Characterization of Adhesive Strength of Carbon Nanotubes to Various Substrates

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ABSTRACT

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The adhesive strength of carbon nanotubes (CNTs) to the substrate on which they are grown is an important characteristic to know in many applications, particularly in biomedical applications where detached CNTs may pose a potential health risk. In this work, we develop a procedure for testing the adhesive strength of CNT films to a substrate, and present initial results of that procedure for CNTs grown on grown on silicon, stainless steel, and titanium. We grew each type of sample in several growth conditions in order to investigate whether this affects CNT adhesive strength, with our primary focus being CNTs grown on stainless steel. The CNTs on silicon and most titanium were grown for times ranging from ten seconds to 25 minutes, while the CNTs on stainless steel were grown at temperatures ranging from 700-800°C and for times ranging from 3-40 minutes. We also conducted tests on a small number of samples which were first grown on silicon and then transferred to titanium with a heat treatment process. The adhesion testing procedure involves pressing a 2x2mm square of adhesive tape onto a CNT sample using an Instron tensile tester. The tensile tester presses up to a 1N force, then raises the tape back up, and afterwards we examine the resulting force data to obtain an adhesive strength. Our procedure proved to be effective for some samples, while for others we obtained only a lower bound on the adhesive strength. In the latter case, we find that even these lower bounds are between 10 and 20 times greater than adhesive strengths measured in silicon and conventional titanium, where the greatest measurements were about 1.1N for a 2x2mm array and 70nN per nanotube. In our stainless steel samples, our data revealed an increase in adhesive strength with increasing growth temperature, with each 50°C step in temperature leading to an approximately 0.2-0.5N increase in our measurements. We also find with the stainless steel that, in general, adhesive strength increases with growth time for a given temperature up to 20 minutes, then levels off, though samples grown at 700°C show somewhat different behavior. While the procedure we describe is not fully effective, it has the advantage of being quantitative and quick to set up where many other tests for measuring the adhesion of thin CNT films are either qualitative or require lengthy preparation. We suggest future steps to work towards the use of antibacterial CNT films, including replicating and refining our procedure.

Keywords: CNT, adhesion, stainless steel

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Chapter 1

Introduction

Carbon nanotubes (CNTs) are sheets of graphene rolled into long, hollow tubes, with diameters ranging from a few nanometers to hundreds of nanometers, and since their discovery they have been shown to have a variety of interesting material properties [1]. One of these more recently discovered properties is the apparent ability of CNT films to inhibit bacterial growth on their surfaces [2] [3]. If such films could be applied to the surfaces of medical implants, they could be extremely helpful in preventing the development of biofilms on their surfaces and reducing rejection in the recipients [4] [5]. Such films would need to remain on the surface of medical implants for the lifetime of the patient, so in order for this use of CNTs to be realized, the adhesive strength of CNTs to the substrates on which they are grown must be well understood.

Several prior works have set out to measure the adhesive strength of the CNT-substrate interface, but with a variety of methods that each have their own strengths and weaknesses. The standard ASTM methods for measuring the adhesion of thin films are straightforward to carry out, but highly qualitative [6]. Some works augment this test with additional quantitative measures [7], but still offer very little in the way of describing the actual stresses the CNTs and substrate are subject to during the tests. Methods that use sonication as a way of measuring adhesive strength suffer a similar problem [8]. Of the methods that do seek to make quantitative measurements of the CNT-substrate adhesion, such as nanoscratching [9], larger scale scratching [10], and tensile testing with atomic force microscopes [11], tape adhesives [12], and epoxy adhesives [13] [14], the variety of testing modes and types of values reported make comparison between works difficult. The literature is also dominated by works that do these measurements for CNTs grown on silicon substrates, which is not a material commonly used for medical implants.

This work presents the preliminary results of our own method to quantitatively measure the adhesive strength of CNTs to a substrate when a tensile load is applied to the CNTs. This method uses an Instron tensile and compression tester to press a piece of adhesive tape into a CNT sample at a known force, after which it pulls the tape back up and measures the forces experienced by the system. We then used the force data to determine the adhesive strength of the CNTs to the substrate, coupled with optical and scanning electron microscopy imaging. While this method is similar to others used in the past, it has the advantage of being quick to prepare, which allowed us to obtain a relatively large number of data points. This method was primarily developed by Michas et al. [15], but its development also continued into this work.

We performed this procedure on four different types of samples: CNTs grown on silicon, CNTs grown on stainless steel, CNTs grown on titanium, and CNTs first grown on silicon and then transferred to a titanium substrate with a heat treatment process. Our main focus was on testing stainless steel samples, since stainless steel is sometimes used in medical implants and previous work suggested such CNTs would have high adhesive strength [16]. We grew and tested several stainless steel samples in a variety of growth environments to understand how changes in the growth environment affect the adhesive strength. Variables in the growth included growth time, growth temperature, and anneal time. Titanium is very commonly used in medical implants, and for this work we grew and conducted tests on a relatively small number of samples. Silicon is the most common growth substrate used in research applications, so we tested a small number of this type of CNTs for comparison.

Our test reports a force that represents a mechanical failure in the system, and the cause of this mechanical failure varies between samples. For the silicon, most of the titanium samples, and some of the stainless steel samples, we definitively measured the adhesive strength between the CNTs and the substrate layer, while for other samples the mechanical failure was most likely a measure of the tensile strength of the CNTs. For this second type of sample, our measurement still represents a lower bound on the substrate-CNT adhesive strength, and we show that even these lower bounds are many times greater than the adhesive strength of CNTs grown on silicon and titanium. The steps necessary to prepare stainless steel for CNT growth make it a non-ideal substrate for use in medical implants, however, and further work must be done to investigate whether other preparation methods can retain the high adhesive strength.

In chapter 2, we will explain in greater detail the method we developed and used to make our measurements, as well as describe the CNT growth process we used. The description of the method will include the adhesion test itself as well as the steps we took to process the collected data and clarify our findings with microscopy techniques. Chapter 3 will present the results of this procedure, establish the nature and limits of our measurements, and point out a few trends that appear in the data. Chapter 4 will discuss the potential meanings of our results for various kinds of samples, present adhesive strength values, and suggest future work to improve our adhesion testing method.

Chapter 2

Methods

Previous works investigating the adhesion of carbon nanotubes to their growth substrate have used a variety of methods and employed many different kinds of experimental apparatus. These different methods have in turn measured this adhesion using several different physical qualities, from force and stress to work and binding energy. This work seeks to measure the adhesive strength of CNTs by applying uniaxial tension with a tensile and compression tester. Some previous works that have measured CNT adhesion strength in this way include Kaiser et al. [13] and Brown et al. [14], in which they embedded the ends of CNTs in epoxy resin and removed them from their substrate once the epoxy had cured. This method is effective, but allowing the epoxy to cure means each test takes several hours to complete. Our method instead uses a piece of double-sided adhesive tape, which means tests can be completed more quickly and a larger number of samples can be tested. This procedure comes with its own set of problems as well and proved not to be effective in all the ways we were hoping, but we were still able to find several interesting results.

Stainless Steel				
Anneal Time (min)	Growth Time (min)	700°C	750°C	800°C
2	3	1	2	2
	10	2	2	2
	20	2	2	2
	40	2	2	2
4	3	2	2	1
	20	-	-	2
	40	2	2	1

Table 2.1 Table showing the number of stainless steel samples created and tested with the adhesion method for this work.

2.1 CNT Growth and Sample Preparation

We conducted tests on 35 samples of CNTs grown on 316L stainless steel. Each sample was grown on a rectangular chip of stainless steel, a few centimeters on each side, using a chemical vapor deposition (CVD) process [17] [18]. The CVD furnace was first brought up to one of the three growth temperatures shown in Table 2.1, and then the chips were placed inside to oxidize in air for either 2 or 4 minutes. The air inside the furnace was then replaced with argon, and we started an ethylene flow into the furnace to begin CNT growth. We varied the growth temperature, growth time, and anneal time for individual samples. The chips were annealed for either 2 or 4 minutes; growth was carried out at 700, 750, or 800°C; and growth lasted for 3, 10, 20, or 40 minutes. Whenever possible, we created and conducted a set of adhesion tests on two samples having a set of unique growth properties. However, due to time and material constraints, this was not always possible, and Table 2.1 gives the number of samples that were tested for each set of growth conditions.

Following the growth process, samples which were in the furnace for longer times accumulated a carbon dust on the side of the chip opposite the CNTs. During the adhesion testing procedure, this side of the sample is taped to an aluminum stub, meaning the dust needed to be removed. When necessary, we cleaned these samples with a cotton swab and acetone.

We also prepared a small number of samples with CNTs grown on silicon and titanium. These samples were grown on similarly sized chips as the stainless steel and in a similar CVD process, though their surfaces were treated with catalyst supports rather than being annealed in air. 200nm of alumina were e-beam deposited onto the surface of the titanium along with 4nm of iron nanoparticles. The same is true of the silicon samples, except the alumina was deposited by reactive sputtering. The silicon and titanium samples were both grown at 750 °C, and for each we tested four samples: one grown for 10 seconds, one for 5 minutes, and two for 25 minutes. We also tested one final type of sample on titanium, where CNTs were first grown and then transferred onto titanium by a heat treatment process. We tested only two samples of this type.

2.2 Adhesion Testing Procedure

The adhesion test procedure made use of several pieces of equipment. The first of these was an Instron 3345 Tensile and Compression Tester, which recorded force data with a 5.6lb load cell (A in Figure 2.1). This machine consists of a column with a space at the top and bottom for clamps (B, Figure 2.1). The bottom of the machine is fixed, but the top is able to move vertically according to user input. Prior to an adhesion test, the tensile tester was set up as follows.

The top clamp housed a 3D-printed post made of polylactic acid (PLA) filament (C, Figure 2.1). The bottom end of this post was square, 2 millimeters on each side. This end of the post, in turn, held a flexible strip of double-sided carbon tape (F, Figure 2.1) typically used for preparing samples for scanning electron microscopy (SEM). This strip of tape was cut to be approximately 2 mm wide,

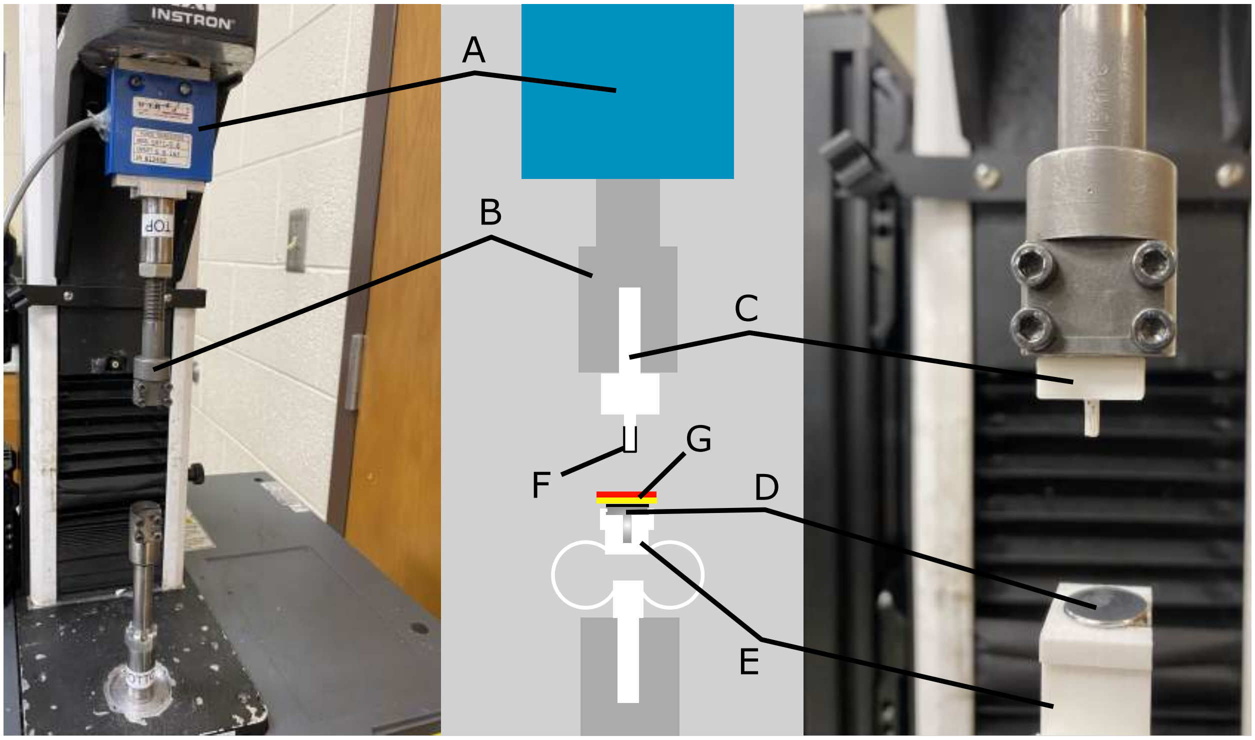

Figure 2.1 Schematic view and photographs of experimental equipment. A is a 5.6lb load cell, B is a clamp, C is a 3D-printed post, D is an aluminum SEM stub, and E is a 3D-printed spring mechanism. F and G (not pictured in photographs) are a piece of double-sided carbon tape and the CNT sample, respectively.

and the excess was wrapped onto the sides of the post. The bottom clamp held another 3D-printed part: a compliant mechanism (E, Figure 2.1). This component was included because it would allow the force applied to the CNT sample to be applied gradually, and the known spring force of the mechanism could be easily separated from the other forces recorded during the test. The top of the compliant mechanism held an aluminum stub used for SEM samples (D, Figure 2.1), and the CNT sample to be tested (G, Figure 2.1) was fixed to this stub with tape similar to the tape on the top post. Once all these pieces were in place, the top part was manually moved downward such that the post was within a few millimeters of the CNT sample surface. See Appendix A for a more detailed set of standard operating procedures.

The tensile tester was run with the software from Bluehill Universal typically used for this type of machine, and our procedure utilized a custom method written in that environment. The method was programmed to move the top arm downwards and press into the CNT sample until the load cell detected a compressive force of 1N. At this point, the arm held its position for 10 seconds and then moved back upward 12mm. While the arm moved upward, the load cell would detect a tension force, indicating that the CNTs had become stuck to the tape on the top arm and were now being pulled up. Figure 2.2 gives a schematic view of the test process. For a given CNT sample, this procedure could be done between 5-9 times depending on the size of the stainless steel chip. In total, we conducted 219 tests with CNTs grown on stainless steel using this procedure, 25 using CNTs grown on titanium, 17 using CNTs grown on Si, and 6 using CNTs transferred to titanium. We also ran 9 tests on a bare stainless steel chip to better understand the behavior of the tape.

2.3 Data Processing and Visualization

Each test completed with this procedure outputs the collected data in a .csv file. This data includes three columns: time in seconds, displacement in millimeters, and force in Newtons. Measurements were recorded by the software at a rate of about 50 measurements per second.

For each test, we obtained a mechanical failure force by finding the maximum tension force recorded during the test. Figure 2.3 shows a few examples of plots generated using the raw data recorded by the tensile tester. We determined the maximum tension force using the MAX function in Microsoft Excel on the column of recorded force values. This maximum force is the force experienced by the system just before some sort of mechanical failure; some possible sources of this failure are the CNT-adhesive interface, the adhesive-post interface, tearing partway through the CNTs, or the substrate-CNT interface. If the source of the failure was the substrate-CNT interface, then we could say with certainty that this peak tension force represents the adhesive strength of the

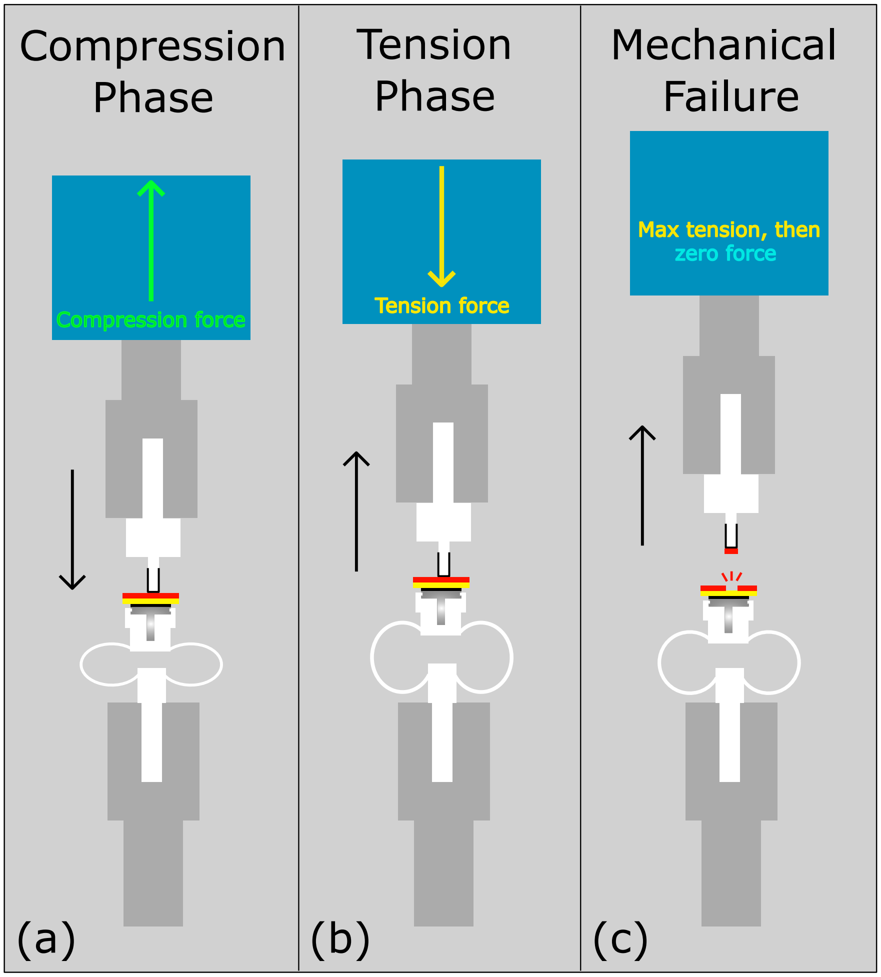

Figure 2.2 Diagram of the adhesion procedure. (a) The top clamp of the tensile tester pushes the post down into the CNT sample and holds for ten seconds, while the load cell detects a compression force. (b) The top clamp pulls back up, and the load cell detects a tension force as the CNTs resist being pulled. (c) A peak tension force is reached before a mechanical failure occurs in the system, and the load cell reads zero force.

CNTs. We imaged the substrate with scanning electron microscopy (SEM) to investigate whether this was the case.

These maximum force measurements, along with identifying information for each test, were recorded in a catalog .csv. A Python script we wrote then sorted these data by growth time, growth temperature, and anneal time, and generated plots of the maximum force with these variables. In

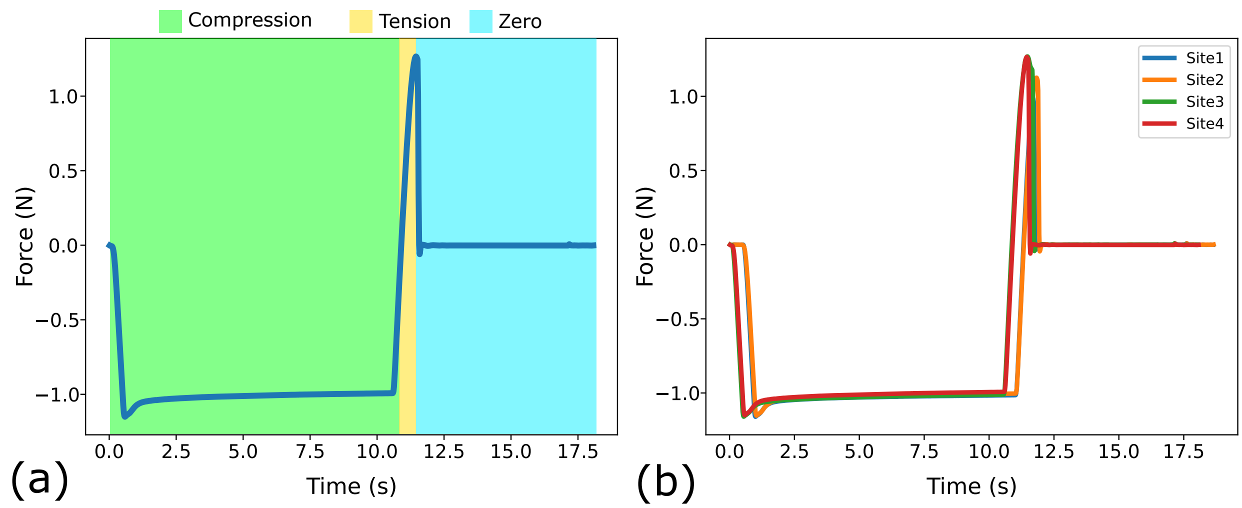

Figure 2.3 Examples of raw data collected from the adhesion procedure. (a) A single test with different stages of the procedure marked with shaded regions (compare with Figure 2.2). The peak tension force represents a mechanical failure in the system during the test. (b) Raw data from several tests conducted on the same sample.

the generated plots, each point is the average maximum force of all data having the appropriate characteristics, with an error of one standard deviation of that data subset.

2.4 Imaging

In order to investigate whether the force we measured was the adhesive strength of the CNTs to the substrate, several of the samples were imaged after testing with an SEM. We compared areas of the sample that had undergone the experimental procedure with areas that were unaffected. If few or no CNTs were present in the tested areas, this would confirm that the CNTs were being completely pulled away from the substrate by the procedure.

A more broadly useful measure of adhesive strength than the force alone is the force per unit area required to lift a thin film from a surface. Obtaining this value for our procedure would be straightforward if the adhesion test uniformly pulled all the CNTs from a given test site. However, visual examination of the samples after testing indicated that, for most tests sites, the tearing off of the CNTs was patchy; while some areas of the test sites were completely bare of CNTs, other parts retained most of their CNTs. This meant that a measure of the adhesive strength as pressure could not be accurately obtained by simply dividing the recorded force by the area of the post. Instead, we took optical images of each of the CNT samples and used them to calculate an approximate affected area for each test. The areas were traced out by hand in the vector graphics program Inkscape, and we used the Measure Path extension to calculate the areas of these traced shapes. Figure 2.4 gives a side-by-side example of an optical image and the areas obtained using the image. While taking SEM images of every test site to find these areas would have been more precise, it also would have been impractical given the number of tests carried out.

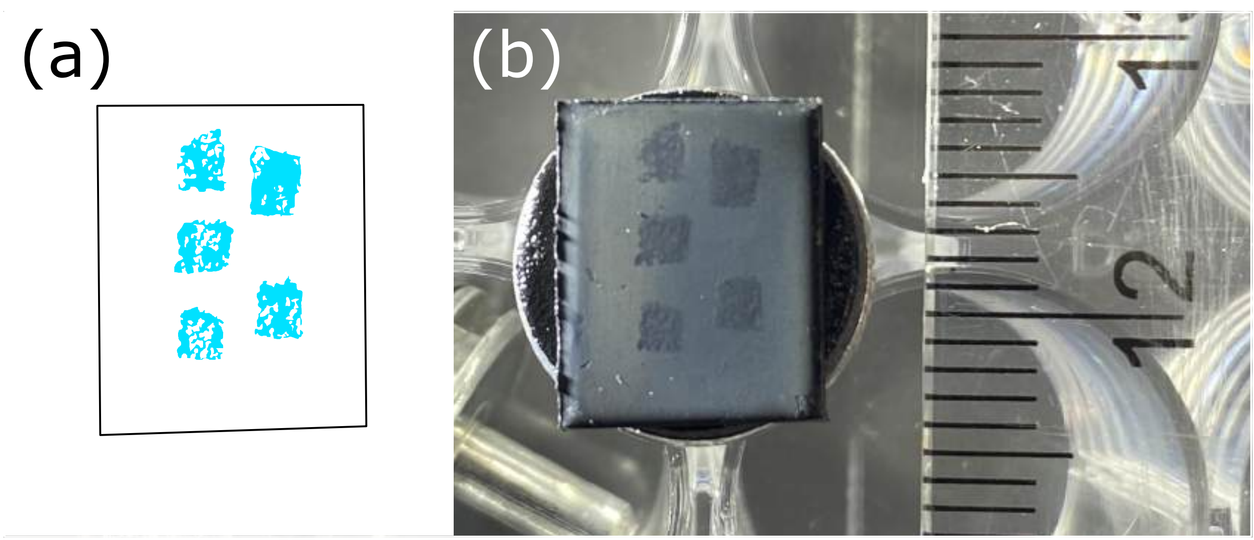

Figure 2.4 Images of one of the CNT samples tested: (a) tested areas, traced out in blue in a vector graphics program, whose areas can be easily calculated, and (b) the optical image of the sample used as the basis for the tracing.

Chapter 3

Results

In order to know exactly what value our adhesion test was measuring, we imaged CNT samples in a scanning electron microscope (SEM), both in areas that were and were not affected by the adhesion test. Figure 3.1 shows one example of these images for a stainless steel sample grown at 700°C. 3.1(a) shows an unaffected area, and 3.1(b) shows an area that underwent the test procedure at a similar magnification. These images clearly show that areas affected by the adhesion procedure are almost entirely bare of CNTs, indicating the adhesion test pulled them completely away from the substrate. This means that the maximum force data we compiled does indeed represent the adhesive strength of the CNTs to the substrate for the 700°C samples. We obtained very similar images for the CNTs grown on silicon, so we successfully measured the adhesive strength for these samples as well.

Figure 3.2, on the other hand, shows an example of SEM images obtained for CNTs on stainless steel grown at 750°C. For these, as well as the 800 °C samples, we much more commonly found that very few CNTs had been removed by the adhesion test, and that instead they had either been broken partway through or simply straightened out. This is further supported by SEM images we took of the tape used in these tests, such as Figure 3.3, which show that short CNTs were present on the tape following a test. In such cases, then, we cannot say that we measured the adhesive strength

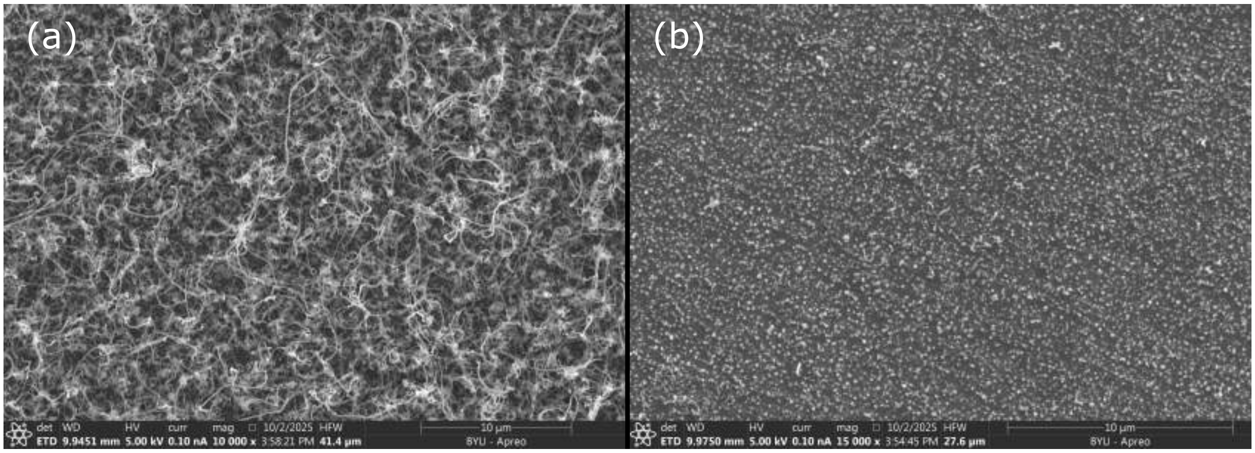

Figure 3.1 SEM images of a CNT sample grown at 700°C for 40 minutes, with a 2 minute anneal. (a) shows an area of the sample unaffected by the adhesion procedure, while (b) shows one of the test sites. Almost no CNTs are left on the right, indicating they were torn off by the adhesion procedure.

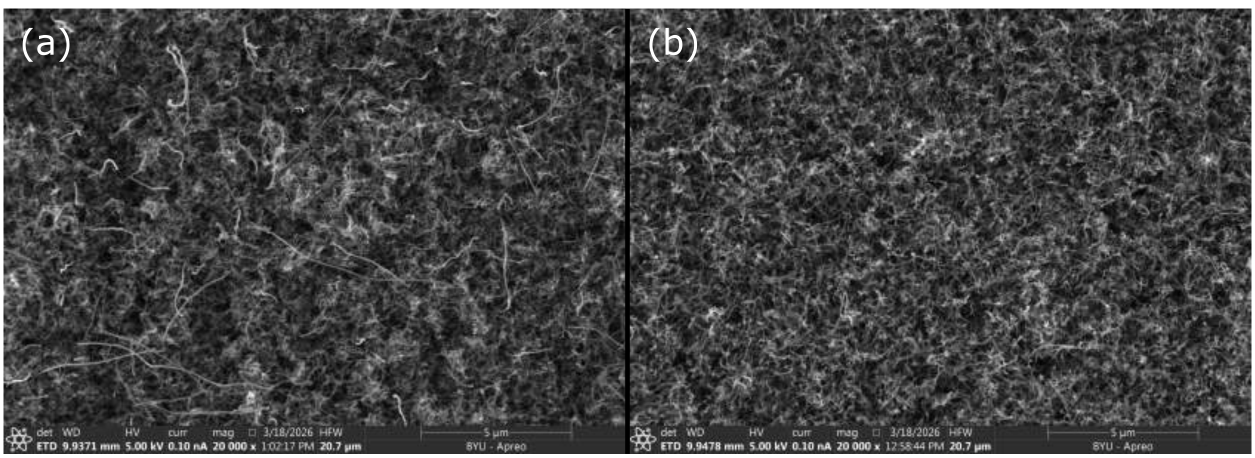

Figure 3.2 SEM images of a CNT sample grown at 750°C for 20 minutes, with a 2 minute anneal. (a) shows an area of the sample unaffected by the adhesion procedure, while (b) shows one of the test sites. We see that very few CNTs have been removed by the adhesion procedure.

of the CNT-substrate interface. The data we collected is still valuable in the pursuit of this goal, however. Since this mechanical failure occurred before the CNT-substrate interface could fail, we know that the adhesive strength must be at least as large as our measured force. In such cases, we instead report that the force measured for these samples represents a lower bound on the adhesive strength of the CNT-substrate interface.

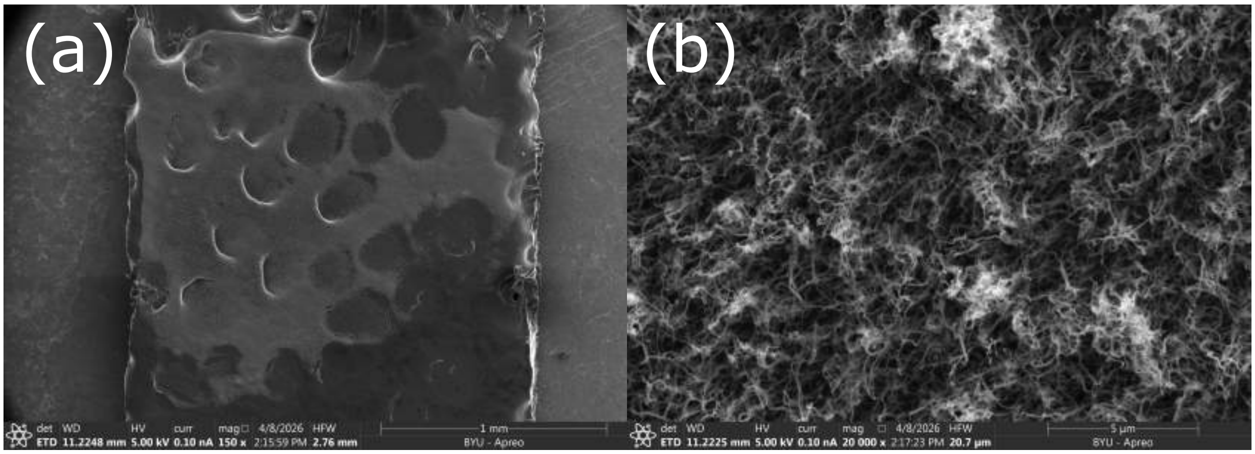

Figure 3.3 SEM image of tape used in an adhesion test, at (a) low and (b) high magnification. This sample was grown on stainless steel at 750°C for 10 minutes, and these images are typical of what the tape looked like following an adhesion test for stainless steel samples grown at 750°C and 800°C. The lighter areas in (a) are areas with CNTs. These images show that there are short CNTs on the tape after adhesion tests, with a similar area density to the CNTs on the substrate. Together with Figure 3.2, this suggests that these tests broke CNTs partway through their length rather than removed them from the substrate.

Figure 3.4 shows a plot of the adhesive strength in terms of force with growth time for each of the three stainless steel growth temperatures. Each point is the average of the adhesive strengths for samples with given growth criteria (e.g. the first blue point is the average of all adhesive strengths measured for tests on samples grown for 3 minutes at 700°C). The error bars on each point represent one standard deviation of that data subset. Here we see that for a given growth temperature, as growth time increases, the adhesive strength increases up to 20 minutes, then levels off between 20 and 40 minutes. The 750°C and 800°C samples closely followed this trend, but the samples grown at 700°C showed unexpectedly high adhesive strengths at 3 minute times and unexpectedly low adhesive strengths at 40 minutes. We discuss some possible explanations for this behavior in the following chapter.

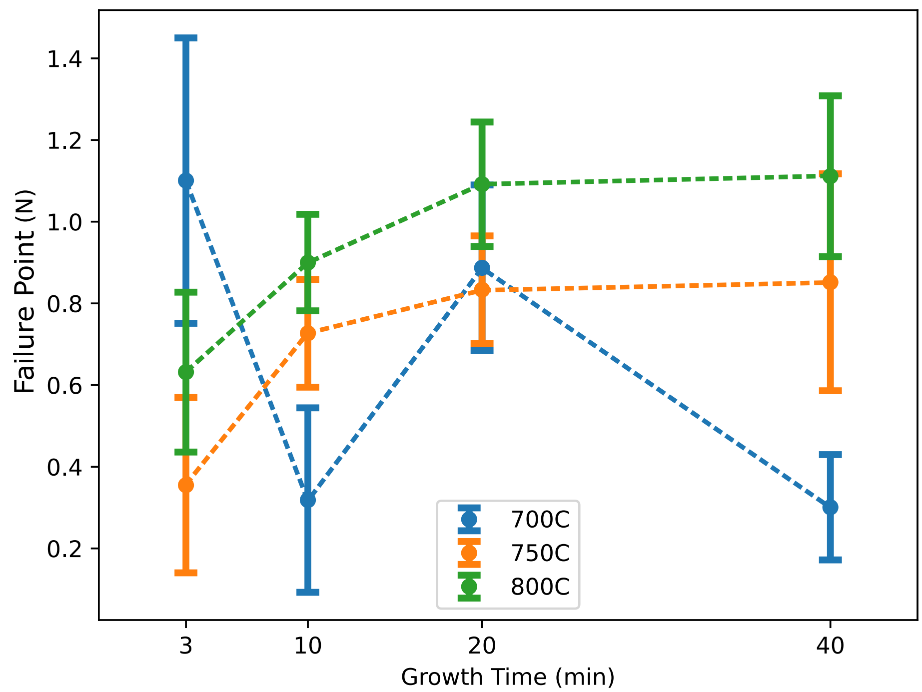

Figure 3.4 Mechanical failure data gathered plotted with CNT growth time. Points are the average of all adhesive strengths measured for samples with matching growth environments, and error bars represent one standard deviation of those data subsets. An upward trend that levels off is clear for the 750°C and 800°C samples, but the 700°C samples behave somewhat differently.

Figure 3.5 shows a similar plot of adhesive strength in terms of force, instead plotted with growth temperature. For improved legibility, the data has been split into two plots. We find that, for a given growth time, adhesive strength tends to increase as growth temperature increases. We once again see that the 700°C samples do not follow this trend, but in this case the 3 and 20 minute growth samples are the anomalies.

As we can see in Table 1, most of our data was gathered using samples that underwent a 2 minute anneal; thus, we cannot make as robust a comparison between the adhesive strength of CNTs grown on 2 minute annealed steel and 4 minute annealed steel. We do, however, have sufficient data to at least compare the shortest and longest growth times for each kind of anneal. This data does

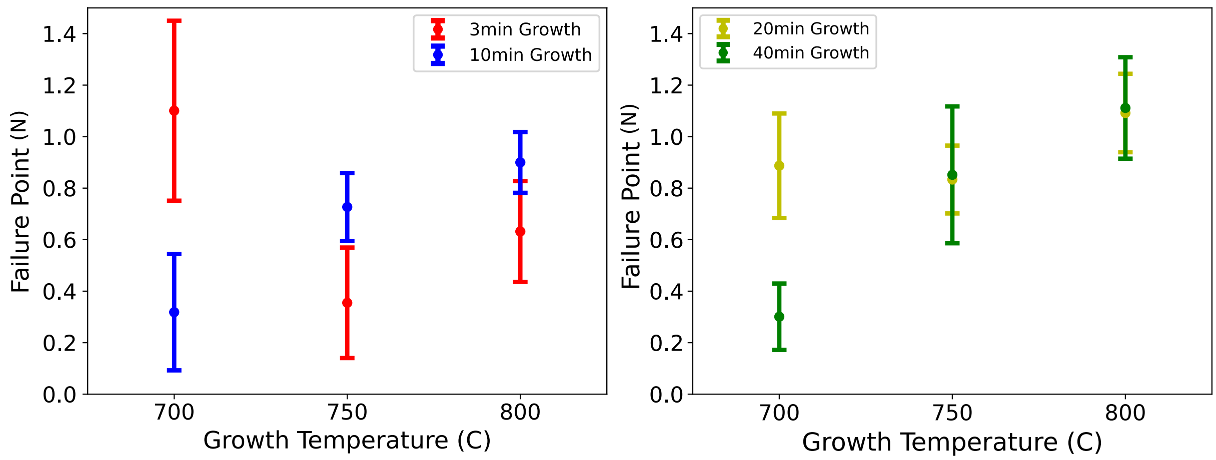

Figure 3.5 Adhesive strength data gathered plotted with CNT growth temperature. Points are the average of all adhesive strengths measured for samples with matching growth environments, and error bars represent one standard deviation of those data subsets. We see that adhesive strength tends to increase with increasing growth temperature, except for samples grown at 700°C for 3 and 20 minutes.

not reveal any consistent trends. As an example, Figure 3.6 shows two plots that compare adhesive strength of 2 and 4 minute anneal samples for two different growth temperatures. Samples grown at 750°C show a decrease in adhesive strength with increasing anneal time for both 3 and 40 minute growths, but the 800°C samples show both an increase and a decrease.

Figure 3.7 shows a plot similar to Figure 3.4, but this figure adds the results for the silicon, titanium, transferred titanium, and bare stainless steel tests. We see that the shortest silicon and titanium growths had maximum forces on par with the stainless steel samples, but were otherwise much smaller. We also see that the adhesion tests on bare stainless steel and transferred titanium had maximum force values with similar magnitudes to the highest forces reported for CNTs grown on stainless steel.

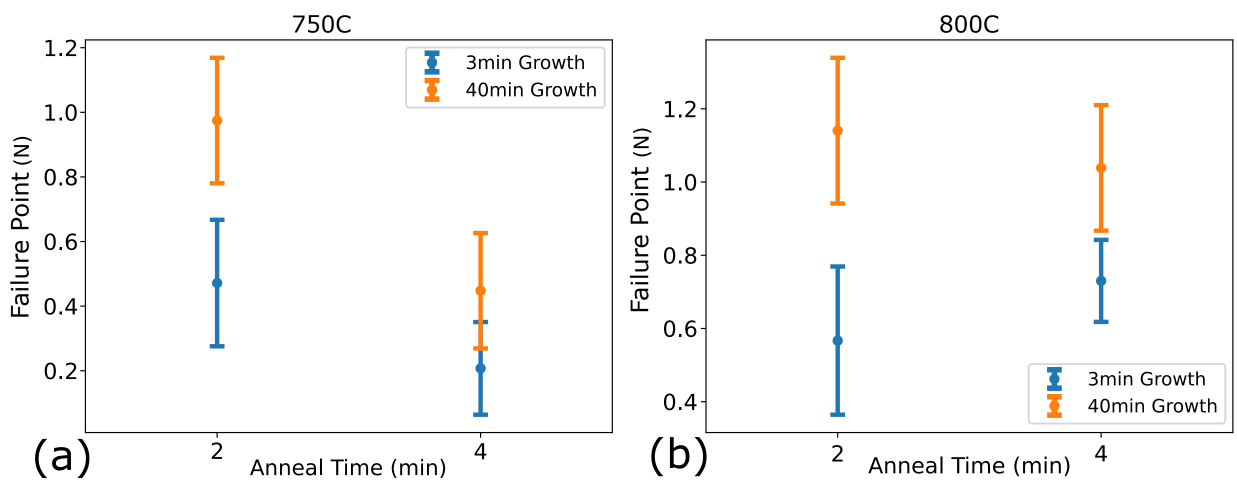

Figure 3.6 Adhesive strength data gathered plotted with anneal time. Points are the average of all adhesive strengths measured for samples with matching growth environments, and error bars represent one standard deviation of those data subsets. Trends for this data are inconsistent. The 750°C samples in (a), for example, show significant decreases in adhesive strength, while the 800°C samples in (b) show both an increase and a decrease.

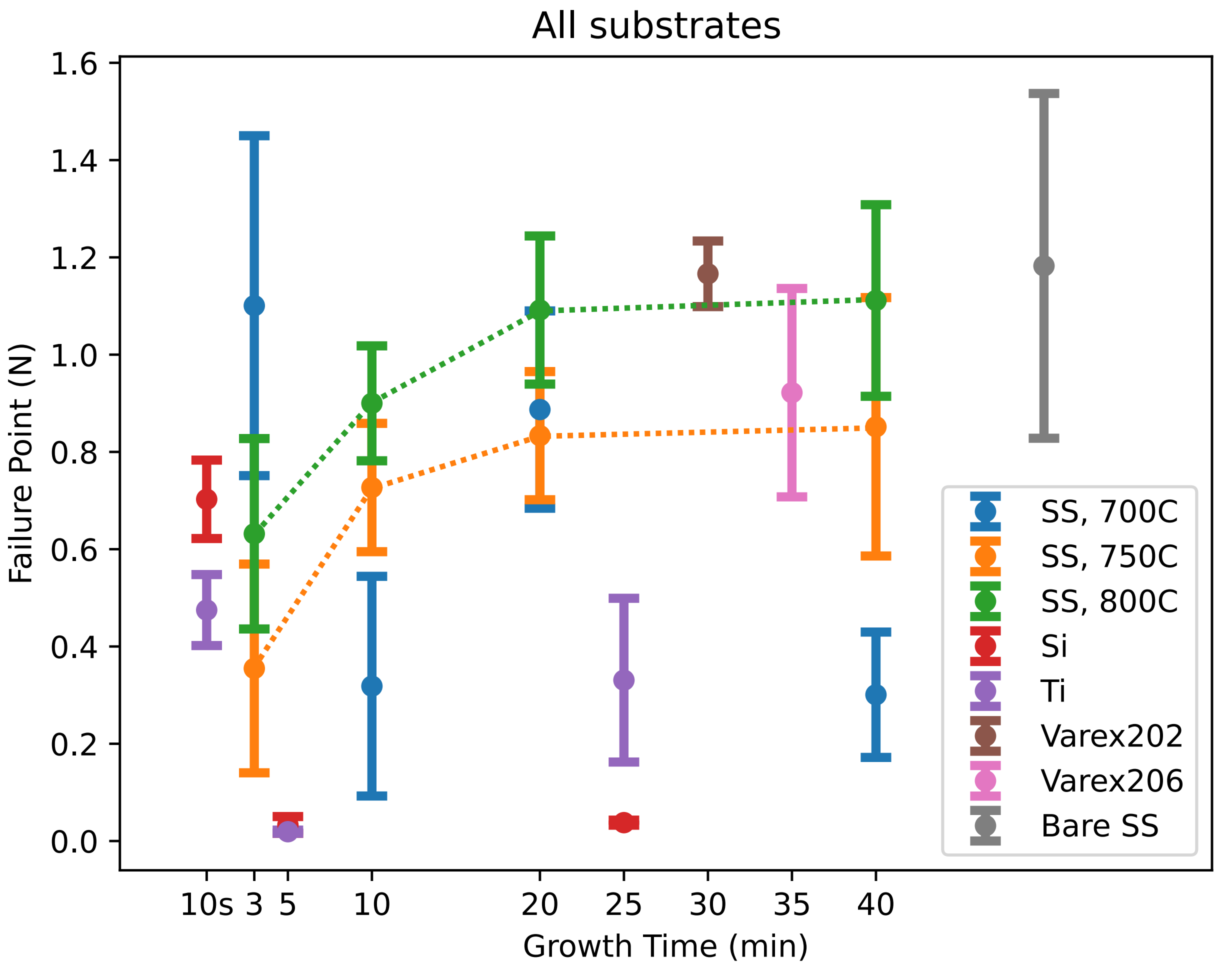

Figure 3.7 Adhesive strength data gathered plotted with growth time, including Si and bare stainless steel substrates. Points are the average of all adhesive strengths measured for samples with matching growth environments, and error bars represent one standard deviation of those data subsets. We see that adhesive strength for most Si and Ti samples in much lower than for stainless steel, and bare stainless steel and transferred Ti report values of similar magnitude or higher than the highest stainless steel values. Growth times for the transferred Ti and bare stainless steel are placeholders and do not reflect actual information about the preparation of these samples.

Chapter 4

Discussion

To this point, we have described our quantitative method for measuring the adhesive strength of carbon nanotubes to the substrate on which they are grown, and we have presented the results of using this procedure for CNTs grown on stainless steel, silicon, and titanium, as well as CNTs transferred to titanium by heat treatment. We clearly measured the adhesive strength with the substrate of the 700°C stainless steel samples, as well as all the silicon samples and conventional titanium samples. We measured only a lower bound on the adhesive strength to the substrate for the 750°C and 800°C stainless steel samples and for the transferred titanium samples. Our results indicated that increasing the growth time for CNTs grown on stainless steel has a commensurate effect on their adhesive strength up to about 20 minutes, after which the strength plateaus with increasing time. We also showed a possible correlation between increased growth temperature and increased adhesive strength.

4.1 700°C Samples

The samples we tested that grew at 700°C challenge both of these trends. The samples grown for 3 minutes and 20 minutes both show a higher average adhesive strength than expected, and the

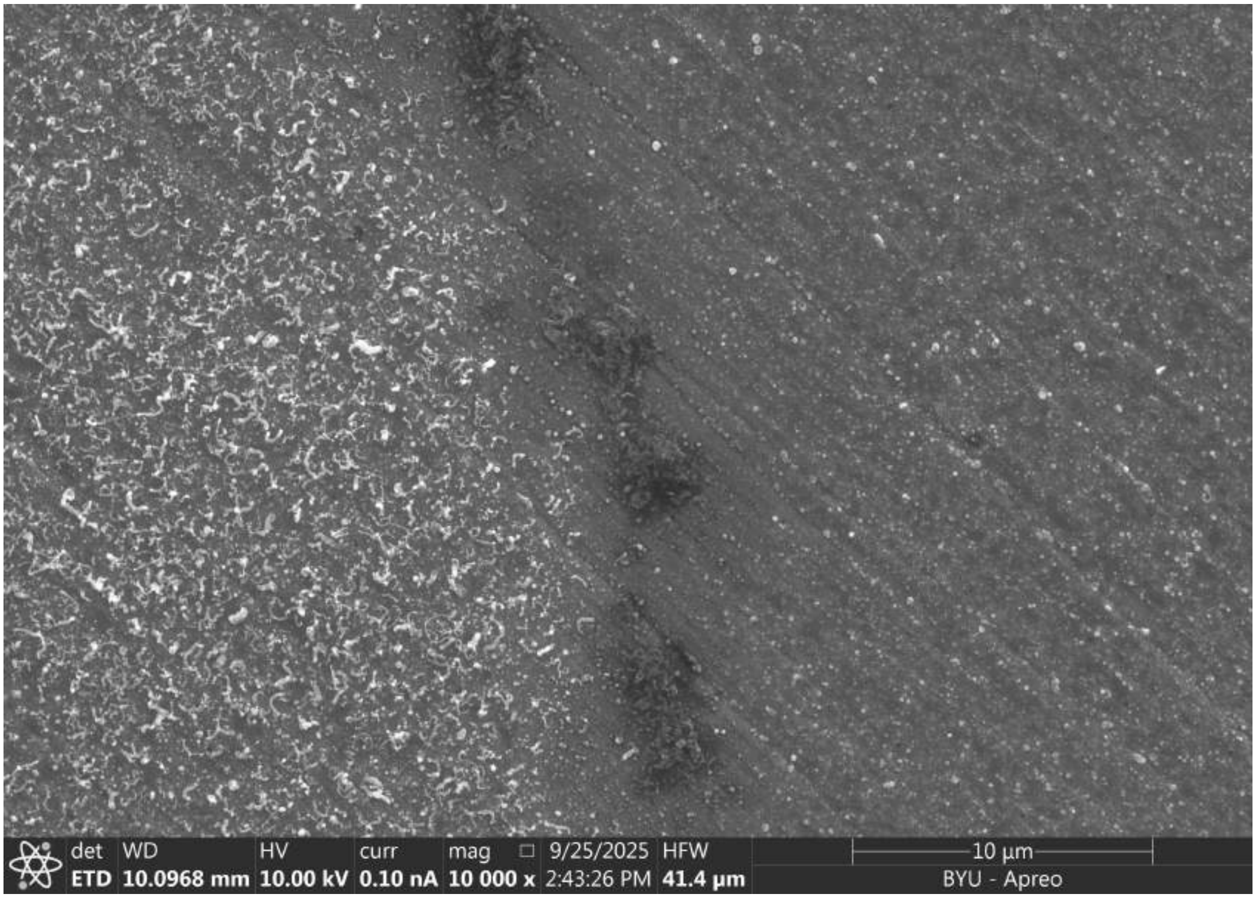

Figure 4.1 SEM image of CNTs grown on stainless steel at 700°C for 3 minutes, showing a typical surface morphology for both the 3 minute and 20 minute samples. The left region shows an area of CNTs untouched by an adhesion test, while the right shows a region where an adhesion test was performed. The left shows much sparser CNT growth than was anticipated for these samples, meaning the tape is likely coming into contact with the substrate itself during tests on these samples. The dark regions in the center of the image are likely adhesive left behind during the test, further supporting this idea.

samples grown for 40 minutes have a much lower adhesive strength than expected. For the 3 and 20 minute samples, the most likely explanation is revealed by the SEM image in Figure 4.1. This image shows that even regions which were unaffected by an adhesion test on this sample (such as the left of the figure) have much sparser CNT growth than would typically be expected. Thus it is likely that, in addition to pulling CNTs from the substrate, the tape is coming into contact with the substrate itself. This is further supported by the dark material in the center of Figure 4.1, which is likely adhesive from the tape left on the substrate, and by the bare stainless steel data in Figure 3.6, which shows that tape adhered to bare stainless steel comes unstuck at forces of a similar magnitude to those measured for 700°C, 3 minute growth samples. If this is true, the forces reported by our adhesion test for these samples are in fact a measure of the adhesive strength of the tape to the substrate rather than that of the CNTs to the substrate.

We also have a possible, though admittedly weaker, explanation for the low adhesive strengths recorded for the 700°C samples grown for 40 minutes. A side effect of growing samples for longer times is that, occasionally, a carbon ash is deposited on the back side of the substrate. In order for the adhesion procedure to work as intended, the backs of the samples must have this ash removed so they can be well-adhered to the SEM stub. If this ash is present on the front side as well as the back, it is possible that the tape is sticking primarily to it rather than the CNTs, which would substantially decrease the recorded adhesive strength. If this were the case, however, we would expect fewer CNTs to be pulled from the substrates of these samples, which is not supported by Figure 3.1.

4.2 750°C and 800°C Samples

The 750°C and 800°C stainless steel samples held on to most of their CNTs, so for these samples we can only say that the recorded force is a lower bound on the adhesive strength. In Figure 3.3, we see that there are CNTs on the surface of the tape used in these tests, which suggests the CNTs themselves are failing on these samples. Our test would in this case be measuring the tensile strength of the CNTs rather than the CNT adhesion to the substrate.

For CNTs grown for the longest times and at the highest temperatures, we also sometimes saw that the tape would come unstuck from the post, meaning both the adhesive strength and the tensile strength of the CNTs were greater than the adhesive strength of the tape to the post. This outcome was uncommon, but could explain why the forces we measured plateau for the 750°C and 800°C samples. At the extreme growth times and temperatures, we may be transitioning into a measurement of the tape strength, which would be a single flat value. This would not, however, explain why this plateau occurs at a lower force for the 750°C samples than for the 800°C samples.

4.3 Adhesive Strength Values

The maximum force recorded during our test is the most direct measurement of the adhesive strength of CNTs to their substrate, either the true strength or a lower bound, to come from our test, and those values are given in Table 4.1.

We also derived a stress measurement (force per unit area), and those values are given in Table 4.2. This measurement of adhesive strength is more broadly useful, but the derivation of it from our test has some issues. The hand-tracing method described in Section 2.4 is somewhat subjective, and when we completed this process for all the samples we found that the error bars on our measurements did not get any narrower than for our force measurements. Also, for most of the silicon samples, patches much larger than the area of the post would be removed by the test, which made determining any area much more difficult. The CNTs on the transferred titanium were mostly flattened when we received the samples, which also made determining the true area affected by the test difficult. For these reasons, these data were not included in our results section, but we include them here for those interested.

We also include one more set of values, Table 4.3, which gives an approximate per-nanotube adhesive strength. From the SEM images we took of the unaffected substrate, we adopt an approximate area density of 10^9 CNTs per square centimeter on stainless steel substrate for all our stainless steel samples. Given that the CNTs on our stainless steel samples tangled considerably as they grew, this is a rough approximation, but it is similar in magnitude to low area densities on silicon growth [19]. We were able to find area densities for our silicon and titanium samples

Stainless Steel, Force (N)			
	700°C	750°C	800°C
3min Growth	1.07 ± 0.36	0.35 ± 0.21	0.64 ± 0.19
10min Growth	0.32 ± 0.23	0.73 ± 0.13	0.89 ± 0.12
20min Growth	0.89 ± 0.20	0.82 ± 0.14	1.07 ± 0.16
40min Growth	0.29 ± 0.14	0.86 ± 0.26	1.11 ± 0.19
Silicon, Force (N)			
10s Growth	0.70 ± 0.08		
5min Growth	0.03 ± 0.02		
25min Growth	0.04 ± 0.01		
Titanium, Force (N)			
10s Growth	0.48 ± 0.07		
5min Growth	0.020 ± 0.003		
25min Growth	0.33 ± 0.17		
Transferred Titanium, Force (N)			
Varex 202	1.17 ± 0.07		
Varex 206	0.92 ± 0.21		

Table 4.1 Table showing the average adhesive strength in terms of force (N) obtained for each type of sample tested, with errors. Values highlighted in blue are true adhesive strength measurements, gray values are likely measurements of the adhesion between the tape and substrate, and yellow values are lower bounds on adhesive strength which are likely measurements of the CNT tensile strength.

individually, and while they varied somewhat between samples they were all of magnitude 10^{10} CNTs per square centimeter. Using these values and the hand-drawn areas for the test sites, we divided the maximum force by the approximate number of CNTs per test site to obtain these values.

Stainless Steel, Stress (MPa)			
	700°C	750°C	800°C
3min Growth	0.61 ± 0.28	0.20 ± 0.11	0.30 ± 0.09
10min Growth	0.18 ± 0.12	0.44 ± 0.07	0.47 ± 0.17
20min Growth	0.52 ± 0.11	0.60 ± 0.12	0.67 ± 0.18
40min Growth	0.16 ± 0.11	0.69 ± 0.31	0.63 ± 0.25
Silicon, Stress (MPa)			
10s Growth	0.33 ± 0.23		
5min Growth	0.008 ± 0.005		
Titanium, Stress (MPa)			
10s Growth	0.190 ± 0.016		
5min Growth	0.0050 ± 0.0008		
25min Growth	0.086 ± 0.058		

Table 4.2 Table showing the approximate average adhesive strength in terms of pressure (MPa) obtained for the various samples types. Values highlighted in blue are true adhesive strength measurements, gray values are likely measurements of the adhesion between the tape and substrate, and yellow values are lower bounds on adhesive strength which are likely measurements of the CNT tensile strength.

Because of the wide variety of ways CNT adhesion to the substrate has been measured in the literature, there are relatively few works we can directly compare our results with. The most similar methods are those used by Brown et al. [14] and Kaiser et al. [13], which both trapped the tops of CNTs in epoxy resin and pulled them from the substrate with a tensile tester. Both of these works used silicon substrate with similar preparation and growth methods to our own. Brown et al. measured an average adhesion force per nanotube of about 12.2 nN, significantly higher than our own silicon measurements, while the measurement from Kaiser et. al. of about 0.43nN for as-grown CNTs is in closer agreement with our results. Ageev et. al. [11] also measured CNT

Stainless Steel, Force per CNT (nN)			
	700°C	750°C	800°C
3min Growth	68.6 ± 21.8	24.7 ± 18.1	36.4 ± 13.1
10min Growth	44.3 ± 27.0	33.0 ± 22.2	68.5 ± 25.6
20min Growth	63.5 ± 37.1	70.3 ± 21.8	68.8 ± 22.4
40min Growth	38.7 ± 26.5	66.5 ± 31.5	61.1 ± 23.4
Silicon, Force per CNT (nN)			
10s Growth	1.84 ± 0.13		
5min Growth	0.012 ± 0.007		
Titanium, Force per CNT (nN)			
10s Growth	1.71 ± 0.14		
5min Growth	0.014 ± 0.002		
25min Growth	0.23 ± 0.16		

Table 4.3 Table showing rough estimates for the force experienced by individual CNTs during adhesion tests for the various sample types. Values highlighted in blue are true adhesive strength measurements, gray values are likely measurements of the adhesion between the tape and substrate, and yellow values are lower bounds on adhesive strength which are likely measurements of the CNT tensile strength.

adhesion with tension force on silicon, instead by using an electric field induced by an atomic force microscope. Their measurements ranged from 92.5-226nN, significantly higher even than the values we measured on stainless steel, though in this case their substrate also included a titanium layer designed to increase adhesion.

4.4 Role of Growth Mechanism in Adhesion

The scope of this thesis is primarily to exhibit the results of the adhesion procedure and to demonstrate connections between the adhesion data and the growth variables we tested; it is not to provide models for the mechanisms behind these trends. We note, however, work done in our research team alongside this work that does investigate the mechanisms of CNT growth on stainless steel, and compares them with growth on silicon [20]. That work finds higher adhesive strength in stainless steel relative to silicon, and, on the basis of various microscopy techniques, proposes that this higher strength is due to the CNTs being anchored into the oxide layer with iron nanoparticles. It is possible that this mechanism is strengthened further by increased growth time, but further work is needed to confirm or refute this.

4.5 Conclusion

A solid understanding of the adhesive strength of carbon nanotubes to the substrate on which they are grown and a reliable method for measuring that strength are crucial for the eventual use of CNT films on medical implants as an antimicrobial agent. This work presented a method for quantitatively measuring this adhesive strength, and we have used this method to test the adhesive strength of CNTs grown on stainless steel in various conditions. Our method shows that the adhesive strengths of CNTs on stainless steel and CNTs transferred to titanium are significantly higher than on silicon and titanium. Our method also shows that, up to approximately 20 minutes, increased growth time leads to greater adhesive strength for stainless steel substrate, and also suggests increased adhesive strength with increased growth temperature, though these trends are for the lower bound on adhesive strength rather than the true adhesive strength.

Future work in the short term should be focused on improving and expanding this method. We are already working on ways to obtain more definitive stress and force per nanotube measurements, and ensuring a stronger bond between the tape and post piece so CNT samples with stronger adhesive strengths can be tested. Adhesive testing on more stainless steel samples should also be done to verify, refute, or adjust the trends we have observed.

According to our results, the most promising path towards applying CNT films to medical implants made of stainless steel is to grow them for long times and at high temperatures. However, a number of problems stand in the way of this goal. The most significant of these is that, in the process that we used to treat the stainless steel for CNT growth, the surface first has to be oxidized. Previous work has shown that this process severely reduces stainless steel's resistance to corrosion, which is problematic for its use inside the human body [16]. Future work should seek new or adjusted growth methods that resolve this issue while also retaining high CNT-substrate adhesion. For medical implants made of titanium, on the other hand, CNTs transferred from silicon to titanium show a great deal of promise, and future work should perform a larger volume of adhesion tests on this kind of sample than we were able to carry out.

Appendix A

Standard Operating Procedures for Adhesion Test

This appendix describes the adhesion procedure in detail. It is primarily intended for the use of future BYU students, and as such makes reference to specific machines and software available at BYU. The overall method, however, should be replicable in other facilities with slight modifications.

1. Prepare Sample

    - If the sample will ever be imaged in an electron microscope, be sure to handle it with powder-free nitrile gloves whenever possible.
    - Clean the back of the sample with a cotton swab and acetone. This will remove any amorphous carbon that may have been deposited, and will ensure the sample sticks well to the SEM stub.
    - Apply double-sided carbon tape to the surface of an SEM stub, then secure the sample onto the stub. When doing this, be careful to touch only the edges and corners of the sample as much as possible, such that the available area for adhesion testing will be maximized.

2. Configure Tensile Tester

   - The Instron mini tensile tester currently available for student use at BYU has several different parts and accessories. For this procedure, the parts in the figure below will be necessary.

Figure A.1 From left to right: 5.6lb load cell, two small bolts, spacer, threaded top/bottom clamp holders, threaded top/bottom clamps

   - Use one of the small bolts to secure the bottom clamp holder into the bottom of the tensile tester. You may also need to use a washer from the large bolt if the small bolt is too long.
   - Screw one of the threaded clamps into the clamp holder. For convenience, the Allen key screws on the clamp should face outward.

- After calibrating the load cell in the tensile tester interface, screw the load cell into the top of the tensile tester. Make sure the load cell is upright (ie, the labels on the side are right-side up).
- Place the bolt into the top clamp holder, put the spacer onto the end of the bolt, and screw the clamp holder and spacer into the bottom of the load cell.
- Screw the second clamp into the top clamp holder.
- Set the 3D printed compliant mechanism into the bottom clamp, and secure it with the clamp screws.
- Slide the SEM stub with the CNT sample into the top of the 3D printed mechanism.
- Cut a 2mm-wide strip of carbon tape, being careful not to remove the protective film on the other side of the strip.
- Stick the exposed side of the strip onto the end of the 3D printed post piece, wrapping the excess onto the sides of the post. Remove the protective film from the tape.
- Set the post into the top clamp and secure it with the clamp screws.

3. Test Sample

    - Use the jog button to lower the tensile tester until the post is close to the CNT sample, about 3-5mm away. Set this position as the zero displacement point in the tensile tester interface.
    - Begin video recording the CNT sample. This is for identifying the individual test site later; alternative methods of identification are also appropriate as long as they do not affect the CNT surface.
    - Run the method "CNT Adhesion Method," which is programmed as follows:

  - Advance downward up to 9mm, while checking if the compressive force has reached the "Target Force" established by the user. The Target Force is set to 1N by default.
  - Stop advancement once the compressive force is greater than or equal to the Target Force
  - Hold position for 10s
  - Retreat upward by 5mm
  - Move any remaining distance up to +7mm displacement from zero. The tensile tester moves more quickly in this phase than in the previous phases.
- Once the cycle is complete, stop video recording, raise the top of the tensile tester, and carefully remove the post.
- Remove the tape from the post. If desired, save the tape (which should have CNTs on its surface) for SEM imaging.
- Export the data taken by the tensile tester and begin a new test.
- Repeat the above steps, adjusting the position of the post piece as needed, until the available area of the CNT sample surface has been exhausted (typically 5-6 tests total). Pressing the "Return" button in the interface will move the tensile tester back to the zero displacement position

4. Image Sample

- Set the sample on a surface such that the top surface is level/
- Place a ruler or other object of known size next to the sample.
- Take a picture of the sample and the ruler using a smartphone camera.
  - Where possible, use the level feature found in the advanced settings of some smartphone cameras to ensure the surface of the sample and the image plane are

parallel. On an iPhone, this feature can be accessed in Settings -> Camera -> Composition.

  - Illumination from the side using a bright LED flashlight helps to clearly reveal areas affected by the testing.

5. Obtain Affected Area

   - Import the optical image into Inkscape.
   - Use the Pencil Tool to trace out the affected areas of each test.
     - It is important that each area be comprised of one shape, so first trace out the entire shape even if there are holes or disconnected areas. Once this is done, trace out any holes as separate shapes, arranged on the canvas such that they are above the overall outline. To use these shapes to cut holes in the outline, select both the outline and one of the hole shapes with Shift+click, then press Ctrl and the – key. Repeat this process until the outline shape correctly reflects the optical image.
   - Using the Pen Tool, draw a straight line along the ruler 3cm long, or any length longer than the sample in the image.
   - Select the affected area shapes and the ruler line, but not the image, and move them to the side.
   - Now select only the line and rotate it so that the line and its bounding box are parallel.
   - Select all your created objects again and change the width of the selection to 3cm (done using the Selector Tool in the field labelled W; make sure the lock icon next to this field is in the locked position)
   - To get the actual area:
     - Select one of the affected area shapes, and from the tool bar select Extensions -> Visualize Path -> Measure Path

- A pop-up window will appear. Set the Measurement Type to Area, Precision to 2, Scale Factor to 1, and Length Unit to mm.
- Press Apply, and a few moments later a text object should appear with the area of the shape. This will go much more quickly if photographs are removed from the canvas first.

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