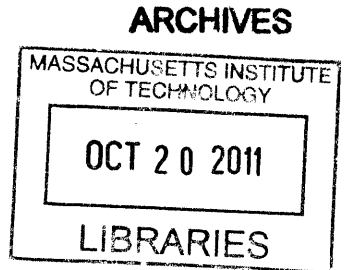**Testing and Characterization of Carbon Nanotubes as Strain Sensors**

By

Juan D. Diaz
B.S. Mechanical Engineering
Massachusetts Institute of Technology, 2011

SUBMITTED TO THE DEPARTMENT OF MECHANICAL ENGINEERING IN PARTIAL
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Testing and Characterization of Carbon Nanotubes as Strain Sensors

By

Juan D. Diaz

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Bachelor of Science in Mechanical Engineering

ABSTRACT

The potential of using carbon nanotube coated flexible cloth as strain gauges was studied. Samples were prepared by sonicating strips of cloth inside a 1mg/ml carbon nanotube in propylene carbonate solution. A dynamic mechanical analyzer was built that applied uniaxial cyclical strains to the samples and recorded the force and strain applied. The DMA also provided a constant voltage to the samples while recording the resistance response of the strain gauges. The samples were tested using the dynamic mechanical analyzer for their response to variables such as strain and time. The samples were successfully tested at strains ranging from 1% to 50%. The conductivity of the samples was measured. We studied the effects that a carboxylate and the sulfonate functional groups of the carbon nanotubes have on the strain sensors, the effect of the sonication time, and the effect that leaving the strain sensors inside the solution for different amount of times has on the strain sensors. It was discovered that the samples dried overtime, thus decreasing the conductivity of the samples and damaging the strain sensors. An encapsulation method was developed and studied to counter the drying effect. The results showed that the encapsulation method did delay the decaying of the samples. Moreover, it was concluded that the sulfonate group had higher changes in resistance than the carboxylate group. While increased sonication time did not seem to have a measurable effect on the resistance of the sulfonate CNT samples, this was not true for the carboxylate group CNTs. The carboxylate group CNTs seemed to have a higher initial resistance with longer sonication time and a lower resistance with increasing time sitting in the solution. Overall, it was concluded that carbon nanotubes have a promising potential as macro level strain sensors for high-elongation applications but more development is yet to be done.

Thesis Supervisor: Ian W. Hunter

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1. Introduction

Carbon nanotubes (CNTs) are molecular scale tubes made out of graphitic carbon. CNTs can be characterized as single walled (SWNT), which have a diameter of less than 2 nm and could be thought of as wrapping a one-atom thick sheet of graphene into a cylinder. Then there are multi-walled CNT's (MWNT), which have diameters of 0.3 to 10 nm and have multiple layers of graphene rolled into a cylinder [1]. They have very interesting properties including great strength, heat conducting capabilities and unique electrical properties. Carbon nanotubes can be semi-conducting or metallic depending on their structure. In theory, metallic carbon nanotubes can carry an electrical current density of 4×10^{13} A/m^2 [2].

Since carbon Iijima first discovered nanotubes in 1991 [3], there has been a myriad of research into how to use them for technical applications. One of these applications has been the construction of strain sensors out of carbon nanotubes. Their strength, super-elasticity and electrical conductivity make carbon nanotubes great candidates for use as strain sensors. More importantly, these properties allow for strain sensors of high-elongation [4].

2. Background

High-elongation strains are sometimes seen with expansion joints or crack openings. These gauges are mostly for strain measurements between 1% and 20%, and are fabricated for industrial application. Problems with high-elongation strain gauges include the durability of the strain gauge material but also the adhesive used to attach the strain gauge. The adhesive must be flexible enough to allow gauge elongation, but also must be rigid enough to prevent gauge creep. For strain gauges exceeding 20%, mechanical flexure devices called clip gauges are usually used. Clips are mounted to the specimen that needs to be measured and the strain gauges are installed on the top and bottom of these clips. As the specimen undergoes a strain, the flexures on the clips cause a resistance change in the strain gauges. Moreover, these devices need to be calibrated to account for their nonlinearity. [5].

Carbon nanotubes can be very hydrophobic, [6] making their adhesion to other materials difficult. To counter this, chemical reactions are created that attach surface functional groups through acid-induced oxidation of the carbon nanotube surface. In this process, oxygen units in the form of carboxylic, phenolic, or lactone are introduced when the carbon-carbon bonded network of the graphitic layers is broken [7]. For this thesis the sulfonate and carboxylate working group CNTs were used. The sulfonate working group has the chemical formula R-SO_2O. The carboxylate functional group has the general formula $RCOO$ [8].

The research on carbon nanotube strain sensors has been substantial. The fact that electrical conductivity of carbon nanotubes is dependent on its mechanical deformation makes it a possible candidate to use as strain sensors. The Raman band shift as a function of stress and strain has been studied for both MWCNT and SWCNT. These experiments have shown the potential of using carbon nanotubes as strain sensors on the nano-scale. Various studies have also attempted to create carbon nanotube strain sensors in the micro scale as well as in the macro scale [9].

Films of randomly oriented SWCNTs have been studied as strain sensors and have shown potential as strain sensors [10]. Other studies have also made multiwalled carbon nanotube films that were directly bonded to specimens in order to measure the health and vibrations of different structures. These tests showed a proportional increase in the resistance as the specimens underwent a uniaxial tensile load thus validating the possibility of carbon nanotubes films as strain sensors [11]. Another study demonstrated "nearly linear trend between the change in voltage, measured using a movable four point probe, and strains" carbon nanotube film sensors. Moreover, due to the random orientation of the carbon nanotubes, multi directional and multi location measurements of strain are possible [10]. Other novel use of carbon nanotubes as strain sensors is making a CNT-polymer nanocomposite flexible strain sensor [13]. One other example of carbon nanotube strain sensors is a spun carbon nanotube yarn that was spun directly from CNT arrays. This sensor showed promise in monitoring crack initiation and propagation. One of the most interesting studies on carbon nanotubes as strain sensors was a study that created millimeter long SWCNT that were directly transferred to a flexible substrate. This experiment demonstrated a strain resolution of 0.004% [14].

3. Testing Methods of the Carbon nanotube Strain Sensors

3.1 Fabrication of the Carbon nanotube Strain Sensors

In the exploration of practical uses for carbon nanotubes, strain sensors have been proposed, and many tests have been concluded, as the pervious sectioned explained. For this thesis, a new type of strain sensor was created in order to test the viability of using carbon nanotubes to analyze the stress and strain of materials. The carbon nanotube strain sensors mentioned here are created out of small rectangular strips of stretchable cloth. The cloth is Darlington Fabrics brand "PowerNet." This fabric is 80 percent "semi dull nylon" and 20 percent spandex [15]. This material is cut into small strips that are 2.78 mm wide, and 30 mm in length. The thickness of the cloth is about 0.48 mm. In order to make the strain sensors, a solution of carbon nanotubes in propylene carbonate is made, and placed into syntillation vials. The concentration of the solution is 1 mg of carbon nanotubes per 1 ml of propylene carbonate. About 2 ml of the carbon nanotube solution is added in each vial, and the small strips of cloth are placed inside. After the small cloth strips were added inside the vials, the vials were sealed and placed in a sonication machine for different amounts of time. The results are flexible pieces of cloth soaked in a carbon nanotube solution that serve as strain sensors. An illustration of the process for making the carbon nanotube covered cloths can be seen in Figure 1 below. The following step was designing the testing device and the various experiments and characterizing the differences in these strain sensors.
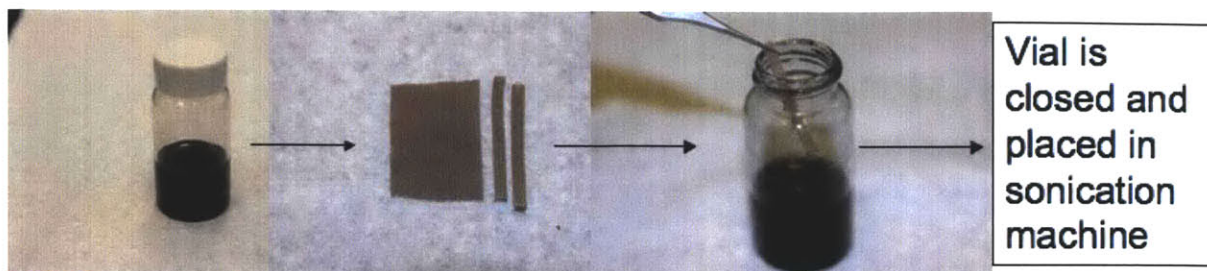
Figure 1: Images demonstrating the steps required in making the carbon nanotube strain sensors. First the carbon nanotube solution is added to a vial, and then the strips of cloth are cut to the required lengths and added to the solution. After the samples are sonicated inside the vial, they are removed and placed in the DMA for testing.
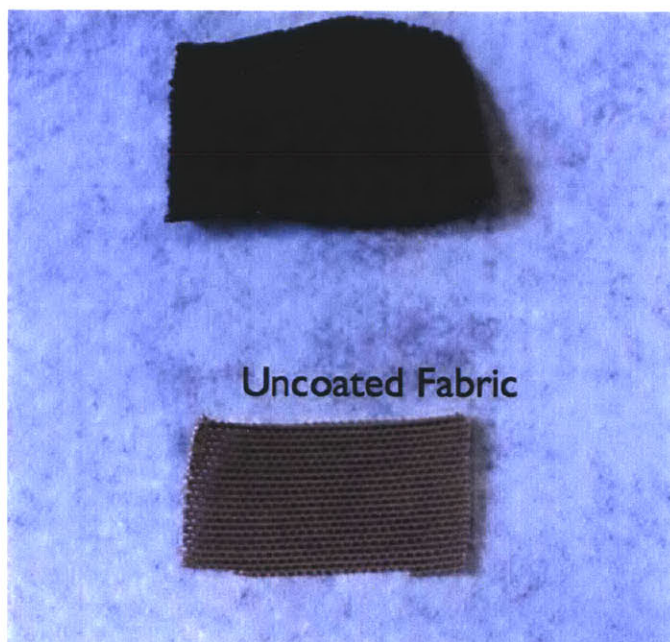
Figure 2: Comparison of the Power Net cloth after being sonicated with the carbon nanotube solution as compared to one that has not been placed in the carbon nanotube solution.

3.2 Fume Hood Dynamic Mechanical Analyzer

Some studies have found carbon nanotubes to be toxic for humans. It has been found that when carbon nanotubes enter cells, they tend to center within the cell nucleus and cause cell

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mortality [16]. Due to this toxic effect, the tests have to be conducted inside a chemical hood, and a new dynamic mechanical analyzer had to be built. The new DMA to be used for testing the carbon nanotube strain sensors had to be small enough to fit inside of the chemical hood, but it also needed the robustness, and durability to undergo a large number of tests. The final design of the hood DMA can be seen in Figure 3 below, the controls of the DMA will be addressed later in this chapter.
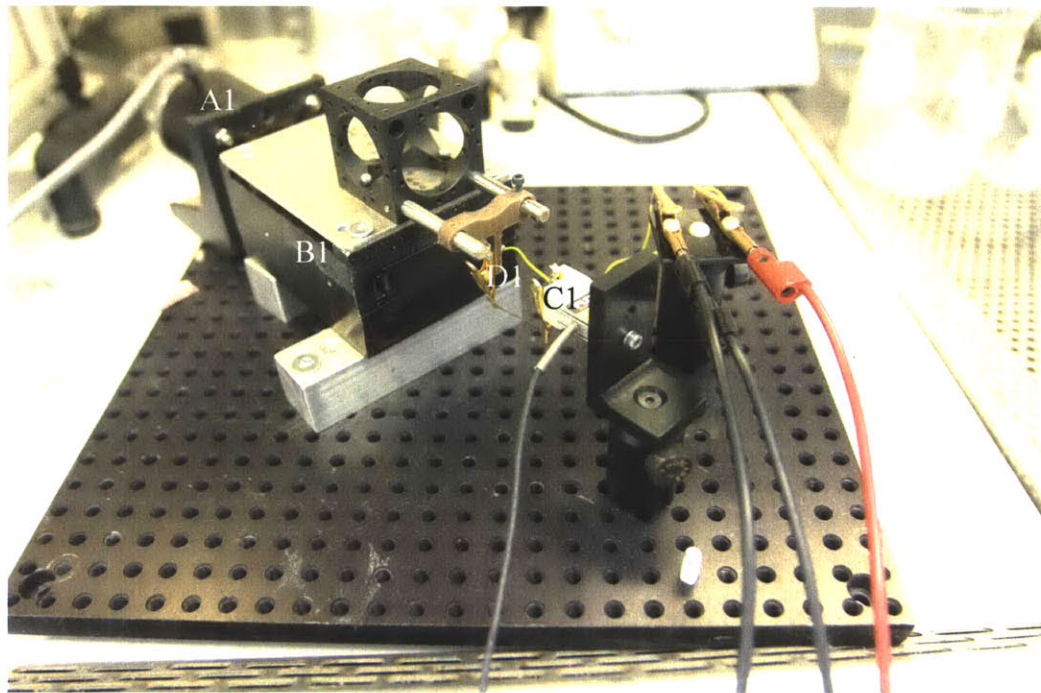
Figure 3: Dynamic mechanical analyzer set up inside of fume hood. The stepper motor (A1), linear stage actuator (B1), force sensor (C1), and electrically conductive clamps that hold the sample and measure electrical current (D1) can be seen.

The entire mechanical actuation of the hood DMA is composed of four main components that sit on top of a flat steel base. The four main components are a stepper motor (A1), a linear stage actuator (B1), a force sensor (C1), and electrically conductive clamps that hold the sample and measure electrical current (D1). The stepper motor is a model "Compumotor 67" which is mounted on the surface of the steel base. The motor is connected to the linear stage that moves

horizontally forward as the stepper motor moves clockwise, and backwards, towards the stepper motor, when the stepper motor rotates counter-clockwise. Attached on top of the linear stage is an aluminum base that holds the supports for one of the clamps that hold the sample. On the opposite side of this set-up is another support that holds a FUTEK brand Model LSB200 load cell that is rated for a maximum of 1 N. Attached to the front of this force cell is another support that holds the second clamp that holds the other side of the sample. In this fashion, as one side of the set up moves horizontally, thus pulling and pushing the sample, the opposite side stays in place applying a uniaxial tensile load and measuring the force on the sample. Each clip that holds the sample is conductive and is attached to a wire that is then connected to a separate set of clamps. This set up can be more clearly seen in Figures 4 and 5. These wires are connected to a potentiostat that applies a constant voltage and measures the change in current that is then correlated to the change in resistance of the samples. These auxiliary devices will be discussed in the following section.
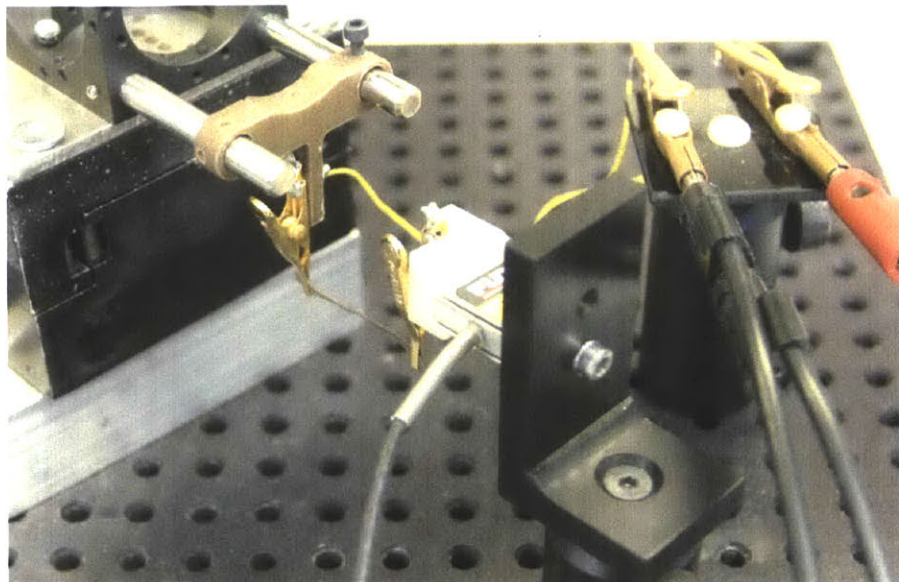
Figure 4: Close up of clamp set up, including the force sensor and the wires that go to the potentiostat. Notice the carbon nanotube strain sensor attached to the clamps

3.2.1 Supporting Hardware Used to Operate the DMA
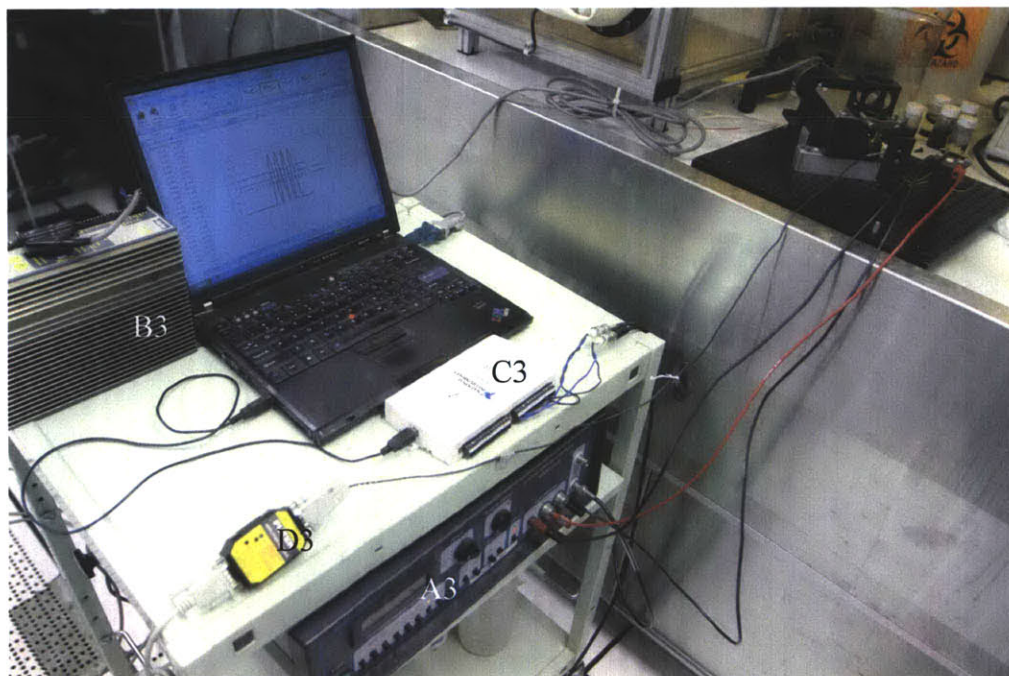
Figure 5: DMA with supporting hardware. The figure shows the AMEL brand Model 2049 potentiostat (A3), the Parker Zeta6104 motor control (B3), the National Instruments 6216 data acquisition device (C3) and the FUTEK amplifier module (D3).
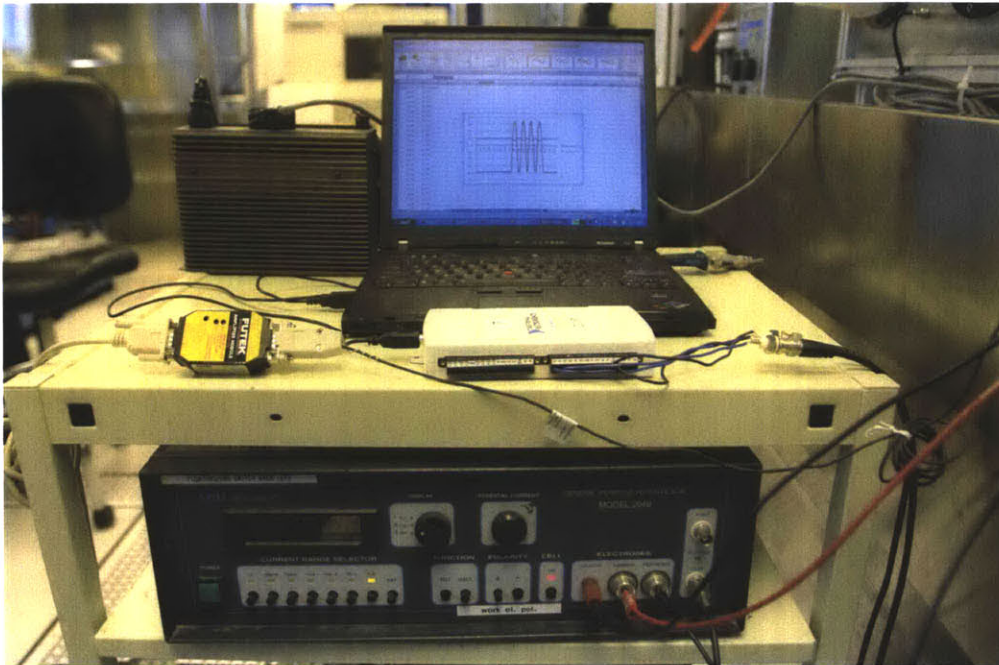
Figure 6: Auxiliary devices to the DMA.

3.2.2 Providing Power to the DMA and Collecting Data:

Figures 5 and 6 show the overall set up of the DMA including the mechanical components, the AMEL brand Model 2049 Potentiostat (A3), the Parker Zeta6104 Motor control (B3), the National Instruments 6216 data acquisition device (C3) and the FUTEK amplifier module (D3). Not pictured in Figures 4 and 5, there is also an Agilent brand model 3633A power supply that is part of the system. The power supply provides a constant 12 V DC to power the FUTEK amplifier module.

The potentiostat and the motor controller receive their power from the wall outlet. The Potentiostat provides a constant 5 V to the sample through the wires and clamps mentioned in the previous section. In addition to providing the 5 V of constant voltage, the potentiostat also measures the current going through the sample. The current data is then collected by the data acquisition device and is saved to the laptop that collects all of the data. The force data is passed

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through the FUTEK amplifier module, and is also collected by the data acquisition device, and saved to the computer.

National Instruments LabView software is used to collect all of the data coming from the data acquisition device. A code was created that collects the data from the two channels of the data acquisition device, the current data and the force data. The user-interface of the data collection can be seen in Figure 7 below.
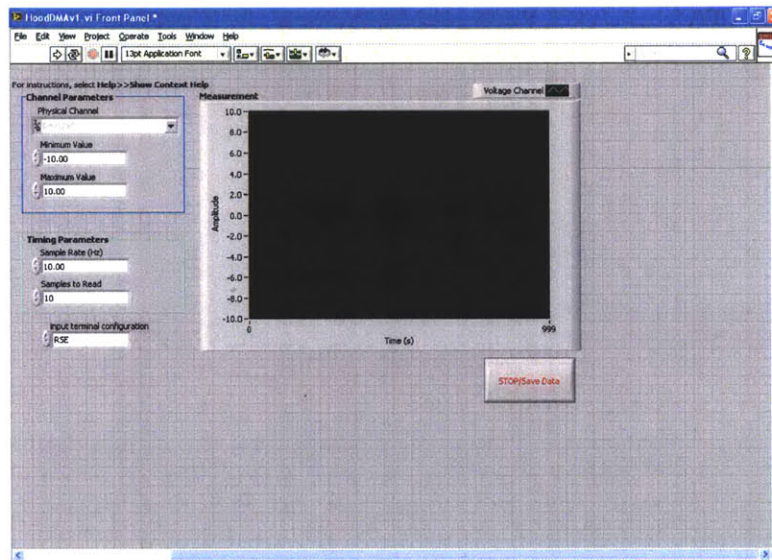
Figure 7: Image of the user-interface of the LabView data collector.
The program automatically saves the data to an Excel spreadsheet

The data from the LabView code is collected at 10 Hz and is saved as an Excel spreadsheet. Both of the inputs from the data acquisition device are in the form of a voltage, therefore the data needs to be calibrated and converted to the correct units of N for the data from the load cell and of Ohms for the data from the potentiostat. In both cases this was done with Matlab. In order to convert the force voltage data, a calibration factor had to be generated. To generate the calibration factor, the load cell was held vertically while its output voltage was being measured. Then, six masses ranging from 4 gm to 100 gm were suspended from the load cell. As a result,

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the voltage that corresponded to different forces being applied on the load cell was known. These values were then plotted, and a linear relationship between force and voltage was established. This calibration factor was then used to plot the force applied to the sample over time. The data from the potentiostat also had to be converted from Volts to Amperes, and then from the current, the resistance was calculated. The Matlab code was then made to plot the resistance of the sample and the change in resistance over time. These results were analyzed and will be explored in the results section of this paper.

3.2.3 Controlling the Linear Stage

The stepper motor is controlled through the Zeta6104 motor controller. Using the "Open Test and Measurement" tool from Matlab, a code was generated that connected the computer to the motor controller, and controlled the stepper motor. This code can operate the stepper motor, and thus the linear stage at a variety of speeds and accelerations. Furthermore, the code could also apply different strains to the samples. For the majority of tests, strains ranged from 1% to 48%. A calibration factor that took into account the number of "steps" that the stepper motor was told to rotate, and correlated it to the horizontal displacement of the linear stage was also generated to accurately control the motor.

The code functioned by first establishing a connection between the USB serial port in the computer and the motor controller. Once a connection was established one could simply input the desired movements of the motor and the Matlab would send them to the motor controller that would then execute the commands, causing motion in the steppe motor. The usual order of command started by writing the number of steps for the motor to rotate, this would be the rotational distance. After the distance that the motor was established, the acceleration and a velocity at which the motor needed to move was written in the code. After all the movements

that one wished for the motor to perform were inputted in the code, the code was asked to run, prompting the controller to power the motor in the desired direction, velocity and acceleration. These commands could be added on top of each other and could be changed at will, thus the motor could move in multiple cycles with just one command. For the long term tests, a while loop was created that commanded the motor to continue operating in a clockwise and counterclockwise cycle until a value was changed. In this way, there was no need to physically type all of the commands that the motor needed to perform, rather, one cycle was written in the code, and the motor was told to perform this cycle until commanded otherwise.

In order to calibrate the rotational motor distance with the horizontal distance that the linear stage moved, different values for the steps of the motor were inputted to the code, and the physical distance that the linear stage moved was measured. After twelve different distances were measured, the data was plotted and a linear relationship emerged relating the code step input to the motor physical distance movement. This data was then used to calculate the strain at which the different samples were tested.

3.3 Understanding the properties of the Carbon nanotube Strain sensors.

All of the tests involved the above-mentioned DMA. After each strip was prepared according to its specific test, the strip was removed from the vial and placed in the DMA. The carbon nanotube covered strips were held by two clips that pinched each end of the strip at a distance of 26 mm. The initial distance separating the two clips that held all of the strips was held constant for all of the tests.

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3.3.1 Conductivity of the Carbon Nanotube Covered Strips

To understand the effect of strain on the resistance of the carbon nanotube samples, and how they can be used as strain sensors, we can explore the conductivity of elastic beams. Conductivity, σ, in this case is assumed to be for an elastic beam, and is defined as Equation 3.1,

$$\sigma = \frac{l_\circ}{R_\circ A_\circ},$$

$$(3.1)$$

where R is resistance, $l_\circ$ is the initial length and $A_\circ$ is the initial cross-sectional area of the strain sensor. Because this is assumed to be an elastic beam, uniaxial stress causes strain in both the axial and lateral directions as governed by Poisson's ratio, (v).

Assuming uniaxial stress, the fundamental linear stress-strain relationships are,

$$\varepsilon_x = \frac{1}{E}\sigma,$$
$$\varepsilon_y = \frac{-v}{E}\sigma = -v\varepsilon_x, and$$
$$\varepsilon_z = \frac{-v}{E}\sigma = -v\varepsilon_x.$$

$$(3.2)$$

Therefore, the cross-sectional area of the sample, A, is variable and is defined as,

$$A = yz = (y_\circ + \delta_y) + (z_\circ + \delta_z)$$

$$(3.3)$$

where δ_y and δ_z represent the deformation of the sample in the y and z directions. We also know that strain, is defined as,

$$\varepsilon_i = \frac{\delta_i}{l_i},$$

$$(3.4)$$

where, δ_i is the change in length of the sample and l_i is the original length of the sample. Substituting into the area, we get,

$$A = A_\circ (1 - v\varepsilon_x)^2 .$$ (3.5)

We can then use the definition of conductivity, and solve for resistance. We can then substitute into this equation the variables for conductivity, and area, thus we get,

$$R = \frac{x}{\sigma A} = \frac{x_\circ + \delta_x}{(\frac{x_\circ}{R_\circ A_\circ}) A_\circ (1 - v\varepsilon_x)^2} .$$ (3.6)

Rearranging the terms, we get,

$$R_s = R_c \frac{x_\circ + \delta_x}{x_\circ (1 - v\frac{\delta_x}{x_\circ})^2} = R_c \frac{1 + \varepsilon_x}{(1 - v\varepsilon_x)^2} \ [12].$$ (3.7)

Thus, the strain applied to a sample is related to its resistance. In order to calculate the conductivity of the carbon nanotube strain sensors, the resistance of a variety of samples was taken before every test. With the values for the cross-sectional area, length and resistance of the strips, the initial conductivity was calculated.

3.3.2 Effect of Functional Groups

Two functional groups were used and tested for their potential as carbon nanotube strain sensors. The first group is the carboxylate carbon nanotube group, and the other one was a sulfonate carbon nanotube group. For these sets of tests, the strips of flexible cloth were soaked in the carboxylate carbon nanotube and in the sulfonate carbon nanotube. Each sample was placed in the sonication machine for 30 minutes. After the samples had been sonicated, seven tests were performed on each sample, corresponding to seven different strains. The strains were 1%, 3%, 6%, 12%, 24%, and 48% strain.

3.3.3 Effect of Sonication Times

The impact that Sonication time has on the performance of the carbon nanotube strain sensor was also studied. In order to perform this experiment, three different samples were made of the carboxylate functioning group, one sample was placed in the sonication machine for 30 minutes, the second sample was placed in the sonication machine for 1 hour and the third sample was placed in the sonication machine for 2 hours. Once again, each sample was tested for seven different strains. Just as the experiments regarding the functional group, these experiments were done with strains of 1%, 3%, 6%, 12%, 24%, and 48%.

3.3.4 Effect of Time Spent "Soaking" in the CNT Solution over a Long-Term Test

In order to better comprehend the functionality of the CNT strain sensors, it is necessary to evaluate their long term potential as strain sensors. For this data, various long-term tests were conducted where the strain sensor was subjected to a cyclical strain over a period of time. This test was continued until the strain sensor ceased to work. The first long term tests were conducted with a cyclical strain of 0.5 Hz, with a strain of 16%. The variable changed when these tests

were conducted was not the sonication time, but rather the amount of time that the strips of cloth were left soaking in the carbon nanotube solution. Three samples were made, and all of them had a sonication time of 30 minutes. However, one sample of cloth was left inside the vial soaking in the CNT solution for 30 minutes, the second sample was left soaking in the solution for 5.5 hours, and the third sample was left soaking in the solution for 25 hours. Unfortunately the data for the 30-minute "sitting" time was not available because the samples dried up before the test could start. After the sample had been left soaking for the required period of time, the strips of cloth were taken removed from the solution and placed in dry vials that were sealed. As it will be later explained in the results section, it was discovered that the drying up of the sample was the biggest factor in the deterioration of the strain sensors over time. Due to this fact an encapsulation technique was developed in order to try to minimize the deterioration due to drying of the strain sensors.

3.3.5 Effect of an Encapsulation of the Samples:

Two materials were explored to fulfill the role of encapsulating the CNT covered cloth samples. The intention was that a simple method of sealing the strip of cloth could be created that prevented the liquid from evaporating, thus keeping the cloth wet, and the strain sensor functional for as long a period as possible. The GLAD brand "Press and Seal" product turned out not to be a viable option for encapsulating the strain samples due to the fact that the seal was easily broken with the solution, and it did not last when placed in the DMA. The second material that was proposed in order to seal the CNT strain sensors was a wrapping of 3M's brand "Scotch Tape." The tape was wrapped around the middle of the cloth, leaving the ends open so that the DMA connections could be attach and could still measure the resistance of the CNT sensor. Figure 8 shows the tape encasing around the CNT covered cloth.
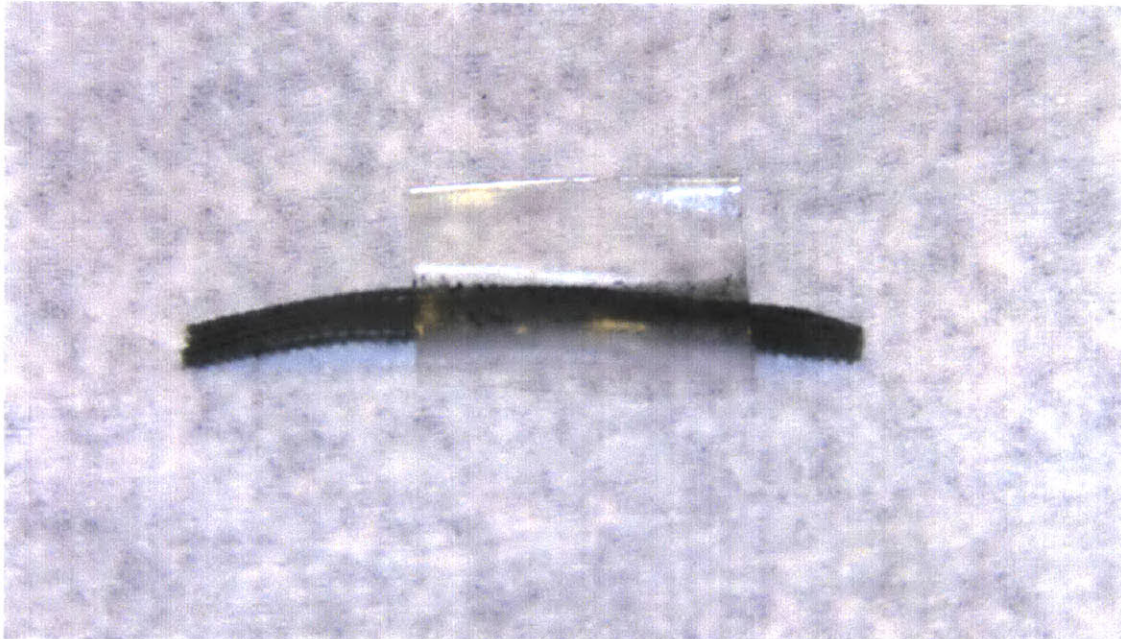
Figure 8: Picture of a carbon nanotube strain sensor encapsulated with Scotch brand tape. The ends are not encapsulated so that the resistance can be measured.

Two different sets of tests were performed in order to examine the effect of the encapsulation on the sample. Samples were sonicated for 2 hours and two long-term tests were conducted. The first sample was encapsulated with the above-mentioned "Scotch Tape" covering, and the second sample that was tested was not encapsulated. Both samples were tested at 38% strain. The second set of tests was performed in order to explore the performance of the resistivity of the samples over time with no strain applied. In these tests an encapsulated and a non-encapsulated sample were attached to the conducting clamps of the DMA but no strain was applied on them. The resistance change over time was measured for both samples. Again, the results will be discussed in the results section.

3.3.6 Gauge Factor

The gauge factor is the ratio of relative change in electrical resistance to the mechanical strain, ε. It is defined as [17],

$$GF = \frac{\frac{\Delta R}{R}}{\varepsilon}. \tag{3.8}$$

The gauge factor of the sulfonate carbon nanotube strain sensors was calculated by doing a set of tests that varied the strain of the carbon nanotube samples. The strain amplitudes applied to the samples were 16%, 21%, 25%, 30%, 34%, 38% and 42%. The tests were performed on multiple that had undergone a sonication time of 30 minutes and 1 hour. The data was collected by measuring the initial resistance of the samples and the change in resistance with the applied strain.

4. Results and Discussion
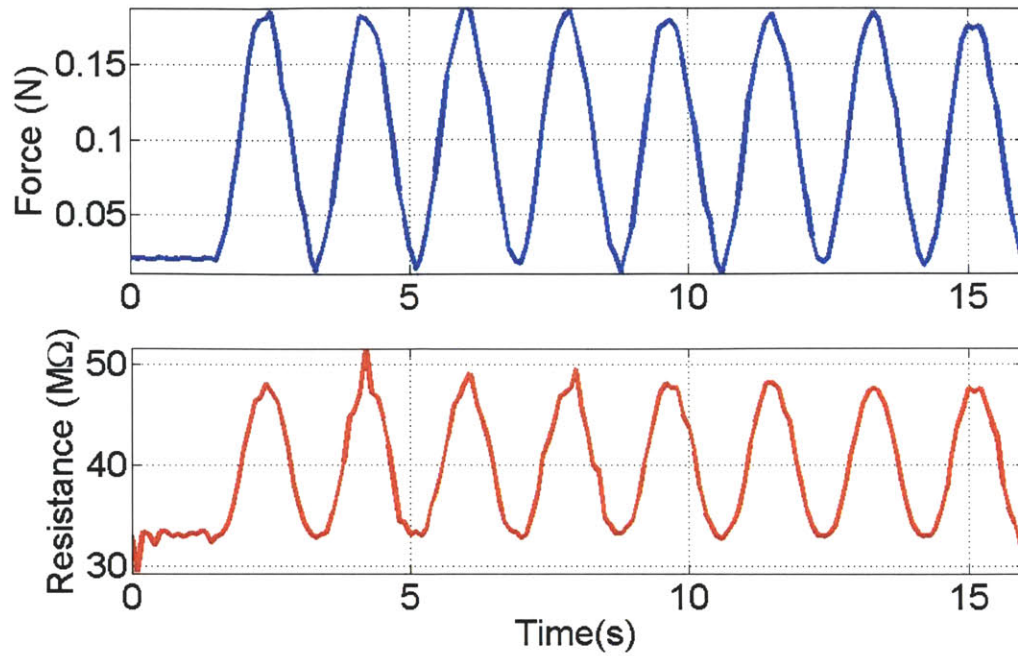
Figure 9: The graphs above show the data which were collected using the LabView code. It shows the change in resistance over time as well as the force felt by the sample over time. The force applied is proportional to the strain applied on the sample. The data shown above is basis for all of the other data analyzed.

4.1 Conductivity
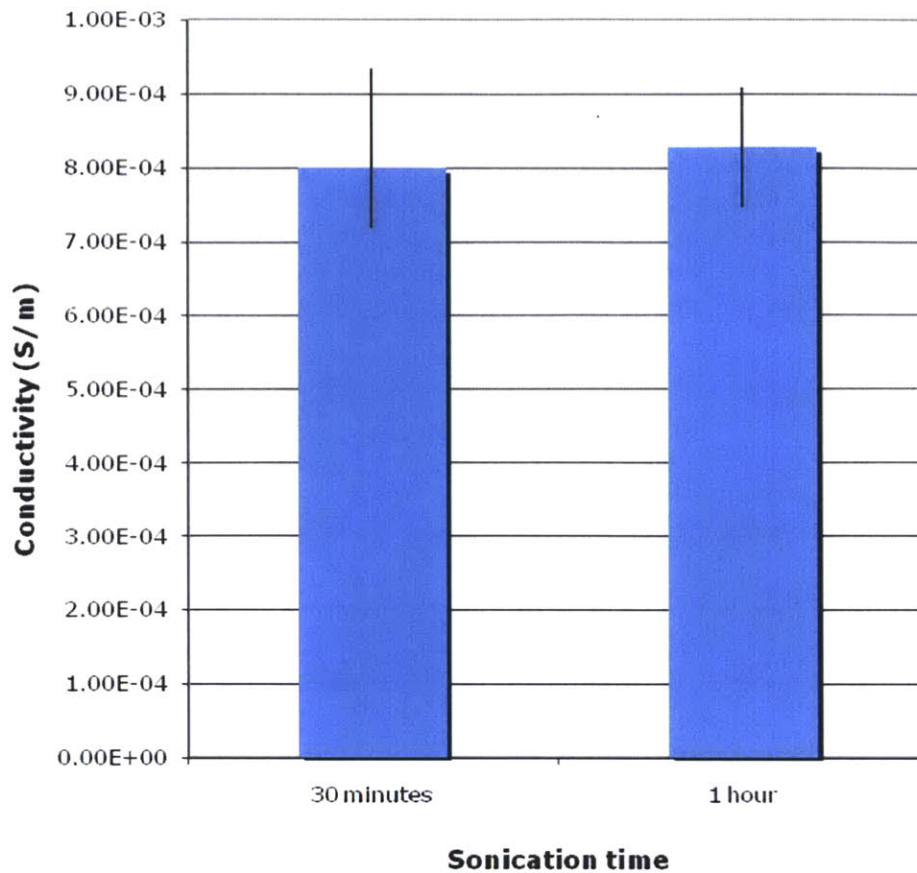
Figure 10: Average conductivity of the sulfonate CNT covered cloths for sonication times of 30 minutes and 1 hour.

Figure 10 above shows the conductivity, as defined by Equation 1.1 for samples of the sulfonate group CNTs. From the data, we can conclude that the conductivity for sulfonate CNT covered cloths with a cross-sectional area of 1.33×10^{-6} m^2 and a length of 26 mm is about 8.0×10^{-4} S/m for 30-minute sonication time and about 8.3×10^{-4} S/m for a 1-hour sonication time. The data from the graph indicates that a longer sonication time, can have an effect on the initial resistance and conductivity of a sample, but it is not very noticeable.

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4.2 Functional Group

Two functional groups were tested for their response regarding their resistance change compared to the strain they had undergone. One functional group was the carboxylate carbon nanotube group, and the other one was a sulfonate carbon nanotube group. The results of this test are plotted in Figure 11 below.
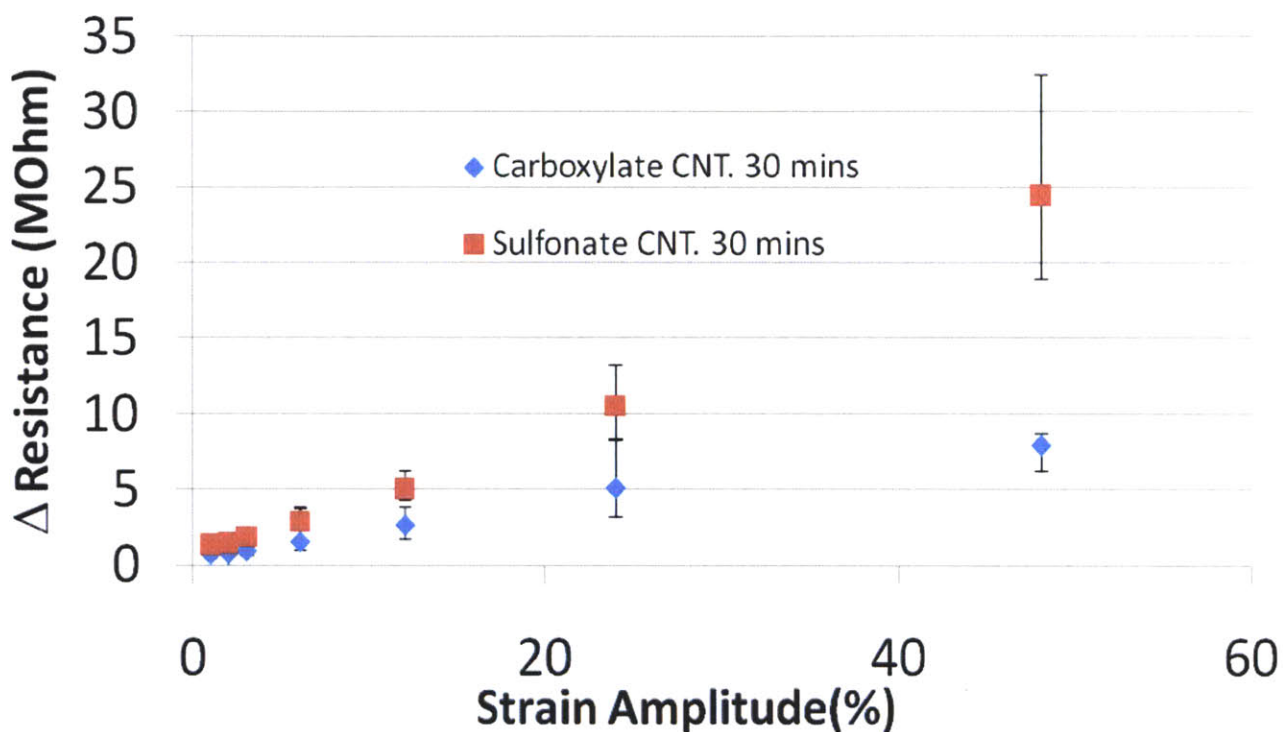
Figure 11: Response of both the carboxylate and the sulfonate CNTs, both exposed to 30 minutes of sonication time and seven different strain amplitudes.

From Figure 11 above, it is clear that the carboxylate group CNT has a lower change in resistance over increasing strain amplitude than the sulfonate group. The carboxylate group CNT had an originally lower resistance than the sulfonate group CNT, and the tests showed that the change in resistance of the sulfonate group increased at a rate about 3 times higher than carboxylate group. This could be due to the carboxylate CNT group being able to attach more

easily to the cloth. The sulfonate group CNT on the other hand could be less likely to attach to the strips of cloth, thus as the strain increases, it is more likely to come apart and create a higher change in resistance than the carboxylate CNT group.

4.3 Sonication Time

In classifying the CNT strain sensors, it was also important to understand the effect that sonication time has on the resistance response. Response of carboxylate CNT covered cloth with three different sonication times; 30 minutes, 1 hour and 2 hours can be seen in Figure 12 below.
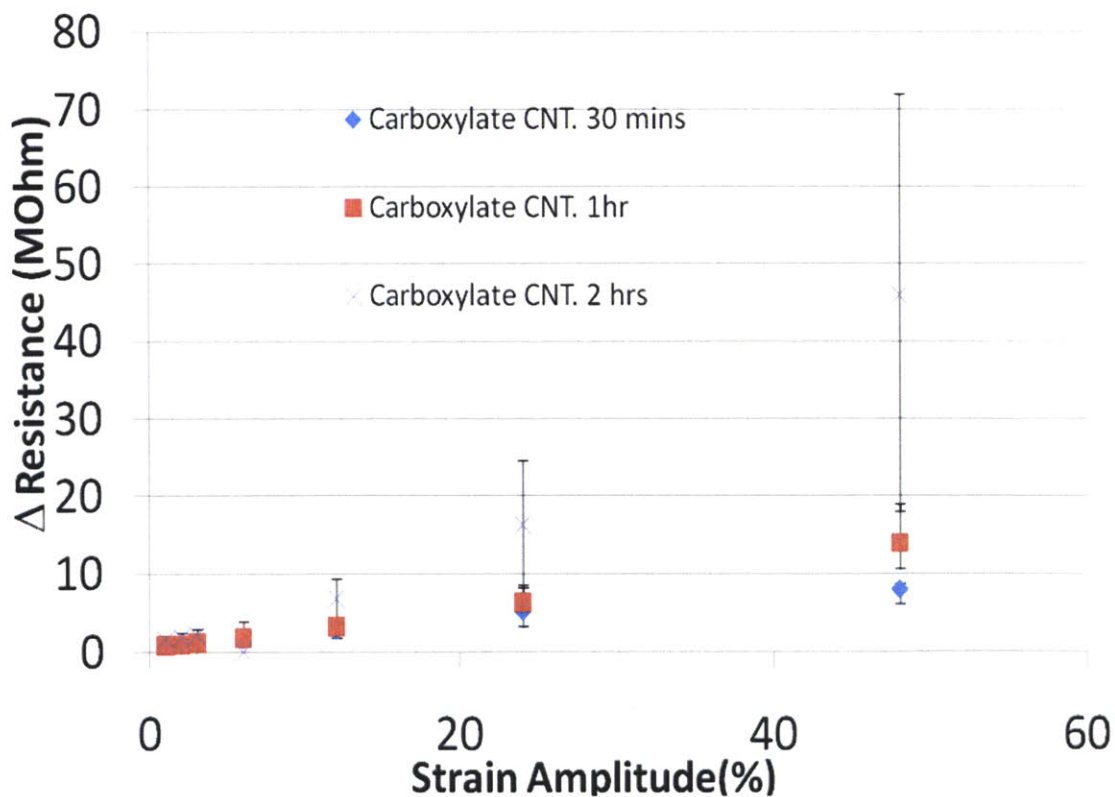

Figure 12: Response of carboxylate group CNTs exposed to three different sonication times and tested at seven different strain amplitudes.

The results of the different tests comparing the effect that sonication time has on the change in resistance of the carboxylate CNTs show that there is a substantial difference in the sonication time and the change in resistance with regards to strain amplitude. It can be concluded that the higher the sonication time of the sample, the higher the change in resistance of the sample. From the data collected it is conclusive that the change in resistance increase with respect to strain amplitude is about 1.5 times higher for the 1-hour sonication time as compared to the 30-minute sonication time. Moreover, the 2-hour sonication time has an increase in change in resistance with respect to strain amplitude that is about 3.5 times higher than the 1 hr sonication time samples. More interesting is the fact that the carboxylate CNTs with the longer sonication time had the higher change in resistance. This is slightly different than the conductivity data, and could be due to the fact that the change in resistance changes in proportion to the strain applied on the sample. It is suggested that the reason for this higher change in resistance over time for the longer sonication time is due to the fact that the carboxylate carbon nanotubes lose adherence to the cloth samples as the strain amplitude increases, and as the sonication time increases. As a result, the carbon nanotubes have a higher change in resistance that gets larger as the strain amplitude is increased.

4.4 Effect of Encapsulation on Samples

It was important to understand how the resistance of the strain sensors increases over time with no applied strain. Previous tests have indicated that the resistance increases as time passes due to the drying of the carbon nanotube solution off of the strips of cloth. Therefore two different tests were conducted that compared the increase in resistance over time for a cloth sample as tested before, and a cloth sample with the majority of the strip encapsulated with

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Scotch Brand tape. Both samples were placed on the DMA and left over a period of time to see their resistance response. The results of the tests with no strain can be seen in Figure 13 below.
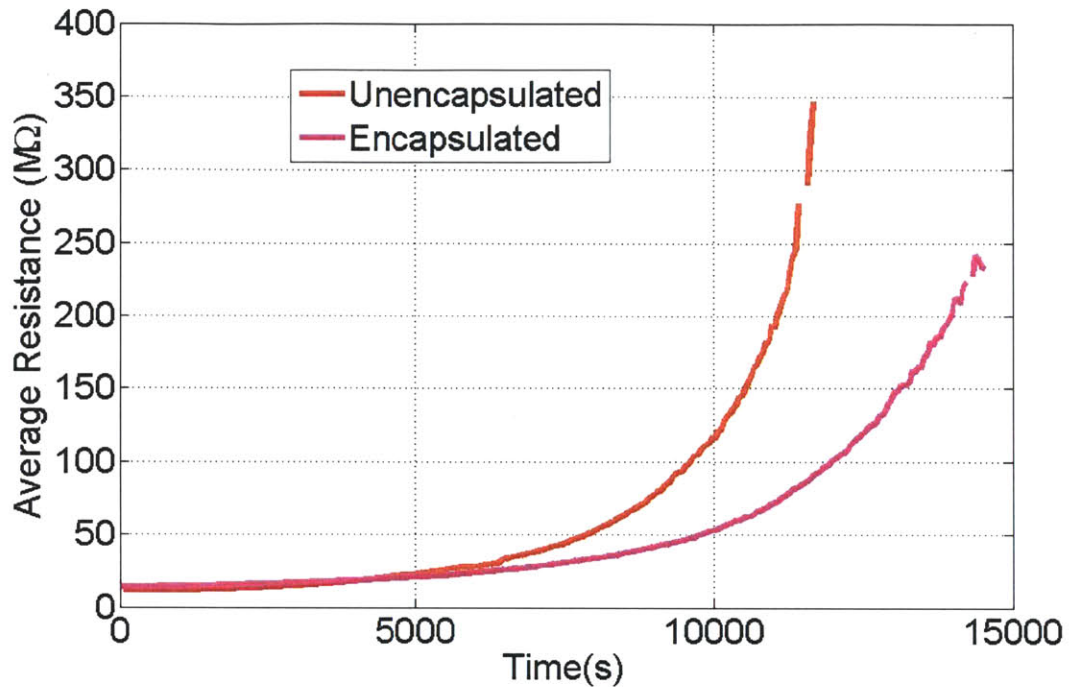
Figure 13: Resistance increase of two strain sensors left over time with no strain amplitude applied. The red curve shows a strain sensor as fabricated in all other tests while the magenta curve shows a strain sensor with an encapsulation. Notice the faster increase in resistance for the sample that was not encapsulated.

The results of the no-strain tests of encapsulated versus non-encapsulated samples lead to the conclusion that the CNT strain sensors have a decrease in conductivity over time. After careful examination of the samples it was concluded that this is due to the fact that the CNT solution dries off of the strips of cloth. Moreover, from the comparison of the tests above, it can be concluded that creating a form of encapsulation around the strain sensors does delay the decaying of the strain sensors. The resistance increase in both tests is exponential. Looking at the data for average resistance over time, the resistance of the non-encapsulated samples increased faster than that of the encapsulated samples. Looking at the data for the encapsulated samples shows that

30

the resistance at 10000 s is only 50 MΩ, while it is about 115 MΩ for the non-encapsulated samples. After 12000 s, the resistance of the non-encapsulated sample reaches about 700 MΩ, while that of the encapsulated sample is close to 102 MΩ. The slower increase in resistance for the encapsulated sample is due to the fact that an encapsulation prevents more air from coming in contact with the sample, thus slowing down the drying of the solution.

4.5 Change in Time that Samples are Left Soaking in Solution

Another variable that was tested in order to characterize the carbon nanotube strain sensors was the effect that time left soaking inside of the solution had on its strain-stress response. The following figures show the results of samples that had 30 minutes of sonication time but stayed inside the carbon nanotube solution for 5.5 hours and 25 hours respectively.
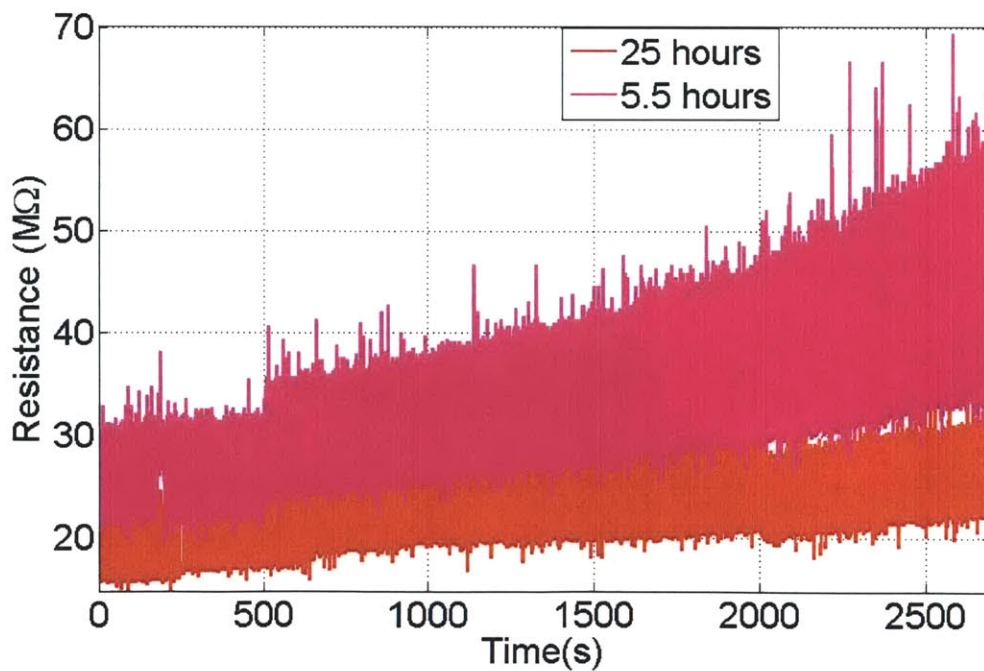
Figure 14: Resistance change over time of samples created with a 30 minute sonication time and with 25 hours and 5.5 hours soaking in the solution tested at 16% strain.

Figure 14 above demonstrate the effect that time soaking inside of the CNT solution has on the sample. The unedited resistance with respect to time data shows that the time left soaking inside of the solution does have an effect on the initial resistance and change in resistance of the sample over time. The sample left soaking inside of the solution for 25 hours had a lower resistance than the sample left soaking inside of the solution for 5.5 hours. Moreover, the 5.5-hour sample had a smaller change in resistance over time than the 25-hour sample. The data above is only recorded until a time of 2700 s because there was an error in the DMA and the samples had to be reset. Once these samples were reset, the tension on them was changed slightly, and it altered the results for the rest of the experiment, therefore only data for time up to 2500s is analyzed. Further analysis of this data is done in Figures 15 and 16 below.
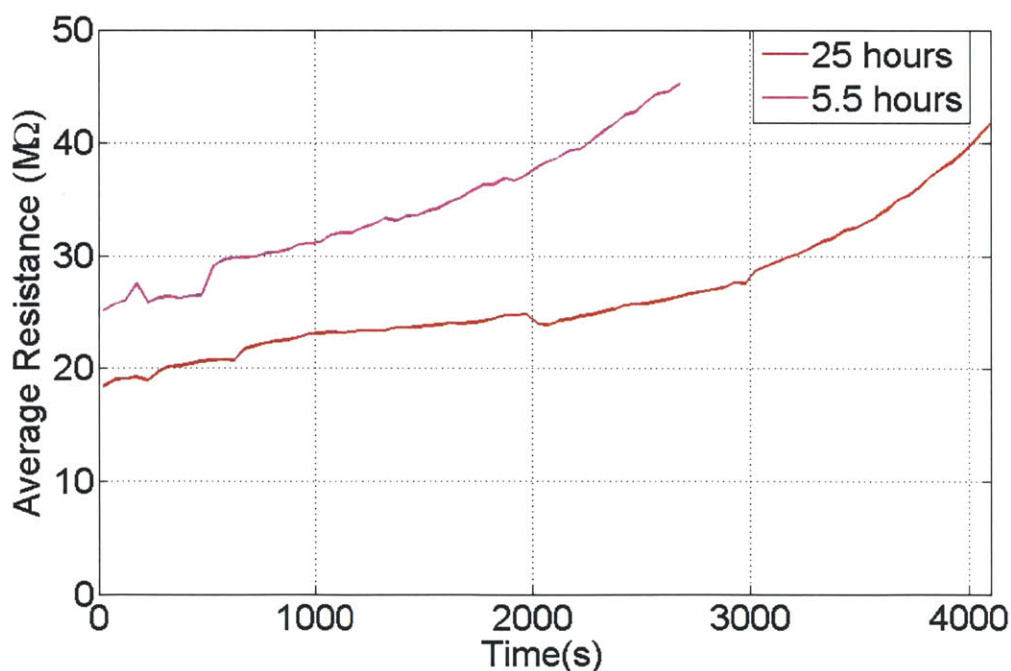
Figure 15: Average resistance increase over time of samples created with a 30-minute sonication time and a difference in time soaking inside of the solution tested at 16% strain. The samples were left soaking for 25 hours and 5.5 hours

Figure 15 above show the average resistance over time. The graph shows that the 5.5-hour sample had a higher initial resistance than the 25-hour sample, and this stayed constant throughout the experiment. Moreover, the graph also illustrates that the 5.5-hour sample has a faster increase in resistance over time for the first 2500 s. After 2000 s the 5.5-hour sample had an average resistance of about 40 MΩ, while the 25-hour sample had an average resistance of only 25 MΩ. This is likely due to the fact that when the samples are left soaking for a long period of time, it allows the carbon nanotubes to settle and attach to the strips of cloth. If there are more carbon nanotubes attached to the strip of cloth, then the resistance of the sample tends to be lower.

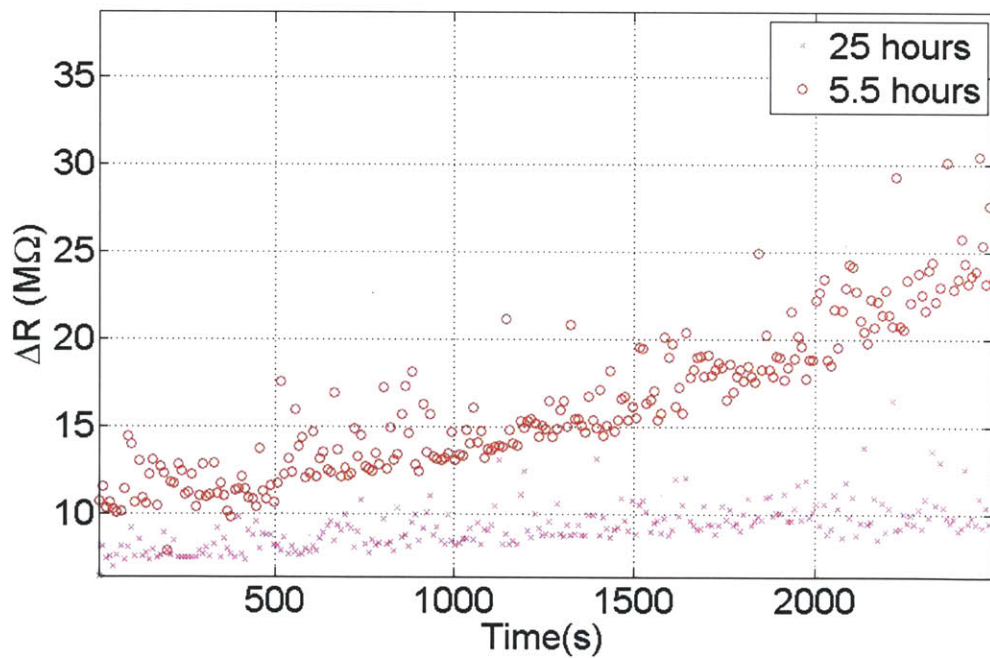Figure 16: Change in the range of resistance over time of a sample created with a 30-minute sonication time and with 25 hours sitting in solution tested at 16% strain

Figure 16 above demonstrates that the increase in the range of the resistance is higher for the 5.5-hour sample than for the 25-hour sample. For the first 2500 s of this test the resistance

difference for the 25-hour sample stayed nearly constant. The resistance difference on the 5.5-hour sample on the other hand, increased constantly over the same period. After 2000 s, the 5.5-hour sample has a range of resistance of about 20 MΩ, where the 25-hour sample only has a resistance range of a little over 10 MΩ. The increasing resistance change of the 5.5-hour sample is consistent with the previous observations that the carboxylate groups CNTs, when not allowed to attach to the sample, create an increase in overall resistance and in resistance change of the strain sensors. All of these results lead to the conclusion that the amount of time the samples are left soaking in the solution does have an effect on the change in resistance over time.

4.6 Encapsulation versus Non-Encapsulation with Strain

The results for the carbon nanotube strain sensors with 2-hour sonication time and tests at 38% strain amplitude are seen below. Each set of data will be compared between the samples encapsulated in Scotch brand Tape and those that were not.

Figure 17: Resistance increase over time of an encapsulated carbon nanotube strain sensor and a non-encapsulated carbon nanotube strain sensor both tested with a cyclical 38% strain

Figure 17 above shows the raw data of the increase in resistance over time of both the encapsulated and non-encapsulated carbon nanotube strain samples. The data shows that the resistance increases at an accelerating rate over time. Additionally of the resistance increasing, the range in resistance from the lowest measured resistance in each strain cycle to the highest measured resistance in that same strain cycle also increases over time. Moreover, it is clear that the encapsulation of the sample does have a positive effect in keeping the resistance constant over a longer period of time. It is important to note that when the resistance gets above 200 MΩ, noise from the potentiostat creates error in the data to the point that the data was invalid. This data will be further analyzed in Figures 18 and 19 below.
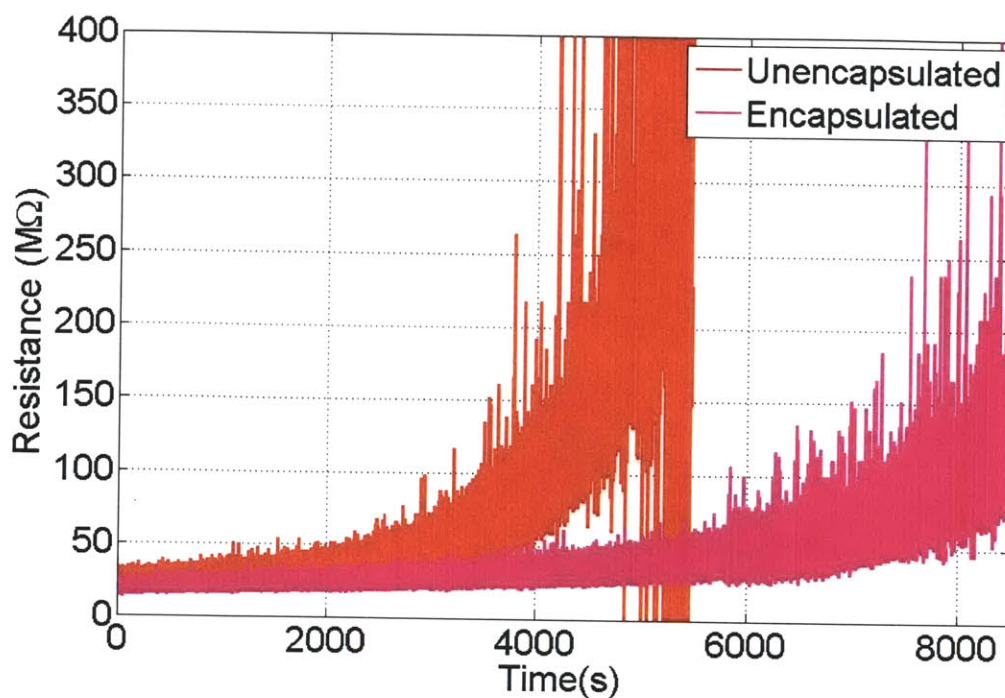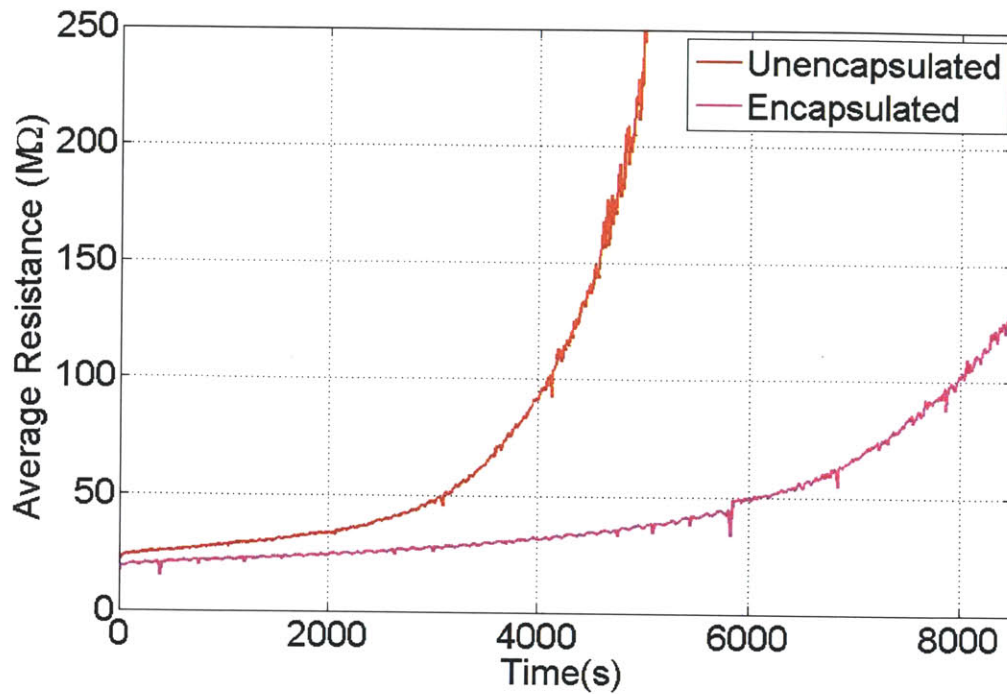
Figure 18: Average resistance of an encapsulated carbon nanotube strain sensor and a non-encapsulated carbon nanotube strain sensor tested at 38% strain.

Figure 18 above show the averaged change in resistance over the entire tests. The data demonstrates that both samples have an exponentially increasing resistance over time. Moreover, further evaluation of the data demonstrates that the non-encapsulated samples have an increase in resistance in the linear portion of the data that is roughly two times larger than the encapsulated samples. This linear portion is the data for up to time 2000 s. This demonstrates that encapsulating the samples does have a significant impact in reducing the rate of resistance increase over time. After the average resistance reaches around 30 MΩ, the average increase in resistance becomes exponential. The encapsulated sample reached 100 MΩ in a period of 8000 s while the non-encapsulated sample had a resistance of 100 MΩ at only 4000 s. Although the encapsulation created in this experiment extended the life of the strain sensor, these rudimentary methods of covering the samples are still not sufficient to prevent the resistance to eventually increase to levels that would make the carbon nanotube strain sensor useless. It is important to

note, the noise seen in both sets of data after the resistance gets over 100 MΩ is caused by the potentiostat.
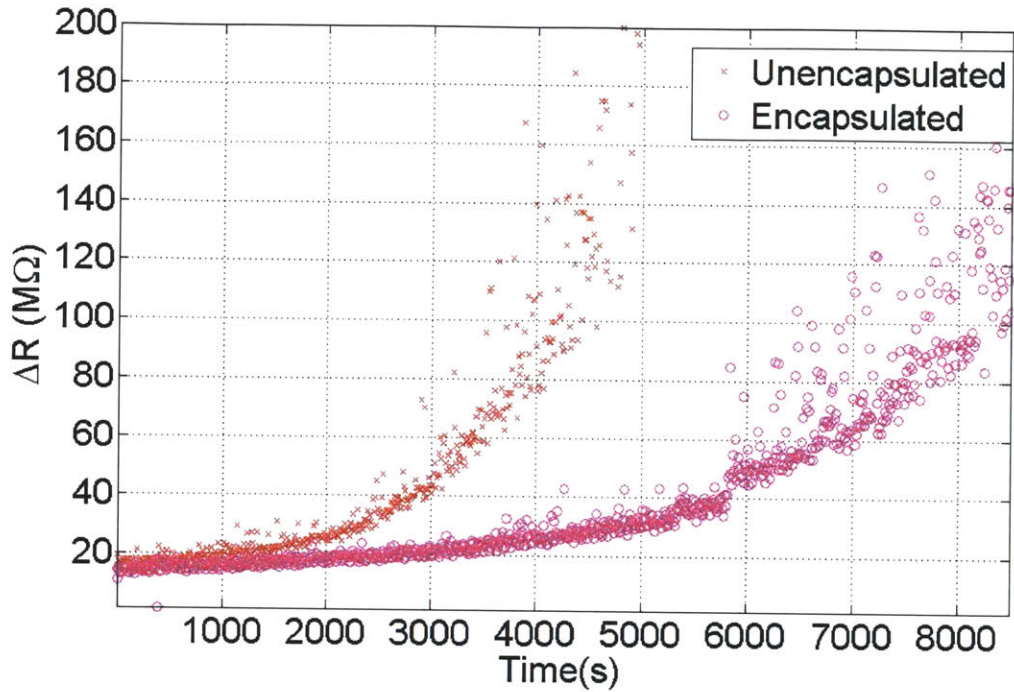
Figure 19: The change in the range in resistance of an encapsulated carbon nanotube strain sensor and a non-encapsulated carbon nanotube strain sensor over time tested at 38% strain.

Figure 19 was created by taking measurements from the data and calculates the range of resistance for various strain cycles. This is done every ten seconds of data and it shows that the range in resistance also increases over time. Again, the sample that is encapsulated shows a slower increase in the range of resistance over time. By the time of 5000 s, the non-encapsulated sample had a maximum resistance range of 1150 MΩ, while the encapsulated sample only had ranges of 50 MΩ. The encapsulation of the samples helps to increase the lifetime of the current samples.

Additionally, when the data for the samples tested at 38% strain is compared to the data of the samples left with no applied strain over time, there are other observations. The encapsulated

samples tested with no strain reached a resistance of 100 MΩ at a time of around 12000 s, while the samples tested with a strain of 38% reached that resistance at about 8000 s. Moreover, the non-encapsulated samples tested with no strain reached a resistance of 100 MΩ at a time of around 9000 s while the non-encapsulated samples tested at 38% strain reached that resistance about 4500 s. This is a decrease of 50% in the useful life of the samples. Therefore, it can be concluded that the constant straining of the samples does decrease the life of the carbon nanotube strain sensors. The cyclical straining of the sensors likely causes separation of the carbon nanotubes in the cloth, thus increasing the resistance at a faster rate.

4.7 Gauge Factor
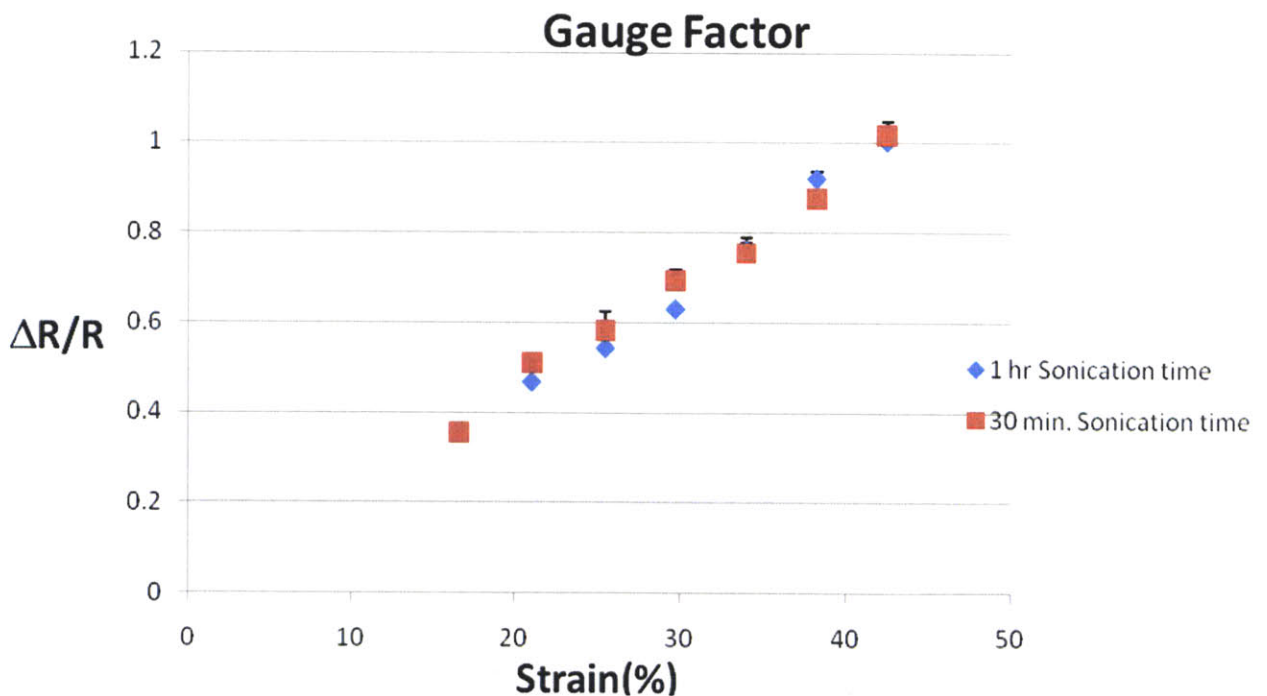
Figure 20: Change in resistance (ΔR), over the original resistance of the samples versus the strain amplitude for sulfonate carbon nanotube strain sensors.

The gauge factor was calculated as the difference in resistance over the original resistance of the sample over the strain. In essence, the gauge factor is the slope of Figure 20. For the

samples tested above the gauge factor was found out to be 2.3. This gauge factor is in the same magnitude of metal foil strain gauges, which range from 2 to 5. It is interesting to note that there is very little difference in the gauge factor of the 1-hour and 30-minute sonication time.

5. Conclusions

The results demonstrate that carbon nanotubes could be effectively used as high-elongation strain sensors. The samples tested were all capable of providing predictable resistance responses at strains of up to 48%. In characterizing the samples, it is clear that the sulfonate working-group CNTs have an overall higher resistance than the carboxylate working-group CNTs. Moreover, the carboxylate CNTs seem to be more susceptible to changes in the sonication time and soaking time of the strain sensors. A higher sonication time did seem not to lead to higher conductivity for the sulfonate CNT strain sensors but the same is not true for the carboxylate CNT strain sensors. It seems that with the carboxylate CNT sensors, the higher sonication time did lead to a lower initial resistance but it also lead to a faster increase in resistance over time and an increasing change in resistance with increasing strains. A longer soaking time for the carboxylate CNT strain sensors led to a higher resistance and a faster increase in resistance. The gauge factor for sulfonate carbon nanotube strain sensors was also calculated to be 2.3, and the conductivity of the sulfonate carbon nanotube strain sensors was measured to be around 8.0×10^{-4} S/m. Overall, it can be concluded that carbon nanotubes have a promising potential as macro level strain sensors for high-elongation applications but more development is yet to be done. Further studies could be done to validate the data of this thesis, as well as to further study the difference between the carboxylate-group CNTs and the sulfonate-group CNTs. Moreover, due to the precision usually needed for strain sensors, different methods could be studied to reduce any drift in resistance of these strain sensors. One proposed solution is the use of a bridge circuit. A Wheatstone bridge could be used to measure the resistance of the carbon nanotube strain sensors without the need of a potentiometer. Knowing the resistance of three legs of a Wheatstone bridge allows for the measurement of a fourth unknown resistance by measuring the

voltage across the bridge. This setup would allow for accurate measurements of the resistance of the of the carbon nanotube strain gauge.

After multiple tests, it was concluded that the carbon nanotube strain sensors decay exponentially over time due to the drying of the carbon nanotube solution off of the cloth. It was shown that a simple encapsulation method using Scotch Brand tape did delay the decaying of the samples by upwards of 100%. While this result is impressive, most carbon nanotube strain sensors tested still reached a resistance that made them useless after a period of about 2.5 hours. Further studies need to be carried out that analyze other methods of encapsulating the strain sensors or developing novel ways to avoid the drying of the solution so that they can have longer useful lives.

Due to this drying of the proposed carbon nanotube soaked cloths, a novel humidity sensor could be studied. It is suggested that with an increasing humidity, the rate of drying of the strain sensors will decrease. Therefore, further studies could test a correlation between the humidity of the atmosphere and the rate of resistance increase of the carbon nanotube covered cloths. If a relationship between humidity and rate of resistance increase in the carbon nanotube covered cloth is found, studies could be carried out to increase the useful life of the carbon nanotube covered cloths and make them reusable.

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