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# Characterization of Polyurethane for Use as Substrate in Nanofiber Sensor for Biomedical Applications

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Characterization of Polyurethane for Use as Substrate in Nanofiber Sensor for  
Biomedical Applications

Megan Theaker

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**Honors Research Project**

Submitted to

*The Honors College*

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## **Executive Summary**

The purpose of this project is to begin to determine properties of polymer nanocomposites that make a suitable substrate for nanofiber sensors. This problem arose when Dr. Chelsea Monty and her research team began examining polyurethane as the substrate for resistance temperature detectors (RTDs). Dr. Monty and her team have developed multiple sensors over the years to detect and monitor parameters on the users' skin such as temperature, pH, sweat sodium concentration, sweat lactate concentration, as well as others. These sensors used electrospun nylon-6 as the substrate with multi-walled carbon nanotubes (MWCNTs) as the conductive (sensing) material. The hypothesis was that polyurethane would perform better than nylon-6, due to properties such as its increased heat resistance. This hypothesis was proven incorrect, therefore, it was important to determine what properties of the polyurethane nanocomposites hinder its performance as a sensing substrate. In this work, sensitivity of a sodium ion selective sensor was used as a benchmark for comparison.

Using an ANOVA analysis, the results showed that the MWCNT type was a significant factor on sensor response both with and without additional functionalization of the polymer by calixarene. The weight percentage of polyurethane in the electrospinning solution was also statistically significant for sensors made with calixarene.

Conclusions made from this project include that the nanotube types affect both the conductivity of the sensor as well as the  $\text{Na}^+$  binding to calixarene. The polyurethane wt.% also affects sensor response, possibly due to the geometry of the sensor. The

experimental parameters (nanotube type, nanotube loading, or PU wt.%) do not have a statistically significant effect on adhesion.

Completing this project has allowed me to grow as a researcher in many ways. As a research and development co-op, I performed my experiments as an individual and, other than the guidance and instruction from my supervisors, I worked alone mostly. Being a part of a research team has taught me how much more efficiently work can get done. I also learned how important and difficult scheduling can be. This difficulty has taught me to be mindful of others schedules when completing a collaborative task, rather than just my own. From a technical standpoint, I have gained many new skills. This project required me to learn about electrospinning and chronoamperometry as well as other polymer characterization methods such as contact angle, scanning electron microscopy (SEM), and thermal gravimetric analysis (TGA). I was drawn to this research as its original intentions were to help diagnose those suffering from cystic fibrosis, as I have a close friend who was not able to be diagnosed until the age of two. Now, the research has broadened its focus and can help with various other matters as Dr. Monty's team continues to improve, develop, and widen the range of use of the sensors.

Future work should continue to verify the results of this paper using contact angle and chronoamperometry. SEM imaging should continue for all polyurethane samples to determine the effect of the fiber size. The sensors should also be tested using TGA to determine the components weight percentages as well as x-ray diffraction (XRD) to study the crystallinity of the sensors.

## Introduction

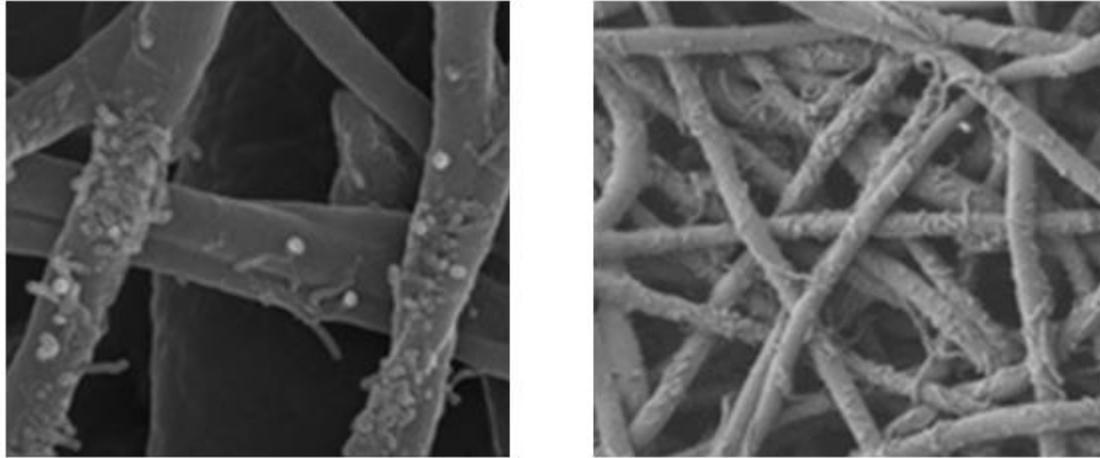
Dr. Monty and her research team have developed nanofiber sensors to measure and monitor different parameters at the surface of the user's skin. These parameters include temperature, pH, sweat sodium concentration, sweat lactate concentration, as well as others. These sensors are currently being fabricated using electrospun nylon-6 polymer for the substrate. Polymers other than nylon-6 were first considered and examined as the substrate for resistance temperature detectors (RTDs) in previous work. RTDs generally use conductive metals such as platinum, copper, or nickel. These stiff materials create pressure points with the body, hence the search to find a more flexible substrate. The RTDs were constructed with both nylon-6 and polyurethane. Polyurethane was chosen as it had superior properties compared to nylon-6, such as better heat resistance, and was expected to outperform nylon-6. The results of the polyurethane sensors can be found in "Construction of Polyurethane Fabric Nanocomposites for use in Resistance Temperature Detectors-Effect of Polyurethane Concentration, Multi-Walled Carbon Nanotubes, and Oxidant" by Jordan Shaffer [1]. The expectations of polyurethane's performance were not met. The purpose of this project, therefore, is to determine what properties of polyurethane nanocomposites hinder its performance as the sensor mat, or conversely, what properties or conditions are conducive of a suitable sensor substrate.

Sensor parameters that were varied include the carbon isomer in the form of multi walled carbon nanotubes (MWCNTs), the concentration of the carbon isomer, the weight percent of the polymer solution used for electrospinning, and whether the sensor was functionalized with calixarene (CAX). The sensors were characterized using scanning electron microscopy (SEM), contact angle, and chronoamperometry.

## **Background**

### *Previous Research*

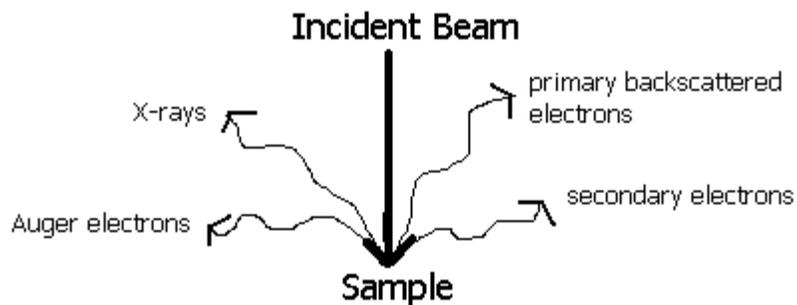
As mentioned above, polyurethane was introduced as a sensor substrate when Jordan Shaffer began examining it for its use in RTDs [1]. RTDs are generally made out of a conductive material; therefore, to create a flexible sensor with a non-conductive polymer substrate, a conductive additive is needed. CNTs meet this requirement. CNTs are an exceptional material due to their mechanical, thermal, and electrical properties, as well as their high aspect ratio [2]. Shaffer's work was a continuation of a Taguchi L36 DOE that varied the substrate polymer between nylon-6 and polyurethane. His initial sensor test examined the relationship between the sensor current and potential (IV relationship). To pass, the sensor needed to show a linear relationship, which would suggest sufficient binding interactions between the polymer and MWCNT. If insufficient binding between the polymer and MWCNT occurs, the sensor will act as a thermistor rather than a resistor, which means that the IV curve will not be linear. Over half of the sensors constructed failed this initial test. The polyurethane and nylon-6 sensors were also compared using SEM imaging. SEM images showed clumping of the MWCNT on the polyurethane fibers. SEM images of nylon-6 showed the MWCNTs wrapped around the nylon-6 fibers. **Figure 1** compares these images. This difference in MWCNT arrangement indicates the MWCNTs are more attracted to themselves than they are to the polyurethane fibers. These repulsive forces prohibit the necessary MWCNT network from forming [1].



**Figure 1** Left: Polyurethane with nanotubes clumped upon the fibers; Right: Nylon-6 with nanotubes wrapped around the fibers [1]. Analysis also shows the polyurethane nanotubes are much shorter than the nylon-6 nanotubes.

### *Scanning Electron Microscopy (SEM)*

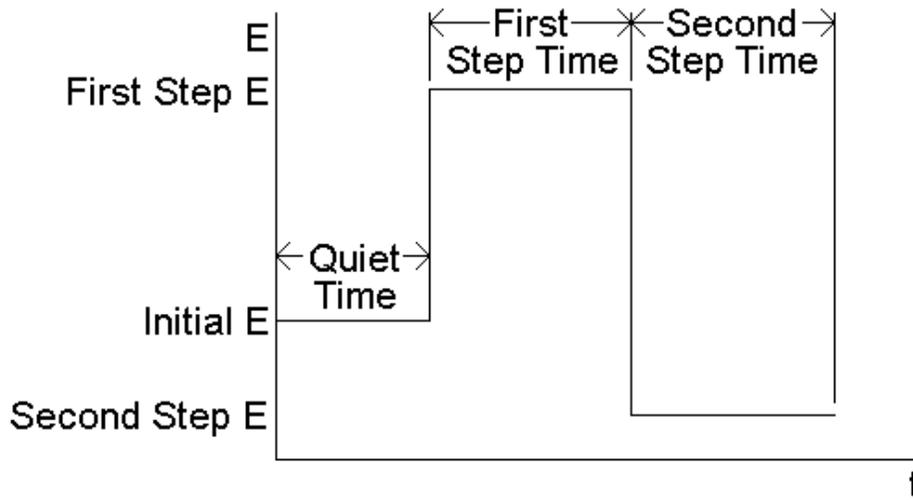
SEM was first discovered in the 1950s. Unlike optical microscopes, SEM can produce a more in depth image of the sample. Using a stream of electrons and electromagnets, rather than light and lenses, SEM has a longer depth of field, higher magnification, and greater control of magnification. **Figure 2** shows the reflected electrons and x-rays that are then absorbed and used to create the SEM image [3].



**Figure 2** A stream of electrons is directed at the sample; the projected electrons and x-rays create the SEM image [3].

### *Chronoamperometry*

Chronoamperometry is a way to measure the change in current of a conductive material when subjected to a stimulus. A constant voltage is applied using a step change waveform, **Figure 3**. The measured variable, current, is plotted against time to reflect the response of the sensor to the stimulus [4].



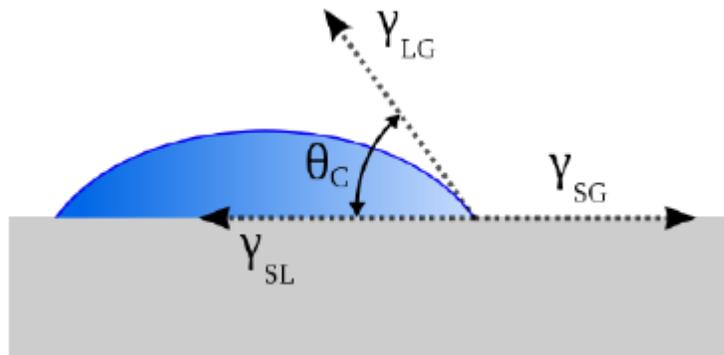
**Figure 3** Depiction of the applied voltage during a chronoamperometry test [4].

For the scope of this document, the stimulus refers to small drops (20  $\mu\text{L}$ ) of ionic solution (dissolved NaCl in DI water) applied in increasing concentrations of 10-60 mM. The sensor was placed on a glass slide and secured by two micro-alligator clips [Nickel-plated steel], which will work as the electrodes. The clips were placed as close to the edges of the sensor as possible to create a distance slightly less than 1 cm between them [5].

### *Contact Angle (CA)*

To measure the contact angle of a liquid solution, a droplet of the solution is placed on a solid substrate. The internal angle the droplet boundary creates with the substrate is its contact angle (**Figure 4.**) Contact angles can tell many things about the

system (solid, liquid, vapor) interactions. The water contact angle indicates if the substrate is hydrophobic ( $CA > 90^\circ$ ) or hydrophilic ( $CA < 90^\circ$ ). CA of any solution describes the wettability of the substrate. Similarly, if  $CA > 90^\circ$ , the surface does not like the solution; if  $CA < 90^\circ$ , the surface likes the solution and will be wetted by it. These behaviors are reactions of the cohesive and adhesive forces of the system. The greater the cohesive forces of the solution are than the adhesive forces between the solid-liquid interface, the greater the CA. Similarly, the smaller the CA, the more the adhesive forces will dominate [6].



**Figure 4** Example of a contact angle that is less than  $90^\circ$  [6].

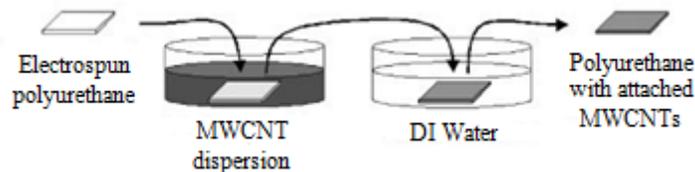
This document is concerned with the systems work of adhesion ( $W_a$ ), also known as the work of the solid-liquid-interface ( $W_{slv}$ ).  $W_{slv}$  is a function of the interfacial tensions of the solid-liquid-vapor interfaces. The interfacial tensions are a result of the interactions of the surface tensions of the individual components (solid, liquid, and vapor). The Young-Dupre equation relates  $W_{slv}$  to CA ( $\theta$ ):

$$W_{slv} = \gamma_{lv}(1 + \cos\theta)$$

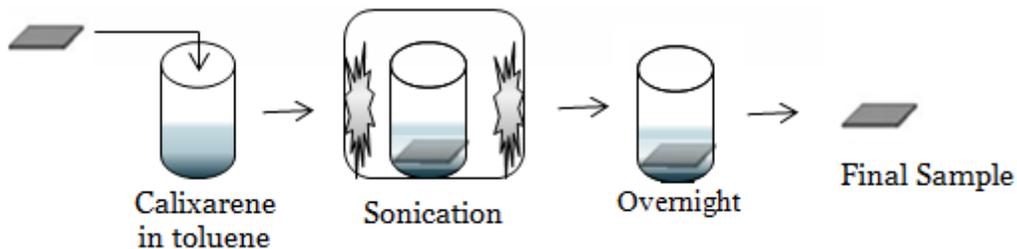
where  $\gamma_{lv}$  [mN/m] is the interfacial tension between the liquid-vapor interface [7].

## Experimental Methods

The polyurethane was electrospun following the procedure found in “Construction of Polyurethane Fabric Nanocomposites for use in Resistance Temperature Detectors-Effect of Polyurethane Concentration, Multi-Walled Carbon Nanotubes, and Oxidant” by Jordan Shaffer. Polymer mats used were spun with 8% wt. and 12% wt. polyurethane (PU) solution. Sensors were fabricated following the procedure found in “Optimized Fabrication and Characterization of Nanofiber Ion Sensors for Biomedical Applications” by Daniel Trowbridge. First, solutions of MWCNT and 0.3% vol. Triton-X-114 were prepared at concentrations of 1, 0.5, and 0.25 g/L. The solutions were sonicated for one hour. The polyurethane was cut into 1 cm by 1 cm square samples. The samples were then dipped in the solution for one minute to allow the MWCNTs to adhere to the polymer. Immediately following their removal, the samples were dipped in DI water to rinse excess MWCNTs, as shown in **Figure 5**. The samples were left over night at atmospheric conditions to dry. After drying, a solution of calixarene (12.5 mg) and toluene (5mL) were mixed using a magnetic stir bar. The samples were added to the calixarene solution and sonicated for 5-10 minutes. The samples were left over night to soak in the solution, as shown in **Figure 6**. The samples were then removed and dried over night at atmospheric conditions. A second set of identical samples were prepared without the calixarene solution. A list of sensors prepared is found below in **Table 1**.



**Figure 5** Sequence of solutions during the dip-coating process (Edited from Trowbridge [5]).



**Figure 6** Depiction of further functionalization by calixarene (Edited from Trowbridge [5]).

**Table 1** The sensors for this experiment were constructed with the following conditions of MWCNTs functional groups, loadings of MWCNTs, and grade of PU. All samples were replicated without the calixarene functionalization step. (CNT=no functional group, CNTOH=hydroxyl group, CNTCOOH=carboxylic acid)

MWCNT	Concentration (g/L)	% PU
CNT	1	8
CNT	1	12
CNT	0.5	8
CNT	0.25	8
CNT	0.25	12
CNTOH	1	8
CNTOH	1	12
CNTOH	0.5	12
CNTOH	0.25	8
CNTOH	0.25	12
CNTCOOH	1	8
CNTCOOH	1	12
CNTCOOH	0.5	8
CNTCOOH	0.5	12
CNTCOOH	0.25	8
CNTCOOH	0.25	12

### *Chemicals and Equipment*

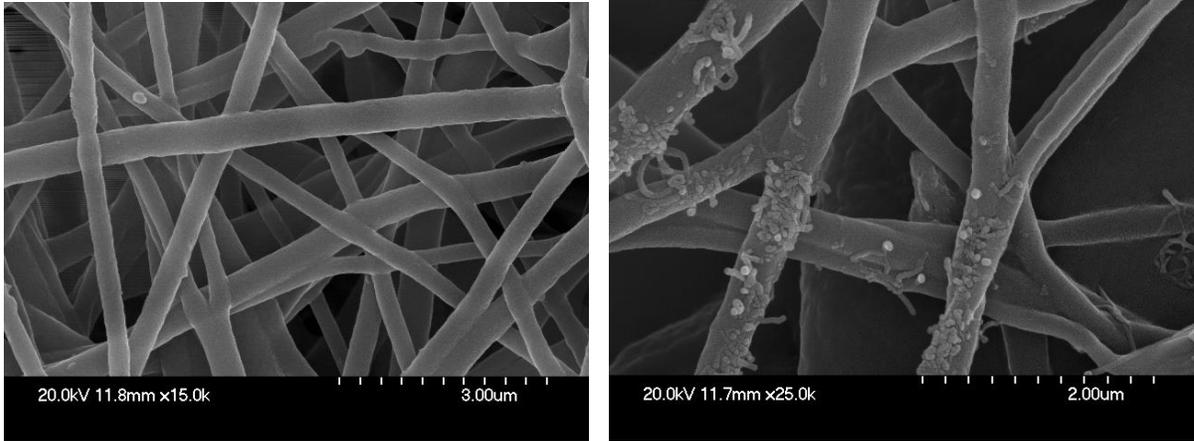
Polyurethane pellets were obtained from Lubrizol Corporation. MWCNTs were acquired from Nanostructured & Amorphous Materials Inc. with a diameter of 10-20 nm, a length of 0.5-2.0  $\mu\text{m}$ , and 95% purity. MWCNTs functionalized with carboxylic acid (-COOH) were also purchased from Nanostructured & Amorphous Materials Inc. with a diameter of 10-20 nm, a length of 10-30  $\mu\text{m}$ , and 95% purity. MWCNTs functionalized with a hydroxyl group (-OH) were purchased from CheapTubes.com with a diameter of

13-18 nm, a length of 3-30  $\mu\text{m}$ , and >99% purity. The surfactant used was Triton X-114, obtained from Acros Organics. The calix[4]arene was purchased from Alfa Ae, 99% purity. The toluene was purchased from Fisher Scientific.

A Branson 1510 Ultrasonic Cleaner was used for sonication. A Gamry Instruments Reference 3000 Potentiostat/Galvanostat/ZRA was used as a direct-current (DC) amperometer with an applied voltage from the potentiostat of 6 V against the open-circuit potential (VOC) of the sensor. The Gamry Framework software was version 6.24. A Kruss Easy Drop with a Stingray Allied Vision Technology camera was used for the contact angle testing. The Drop Shape Analysis software, version 1.91.0.2, was used to record the test. Images were then taken from the video for measurement. Contact angle and SEM images were measured using ImageJ software from the National Institutes of Health (NIH).

## Data and Results

### SEM



**Figure 7** SEM images of CNTCOOH 0.5g/L 8% PU. Left: PU fibers, Right: PU fibers with MWCNT.

**Table 2** Summary of analysis on images in Figure 7.

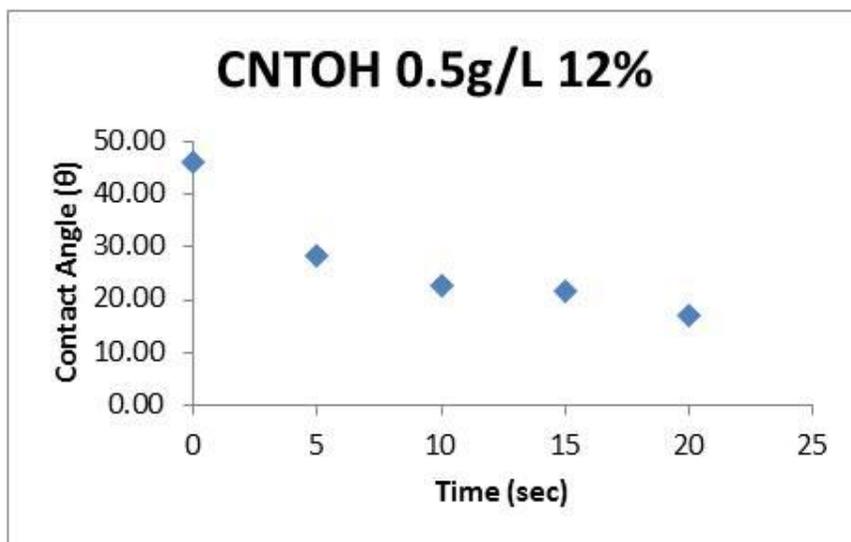
	Fiber Diameter (um)	MWCNT Diameter (um)	MWCNT Length (um)
<b>Avg.</b>	0.311	0.050	0.244
<b>St. Dev.</b>	0.071	0.005	0.022

**Figure 7** displays SEM images of CNTCOOH 0.5 g/L 8% PU. **Table 2** shows the measurements for the SEM data available for polyurethane. Further analysis needs to be done to determine the effect of fiber size on the sensitivity of the sensor.

### Contact Angle

Using the Kruss Easy Drop machinery, a 5.00  $\mu\text{L}$  droplet of the corresponding MWCNT + 0.3% Triton X-114 solution was placed on a neat polyurethane fiber mat using a 500  $\mu\text{L}$  syringe. A video was taken to record the rate of wetting in addition to the contact angle. The contact angle was measured every 5 seconds for 20 seconds after the droplet left the tip of the needle, for a total of 5 frames per solution. Plotting the CA versus time should produce a trend as seen below in **Figure 8**. As mentioned previously,

the CA is used to calculate the  $W_{slv}$ , which will be used in the statistical analysis of the results.

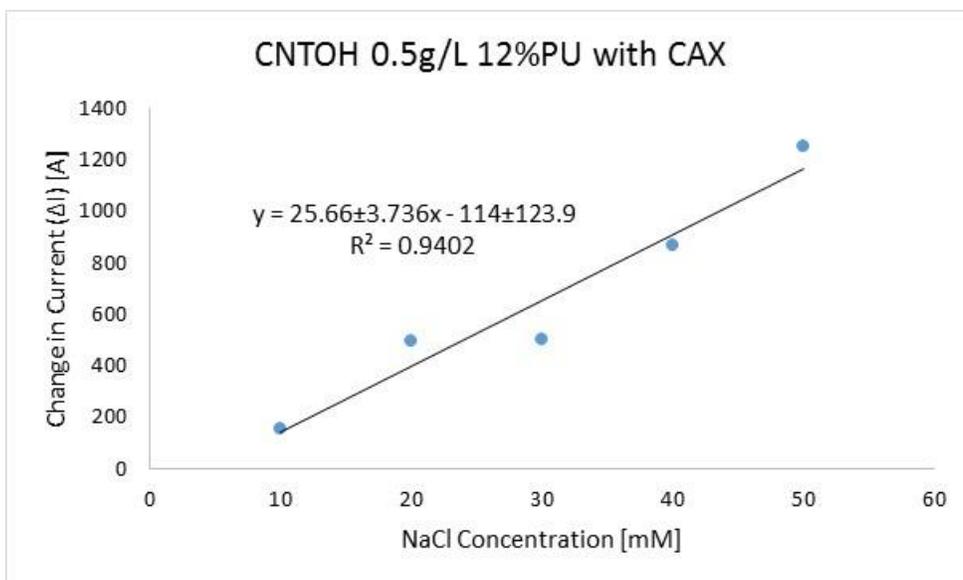


**Figure 8** Graph of the contact vs. time for CNTOH 0.5 g/L 12% PU.

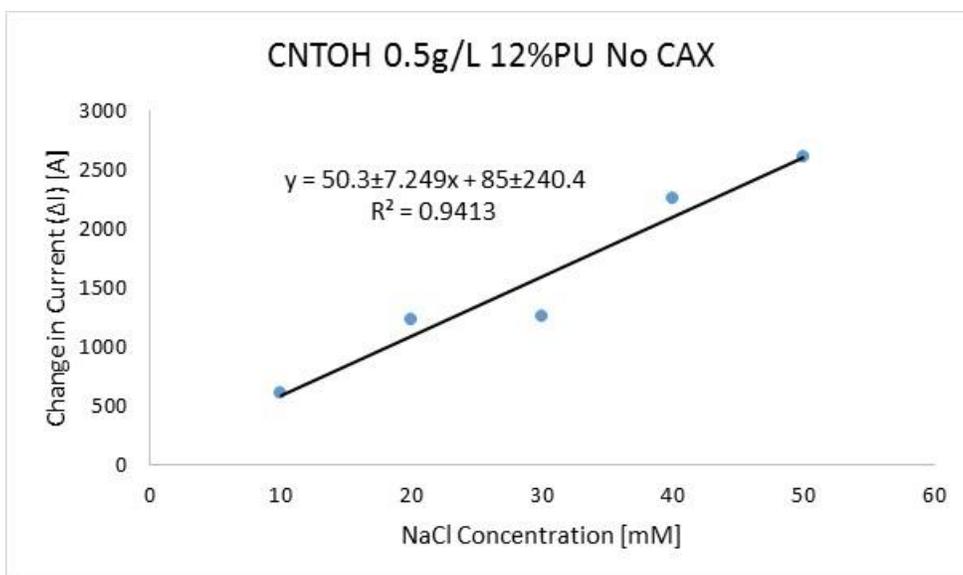
### *Chronoamperometry*

As mentioned previously, the functionalized sensor mat was secured to a glass slide with alligator clips, which act as the electrodes. The applied voltage from the PSAT was 6 V. The sensor was wetted with DI water before applying the voltage. The NaCl solutions were then dropped with a 20  $\mu$ L pipette in series by increasing concentration. The change in voltage after the drop of solution was recorded and plotted against the NaCl solution concentration. The data should produce a linear trend with a positive slope. Many times, one out of the six data points will need to be omitted as an outlier, as is seen by the five data points below in **Figures 9 & 10**.

The polyurethane exhibited increased sensitivity to sodium concentration changes, as opposed to nylon-6. This trend was also apparent for polyurethane that had not been functionalized with calixarene. The calixarene's purpose is to make the sensor selective to only sodium.



**Figure 9** Graph of the change in current versus the NaCl concentration during the chronoamperometry test for CNTOH 0.5 g/L 12% PU with calixarene. This is for one set of measurements for the sensor. Note: the error for the regression intercept is too large; more measurements are required.



**Figure 10** Graph of the change in current versus the NaCl concentration during the chronoamperometry test for CNTOH 0.5 g/L 12% PU without calixarene. This is for one set of measurements for the sensor. Note: the error for the regression intercept is too large; more measurements are required.

### Summary

**Table 3** summarizes the results of the contact angle and chronoamperometry tests. This data is used in a statistical analysis to determine the significance of the nanotube type, additional functionalization using calixarene, the weight percentage of polyurethane

in the electrospinning solution, as well as adhesion between the MWCNT solution and the polymer.

**Table 3** Summary of test results for polyurethane sensors, including the initial CA, initial  $W_{slv}$ , and the slope of the change in current vs. concentration graphs generated from the chronoamperometry tests. Further testing should be done to verify these results.

MWCNT	Concentration (g/L)	% PU	Initial CA (°)	Initial $W_{slv}$ (mN/m)	$\Delta I/C$ Slope (w/ CAX)	$\Delta I/C$ Slope (w/o CAX)
CNT	1	8	48.78	49.77	16.07	N/A
CNT	1	12	36.66	54.07	6.46	3.16
CNT	0.5	8	39.82	53.04	4.26	11.86
CNT	0.25	8	32.42	55.32	20.34	6.81
CNT	0.25	12	58.16	45.83	5.30	6.64
CNTOH	1	8	47.52	50.26	16.73	21.75
CNTOH	1	12	30.62	55.82	1.77	0.79
CNTOH	0.5	12	46.16	50.78	21.19	35.89
CNTOH	0.25	8	33.00	55.16	17.46	21.61
CNTOH	0.25	12	31.84	55.48	12.57	19.20
CNTCOOH	1	8	42.82	52.00	2.00	3.90
CNTCOOH	1	12	50.14	49.23	1.55	7.67
CNTCOOH	0.5	8	41.10	52.61	12.41	11.49
CNTCOOH	0.5	12	27.07	56.71	11.71	2.21
CNTCOOH	0.25	8	39.52	53.14	17.34	18.52
CNTCOOH	0.25	12	29.24	56.18	6.77	3.10

### ANOVA Analysis

Using an ANOVA analysis, it was found that the nanotube types were a significant factor both with and without calixarene as well as the weight percentage of PU for sensors made with calixarene. The p-values were 0.031, 0.004, and 0.108, respectively with an alpha value of 0.05. While the p-value of 0.108 is higher than the alpha value, it was concluded to be significant due to its close proximity. Adhesion between the solution and polymer showed no significance between the experimental parameters. The sensitivity of the sensor (the change in current) simply increased with increasing adhesion.

## Discussion

The statistical analysis shows that the nanotube type affects the performance of the sensor both with calixarene and without calixarene. This means the nanotube types affect both the conductivity of the sensor as well as the Na<sup>+</sup> binding to calixarene. The analysis also showed the polyurethane weight percentage was significant for sensors with calixarene. This means the PU wt.% affects sensor response. Adhesion showed no significance during the analysis. This means the experimental parameters (nanotube type, nanotube loading, or PU wt.%) do not have a statistically significant effect on adhesion. Or in other words, the experimental parameters do not have a strong or abnormal effect on the adhesion of the sensors.

Future work should continue verifying contact angle and chronoamperometry results. SEM and XRD analysis should be done to help quantify the sensor properties under different experimental conditions. This data should also be used to evaluate their effect on the sensors or to determine if there is a correlation between adhesion and fiber size or adhesion and crystallinity. Also, now that significant parameters have been identified, work should be continued to find the optimum conditions for polyurethane sensors. These statistical results should also be compared to nylon-6 to help determine polymer properties that may play a role in sensor performance.

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