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Analysis of variance on thickness and electrical conductivity measurements of carbon nanotube thin films

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Abstract

One of the major challenges towards controlling the transfer of electrical and mechanical properties of nanotubes into nanocomposites is the lack of adequate measurement systems to quantify the variations in bulk properties while the nanotubes were used as the reinforcement material. In this study, we conducted one-way analysis of variance (ANOVA) on thickness and conductivity measurements. By analyzing the data collected from both experienced and inexperienced operators, we found some operation details users might overlook that resulted in variations, since conductivity measurements of CNT thin films are very sensitive to thickness measurements. In addition, we demonstrated how issues in measurements damaged samples and limited the number of replications resulting in large variations in the electrical conductivity measurement results. Based on this study, we proposed a faster, more reliable approach to measure the thickness of CNT thin films that operators can follow to make these measurement processes less dependent on operator skills.

Keywords: carbon nanotube, carbon nanotube thin films, analysis of variance, measurement protocol, nanomaterial, statistical analysis

(Some figures may appear in colour only in the online journal)

1. Introduction

Carbon nanotubes (CNTs) have attracted the attention of many researchers for their extraordinary mechanical, electrical and thermal properties [1–3]. They are considered one of the most promising next-generation reinforcement materials. Electrical and thermal conductivity characterization of CNT thin films has been an active area of research in the recent years [4, 5]. Conductivity measurements rely on accurate knowledge of the thickness of the material. Although standard protocols exist for film thickness measurements of materials including

polymers and metals [6–8], some unique natures of CNT thin films, such as ultra-thin thickness and soft nanoporous structure, have made the measurement process challenging. Therefore, obtaining accurate measurements of thickness of CNT thin films to evaluate the properties of the nanocomposites is critical.

Resistance measurement is an essential test when characterizing conductivity of materials. The resistivity of a material and the thickness of a thin film can be inferred from the resistance measured. If a thin film is processed into an isometric electronic circuit, the dimension of the circuit can also be calculated by resistance measurement. The resistivity of a material is highly sensitive to variations by factors such as temperature, humidity, and thickness; therefore, the stability of these parameters is important for providing repeatable evaluations of the material properties.



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The commonly used method to measure the resistance of a material is known as two-point probe measurement [9]. Despite the convenience, obtaining the electrical properties of materials is often unreliable because the resistance obtained by two-probe measurement cannot determine the accurate resistivity of a material. The main reason is that the same probe that determines the voltage also provides the current. This issue can be solved if the functions of the probes are separated so that two probes provide the current path and another two determine the voltage. This configuration is the so-called four-point probe measurement. The four-point probe approach provides more reliable test results compared to the conventional two-point probe method; however, careful setup is required to ensure accurate resistance measurements by factoring in equipment calibration, sample structure, sample size and environmental conditions.

While we have some clear thoughts on how to conduct resistance measurements, few standards or protocols are available to measure the thickness of soft ultra-thin CNT films due to their fragile characteristics. For example, CNT thin films are easy to deform permanently and are sensitive to moisture due to nanoporosity. Consequently, the experimental data collected usually differs from operator to operator. Test methods and standards for measuring thickness of various metal and polymer coatings are well-established and can be easily found in directions such as ISO 2808 [8], ASTM D1005 [10], SS 184160 [6]. Some standards and protocols exist, such as ASTM E252 [7], for measuring thickness of thin (<0.015 inch) metal films by measuring the mass of a sample of known area and density. ASTM F2251 [11] contains standard procedures for thickness measurements of flexible packaging material; however, the contact micrometers may damage the soft ultra-thin films. Ultrasonic handheld devices provide a non-destructive approach to measure the thickness of materials, which seems to be ideal for fragile thin films [12]. However, the nanoporosity, ultra-softness, and surface roughness often lead to the attenuation of sound energy and irregular sound velocity, which may consequently have negative impacts on the accuracy of measurements. Standards regulating the test methods using ultrasonic thickness gauge can be found in ASTM E797M [13], ISO 16831 [14] and BS EN 14127 [15].

Many researchers have found that the electrical properties of CNTs are highly sensitive to structural variations [16–18]. Ebbesen [19] and Shimizu [20] managed to measure the conductivity of individual multi-walled carbon nanotubes (MWCNTs) using a four-probe approach and CNT bridge between thermocouples. IEEE proposed a set of test methods for measuring the conductivity of individual carbon nanotubes (IEC/IEEE 62624 [21]). However, no standard exists for conductivity measurement of CNT thin films. In recent years, the four-point collinear probe arrangement has been widely used to evaluate the electrical performance of CNT thin films. Standards for four-point probe arrangement to measure sheet resistance of thin film semiconductors can be found in ASTM F390-98 [22], ASTM F1711-96 [23].

While these are the standard currently followed, thin film semiconductors and CNT thin films have essential differences. As we have reviewed above, challenges exist in standardized

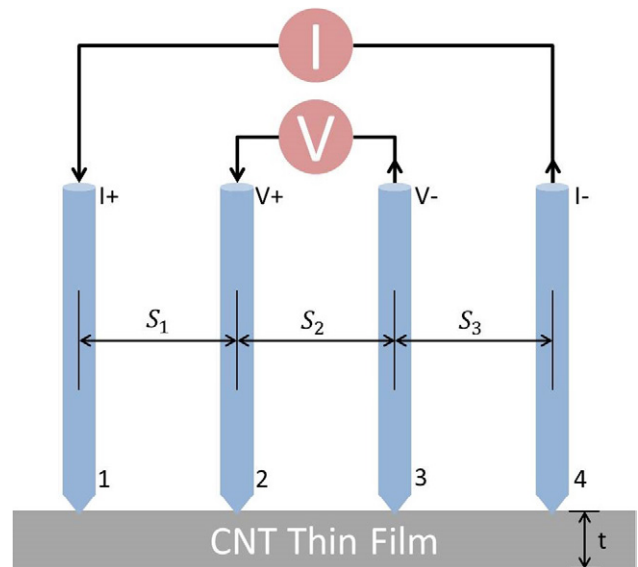


Figure 1. An illustration of typical four-point probe arrangement.

measurements of conductivity of CNT thin films. In this study, a protocol to obtain accurate thickness measurements for CNT thin films was proposed. As a case study, we used MWCNT thin films as samples for the CNT thin films. We demonstrated how some small variations in thickness measurements can cause large fluctuations in electrical conductivity measurements. We found with our proposed approach, trained operators can obtain highly consistent measurement results that are close to true values while minimizing human errors during the experiments.

2. Theoretical background

2.1. Four-point probe conductivity measurement arrangements

The four-point probe arrangement was introduced in order to overcome the drawbacks of the two-point probe arrangement [24]. Figure 1 is a schematic of the four-point probe arrangement where the probes were set collinearly at equal interval S . The mathematical expression for the setup can be written as

$$V = \frac{\rho I}{2\pi r} \quad (1)$$

where V is the voltage potential adjacent to a probe carrying current, ρ is the surface resistivity, I is the current in the probe, r is the distance between the current probe and the voltage probe.

The voltage at probe 2 is

$$V_2 = \frac{\rho I}{2\pi} \left(\frac{1}{S_1} - \frac{1}{S_2 + S_3} \right) \quad (2)$$

and at probe 3, the voltage becomes

$$V_3 = \frac{\rho I}{2\pi} \left(\frac{1}{S_1 + S_2} - \frac{1}{S_3} \right) \quad (3)$$

Therefore, the total measured voltage

$$V = V_2 - V_3 = \frac{\rho I}{2\pi} \left(\frac{1}{S_1} - \frac{1}{S_2 + S_3} - \frac{1}{S_1 + S_2} + \frac{1}{S_3} \right) \quad (4)$$

Since the intervals are equidistant, i.e. $S_1 = S_2 = S_3 = S$, the resistivity ρ can be found by

$$\rho = 2\pi S \left(\frac{V}{I} \right) \quad (5)$$

According to equation (5), the resistivity of a sample can be obtained with known probe distance, application of constant current and the total voltage measurement.

The theoretical derivation of the measurement is intuitive; however, large discrepancies were often found between the theoretical values and the experimental data due to two major factors that affect the measurement results. Firstly, the capacity of the equipment was overestimated. Most measuring gauges came with their stable range of power output and resolution of measurement. The discrepancy can be inaccurate if they were operated out of range and resolution. If the measurement system consists of multiple measuring gauges, it is important to make sure that the measurements were handled carefully within the range and resolution of every gauge in the system so that proper results can be guaranteed. Another reason is that the properties of the test samples were idealized and assumed consistent as the measurement conditions changed. In our case, for example, if some surfactant was not fully washed from a CNT thin film, it is very likely that the measured resistivity will be much lower than the true value. In addition, a CNT thin film sample stored in a humid environment or is not completely dry will overestimate the test results because of the moisture within the sample or in the air.

2.2. Correction factors for finite volume samples

One major assumption in equation (5) is that the sample is assumed to be of semi-infinite volume. Since the samples are in fact of finite size, Valde derived correction factors for six different boundary compositions [25] and produced two major findings: (1) if the distance from any probe to the nearest boundary is at least $5S$, no correction is needed, and (2) for samples less than or equal to $5S$ in thickness, the true resistivity is given by

$$\rho_0 = ab\rho \quad (6)$$

where ρ_0 is the true resistivity of the sample, a is the thickness correction factor, and b is the geometry correction factor which is used when the sample is not large enough compared to probe spacing. The geometry correction factor b can be found from Smits' work [24] for a given D/S where D is the dimension (diameter or width) of the sample. Smits also showed in his work that for $t/S < 0.5$, a is proportional to t/S and shows a linear relationship, which can be written as

$$a = K \left(\frac{t}{S} \right)^m \quad (7)$$

where K is the value of a at $t/S = 1$, m is the slope of the $a - t/S$ curve, and t is the thickness of the sample being tested. In

our case, a Jandel Universal Probe (Jandel Engineering Ltd) with 1 mm probe spacing was used to perform electrical conductivity measurements. To determine the value of K , first we considered the resistance R in the system. Since in thin film case $t \ll S$, a propagation ring was generated instead of a propagation sphere

$$R = \int_{S_2}^{S_3} \rho \frac{dx}{2\pi xt} = \frac{\rho}{2\pi t} \ln 2 \quad (8)$$

In addition, due to the superposition of the currents from two outer probes,

$$R = \frac{V}{2I} \quad (9)$$

Considering equations (5), (8) and (9), we have

$$a = \frac{1}{2 \ln 2} \left(\frac{t}{S} \right) \quad (10)$$

The correction factor is $m = 1$ and the constant $K = \frac{1}{2 \ln 2} \sim 0.7213$. From equation (5) and (10), the resistivity of a thin film sample can be calculated as

$$\rho = \frac{t\pi}{\ln 2} \frac{V}{I} = 4.53t \frac{V}{I} \quad (11)$$

Hence

$$4.53 \frac{V}{I} = \frac{\rho}{t} = R_s \quad (12)$$

where R_s is the sheet resistance of the sample. Two observations should be noted here: (1) the derivations are based on a fact that $t/S < 0.5$, and (2) R_s is independent from all the geometrical parameters and can be consider as a unique property of the material. Note the geometrical meaning of R_s from the definition of resistance

$$R = \rho \frac{l}{wt} \quad (13)$$

where l and w are the length and width of the sample, respectively. Given a square sample, we have

$$R = \frac{\rho}{t} = R_s \quad (14)$$

Equation (14) also implies the reason the unit of R_s is Ω/Sq , and the importance of using a square sample when possible to avoid round-off errors.

3. Proposed approach

3.1. Thickness measurement

To demonstrate how small variations in thickness measurement have impacts on the electrical conductivity measurements, equations (6) and (7) show that a is proportional to t^m , i.e. any change in t will result in an exponential effect on a . In cases where t is tiny such as CNT thin films, a becomes very sensitive to t due to the closeness between the thickness unit and the resolution of the measurement equipment. For example, the average resolution of measurement gauge is

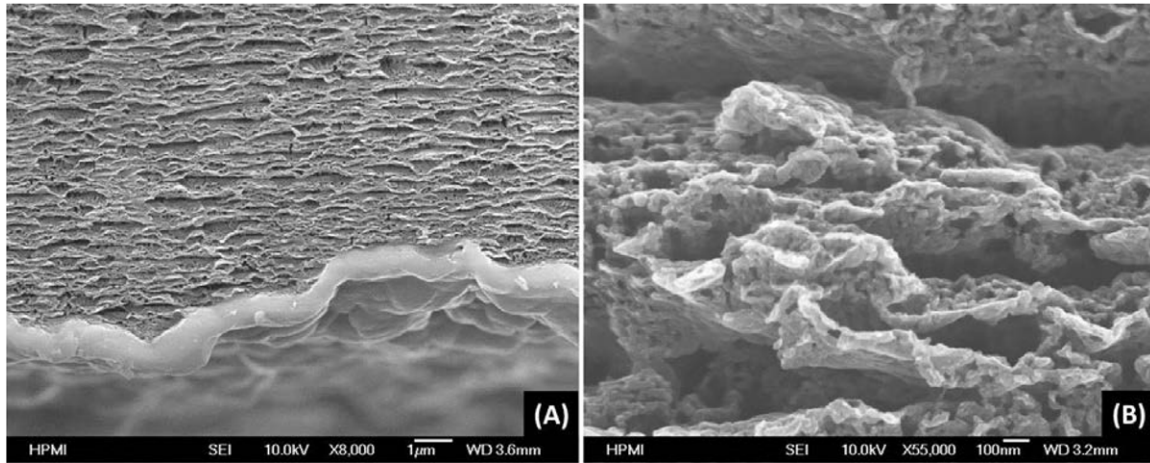


Figure 2. Cross-sectional SEM images of MWCNT thin films that show (A) layered and (B) nanoporous structure.

$\sim 1 \mu\text{m}$. Such an error is usually negligible when measuring general-purpose metal sheets ($\sim 2 \text{ mm}$ in thickness); however, the resolution may account for $\sim 5\% - 10\%$ inconsistency of the test results when determining the ultra-thin thickness of CNT thin films. Due to the unique layered and nanoporous structure (see figure 2), CNT thin films can easily be deformed [26] by a measurement gauge, which leads to inconsistent thickness measurement results from operator to operator.

One of the most commonly seen damages in CNT thin film samples is compression deformation when the plunger of the gauge was released onto the sample surface. This damage is device independent and inevitable due to the rough surface and nanoporous structure of 3D entangled CNT networks. In this study, we proposed adding one or multiple layers of cushion sheets as a solution to overcome this drawback and reduce the human error caused by operators of different skill levels conducting experiments. An ideal cushion sheet placed on the surface of the test sample should be resilient enough to absorb and distribute the compressing force, and bounce back when the force was removed. We chose polyimide sheets as cushions because of their resilience, thinness, flexibility, and availability. In order to observe the changes in thickness of the test samples, four sets of tests were conducted by operators: CNT thin films with zero, one, two, and three layers of cushion sheets. From the measurements of the cushion sheets and the measurements of the total thickness, the thickness of CNT thin film for a case of x layers of cushion sheets was found by

$$t_S = t_T - x * \mu_{CS} \quad (15)$$

where t_S is film thickness, t_T is total thickness, and μ_{CS} is the mean thickness of the cushion sheets. Figure 3 shows the schematic of our proposed experiment. The MWCNT thin films used in the experiments were fabricated by HPMI researchers [27]. The thin films and polyimide cushion sheets were cut into 2-inch squares to ensure that round-off errors can be avoided, as discussed in section 2, and randomly assigned to two experienced and two inexperienced operators. Note that all the MWCNT square thin film samples were cut from the same large buckypaper (BP) to prevent inter-sample variations. Each thickness test set was performed 30 times

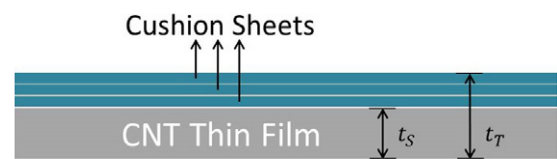


Figure 3. Schematic of the proposed thickness measurement setup.

using a HEIDENHAIN MT 1200 length gauge (Heidenhain Corp.). The results were plotted and summarized in figure 4 and table 1, respectively. In this paper, BP + x CS refers to the case with x layers of cushion sheets laid on the MWCNT thin film BP sample.

Figure 4 shows individual thickness measurements conducted with the four operators, and table 1 gives the sample mean and standard deviations of the observations. Operators 1 and 2 were experienced users who received their training by professionals and had extensive hands-on experiences in thickness measurements of various kinds of materials. Operators 3 and 4 were inexperienced users who were also professionally trained, but never conducted any thickness measurements. The 30 test repeats ensured the stability of the data obtained, and the central limit theorem (CLT) can be applied. Figure 4 also shows that the well-trained operators provided consistent measurements—almost all data points from operator 1 and 2 were plotted within an interval of $\sim 2 \mu\text{m}$ in width. In addition, the measurement results became stabilized when two or more cushion sheets were used. Note that the inexperienced operators sometimes gave larger variations (e.g. figure 4(B)) and human errors (figure 4(C)) that can be easily observed. To determine if there are any statistically significant differences among the results, ANOVA [28] with Box-Cox transformation and a significance level of 0.05 was conducted for each case and summarized in table 2. Figure 5(A) shows the normal probability plots of residuals, which suggests the error terms were normally distributed, and based on figure 5(B), it can be concluded that the results were not affected by the test sequence.

Tukey's HSD (honest significant difference) test [29] was performed to conduct multiple comparisons of the mean thickness measurements of different operators for different

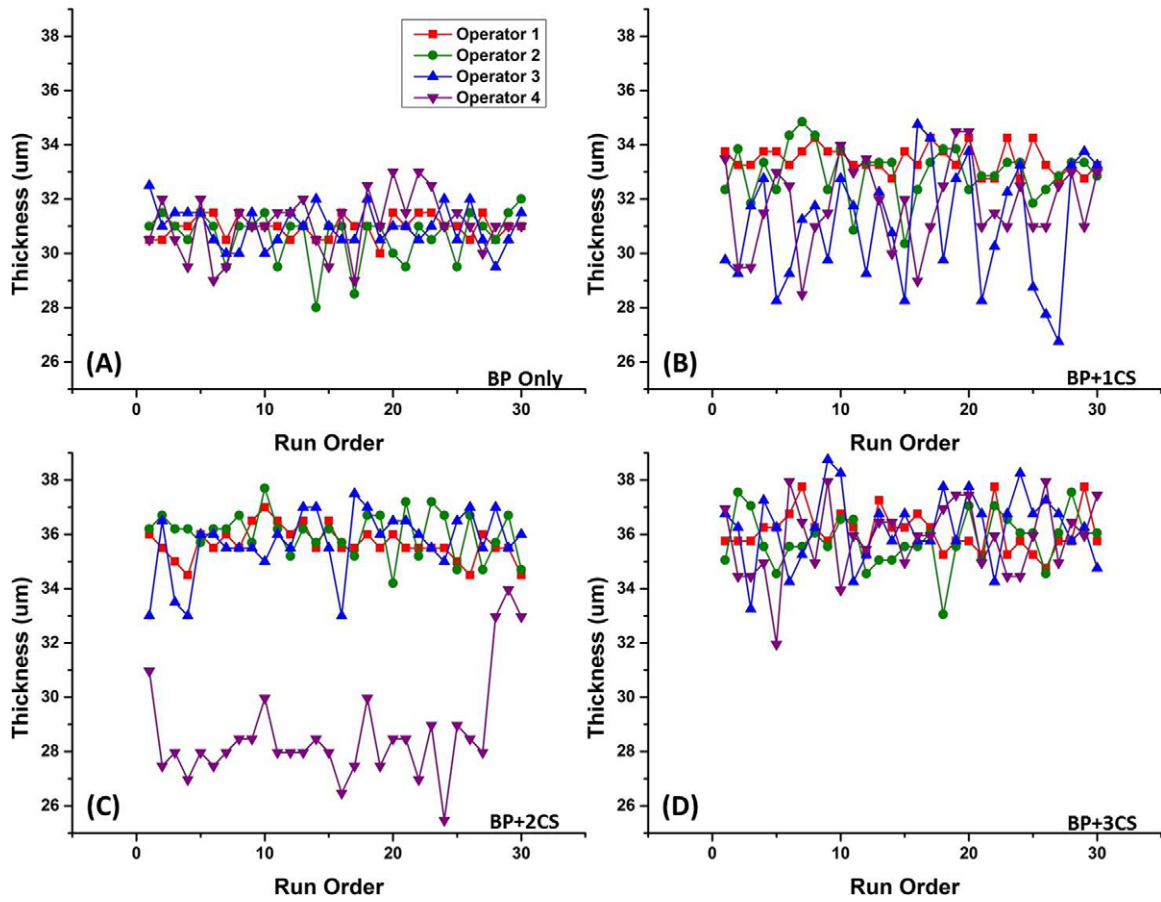


Figure 4. Plots of thickness measurements. (a) Buckypaper only, (b), (c), (d) Buckypaper with 1, 2, and 3 layers of cushion sheets, respectively.

Table 1. MWCNT thin film thickness measurement results.

| Thickness (μm) | Cushion sheet | | BP only | | BP + 1CS | | BP + 2CS | | BP + 3CS | |
|-----------------------------|---------------|----------|---------|----------|----------|----------|----------|----------|----------|----------|
| | μ | σ | μ | σ | μ | σ | μ | σ | μ | σ |
| Operator 1 | 50.25 | 0.39 | 30.97 | 0.41 | 33.45 | 0.5 | 35.67 | 0.61 | 36.1 | 0.78 |
| Operator 2 | 50.15 | 0.37 | 30.65 | 0.92 | 32.98 | 0.98 | 36.03 | 0.83 | 35.8 | 0.98 |
| Operator 3 | 49.75 | 0.31 | 30.98 | 0.72 | 31.05 | 2.2 | 35.7 | 1.21 | 36.25 | 1.3 |
| Operator 4 | 51.48 | 0.52 | 31.07 | 1.07 | 31.78 | 1.56 | 28.63 | 1.9 | 35.85 | 1.39 |

Table 2. ANOVA table of thickness measurement results¹ ($\alpha = 0.05$).

| Source | DF | Adj. SS | Adj. MS | F-value | P-value |
|----------------|-----|---------|---------|---------|---------|
| Operator | 3 | 322.7 | 107.552 | 79.74 | 0.000 |
| Parts | 3 | 1856.0 | 618.655 | 458.65 | 0.000 |
| Operator*parts | 9 | 789.8 | 87.752 | 65.06 | 0.000 |
| Error | 464 | 625.9 | 1.349 | | |
| Total | 479 | 3594.3 | | | |

cushion layer cases. Table 3 compiles the results of Tukey’s test, where 0 denotes no significant difference, and 1 denotes a statistically significant difference between the mean thickness measurements by the pair of operators being compared under a 0.05 significance level.

¹ In ANOVA tables in this paper, DF, Adj. SS, and Adj. MS refer to degrees of freedom, adjusted sum of squares, and adjusted mean square, respectively.

An important observation was immediately noticed in table 3 that no statistically significant difference can be found between the experienced and inexperienced operators in both BP only and BP + 3CS cases. This can also be observed from the interaction plot, as shown in figure 6. The parallel green and purple lines suggest that no operator-part interactions, and these test results were operator independent. The only factor that affected the experiment outcomes was the sample differences. Such an observation reflected the fact that CNT thin films are so soft and fragile that even experienced operators may cause a similar level of damage to the samples compared to inexperienced operators. On the other hand, for experienced operators, the measurement results were highly consistent while those of inexperienced operators showed fluctuations. One possibility is that the locations being tested were rationally chosen by experienced operators. Considering the properties of CNT thin films previously discussed, the position of the test points should be scattered uniformly over the sample to prevent the deformed areas from being measured again.

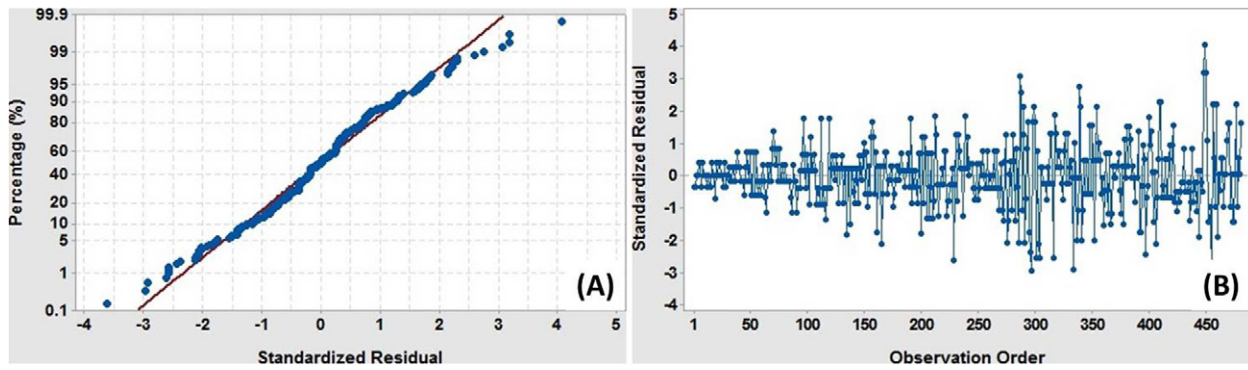


Figure 5. (A) Normal probability plot of residuals and (B) residuals versus order of thickness measurements.

Table 3. Tukey’s HSD test results of thickness measurements ($\alpha = 0.05$).

| Operator | Cushion sheet | BP only | BP + 1CS | BP + 2CS | BP + 3CS |
|------------|---------------|---------|----------|----------|----------|
| 2 versus 1 | 0 | 0 | 0 | 0 | 0 |
| 3 versus 1 | 1 | 0 | 1 | 0 | 0 |
| 3 versus 2 | 1 | 0 | 1 | 0 | 0 |
| 4 versus 1 | 1 | 0 | 1 | 1 | 0 |
| 4 versus 2 | 1 | 0 | 1 | 1 | 0 |
| 4 versus 3 | 1 | 0 | 0 | 1 | 0 |

Another possibility is the care taken when placing the samples. According to table 1, the test results by operator 3 and 4 have larger standard deviations in general, especially when the cushion sheets were added. Since polyimide structures tend to bounce back when the compression force was removed, the large variations can be resulted from the air gap between the sample layers when placing the cushion sheets onto the CNT thin films. Yet another possibility to be considered is the familiarity with the measurement gauge. For example, experienced operators were able to control the timing of pressing and releasing the plunge of the gauge more accurately so that the damages to the test samples were minimized. This inconsistency due to different operator skill levels, however, can be corrected by using a motorized measurement gauge.

A critical issue here is to decide the appropriate number of layers to use for thickness measurements of CNT thin films. Based on BP + 1CS case in table 3, no statistically significant difference between operator groups (namely, we have 0s for both 2 versus 1 and 4 versus 3 cases) were found; however, inconsistency can be seen in the other comparisons among operators. This observation suggest that the cushion sheets absorbed some energy, but part of the compression force was still transferred to the samples and caused some damage of different degree that differed from operator to operator. In BP + 2CS case, inexperienced operator 3 gave consistent results with experienced operators, while operator 4 provided irregular numbers that were apparently too low, as shown in figure 4(C). Reviewing the red and green lines in figure 6, operators 1 and 2 results were close and formed a small ‘X’ shape, meaning that the test results are almost operator and part independent, and only the operator-part interaction fluctuated slightly. For operator 3, the gap between the red and green dots was a slightly larger but still close. However, the

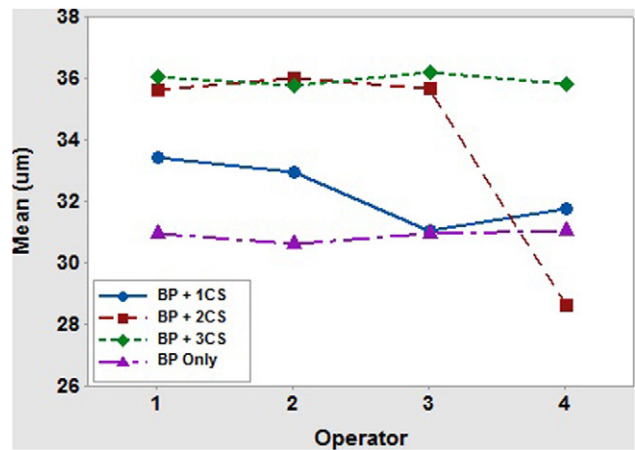


Figure 6. Interaction plot for thickness measurements.

Table 4. Grouping information using the Tukey method and 95% confidence.

| Parts* operator | Mean (μm) | Grouping |
|-----------------|------------------------|----------|
| BP + 3CS, 3 | 36.2949 | A |
| BP + 3CS, 1 | 36.1163 | A |
| BP + 2CS, 2 | 36.0519 | A |
| BP + 3CS, 4 | 35.9013 | A |
| BP + 3CS, 2 | 35.8258 | A |
| BP + 2CS, 3 | 35.7395 | A |
| BP + 2CS, 1 | 35.6766 | A |
| BP + 1CS, 1 | 33.4573 | B |
| BP + 1CS, 2 | 33.0114 | B |
| BP + 1CS, 4 | 31.8566 | C |
| BP + 1CS, 3 | 31.1989 | C D |
| BP only, 4 | 31.1023 | C D |
| BP only, 3 | 30.9997 | C D |
| BP only, 1 | 30.972 | C D |
| BP only, 2 | 30.6764 | D |
| BP + 2CS, 4 | 28.7583 | E |

red line shows a drastic drop for operator 4, which suggests the main effects and interactions were both too large and irregular to be natural, so we need to consider the possibility of human error. Judging from the facts above, the inconsistent data provided by operator 4 in BP + 2CS case were biased and very likely caused by human error.

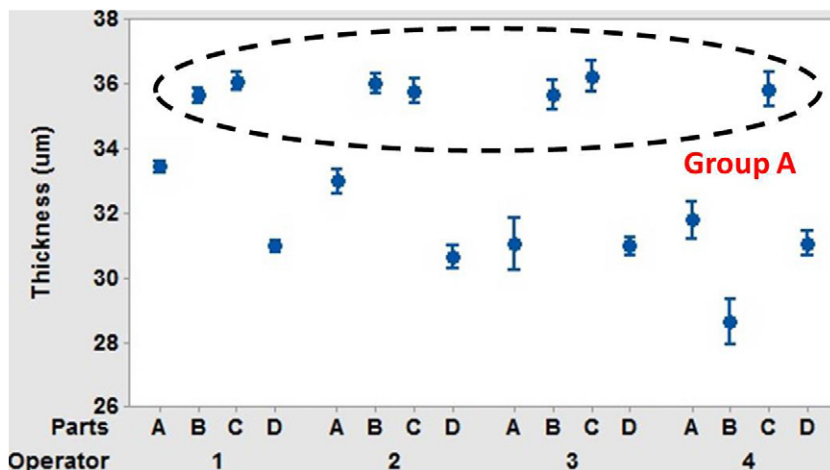


Figure 7. Interval plot of thickness² ($\alpha = 0.05$).

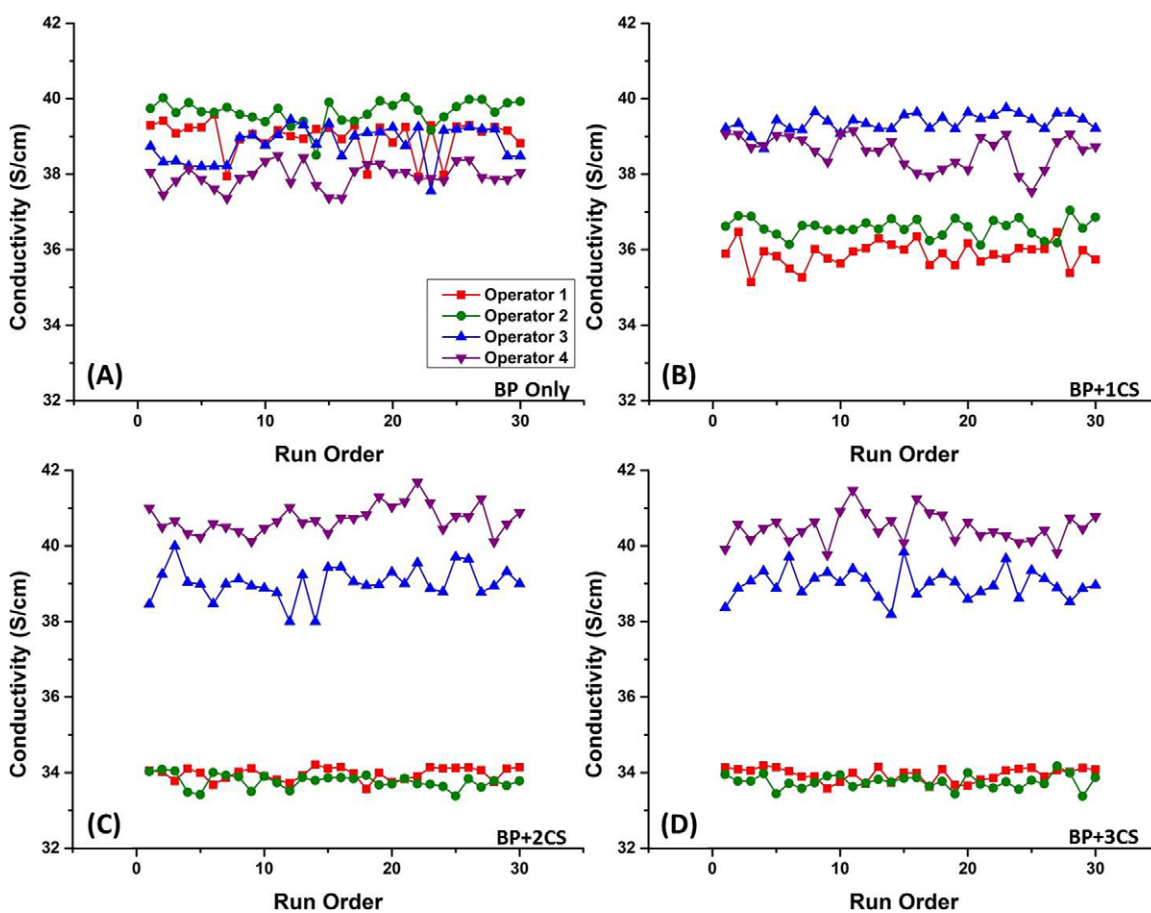


Figure 8. Plots of electrical conductivity measurements. (a) Buckypaper only, (b), (c), (d) Buckypaper with 1, 2, and 3 layers of cushion sheets when measuring thickness, respectively.

The Tukey’s test in table 3 compared sample means by different operators within the cases of different number of cushion layers. In order to study the differences in operators across the different cushion layer cases, all 16 possibilities should be taken into account. Therefore, another Tukey’s HSD test was performed for all the data in table 1. Table 4 compiles the grouping

information of Tukey’s HSD test, and figure 7 shows the interval plot that visualizes the grouping results.

Based on the grouping information and the interval plot, no statistically significant difference was found among the test results of BP + 2CS and BP + 3CS except for those by operator 4 in BP + 2CS case that were thought to be human error, as shown in Group A in figure 7. This finding also revealed that the thickness measurements of CNT thin films began to stabilize when at least two layers of cushion sheets were used.

² A, B, C, and D on the horizontal axis refer to BP + 1CS, BP + 2CS, BP + 3CS, and BP only cases, respectively.

Table 5. MWCNT thin film electrical conductivity measurement results ($\alpha = 0.05$).

| Conductivity ($S\text{ cm}^{-1}$) | BP only | | BP + 1CS | | BP + 2CS | | BP + 3CS | |
|-------------------------------------|---------|----------|----------|----------|----------|----------|----------|----------|
| | μ | σ | μ | σ | μ | σ | μ | σ |
| Operator 1 | 38.99 | 0.45 | 35.88 | 0.32 | 33.97 | 0.17 | 33.99 | 0.16 |
| Operator 2 | 39.65 | 0.32 | 36.59 | 0.24 | 33.77 | 0.19 | 33.76 | 0.18 |
| Operator 3 | 38.81 | 0.46 | 39.37 | 0.24 | 39.03 | 0.44 | 39 | 0.38 |
| Operator 4 | 37.95 | 0.31 | 38.61 | 0.43 | 40.72 | 0.37 | 40.47 | 0.4 |

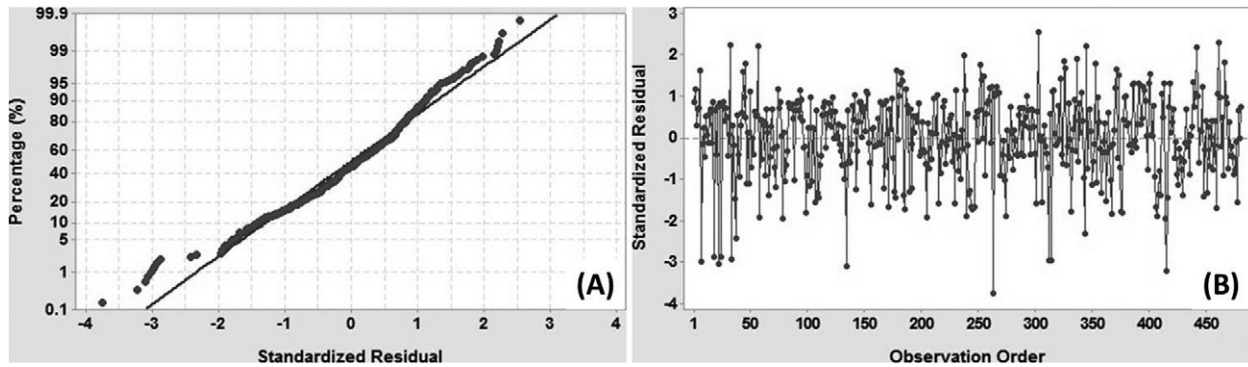


Figure 9. (A) Normal probability plot of residuals and (B) residuals versus order of conductivity measurements.

Table 6. ANOVA table of conductivity measurement results ($\alpha = 0.05$).

| Source | DF | Adj. SS | Adj. MS | F-value | P-value |
|----------------|-----|---------|---------|---------|---------|
| Operator | 3 | 1658.00 | 552.666 | 5592.47 | 0.000 |
| Parts | 3 | 497.36 | 165.786 | 1677.60 | 0.000 |
| Operator*parts | 9 | 1171.98 | 130.220 | 1317.70 | 0.000 |
| Error | 464 | 45.85 | 0.099 | | |
| Total | 479 | 3373.19 | | | |

Table 7. Tukey’s HSD test results of thickness and electrical conductivity measurements ($\alpha = 0.05$) (t = sample thickness, EC = electrical conductivity).

| Operator | BP only | | BP + 1CS | | BP + 2CS | | BP + 3CS | |
|------------|---------|----|----------|----|----------|----|----------|----|
| | t | EC | t | EC | t | EC | t | EC |
| 2 versus 1 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 |
| 3 versus 1 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 1 |
| 3 versus 2 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 1 |
| 4 versus 1 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 1 |
| 4 versus 2 | 0 | 1 | 1 | 1 | 1 | 1 | 0 | 1 |
| 4 versus 3 | 0 | 1 | 0 | 1 | 1 | 1 | 0 | 1 |

3.2. Electrical conductivity measurement

The electrical conductivity of each CNT thin film sample was measured by the four operators using a Jandel Universal Probe after the cushion layers were removed. The results were plotted and compiled in figure 8 and table 5, respectively.

As previously discussed, an increase in thickness will decrease the electrical conductivity of the same sample. The test results obtained from experienced operators agreed with this conclusion. Figure 8 shows that experienced operators provided stable and highly consistent test results as the number of cushion sheets used increased. For inexperienced operators, however, the conductivity data had larger variation. Moreover, a ~20% discrepancy between the data obtained from the two operator groups can be observed in figures 8(C) and (D). In order to have a clearer picture of the experimental data, ANOVA and Tukey’s HSD test were performed with Box-Cox transformation and a significance level of 0.05 to determine if there are any statistically significant differences among the datasets. Figure 9 shows the plots of normal probability and residual versus runs of electrical conductivity measurements. The ANOVA results in table 6 indicated that the electrical conductivity was affected by operator and the number of cushion sheets used, and there is a significant

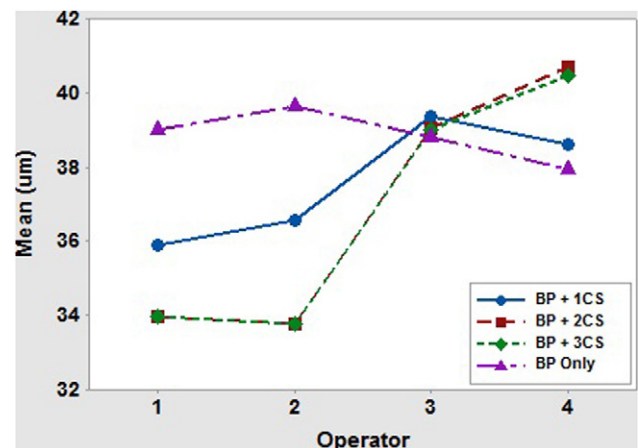


Figure 10. Interaction plot for conductivity measurements.

interaction between operator and cushion sheet effects. The large interaction implies that the effect of cushion sheets depends on the operator.

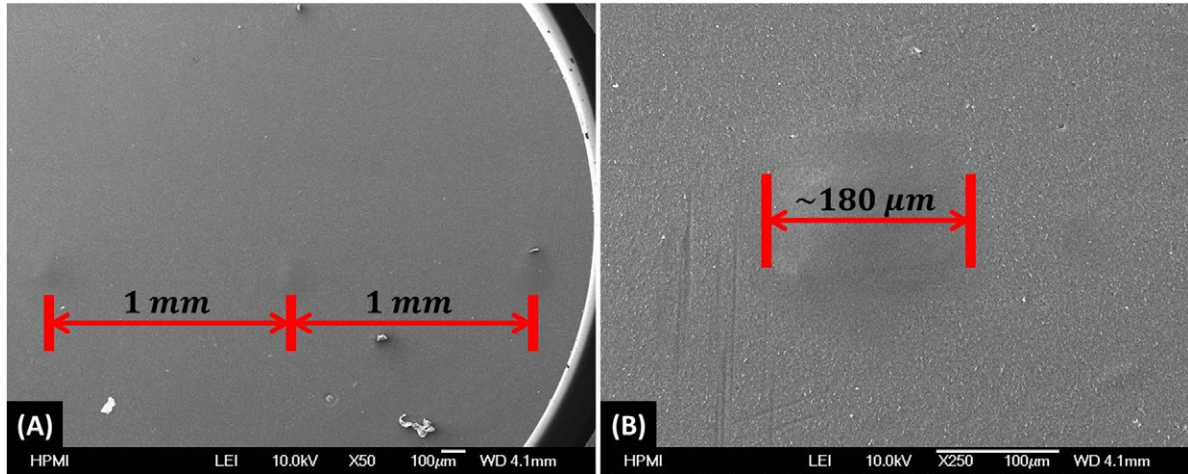


Figure 11. Compression damage caused by the probes of the measurement gauge at (A) 50 × and (B) 250 × magnification.

Table 8. Tukey’s HSD test results of electrical conductivity measurements by different operators ($\alpha = 0.05$).

| Test repeat | Operator 1 | Operator 2 | Operator 3 | Operator 4 |
|--------------------------|------------|------------|------------|------------|
| BP + 1CS versus BP only | 1 | 1 | 1 | 0 |
| BP + 2CS versus BP only | 1 | 1 | 0 | 1 |
| BP + 2CS versus BP + 1CS | 1 | 1 | 1 | 1 |
| BP + 3CS versus BP only | 1 | 1 | 0 | 1 |
| BP + 3CS versus BP + 1CS | 1 | 1 | 1 | 1 |
| BP + 3CS versus BP + 2CS | 0 | 0 | 0 | 1 |

Table 7 summarizes the results of Tukey’s HSD test for the pairwise comparison of thickness (t) and electrical conductivity (EC) measurements (the thickness results were the same as those given in table 3). For the latter, Tukey’s HSD test indicated statistically significant differences between experienced operators in case BP only and BP + 1CS. This result suggest that in the both cases, the compression force from the plunge of the gauge either damaged the sample directly or was transferred through the cushion layer and caused some indirect damage. Although the thickness measurement results showed no significant differences in the statistical tests, the damaged regions on the sample led to the inconsistency in electrical conductivity tests. On the other hand, for cases BP + 2CS and BP + 3CS, experienced operators obtained consistent results. This observation confirmed our previous finding that the thickness measurement results began to converge when two or more polyimide cushion sheets were used. Based on the observations, it can be concluded that the compression force applied to the sample was minimized to a statistically negligible degree with 2 or more cushion sheets used such that it did not affect the conductivity measurement.

The interaction plot in figure 10 indicated that there is significant operator-part interaction. The zig-zag purple and blue lines suggest that the interaction from case BP only and BP + 1CS were large; therefore, operator skills in these two cases played an important role in the measurements. On the other hand, by analyzing the red and green lines corresponding to case BP + 2CS and BP + 3CS, the overlapping and approximately horizontal segments for operators 1 and 2 suggest that the test results were highly stable and repeatable. For operators 3 and 4, although the segments are also close, the sloping trend implies that differences between both operators and parts exist. The lack of hands-on experience could be the explanation for this phenomenon.

Note that the inexperienced operators gave different electrical conductivity measurements for all cases. One of the possible reasons is the samples were damaged by the tweezers when moving the samples. As previously discussed, CNT thin films are soft and fragile; therefore, any outside force can damage the samples and cause permanent deformation. The 3D entangled CNT networks became more densely packed when compressed, hence the electrical conductivity increased if the compressed areas were again tested by the four-point probe. This theory can be verified by re-measuring the thickness of the samples operators 3 and 4 used in case BP + 3CS. We found that the thickness of those samples decreased by ~5%–8%, which could have caused the differences. Based on the experimental data, we would suggest operators place one layer of cushion sheet on both top and bottom of the samples when moving them with tweezers. Another possibility that inexperienced operators gave the fluctuated results is the selection of the test area. According to our observation, although the samples were rotated to obtain electrical conductivity data from different directions, inexperienced operators tended to conduct the tests around the center area, while experienced operators selected regions that were uniformly distributed throughout the sample most of the time. For 30 test repeats within a 2-inch square sample, it is very likely to select regions that have already been measured if they gathered around the center area. As previously discussed, samples can be damaged

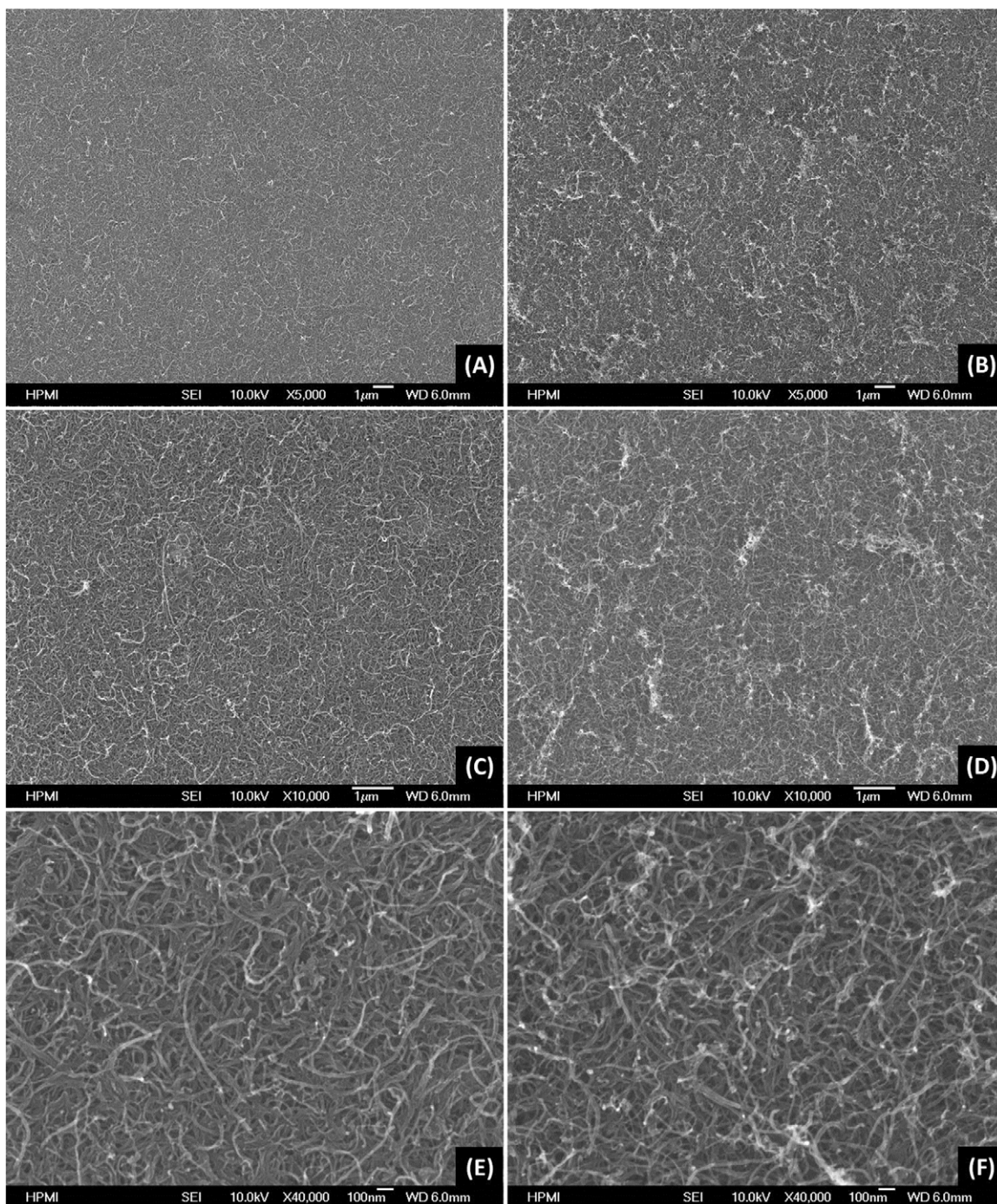


Figure 12. SEM images that show (a), (c), (e) inside and (b), (d), (f) outside the compressed areas at different magnifications.

by the probes of the gauge; therefore, a re-test on those points will cause heavier compression damage and lead to higher electrical conductivity measurement results. Figure 11 shows the SEM images that show the compression damages caused by the probes. Note that the tip end width of the probes used was $100\ \mu\text{m}$, so the damaged areas were actually larger than expected.

To further examine the possible effects that compression damage could have, we took SEM images at higher magnification to check whether the network structures inside and outside the compressed areas were changed, as shown in figure 12.

Figures 12(A), (C) and (E) shows areas inside and outside the compressed points at $\times 5000$, $\times 10\ 000$, and $\times 40\ 000$ magnification. Figures 12(B), (D) and (F) show areas outside the compressed points at the same magnification level. The outside areas contained more white regions due to edge effects [16, 30, 31]. However, figures 12(A), (C) and (E) show a more uniform and darker color tone than those in figures 12(B), (D) and (F) since these surface areas have been flattened. In other words, figure 12 shows evidence that the 3D network structures of CNT thin films were drastically changed after a compression force was applied. Considering that a change in thickness will have an exponential effect on electrical

conductivity, with changes in network structure and thickness, a large impact on the electrical conductivity performance of CNT thin film can be expected.

Finally, we checked the test repeats to propose an optimal setup for electrical conductivity measurements of CNT thin films. Table 8 shows the results of Tukey's test to find a statistically significant difference among the test sets between operators. For experienced operators, table 8 shows quite consistent results with table 7, which leads to the conclusion that accurate and stable test results can be obtained by using two or more polyimide cushion sheets. However, applying too many layers of cushion sheets is not recommended, because, as seen in equation (15), standard deviation of cushion sheet thickness was not taken into account when determining sample thickness used for electrical conductivity measurement. Therefore, the discrepancy between true and calculated values of CNT thin film sample thickness will increase as the number cushion sheet layers used increased.

4. Conclusion

Accurate characterization of electrical conductivity is crucial for repeatable manufacturing of CNT reinforced nanocomposites. In this study, we proposed an ANOVA methodology to analyze characterization data of CNT thin films to determine the setting for the measurement procedures that provided most repeatable results. The study involved a series of thickness and electrical conductivity measurements of CNT thin films to demonstrate the discrepancies between the test results of operators with varying experience levels. It is shown that electrical conductivity outcomes can be affected significantly by small variations in thickness measurement and therefore it is important to quantify measurement errors in thickness gages. Some common mistakes inexperienced operators could make were pointed out, and possible actions to avoid these errors were suggested. We proposed to use polyimide cushion sheets in thickness measurements of CNT thin films and showed that both thickness and electrical conductivity measurement results of CNT thin films were stabilized when two or more polyimide cushion sheets were used. In particular, we suggested experienced operators apply two layers of polyimide cushion sheets on the test sample, while inexperienced operators need three when conducting thickness measurement of CNT thin films until they accumulated enough hands-on experience. In addition, we also recommended operators place one layer of cushion sheet on both top and bottom side of the test sample when moving it using tweezers to prevent the CNT thin films from deforming that leads to changes in both thickness and network structures. Finally, we showed that with our suggested system setup applied, no statistically significant differences among the experimental data were found from experienced and inexperienced operators.

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