Mechanical-electrical characterization of carbon-nanotube thin films for structural monitoring applications

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ABSTRACT

To measure component-level structural responses due to external loading, strain sensors can provide detailed information pertaining to localized structural behavior. Although current metal foil strain sensors are capable of measuring strain deformations, they suffer from disadvantages including long-term performance issues when deployed in the field environment. This paper presents a novel carbon-nanotube polymer composite thin film that can be tailored for specific strain sensing properties. Beginning at the nano-scale, molecular manipulation of single-walled carbon nanotubes (SWNT) is performed to control chemical fabrication parameters as a means of establishing a relationship with macro-scale bulk sensor properties. This novel strain sensor is fabricated using the Layer-by-Layer (LbL) self-assembly process. A rigorous experimental methodology is laid out to subject a variety of thin films to tensile-compressive cyclic loading. In particular, SWNT concentration, polyelectrolyte concentration, and film thickness are varied during the fabrication process to produce a variety of strain sensors. This study correlates fabrication parameters with bulk strain sensor properties; sensor properties including sensitivity (gauge factor), linearity, and hysteresis, are explored.

Keywords: Layer-by-Layer assembly, nanotechnology, carbon nanotubes, strain gauges, structural monitoring.

1. INTRODUCTION

Over the past few decades, researchers among the structural monitoring community have devoted their time and efforts towards the development of novel, high-performance sensors for structural monitoring. A variety of sensors have been developed in recent years including microelectromechanical system (MEMS) sensors, fiber optic strain gauges and wireless sensors. Currently, metal foil strain gauges still remain one of the few sensor transducers that can measure strain in civil structures at low-cost. As a result, metal foil strain gauges are widely used in the laboratory and in the field to obtain component strain measurements. While metal foil strain gauges are capable of accurately measuring strain, their use in the challenging field environment often degrades their performance with extreme temperature dependencies, among other issues. This study will explore the design of a novel strain gage based upon the use of tools under development in the nanotechnology field.

Researchers have developed a new generation of sensors for structural monitoring using a “top-down” approach, as in microelectromechanical systems (MEMS). MEMS technology allows for the scaling down of macro-scale sensor designs to micrometer length scale. Recent MEMS sensors to have impacted the structural monitoring field includes MEMS accelerometers and MEMS ultrasonic transducers. However, MEMS sensors generally suffer from high capital costs associated with fabricating such sensors in advanced clean rooms. As a result, this paper presents a different strategy towards tailoring sensor designs from a “bottom-up” approach. Chemical fabrication parameters can be tailored at the molecular scale to yield macro-scale bulk sensor properties. This paper presents a novel carbon-nanotube-based polymer composite thin film strain sensor. Using a simple and low-cost self-assembly Layer-by-Layer (LbL) fabrication process, such sensors can be designed with specific output parameters controlled by the chemical properties of its ingredients.

Using a “bottom-up” approach beginning at the nano-scale, molecular manipulation of single-walled carbon nanotubes (SWNT) can be employed to fabricate novel sensors. In this study, the impressive mechanical, chemical, and electrical properties of SWNTs will be utilized to form nano-composites with various polyelectrolytes (PE) for strain sensing.
Particularly, a methodical LBL process, utilizing single walled carbon nanotubes and various polymers, is employed to fabricate a variety of SWNT-PE thin films. These LBL SWNT-PE thin films have been demonstrated to show orders of magnitude greater strain sensitivity (gauge factor) as compared to traditional metal foil strain gauges [1]. More importantly, the ability to control the concentration of SWNTs, polyelectrolyte, among other fabrication parameters, allow for the fine-tuning of bulk strain sensor properties. In this study, thin films fabricated from different phase concentrations are subjected to laboratory validation tests. By tuning individual parameters during the nano-fabrication process and subsequently testing each SWNT-PE thin film, nano-scale parameters will be correlated to desired macro-scale strain sensor properties.

2. SWNT-PE THIN FILM SENSORS

Since the discovery of carbon nanotubes in 1991 by Iijima [2], researchers have come to realize their unique electrical, chemical, and mechanical properties for various engineering applications. Their optimal properties in electrical conductivity, mechanical strength, and mass density stem from their high length-to-diameter aspect ratio and carbon-to-carbon chemical bond structure. Individually, each SWNT is a graphene sheet rolled to form a cylindrical structure whose diameter can vary between 0.7 to 10.0 nm and whose length-to-diameter aspect ratio ranges from $10^4$ to $10^5$ [3, 4]. At such length scales, its physical structure approaches that of a one-dimensional structure, leading to high electrical conductivity and other impressive material properties [5]. In fact, the SWNT one-dimensional structure allows electrons to travel greater distances before scattering occurs, approaching that of a ballistic transport-type behavior and thereby increasing electrical conductivity. Moreover, the hexagonally-bonded carbon honeycomb structure of SWNTs contributes to their high mechanical strength, surpassing that of structural steel in terms of elasticity and ultimate strength [6].

In the past decade, many researchers have been motivated to take advantage of SWNT’s impressive material properties for structural monitoring, and in particular, strain sensing. Dharap et al. [7] have proposed the design of strain sensors based on a homogenous deposition of SWNTs known as “buckypaper”. Their work has demonstrated the potential of SWNTs for the design of novel strain sensors based on their high degree of linearity in response to applied strain. Other researchers have utilized multi-walled carbon nanotubes (MWNT) for the development of mechanical sensors [8]. Although experimental results from those studies indicate linear mechanical-electric behavior at low levels of strains, MWNTs suffer from nonlinear effects at higher strain due to pullout of its concentric graphene tubes [9]. While these studies demonstrate the potential of carbon nanotubes, a key factor that has yet been proposed is to achieve the ability to tune nanotubes at the molecular level to control macro-scale sensor properties.

In a previous study, SWNT-PE Layer-by-Layer composites have been designed and validated for strain sensing [1]. The LBL assembly process creates a thin film whose molecular structure consists of alternating layers of SWNTs and a polyelectrolyte defined by a high molecular weight [10]. The piezoresistive behavior of SWNT-PE thin films under applied strain allows for direct conversion from changes in resistivity to changes in strain. While SWNT-PE thin films show promise for strain sensing, little has been done to accurately tailor these composites during fabrication to ensure desired strain sensing properties. This study takes a first step to experimentally characterize key LBL fabrication parameters and correlate them to bulk strain sensor properties. In particular, sensitivity, linearity, hysteresis, and full-scale range are the primary four strain sensor properties of interest in this study.

3. LAYER-BY-LAYER ASSEMBLY OF SWNT-PE THIN FILMS

To fabricate sensors capable of withstanding high applied strains in structural monitoring applications, a sufficiently thick and uniform film is crucial. Furthermore, a thick film is necessary for easy manipulation by hand and for installation upon structural surfaces. In general, LBL assembly is a simple and efficient assembly process for fabrication of thick SWNT-PE composite thin films. LBL employs the sequential deposition of multiple layers of SWNT and PE materials upon a charged substrate (e.g. glass, silicon, among others). With alternating electrically charged particles deposited on each layer, each film monolayer is adsorbed by the layer below through electrostatic and van der Waals forces [5, 11].

Initially, a bare glass substrate is immersed in Piranha ($\text{H}_2\text{O}_2$ and $\text{H}_2\text{SO}_4$) solution to remove microorganisms and impurities while creating the initial charged surface for LBL assembly. To provide for the sequential deposition of
alternating charged monolayers, two solutions of opposite electrical charge are prepared. First, the bare substrate is immersed in a polyvinyl alcohol (PVA) solution, where PVA is the polyelectrolyte counterpart of the LBL thin film. After dipping the substrate for a set period of time (five minutes), the substrate is removed and rinsed in deionized water to remove clumped particles and to prevent cross-contamination between different chemical solutions. Second, to deposit a monolayer of SWNT, the substrate is then dipped in a fully dispersed SWNT solution. The opposite charge (compared to PVA) is provided by employing poly(styrene 4-sulfonate) (PSS), where it also acts as an agent to facilitate dispersion of SWNTs. Following the dipping of the substrate in the SWNT-PSS solution (five minutes), the substrate is removed and, again, rinsed in deionized water to remove clumped SWNT nanoparticles. The described process completes the deposition of the first LBL SWNT-PVA bi-layer. This process is repeated numerous times to fabricate thin films of desired thickness which is controlled by the substrate dipping time in each solution.

In this study, highly purified (i.e. ash < 15 wt.%) HiPco single-walled carbon nanotubes have been obtained from Carbon Nanotechnologies, Inc. (CNI), (Houston, TX). The selection of CNI SWNTs as opposed to other forms of carbon nanotubes is primarily based on their low impurity content leading to systematic achievement of film mechanical and electrical properties in the laboratory. However, one challenge associated with processing ultra pure SWNTs is their tendency to clump together in solution resulting in quick precipitation. Clumping to form large chunks of carbon nanotubes during LBL assembly can dramatically reduce the overall strain sensing performance, quality, and uniformity of SWNT-PE thin films. A series of experiments have been carried out to determine the optimal method to maintain adequate dispersion. Three hours of ultra-sonication bath and one hour each of deep sonication at 30% and 35% amplitude, respectively, is applied to each 20-mL SWNT-PSS solution to achieve dispersion. Deep sonication outputs a frequency of 20 kHz and is set at 5-sec on and 5-sec off. The resulting SWNT solutions remain adequately dispersed for at least one week’s time. Furthermore, previous experiments reveal that SWNT dispersion quality in the polymer (PSS) solution is directly related to its concentration.

4. PRIOR LBL THIN FILM STRAIN SENSOR VALIDATION

As presented in a previous study [1], LBL SWNT-PE thin films exhibited piezoresistive behavior with a proportional change in resistivity due to applied strain. This early study demonstrated that a variety of bulk sensor properties could be attained depending on changes in the fabrication parameters of the SWNT-PE composite film. Early experiments to achieve adequate SWNT dispersion fabricated SWNT-PE thin films using a 0.5 mg/mL SWNT concentration solution dispersed in 0.5% PSS with a total thickness of 35 bi-layers. The study sought to quantify the behavior of SWNT-PE thin films under applied strain. However, optimization of the fabrication properties were not explored. Upon completion of the LBL fabrication process, the SWNT-PE thin film was etched off the glass substrate using HF. The conformable thin film was set to dry and subsequently mounted to a 1.9-cm diameter aluminum rod for monotonic tensile testing. Single-strand electrical wire and silver paste was utilized to establish electrical connections to the thin film, where an Agilent 34401A Multimeter was employed to interrogate the resistance of the thin film at a 1 Hz sampling rate. The mounted thin film and aluminum rod was monotonically loaded until failure (load rate $\approx 0.085$ mm/sec). As a baseline comparison, an MTS extensimeter was also attached firmly to the aluminum rod.

In particular, one of the initial goals of the validation study was to achieve a high gauge factor for SWNT-PE thin film strain sensors. As shown in Figure 1(a), a gauge factor of $GF = 208.33$ was achieved; a gauge factor nearly two orders of magnitude higher than current metal foil strain gauges ($GF = 2.1$). Although high gauge factor can be optimal in certain local-based structural monitoring settings, lack of control of the fabrication parameters resulted in a slight nonlinear piezoresistive behavior as displayed in Figure 1(b). Nonlinear behavior can be advantageous if the response of the thin film can be described mathematically, but clearly, the degree of nonlinearity shown in Figure 1(b) cannot be easily characterized. As a result, a rigorous analysis to relate fabrication processes to controlling bulk strain sensor properties is crucial to the success of SWNT-PE thin film sensors.

5. OPTIMIZATION PARAMETERS

Hidden in the discussion of the LBL assembly method are various fabrication variables and parameters that determine the strain sensing properties of SWNT-PE films. The power of this “bottom-up” approach is the ability to tune specific chemical properties at the molecular-scale to control desired macro-scale bulk strain sensor properties. Desirable strain
sensor properties may be specific gauge factors, linearity, hysteresis, temperature and light sensitivity, and full-scale measurement range. For instance, researchers have studied electrical conductivity through carbon nanotube networks, and it has been shown that conductance is strongly related to the number of nanotube-nanotube junctions in the network [12]. Multiple inter-junctions between carbon nanotubes provide more paths to the connecting electrodes, thus increasing conductance. Thus, it is hypothesized that increasing carbon nanotube concentration in LBL thin films can possibly scale with increasing gauge factor. Moreover, to increase the full-scale range of the thin film strain sensors, greater thickness of the film (number of layers) can potentially provide for more strength to withstand higher stresses and strains, thus increasing the durability of the film.

To verify these hypotheses, three key fabrication parameters are identified in this study: (1) dispersion of the SWNT, (2) thin film carbon nanotube concentration, and (3) thickness of the thin film. Preliminary experiments reveal that SWNT dispersion quality in the polymer (PSS) solution is directly related to its polymer concentration. Absorption spectroscopy is employed to investigate the dispersion of a fixed concentration of SWNT in varying concentrations of PSS solution (ranging from 0.1% to 1.0%). Simply speaking, absorption spectroscopy measures the absorption of light by some chemical substance across a full spectrum of light wavelengths. For a fixed amount of carbon nanotubes in solution, as dispersion quality increases, SWNTs cover greater surface area in the volume of liquid. Clumping of nanotubes is reduced as dispersion quality increases, and each clump, on average, contain less volume than a low quality dispersed sample. According to the Beer-Lambert law, the intensity of absorption of light is linearly proportional to the concentration of the chemical substance and the size of the particles in solution [13]. Figure 2 presents the theoretically linear relationship between SWNT solution concentration and UV-absorbance. Experimental data in Figure 2 indicates that various concentrations of SWNT solution in fact follow the Beer-Lambert Law.

Thus, by measuring the adsorption of varying PSS concentrations of SWNT solution, the adsorption spectra can shed light on preferred PSS concentration for dispersion. Figure 3(a) shows the adsorption of 650-nm wavelength light for SWNT dispersed in increasing concentrations of PSS solution. Figure 3 suggests a sigmoidal relationship exists between absorbance (hence dispersion) and PSS solution concentration. From Figure 3(a), the dispersion of SWNT in 0.7% PSS concentration marks a large jump as compared to lower concentrations of PSS. Thus, 0.7% PSS solution will be utilized for thin film fabrication to achieve maximum dispersion without compromising excessive PSS deposition on LBL thin films. The motivation for utilizing a highly dispersed SWNT solution is to seek maximum linearity between changes in film resistivity and applied strain in bulk strain sensor properties. Figure 3(b) shows a scanning electron microscopy (SEM) image of a 0.80 mg/mL SWNT concentration dispersed in 0.7% PSS 60-layer thin film on a silicon substrate. SWNTs appear adequately dispersed and deposited throughout the substrate to form the thick film.

Figure 1: (a) Changes in SWNT-PE resistance as a function of time during monotonic tensile test (strain measured by extensometer). (b) Change of resistance as a function of strain indicating some inherent nonlinear behavior of the thin film.
To investigate the relationship between SWNT concentration and strain sensor sensitivity (or gauge factor), three SWNT concentrations will be used to fabricate SWNT-PVA thin films, namely 0.25, 0.50, and 0.80 mg/mL. Selection of these concentrations is based on previous experiments indicating that the maximum SWNT concentration to achieve reasonable dispersion is 1.0 mg/mL. Finally, for each SWNT concentration dispersed in 0.7% PSS, films of 50, 100, and 200 layers are fabricated to assess their strain sensing range up to 0.01 mm/mm strains (1.0%). The various thin films are summarized in Table 1.

Table 1: Matrix of seven different combinations of SWNT-PVA thin films.

<table>
<thead>
<tr>
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<th>0.25 mg/mL SWNT</th>
<th>0.50 mg/mL SWNT</th>
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<tr>
<td><strong>50 Layers</strong></td>
<td>2 Specimens</td>
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<td><strong>100 Layers</strong></td>
<td>1 Specimen</td>
<td>1 Specimen</td>
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<tr>
<td><strong>200 Layers</strong></td>
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6. CYCLIC TENSILE-COMPRESSION TESTING OF STRAIN SENSOR

In order to evaluate fabrication parameters that control the performance of the produced SWNT-PVA thin films, tensile-compressive cyclic tests are performed. Although the conformable thin films can be etched off the glass substrate with hydrofluoric acid (HF) and cut to any desired shape, monotonic tensile tests on the etched films exhibit some nonlinearity and noise [1]. Wrinkling of the thin films during mounting is captured with SEM imaging as shown in Figure 4. This unevenly mounted etched sample shows poor behavior in compression and exhibits a high degree of nonlinearity and noise. The wrinkled mounted film is essentially overlapped; as the specimen is strained, SWNT-PVA thin films no longer elongate or shorten under strain but rather changes from a folded to an unfolded state. Rather, the substrate is cut with the thin film still firmly attached to produce small sensor samples. Once a small SWNT-PVA-on-glass sample is cut using a diamond-tip scriber, the sample is epoxy mounted on 3.8-cm wide x 30.5-cm long x 1.9-cm thick PVC bar, as shown in Figure 5(a). Although glass can fail in a brittle manner under tension, the small glass substrate size and low strain (≤1.00%) applied to the substrate ensures the integrity of the glass substrate.

Once the SWNT-PVA thin film and glass substrate have been mounted to the PVC specimen surface, single-strand electrical wires are attached to the two ends of the film using silver paste. The two thin wires are mounted at the ends of the thin film sample for a two-point probe resistivity measurement. The silver paste is allowed to dry for at least two hours prior to testing. This drying time ensures that the silver paste establishes a firm adhesion to both the wire and thin film while maintaining a low, fixed contact resistance. For tensile-compressive cyclic testing, a Material Test System MTS 810 load frame is employed to apply precision displacement controlled loading to the samples. Displacement is applied to the PVC specimen to generate ±0.01 strain across the length of the specimen. Furthermore, the MTS 810 load frame is operated with both 0.1 mm/sec and 0.05 mm/sec displacement rates to illuminate any sensor rate effects. To measure the change in conductivity during applied strain, an Agilent Multimeter 34401A digital multimeter is utilized to sample thin film resistivity at a 1 Hz sample rate. In addition, to provide for a baseline comparison, the TestWare-SX v. 4.00 software package controls the MTS 810 load frame while collecting displacement (resolution ±0.005 mm) at a 1 Hz sample rate.

From previous experiments, it is known that light and temperature can cause changes in resistivity of SWNT-PVA thin films. Shielding of light is achieved by wrapping aluminum foil tightly around the load frame during the entire duration of testing as shown in Figure 5(b). Mild ambient temperature control is simultaneously offered by the aluminum foil. The aluminum foil slows the heating and cooling of the specimens during testing while shielding airflow from the laboratory’s centralized air conditioning unit. Nevertheless, a temperature drift is expected since the Agilent Multimeter provides a constant current (10 µA) while determining the resistivity of the thin film in the two-point probe setup. The
constant current supply causes the film to heat up and the resistivity to change. Nevertheless, this temperature-dependent drift in resistance, \( R_T \), can be easily removed from results by fitting an exponential curve to model the temperature effects

\[
R_T = Ae^{-Bt} + C
\]

where \( A, B, C \) are constants and \( t \) is time. The temperature drift is measured over a period of seven hours to determine the extent to which temperature will affect measurement results. Figure 6 plots the temperature drift of one unloaded SWNT-PVA thin film specimen. It can be observed that the temperature drift follows a near-perfect exponential curve which justifies the exponential modeling of experimental data.

Once the specimen and sample are firmly mounted in the load frame, a multiple-cycle tensile-compressive (±0.01 strain) load pattern is applied to the PVC plate. Two tests are conducted with varying load rates, namely 0.1 mm/sec and 0.05 mm/sec, to assess any film rate-dependent effects. During loading of the specimens, the electrical resistance of the SWNT-PVA thin film is measured. Figure 7 overlays the SWNT-PVA thin film electrical resistance time history upon the time history plot of the specimen strain (calculated from the unsupported length and the applied displacement). Temperature drift due to the applied current is removed by mathematically fitting an exponential relation to describe this temperature effect.
During cyclic loading, the film resistance undergoes an increase and decrease in tandem with increasing and decreasing plate strain, respectively. From Figure 7, the ductile specimens respond to a maximum of ±0.01 applied strain throughout all cycles. The results from these plots confirm that even a 50-layer thin film can withstand the full-scale range of applied ±0.01 strain. Although the plots in Figure 7 overlay with the strain time history calculated from the MTS loading frame, actual strain at the midsection of the PVC plate may not be so ideal. As a result, a separate PVC specimen is mounted with a traditional metal foil strain gauge and then subjected to the same load patterns shown in Figure 8(a). A representative plot of the metal foil strain gauge overlaid with the MTS load frame calculated strain is shown in Figure 8(b). Results from Figure 8(b) indicate that while the MTS load frame calculated strains give reasonable estimates of applied strain, some permanent residual strain is observed after every cycle of loading. A slight mean drift can be observed from the strain gauge time history plot, indicating the PVC specimen is strained slightly past its yield point to cause a minor permanent set. As a result, this slight drift can be extended to results captured by the SWNT-PVA thin film, where from Figure 7, both plots indicate a slight mean drift whereas the MTS load frame data
does not reveal this information. It should be noted that, to provide the same testing conditions for the metal foil gauge as offered to the SWNT-PVA sensors, the MTS 810 load frame is again wrapped in aluminum foil to provide the same ambient temperature and no-light testing conditions.

More insight can be gained by plotting the change in resistance of the thin film as a function of the measured strain. In Figure 9, the change in resistance of the SWNT-PVA thin film is linearly proportional to the strain. By fitting a straight line to the resistance(R)-strain(ε) data, the gauge factor (Gauge Factor = (∆R/R)/ε) of the thin film can be estimated. The experimental data fits a least-squares linear model nicely, indicating that the SWNT-PVA thin film behaves in a fairly linear manner with strain (after removing any temperature-dependent effects).

In total, seven SWNT-PVA samples are tested (as shown in Table 1). The seven samples each represent a different combination of the various optimizing properties mentioned earlier, namely SWNT concentration and the number of LBL layers. The strain sensing parameters of interest are: (1) full-scale range, (2) gauge factor (sensitivity), (3) linearity, (4) repeatability, and (5) hysteretic behavior. First, all seven samples have been subjected to tensile-compressive loading up to ±0.01 strain. Based on the time-history overlays, all of the thin film strain sensors tested are capable of operating within this range.

By plotting the change in film resistance as a function of measured strain during the first tensile cycle of loading, the gauge factor can be determined from the slope of the least-squares fitted line. Each thin film specimen is tested and plotted to determine its gauge factor as presented in Table 2.

From Table 2, no conclusions can be drawn from the calculated gauge factors for the 50-layer strain sensors; however, a clear increase in the gauge factor can be observed for the 100-layer films as the carbon nanotube concentration is increased (from 0.25 to 0.80 mg/mL). This coincides with the initial hypotheses that increasing the concentration of carbon nanotubes provides for more nanotube-nanotube junction mechanisms within the thin film, thereby increasing its sensitivity to strain. This initial carbon nanotube in PSS solution concentration to gauge factor relationship allows for the tuning of one fabrication parameter to attain the desired sensor gauge factor. Furthermore, for all specimens of one

| Table 2: SWNT-PVA thin film gauge factor (sensitivity). |
|-------------|----------------|----------------|----------------|
|             | 0.25 mg/mL SWNT | 0.50 mg/mL SWNT | 0.80 mg/mL SWNT |
| 50 Layers   | 0.1279          | 0.1107          | 0.1195          |
| 100 Layers  | 0.0670          | 0.0817          | 0.0993          |
| 200 Layers  | -               | 0.0568          | -               |

Figure 9: (a) 0.80 mg/mL SWNT-PVA 50-layer subjected to five-cycle tensile-compressive loading (±0.01 strain) at 0.05 mm/sec change in resistance versus strain. (b) 0.50 mg/mL SWNT-PVA 50-layer subjected to 10-cycle tensile-compressive loading (±0.01 strain) at 0.05 mm/sec change in resistance versus strain.
concentration, increasing the number of layers reduces its sensitivity to strain. Within the full-scale range of ±0.01 strains, a thinner film can attain higher gauge factor.

Although SWNT-PVA strain sensors perform linearly to applied tensile and compressive strain (after removal of temperature effects), some inherent hysteretic behavior is observed after each additional loading cycle. The cause of the hysteretic behavior is hypothesized as individual SWNTs reorganizing in the polymer matrix under strain. After SWNT-PVA thin films are strained to the maximum tensile strain, unloading requires the nanotubes to deform and retrace back to their initial positions. Since SWNTs are long, thin tubular nanoparticles of high aspect ratio, their retracing steps are not perfect, thus causing slight permanent damage after each additional loading cycle. The hysteretic behavior can be further understood by plotting one cycle of normalized SWNT-PVA change in resistance as a function of applied strain as presented in Figure 10.

Figure 10 shows representative hysteresis loops for two of the seven specimens tested in this study. It can be immediately noted that by comparing Figure 10(a) and Figure 10(b), increasing the number of thin film layer from 50 to 100 respectively increases the hysteresis behavior. This follows with the previous discussion that thicker films are subject to higher probability of defects during the fabrication process. When the thin films are stretched, clumps can cause excessive local tears within the thin film. From [14, 15], a one-cycle hysteresis, \( h \), can be quantified by identifying the largest deviation between measurements taken during the loading and unloading cycle at the same applied strain. Calculations for Figure 10 show that the hysteresis, \( h \), is in fact increased from 0.0022 to 0.0028 mm/mm between the 50- and 100-layer SWNT-PVA films respectively. Furthermore, comparing Figures 10(a) and 10(b), the hysteresis plot for the 100-layer SWNT-PVA film is clearly smoother than the 50-layer one. Ignoring the hysteretic behavior, the smoothness of the curve alone indicates stronger linearity between changes in film resistance to changes in strain.

### 7. CONCLUSIONS

The use of carbon nanotubes in the design of novel structural sensors is motivated by SWNT's impressive mechanical and conductive electrical properties. SWNT-PE thin films fabricated with the Layer-by-Layer assembly process allows for simple fabrication at low cost, and more importantly, the ability to tune chemical fabrication parameters at the nanoscale to directly affect bulk macro-scale sensor properties. The resulting LBL methodology is capable of producing SWNT-PE thin film of desired sensitivity, linearity, hysteresis, and thickness controlled by turning certain fabrication parameters. In this paper, a methodical process to compare SWNT-PVA thin film strain sensing performance under applied cyclic loading to ±0.01 strains is investigated. The SWNT-PVA thin films, fabricated with the LBL process, show significantly different macro-properties as individual fabrication parameters are altered. Bulk electrical and mechanical properties of the films can be tailored based on the concentration of SWNT, number of layers, and by using highly dispersed SWNT in 0.7% PSS to maximize SWNT dispersion. The result is a conformable SWNT-PE strain sensor well suited for monitoring the strain deformation of structural elements.
Although the conformable SWNT-PE thin films can be etched off their substrates and mounted for strain sensing, SEM images (Figure 4) have identified wrinkling and overlapping of the thin films, resulting in difficult to characterize nonlinear behavior. Consequently, thin films are left un-etched on their original substrates and directly mounted to specimens for testing. The full-scale range of ±0.01 mm/mm strain (well within strain levels experienced by typical structures) has been demonstrated to be within limits of all SWNT-PVA thin films tested. Cyclic load tests are performed on structural elements with the SWNT-PVA thin films mounted to characterize their properties. As shown in Table 2, a clear trend exists between gauge factor and SWNT concentration and SWNT-PVA film thickness. The results indicate that as carbon nanotube content is increased, a thicker film exhibits higher gauge factor. On the other hand, as film thickness is increased, gauge factor decreases. Hysteric behavior of SWNT-PVA thin films are quantified and plotted in Figure 10. The findings indicate stronger hysteretic behavior for thicker films of the same SWNT concentration; however, the smoother curve for the thicker film (Figure 10(b)) indicates stronger linearity between normalized changes in resistance to changes in measured strain. Nevertheless, SWNT-PVA thin films’ resistivity shows a strong temperature dependency. However, as shown in Figure 6, this temperature effect can be modeled accurately by fitting an exponential function to describe its behavior. Thus, any temperature nonlinearities can be completely removed from the collected experimental data to relate changes in film resistivity with changes in applied strain. After removing the fitted temperature effect, in all tested cases, SWNT-PVA thin films show that their time histories coincide with measured strain.

In the near future, various studies will be performed to further enhance the properties of the SWNT-PE thin film strain sensors. In particular, the strain sensor will be fabricated with varying concentrations of PSS to quantify the relation between dispersion, linearity, and gauge factor. It is anticipated that by reducing the PSS concentration, less polymer will be deposited during the LBL process, thereby increasing the overall carbon nanotube concentration; this should increase the film sensitivity significantly. However, the price of higher gauge factor may come at the cost of reducing linearity as dispersion of SWNTs in lower PSS concentrations have been deemed of lower quality. Furthermore, strain sensors will be fine-tuned using specific polymers and different SWNT to PE concentrations to reduce signal-to-noise ratios and to eliminate the observed hysteretic behavior. To address the thin film temperature dependency, future tests will include measuring thin film temperature as a function of time. By establishing a mathematical relation between different temperatures and the various types of thin films, the derived equations can be generalized to all films fabricated with different initial parameters. More elaborate laboratory and field validation experiments will be performed to further assess the performance of SWNT-PE strain sensors.

8. ACKNOWLEDGEMENTS

This research is partially funded by the National Science Foundation (Grant Number CMS – 0528867). The authors would like to express their gratitude to Professor Victor Li, Mr. Shunzhi Qian, and the entire ACE-MRL group for assistance with operating the MTS 810 load frame.

9. REFERENCES


