test was performed on the Test Resources tensile testing machine in Perkins. The PET and PDMS specimens were cut from a flat sheet of material. The latex was molded as cutting it left a very uneven edge. The specimens were loaded into a tensile testing machine. Their respective gage lengths and cross sectional area were determined and entered into the software that controls the machine. This way a real-time stress strain curve was formed. These curves were then compared to determine which substrate could withstand large elastic strain.

### **2.2 Nanowire Growth**

The growth of nanowires was performed by template-assisted electrodeposition using a four-electrode setup on a Keithley 2400 series SourceMeter power supply with the potential set at 1V. The template used for this was an anodized alumina oxide (AAO) filter with 0.100 $\mu$ m holes. The filter had a plastic ring around the outside for ease of holding with tweezers. One side of the AAO filter was sputtered with gold three times at 200mTorr with 55mA for 40 seconds to act as a seed layer for the nanowires. Then a glass slide was covered with a layer of copper tape to act as an electrode and the gold side of the template was placed on it. A piece of plexi-glass with a hole slightly smaller than

the size of the AAO filter was placed over the slide with the filter in between. This is to reduce the area of contact with the solution. Once everything is in place, all the edges were sealed with vinyl tape. This template setup was then put in a beaker with the deposition solution and put in the sonicator on the degas cycle for 5 minutes. Once complete, the template was moved to the fume hood, where deposition solution was contained in a larger beaker. The two ground cables from the power supply were connected to the copper tape lead from the template. The other two were connected to the two electrodes in the solution, platinum and reference. The template was placed 1in. away from the platinum electrode with the reference electrode in between them off to the side. Then the Keithley was set to keep a constant potential of 1V and to record data points at specified time intervals over the deposition time. Once complete, the power supply was shut down and the template is removed from the solution and rinsed with DI water. The remaining solution was poured back into its bottle to be reused again. The AAO filter was then broken and put into a vial with sodium hydroxide (NaOH) to dissolve it. Then the NaOH was removed and the nanowires were rinsed and ethanol was added to the vial. It was at this time that the nanowires were sonicated to break them apart from each other. Once sonicated, the nanowires were free and dispersed in ethanol and ready to form networks (see Figure 1).



**Figure 1: Nanowire electrodeposition setup (left) and nanowires in ethanol solution (right)**

### **2.3 Nanowire Length Measurement**

The nanowires were divided into batches based on deposition time and sonication time. The batches were denoted as a letter corresponding to the deposition time (H-10mins, G-20mins, E-30mins, D-40mins) paired with the amount of seconds they were sonicated (i.e. H6 was the batch that had a deposition time of 10 minutes and was sonicated for 6 seconds). Initially, four batches were made (H, G, E and D). Then once the nanowires were in ethanol, they were sonicated in 3 second increments, each time pouring off 20 mL into a vial and labeling accordingly. Then one drop of each batch was placed on a small piece of Si wafer and examined under a scanning electron microscope. The images were then analyzed using the open-source program ImageJ, which allowed, once a scale was set, to collect spreadsheets of length measurements of the nanowires on

an SEM image by simply clicking and dragging over the wires individually. From there, averages and standard deviations were calculated.

## **2.4 Nanowire Network Formation**

To form the nanowire networks, a vacuum filtration method was used. A soft polycarbonate filter was placed on a mesh grate over a flask. A vacuum pump was connected to the flask and the nanowires in the ethanol were poured over the filter with a pipette (see Figure 1). The nanowires, once on the polycarbonate filter, were ready to be transferred to the substrate. For PDMS and latex, the transfer process was very simple. The liquid polymer was poured into its mold and the polycarbonate filter was placed face down on it, in the desired location (see Figure 1). This was then left to dry for approximately two to three days. The filter was then peeled off, leaving the nanowires embedded in the top layer of the polymer. The transfer process for PET was different from PDMS and latex due to that fact that it was already solid. The PET was heated to  $\sim 120^{\circ}\text{C}$ . Then a PDMS stamp was pressed hard against the polycarbonate filter and slowly peeled away to pick up the nanowires and placed on the heated PET substrate and held, under pressure, for a minute, then slowly peeled away, leaving the nanowires embedded in the PET. Once the transfer process was completed, gold electrodes were sputtered on to the edges of the network and copper tape was attached as leads.



**Figure 1:** Vacuum filtration setup (left). Using pipette to pour nanowire ethanol solution on filter (middle). Liquid latex mold with nanowires on filter face down (right). These show the simplicity of the nanowire transfer process for the liquid polymers

## 2.5 Electrical Performance under Strain

Electrical performance was characterized under strain and no strain. In both cases, the latex sample was connected to a power supply using a four-wire setup using copper tape as leads and a sputtered gold layer to help contact between copper tape and the network (see Figure 2).



**Figure 2:** Four-wire setup for electrical testing

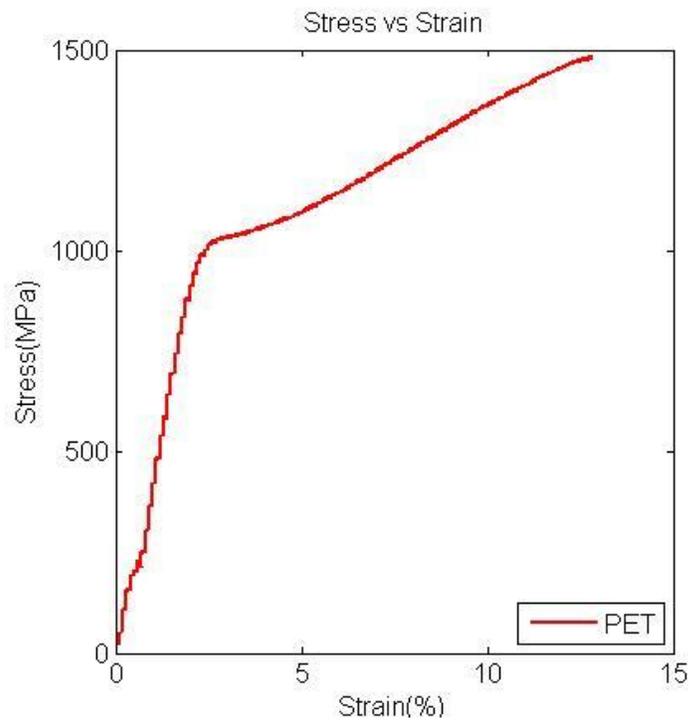
Then a sweep function was used, incrementally going from -1V to 1V and the current through the network was measured. This gave a control I-V curve for reference. Then, a controlled, increasing strain was applied to the sample using a low-force tensile

testing machine available in the School of Engineering lab in Perkins that is capable of measuring forces and strains in soft polymer specimens. A constant 5V potential was put across the sample using the power supply so the current passing through the electrodes could be measured while the sample was mechanically deformed. The current through the composite was measured while the strain increased to see the effect of strain on the composite's ability to conduct electricity.

## CHAPTER 3: RESULTS

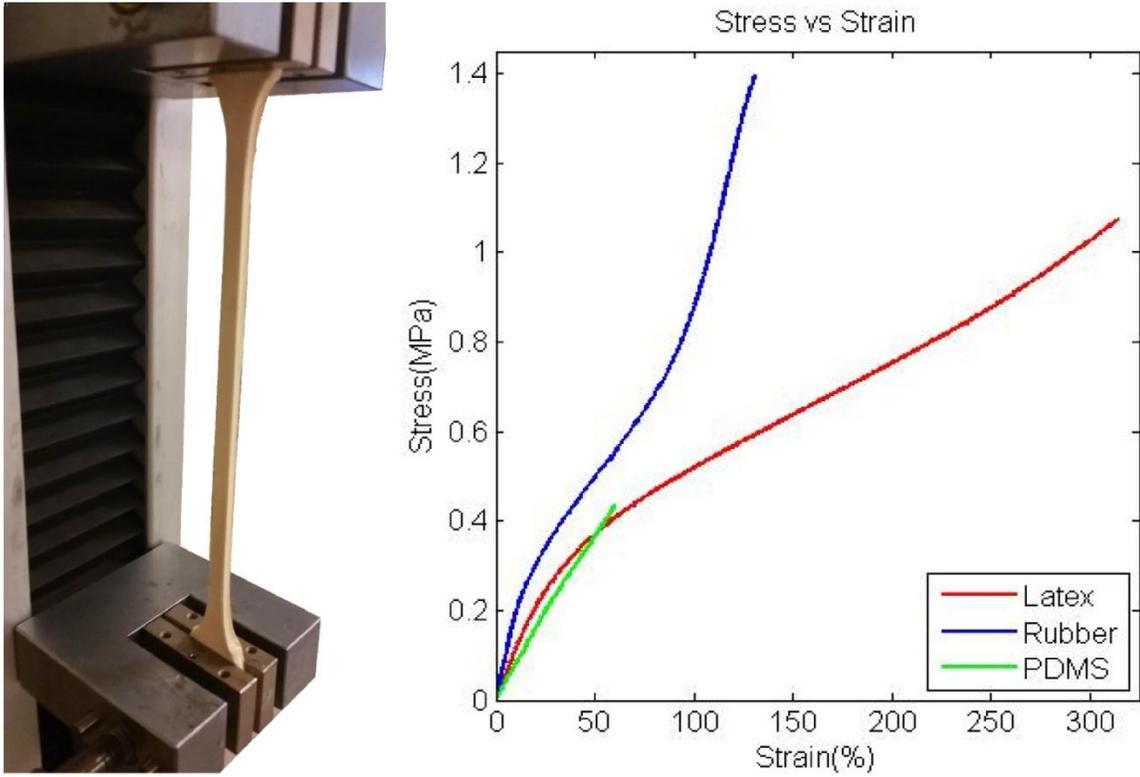
### 3.1 Substrate

The results from the tensile testing showed that the PET was by far the strongest material of the ones looked at, but hardly stretchable. It failed at ~13% strain (see Figure 3). For a flexible, stretchable device, this isn't ideal.



**Figure 3: Stress vs strain curve for PET shows the strength of the material, but also its lack of stretchability**

The PDMS and rubber performed better, failing at ~60% and ~130% strain respectively. The latex, however, never failed. It reached over 300% strain and hit the limit of the testing machine. It has lower strength than the rubber, but can withstand much more deformation (see Figure 4).

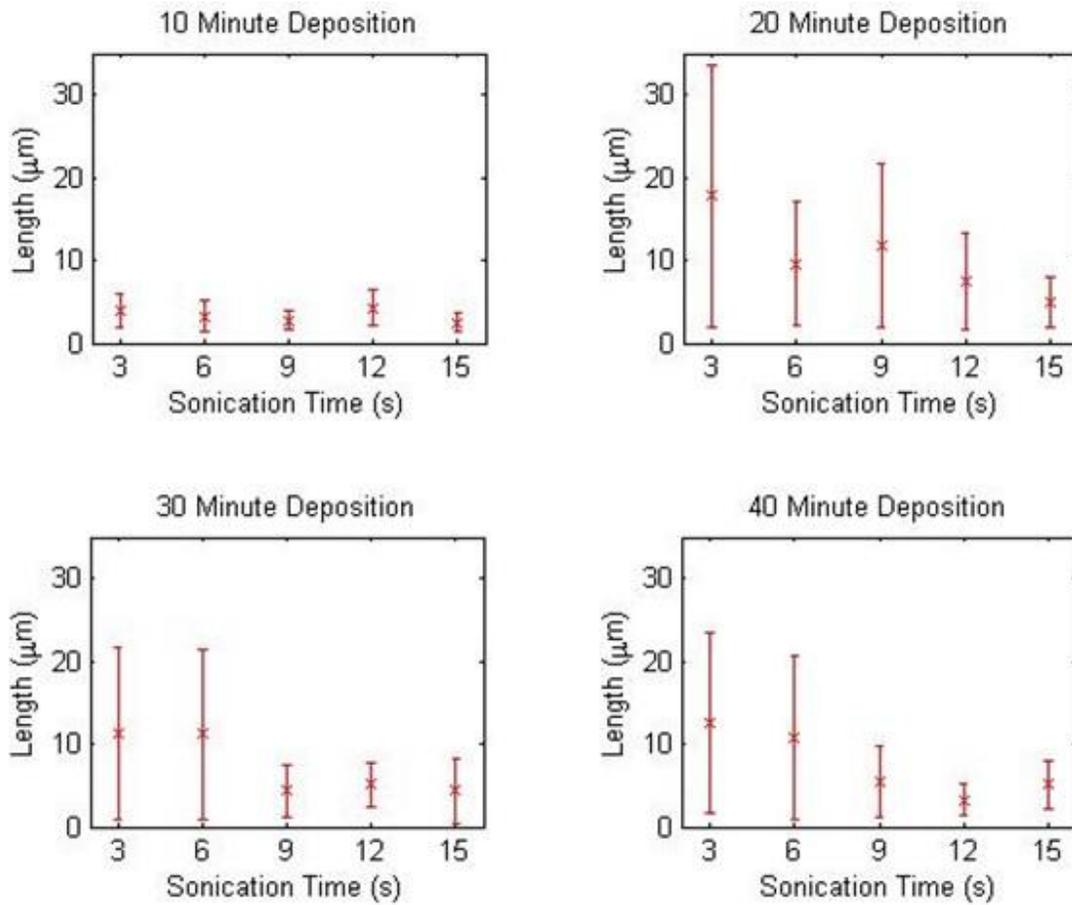


**Figure 4: Tensile test results show that latex can withstand up to 300% strain without failure**

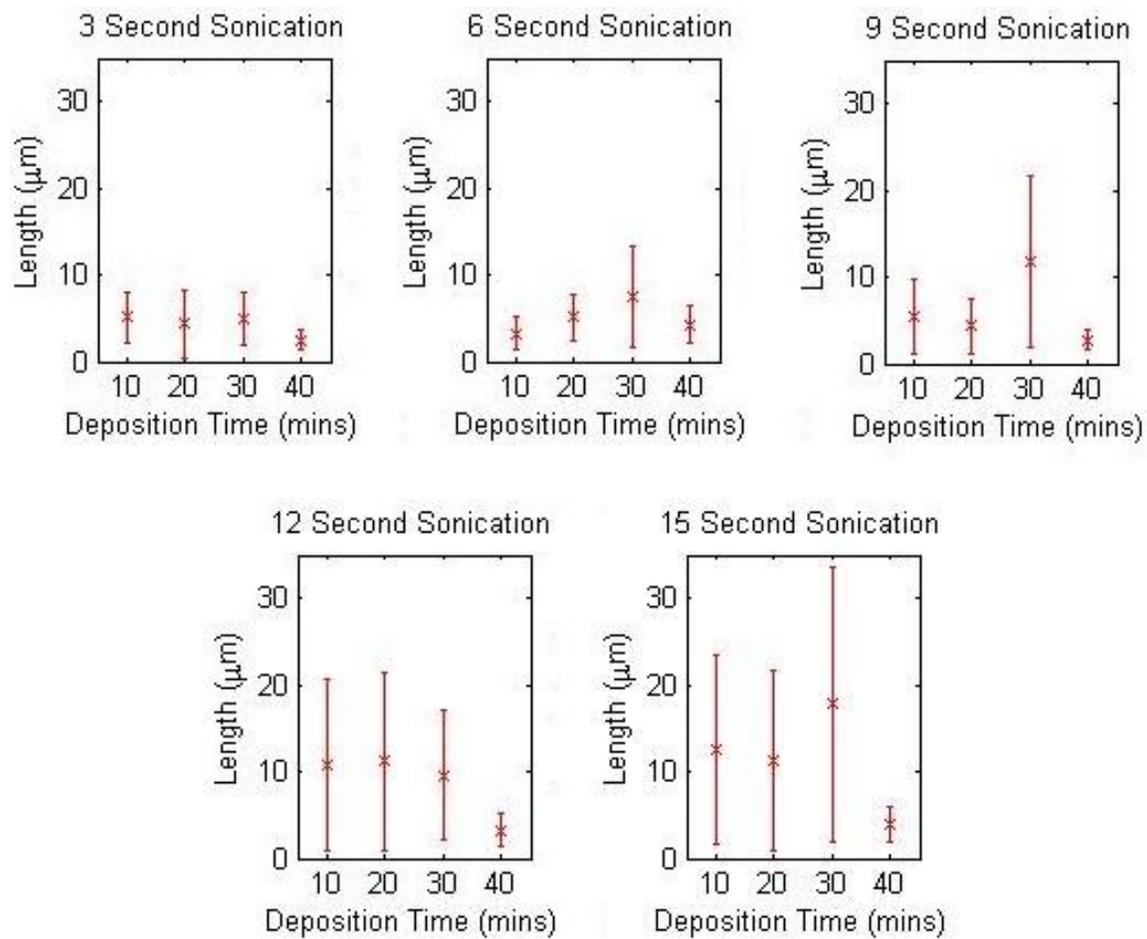
On top of elastic performance, the latex nanowire transfer process was simpler than the PET process and showed better transfer success than PDMS. When the filter was placed on top of the liquid polymers, the ones on the PDMS tended to sink into the material due to its low initial density. This is problematic as it is desired to have the filter stay on top of the material for ease of removal. The latex did not have this issue.

### 3.2 Deposition and Sonication Times

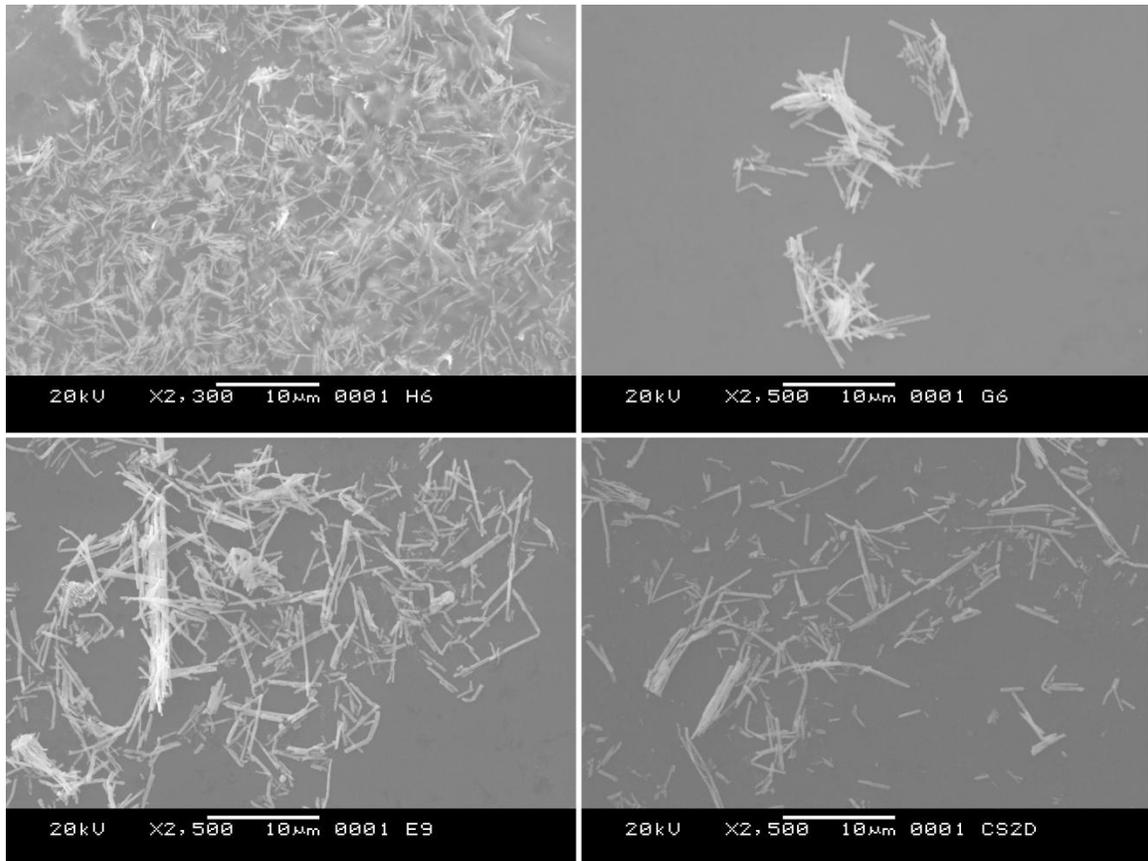
The largest issue with calculating the average lengths of the nanowires for each batch was the sample range and distribution. The clusters of nanowires skewed the data for most batches, indicated by the large error bars (see Figures 5-8). The lower sonication times clearly have a larger average length, but also a much larger standard deviation. There were many small broken wires mixed with large clumps of longer wires not yet separated. These results clearly show that sonicating the wires makes them shorter, but is necessary to break apart the clusters. It is also clear from these plots that a 10 minute deposition time is too short. The nanowires did not have enough time to grow in the template. The batch chosen to be used in the strain test was the 20 minute deposition time sonicated for 6 seconds. When compared to the other batches, it had a relatively high average with a low standard deviation. The histogram for that batch also showed that although most of the nanowires are in the 0-5 $\mu\text{m}$  range, many are also within the 5-10 $\mu\text{m}$  range, which is desired (see Figure 9).



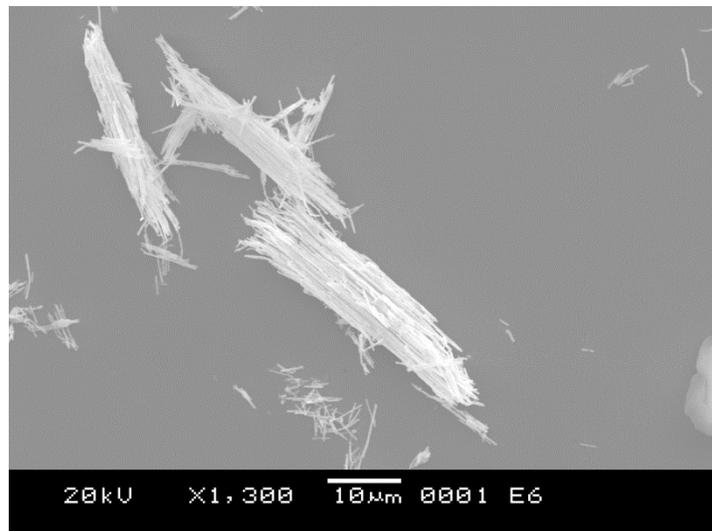
**Figure 5: Average length vs sonication time for 10 minute (top left), 20 minute (top right), 30 minute (bottom left), and 40 minute (bottom right) deposition times**



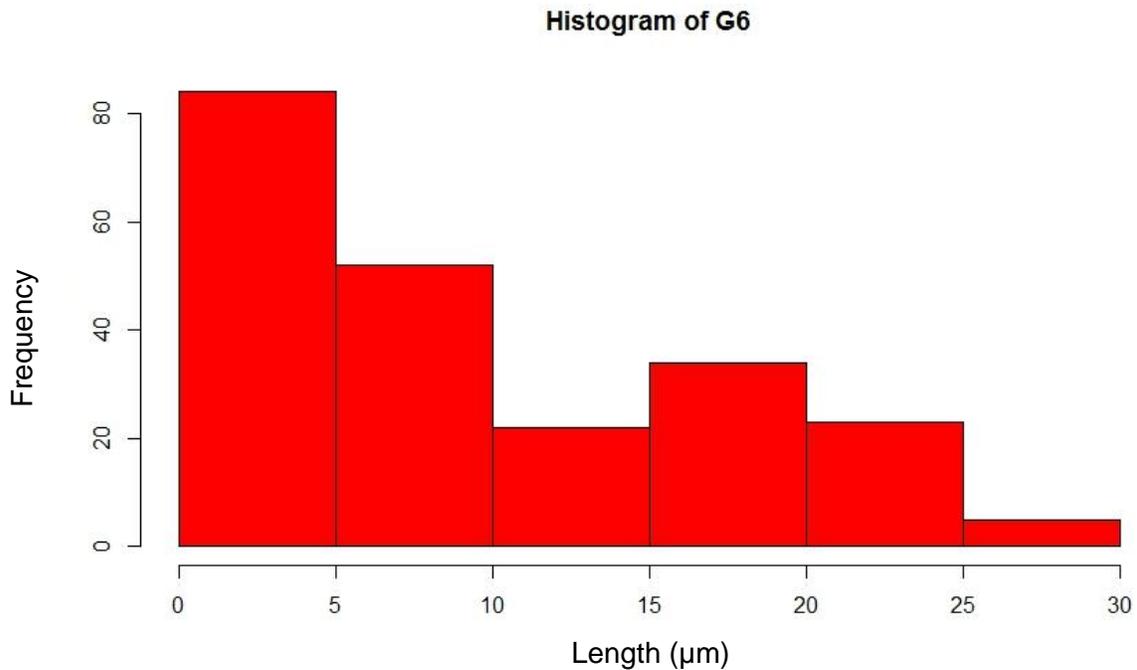
**Figure 6: Average length vs deposition time for 3 second (top left), 6 second (top middle), 9 second (top right), 12 second (bottom left) and 15 second (bottom right) sonication times**



**Figure 7: SEM images of nanowires electrodeposited for 10 minutes (top left), 20 minutes (top right), 30 minutes (bottom left), and 40 minutes (bottom right)**



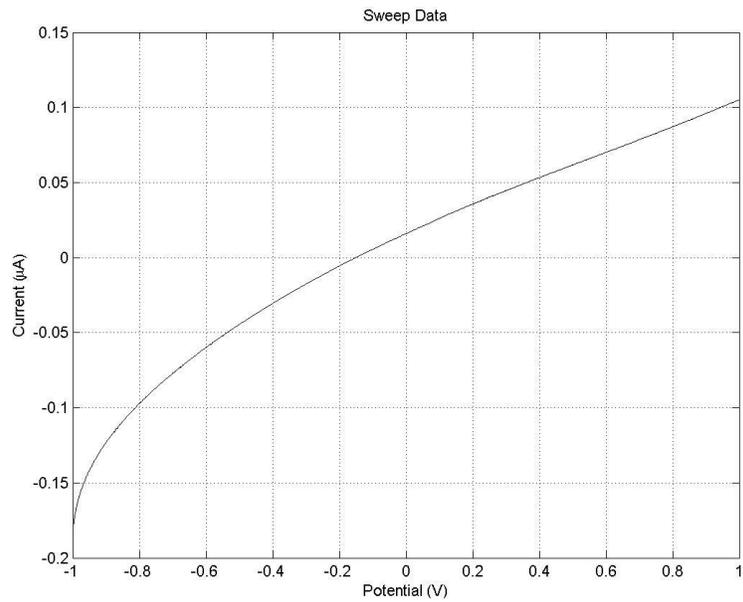
**Figure 8: SEM image showing clusters of nanowires**



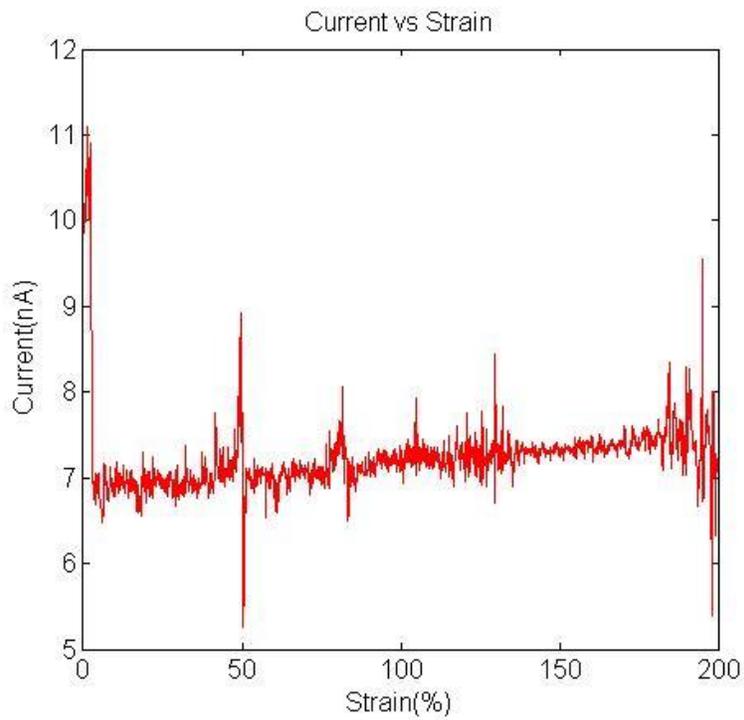
**Figure 9: Histogram of batch deposited for 20 minutes and sonicated for 6 seconds**

### **3.3 Results of Electrical Performance under Strain**

Before the sample was placed under strain, a voltage sweep was done to obtain a control I-V curve. This was to make sure there was conduction in the network. The I-V curve (see Figure 10) showed that there was current in the network, however it also suggests that the resistance increases due to the drop in current from negative to positive voltage. When placed under a controlled, increasing strain while a constant 5V potential was across it, the nanowire network showed an initial decrease in current. But as strain increased, the current showed an upward trend (see Figure 11). The test was performed with a 2-wire setup as opposed to a 4-wire setup for ease of execution. This explains the “noise” in the plot. The larger spikes resulted from having the electrode cables move while the test was running



**Figure 10: I-V curve of sample under zero strain**



**Figure 11: Current vs. strain plot shows that after initial drop, current has an upward trend**

These results show that electrical conductivity remains stable under an increasing strain, although the current initially drops, which implies that conductivity has decreased in the first stage of deformation. This could be due to alignment of the nanowires in the network. The width of the specimen decreases as it is strained, as dictated by Poisson's effect which could be bringing the nanowires in the network closer together, slowly increasing conductivity. In any case, the fact that the current doesn't drop to zero, but in fact increases as strain does is a step in the right direction for wearable electronics.

Another interesting observation is that in the I-V curve under no strain, there is a non-zero current at zero voltage. This could be attributed to thermoelectric effects in the system. When two conducting metals are connected and voltage is applied over them, the junction generates heat and possible current. The clips from the power supply are zinc, the leads are copper, there is a gold seed layer and the nanowires are thermoelectric indium-antimonide. These are four conducting materials all connected to each other, making six of these thermoelectric junctions. It is believed that the current is being generated at these many junctions and creating a non-zero current at zero voltage.

## **CHAPTER 4: CONCLUSIONS & FUTURE WORK**

In conclusion, latex was found to be the best candidate for the nanowire network substrate. It was able to withstand much more strain than the others tested and its transfer process is simple and has high recovery. The ideal deposition and sonication times were found to be 20 minutes and 6 seconds, respectively. This was determined after looking at SEM images and comparing average nanowire length and histograms. The I-V curve performed while under no strain proved that there was conduction in the network. The current vs strain plot showed that after a slight drop, the current remained stable in the network under small strains, and even increased moderately at large strains. Therefore understanding the processes leading to strain-dependent electrical conductivity in our stretchable nanocomposites is crucial for the development of wearable thermoelectric energy harvesters.

Future work could look into the thermoelectric properties of these nanowire networks. Specifically, determining the Seebeck coefficient and figure of merit used to characterize the thermoelectric property of a material. Also further study should be conducted to understand why there is an increase in resistance while both voltage and strain are applied to these networks. Possible hypotheses could include nanowire alignment, joule heating, heating of the latex matrix, and nanowire oxidization.

## CHAPTER 5: REFERENCES

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