



**MONOTONIC LOAD AND CREEP
PROPERTIES OF CARBON NANOTUBE
SHEETS**

THESIS

Matthew T. LeSaint, Captain, USAF
AFIT-ENY-MS-17-D-024

**DEPARTMENT OF THE AIR FORCE
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THESIS

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Degree of Master of Science in Materials Science

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Abstract

Carbon nanotube (CNT) sheets are a new and promising material with properties such as high tensile strength and low density that are ideal for future applications in the aerospace industry. Before those materials can be implemented in future air- and spacecraft, their mechanical properties must be fully understood. Tensile and creep tests are the first and necessary steps to being able to better understand the properties and failure mechanics of any new material. This research is to understand the long term effects and performance of CNT sheets under tensile load, specifically through tensile tests, creep, and tensile tests after exposure in a space like environment. The data was used to create stress vs strain plots in order to mathematically quantify the tensile and creep behavior of the CNT sheets. The sheets were also exposed to ultraviolet (UV) radiation in order to understand how the ultimate tensile strength (UTS) changes under relevant space like conditions.

Acknowledgments

This paper might have my name in the title but that does not fully represent all the people whose ideas, insights, and assistance have touched what is written inside. I would first like to thank my wife, Jane. Without her none of this would have happened. Her constant love, courage, and support were what gave me the determination to keep going and her own drive and perseverance set a benchmark from what I should expect out of myself. I would also like to thank my committee as well as the Material Science professors for their professional and personal mentorship that they all have given me through this process. Finally I would like to thank Dr. Mall as the creator of this line of research and for giving me the chance to study it.

Matthew T. LeSaint

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List of Acronyms

ATOX Atomic Oxygen

CNT carbon nanotube

CVD chemical vapor deposition

EDS Energy-dispersive X-ray spectroscopy

EM electromagnetic

EMI electromagnetic interference

LEO Low Earth Orbit

MWCNT multi-walled carbon nanotube

MWNT multi-walled carbon nanotube

NP nanoparticles

NTI Nanocomp Technologies, Inc

SEM Scanning Electron Microscope

SWNT single-walled carbon nanotube

UTS ultimate tensile strength

UV ultraviolet

List of Symbols

$\{C\}$	Chiral Vector	d	Tube Diameter
δ	Displacement	E	Modulus of Elasticity
ϵ	Strain	E	Young's Modulus
σ	Stress	GPa	gigapascal
σ	Stress	K	Strength Coefficient
ν	Poisson's Ratio	L	Length
A_0	Original Area	MPa	megapascal
a_{cc}	Bond Length	n	Integers
L_0	Original Length	n	Strain Hardening Exponent
a	Vector Components	P	Load
C	Chiral Vector	TPa	terapascal

MONOTONIC LOAD AND CREEP PROPERTIES OF CARBON NANOTUBE SHEETS

I. Introduction

1.1 Introduction

Carbon nanotubes (CNTs) have garnered a great deal of interest from scientists and researchers since their recent discovery in 1991 by S. Iijima of Japan.[13] From that time, people all over the world have been intrigued by CNT manufacturing and how to harness their properties to maximize their potential. Different forms of nanotubes have been identified and their uses have been incorporated into several types of disciplines from electrical engineering to medicine to spacecraft design [14] [15] [16]. While new uses for CNTs are being developed, scientists are continuing to study new methods to manufacture the nanotubes as well as finding new applications for them such as energy conversion devices, electric discharge protection, and its use in varying fields from material science to biology and medicine. [16] [17]. All of this potential comes from the CNT's graphite sheet structure and the sp^2 honeycomb hexagon shaped covalent triple carbon bond types [18]. The arrangement of the carbon atoms where each carbon is bonded to three others is directly related to the corresponding material properties. Diamond has the strongest lattice structure with its carbon atoms in four coordinated states [19], and as a result of this structure it is one of the hardest materials on earth. Graphite, on the other hand, has strong in plane sp^2 bonds but weak bonds between adjacent planes. The weak bonds make it ideal for lubricant and pencil lead but have little mechanical strength. The carbon

bonds that make up CNTs are different from any other type of carbon based material, which is what drew the attention of S. Iijima when he discovered CNTs looking at carbon soot through a microscope after it had been electrified [13]. What he noticed as he studied the soot were helical structures made purely of carbon. Carbon sp^2 bonds in the shape of a tube are not formed in nature, giving the CNTs a unique molecular shape and creating a whole new type of carbon solid. The nanoscale size of new individual tube structures and the forces that bond them together, enabled the CNTs to behave as both a single molecule and a solid. These characteristics, combined with the carbon matrix formed by the honeycomb hexagonal shape of the CNTs, allows CNTs to exhibit great strength potentials along with high electrical and thermal conductivities.

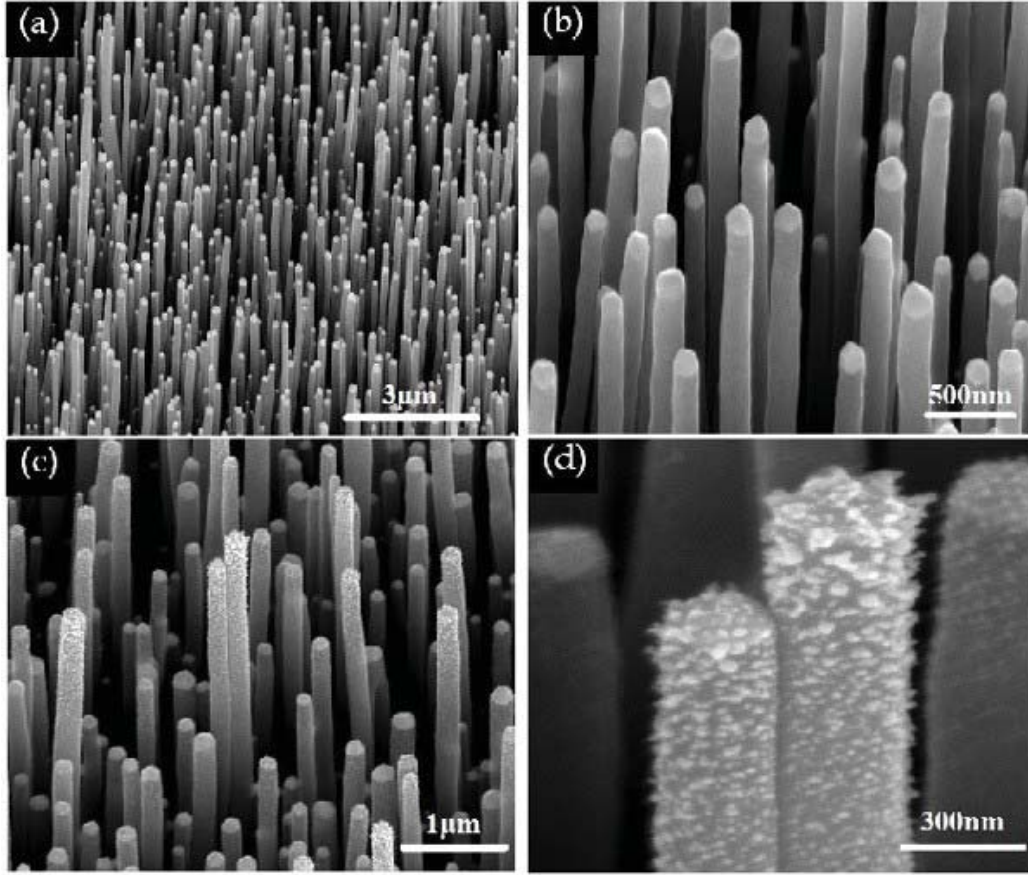


Figure 1.1. 1 SEM images of as-grown multi-walled carbon nanotube (MWCNT) arrays on a silicon substrate at (a) lower magnification and (b) higher magnification; (c) evidence of nanoparticles (NP) coating CNTs at a lower magnification and (d) a higher magnification image of a region in image (c), showing NP deposited on the external surfaces and tips of the MWCNT

The method of creating CNTs has been refined since the accidental discovery in the early 1990s. While arc discharge was proven to be effective, it was not efficient and scientists have looked for other options. Over the past few years, chemical vapor deposition (CVD) growth has become the standard for manufacturing CNTs[20]. This method involves using a carbon source to grow CNTs onto a substrate [21] and has proven itself to be a viable method of manufacturing for several companies. Through continuous research and improvement CNTs have been molded into many forms over the past few years. The first effort to create a more textile form was to extruded the CNTs into fibrous materials and woven together to form yarns. The

next step after yarn was to create large sheets that could have more practical uses and applications. Subsequently, there have also been numerous studies performed to analyze CNT properties of both sheets and yarns. These studies have explored how CNTs yarn and more importantly sheets could be used in different fields, such as in the development of lightweight tethers for space-based applications, shielding protection in space, as acoustic transducers, water purification, protective equipment, car bodies, and satellite structures[22] [23] [24]. CNTs have also been integrated into composites to create new materials with extra strength and durability. These composites incorporate CNTs into a composite matrix and the mechanical properties of the CNT materials are critical to these structures.

1.2 Justification

The research presented here focuses on the mechanical creep behavior of CNT sheets. Creep is the time dependent deformation of a material under mechanical stress. Most applications of CNT sheets involve stretching the sheets for extended periods of time or, in some cases, their entire design life. CNT sheets are a new material and the effects of long term mechanical stress have not yet been characterized. The ultimate tensile strength (UTS) of individual CNTs reported in literature has been difficult to replicate on a larger scale, and the CNTs' properties diminish as they are made into usable materials like yarns or sheets because of increases in defects and, in the case of yarns, strands slipping [25]. By studying the creep behavior of the CNT sheets, further information can be provided to help bridge the gap in understanding the discrepancies between the strength of individual CNT fibers versus bulk CNT materials.

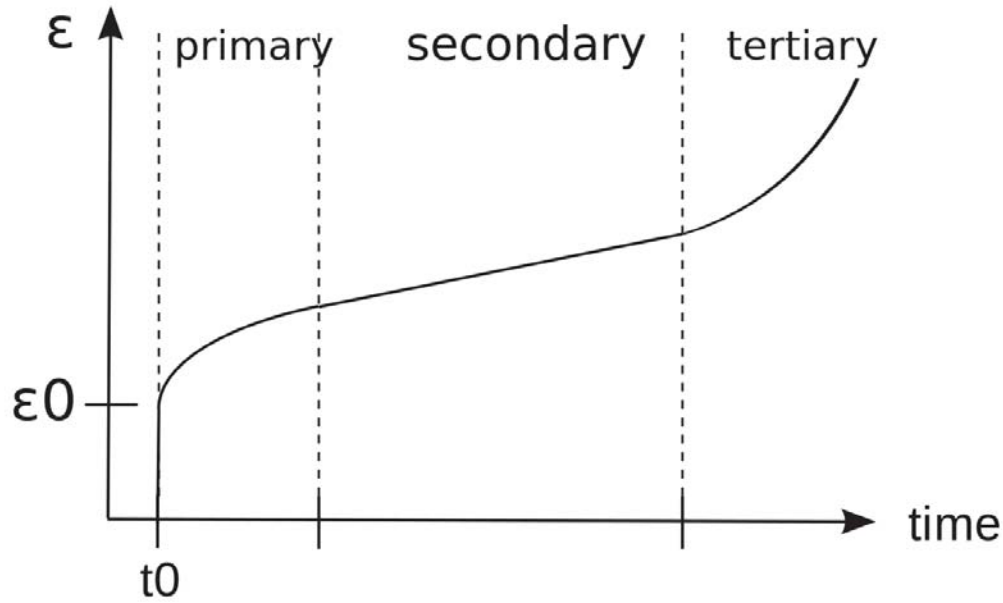


Figure 1.2. A graph showing the three regions of creep related to strain vs time.

Studying creep involves applying a tensile load on a test subject for an extended period of time in order to understand how the material changes under constant stress [26]. These changes can be external, which will effect the shape and size of the material and internal, which effects the structure of the fibers from tensile load and have an impact on its mechanical, thermal and electrical properties over time. Testing methods for creep and tensile tests and analysis of results were developed and refined during World War II to test aircraft materials that would have a high rate of use or be loaded for extended periods [27]. The collected data is used to create a strain vs time graph that can be divided into three sections or phases as shown in Figure 1.2. The first phase is where the initial force is applied and typically has a linear relationship with stress vs strain for an elastic material like CNTs and has a decreasing strain rate. The second phase is characteristically stable with a constant strain rate for an extended period of time. Depending on the load applied and the length of the test the material might never make it out of the second phase. If the stress is high enough and/or the test is allowed to go on long enough, the material will eventually go into

phase three where it will see an increase in strain rate and begin to stretch out and eventually rupture. Creep tests have been used for almost every material as a baseline for understanding basic material properties. The test can be set up to hold either displacement or load constant, where constant load is more commonly accepted and the method used in this research.

Before a creep test is done, tensile tests must be performed in order to find the yield strength, modulus of Elasticity, and ultimate tensile strength (UTS) of the material and establish a testing baseline. The UTS of the material can change depending on the material's working environment. Since CNTs are currently being looked at as possible replacement candidates for current materials used in extreme environments such as space, understanding the expected strength and life cycle of the CNT sheets can impact how they are used and the design and engineering behind them.

1.3 Problem Statement

CNT sheets are a new and promising material with properties, including high tensile strength and low density, that have potential for future applications in the aerospace industry. Before those materials can be implemented in future air and spacecraft, their material properties must be fully characterized. Mechanical tensile tests are the first test necessary to characterize the mechanical properties and failure mechanics of any new material. The goal of this research is to understand long term effects of creep on CNT sheets. These tests will serve to demonstrate real world applications and provide engineers and scientists crucial data to inform them of the potential of CNT sheets for scientific and commercial uses.

1.4 Summary

This thesis has been divided into five chapters. The first chapter includes an introduction that describes CNTs and the problems being addressed. The second chapter includes a literature review of previous work on CNT-based materials and a discussion about the potential uses of CNT sheets that will be improved by knowing the creep behavior. Chapter three will discuss testing methodology. Chapter four will review the results of the test and provide analysis. The final chapter will review the entire work and suggest further studies that could be done.

II. Background

2.1 Chapter Overview

This chapter will discuss the current state of research of CNT-based materials by looking at their physical properties and their current applications. An extensive literature search was performed to examine current trends and areas of examination of carbon nanotube (CNT) yarns and sheets. Relevant findings of this previous research are presented in this chapter.

2.2 Carbon Nanotube Structure

2.2.1 Background

CNTs have a complex structure that does not occur through natural processes. By understanding how CNTs are formed and their growth patterns, there have been major advances in how engineers can manufacture CNT in various shapes and sizes. With a better understanding of CNT's structure, they can be more easily integrated more effectively into other technology. Through studying CNTs, scientists have been able to identify key factors that provide their special properties.

Carbon structures can take many unique and distinctive shapes. As seen in Figure 2.1, diamond is formed when each carbon atom is covalently bonded to four other carbon atoms in a tetrahedron [28]. These bonds give diamond strength and rigidity greater than any material found on earth. When each carbon atom is covalently bonded to just three other carbon atoms, graphene is formed, which is a 2D-planar crystalline structure [14]. This configuration resembles a chicken wire mesh that contains strong in-plane sigma-bonds formed in sp^2 orbitals. When multiple layers of graphene "stack" on top of each other, the pi-bonds are formed through $2pz$ orbitals and graphite is formed. Because the plane to plane $2pz$ orbital bond is much

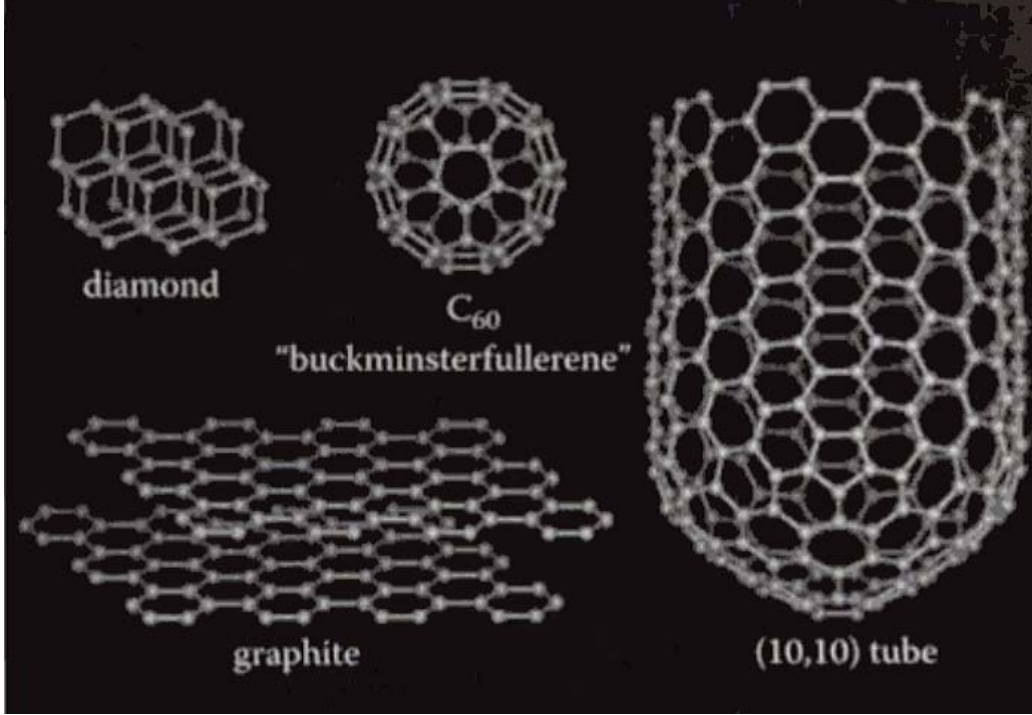


Figure 2.1. Comparisons of different bond structures of carbon. [?]

weaker than the stronger in-plane sp^2 bonds, the out-of-plane bonds that connect each graphene layer can easily be separated from each other causing fractures with minimal load.

CNTs differ in that they are made of one continuous graphene structure but, instead of being flat, they wrap around to create an individual cylinder. The sp^2 carbon bonds keep the same atomic hexagon configuration as graphene but now form a seamless tube [16]. While CNTs are not actually formed this way, this description helps contextualize the CNT structure and describe the different arrangements the CNT can have [29]. Based on where these rolled up sheets overlap and the orientation of the bonds to the direction of the tube, a degree of twist can be identified, which will define the chirality of the CNT as one of three different unique arrangements that have been classified; zig-zag, armchair, and chiral seen in Figure 2.2. The wrapping degree is measured by the chiral vector, as it goes from one point to another following

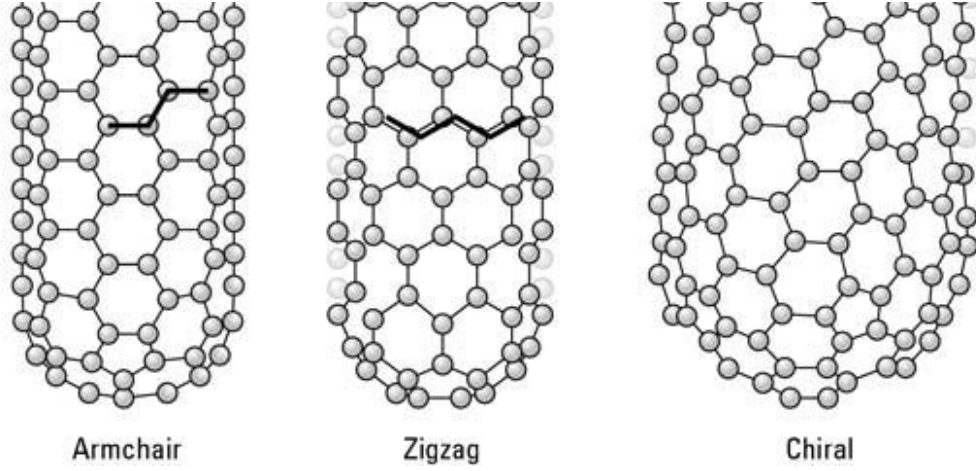


Figure 2.2. Comparison of the Armchair, Zigzag and Chiral forms of CNTs. [1]

the circumference of the hypothetical sheet, as if it were rolled up. This vector is classified by equation 2.1 [30]:

$$C = n * a_1 + m * a_2 \quad (2.1)$$

Where

C = Chiral Vector

a_1, a_2 = vector components

n, m = integers

CNTs have two different tubular forms that they can take, single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) [31]. The difference between these two is the amount of layers in each tube. As the name implies, SWNTs consist of a single layer of CNT. SWNTs have three distinct shapes depending on the chiral vector: zig-zag ($m = 0$), armchair ($n = m$), or chiral pattern (Figure 2.2) [32]. The patterns of the honeycomb structure most impact the electrical properties of the CNTs. An example of these differing properties is that armchair oriented CNTs have metallic like conductivity where zig-zag and chiral act more like semi conductors. There has not been any documentation of effects on strength properties

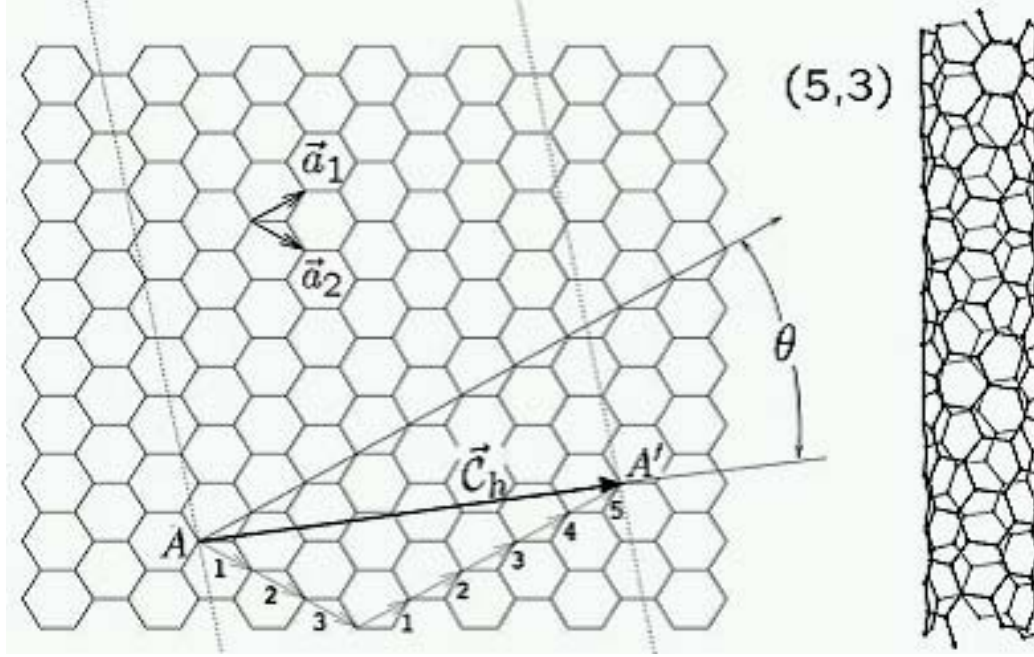


Figure 2.3. Comparisons of different bond orientation of carbon. [2]

based on the orientation of the carbon atom bonds. CNT yarns and sheets are made up of countless of CNTs and each individual tube can be classified as one of the three types of CNT, including the sheets that were tested in the research. MWNTs consist of multiple tube layers and come either as a Russian doll model or a scroll model (Figure 2.4). The Russian doll model involves a CNT core that is surrounded by multiple CNTs of increasing size. The Scroll model involves a single graphene sheet that is rolled into many layers, like a rolled up piece of paper [33]. MWNTs have been found to have less strength in tension from the slipping between layers, but the extra layers have been found to help protect the innermost layers from chemical reactions occurring at the surface [34]. Engineers are able to grow specific types of CNTs through highly-specialized growing processes giving them the flexibility to engineer materials with the properties they desire.

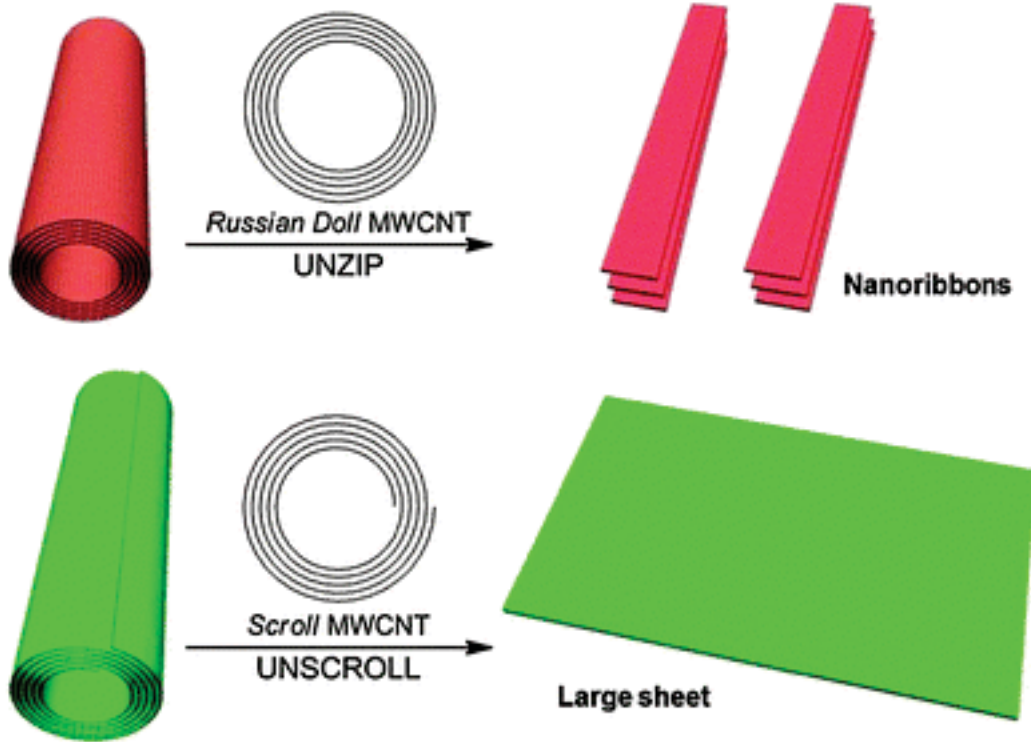


Figure 2.4. Russian Doll and Scroll MWNT [3]

2.2.2 Carbon Nanotube Synthesis

As noted earlier, these variations of CNT geometry come from the detailed manufacturing processes that have been refined in the making of CNTs. As advances and new applications are found for CNTs, manufacturers must keep on the forefront of creating new materials in more effective ways. Since the early 1990s, several techniques have been created and refined to manufacture CNTs: chemical vapor deposition (CVD), arc discharge and laser ablation. Of the three, the most common methods that are currently still used and improved upon are CVD and arc discharge [35] These are the most common because they have been found to be most consistent and economically viable by industry.

The CVD method uses a specially-chosen metal substrate as a catalyst to grow both SWNTs and MWNTs (Figure 2.5). The process begins by preparing a substrate through slow sputtering operations that lays down a metal, usually cobalt, nickel,

or iron, on a prep surface [36]. This substrate is then etched to create the base on which carbon nucleation can begin and CNTs will grow [37]. Using a gaseous carbon compound such as carbon monoxide, methane, or acetylene that is mixed with an inert gas. Then the gases and the etched metal are exposed to heat, which causes the alloy to melt and the carbon in the gas to decompose [38]. The carbon will then diffuse into the metal catalyst, until the concentration of carbon exceeds solubility. At that point, a carbon structure will be extruded out of the metal in the form of a CNT and, depending on the etching process, SWNTs or MWNTs will begin to grow [39]. The ability to control the type of CNT produced, as well as the scalability of this procedure, has made it common in industry.

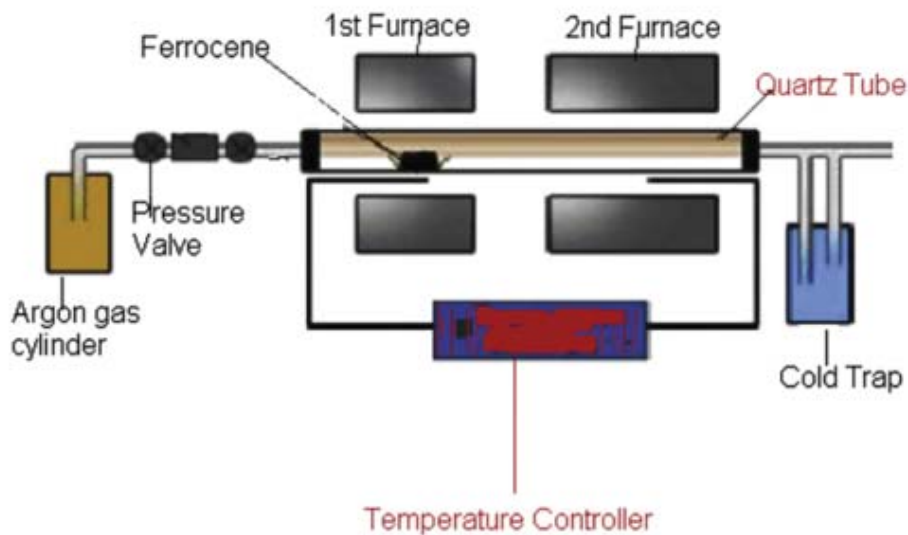


Figure 2.5. A diagram depicting the CVD process to grow CNTs. [4]

The arc discharge method is similar to CVD, because it relies on the diffusion of carbon into a heated alloy catalyst, typically nickel, copper, or iron, while in the presence of an inert gas [40]. The difference is that rather than the reaction happening in a heated environment, the energy comes from an electric arc. Inside an arc vacuum chamber, an anode and cathode create a plasma in the presence of the carbon gas

[4]. The catalyst is typically embedded into the anode and this is where the growth of the CNT begins [29]. This method is one of the original approaches for creating CNTs and, with it, scientists were able to manufacture both SWNTs and MWNTs. Arc discharge is starting to be phased out in favor of CVD, because the quality of CNTs produced from arc discharge is less than that of CVD, the time to make them is greater, and the energy it takes to make them is much higher. [38]

2.2.3 Carbon Nanotube Properties

The makeup of CNTs and their strong carbon-to-carbon sp^2 bonds gives the compound a unique set of properties [41]. These properties allow CNTs to be used in a variety of fields and have spurred innovative research of potential applications. The mechanical strength was the first indication that something about this material was unique and worth investigating. When testing individual strands of perfect SWNTs, Young's Modulus of 1 TPa is the current accepted value, while tests have shown it to go as high as 1.8 TPa [42]. This would classify the material as very stiff, compared to steel which has a Young's Modulus of 760 MPa or .00076 TPa. Individual strands also have a recorded max strength of 30 GPa [43]. MWNTs have a measured Young's Modulus of up to 950 TPa and max strength of 63 GPa. [44] This is compared to the modulus of elasticity of carbon fiber that is 220 GPa [45]. The differences between the mechanical properties of SWNTs and MWNTs come from their respective structures. Due to the orientation of the multiple layers of tubes that form the MWNT, MWNTs do not stretch easily. This comes from the increase in axial strain seen as the wall of the CNTs decrease in diameter causing the different layers to come into contact with one another. When the CNTs are formed into a bulk structure such as sheets and yarn, their performance dramatically decreases with recorded values only up to 2.5 GPa [46]. Discrepancies between the predicted and actual strengths of CNT yarns

have been attributed several factors such as defects in individual CNTs that make up the yarn, the compression pressure each tube puts on the tubes around it when the yarn is subjected to tension, and the slippage that occurs as the individual tubes are pulled tighter together. [47] [48]. As production quality has improved, there have been improvements in controlling changes in orientation and fiber connectivity which may allow CNT materials to reach their full potential.

The mechanical properties are not the only desirable aspect of CNTs. Their electrical conductivity has also been an attribute of high value, with studies showing CNTs may be able to reach and exceed the conduction abilities of copper [49]. Based on its chirality, a CNT can act as a metal or a semiconductor. A CNT acts as a metal if $(2n+m)$, as described in the chirality Equation 2.1, is a multiple of 3. If it is anything else, then it will act as a semiconductor [50]. Figure 2.6 shows the band gap structure and how it relates to the electrical properties of different CNT configurations based on chirality. In Figure 2.6 photos (a) and (d) are a graphical and pictorial representation respectively of an armchair SWNT and present its metallic nature. The zig-zag form of CNT is classified as a semiconductor, having both properties of a metal and non-metal. This semiconductor property is seen in Figure 2.6 photos (b) and (e) which depicts metallic zig zag SWNTs, while (c) and (f) which depicts non-metallic zig-zag SWNTs. The SWNT electronic structure is better characterized by the energy dispersion of the graphene. Due to the limited number of states near the atomic circumference and the small boundary, there is an overlap in the π orbitals with a band structure [5].

The information presented in the graphs found in Figure 2.6 determine if the CNTs have metallic or semi-conducting properties. Metallic features occur when the energy bands intersect the Fermi energy stem and the CNT will have two channels of conduction. The Fermi energy stem is depicted as the origin line (labeled as 0) in (a-c)

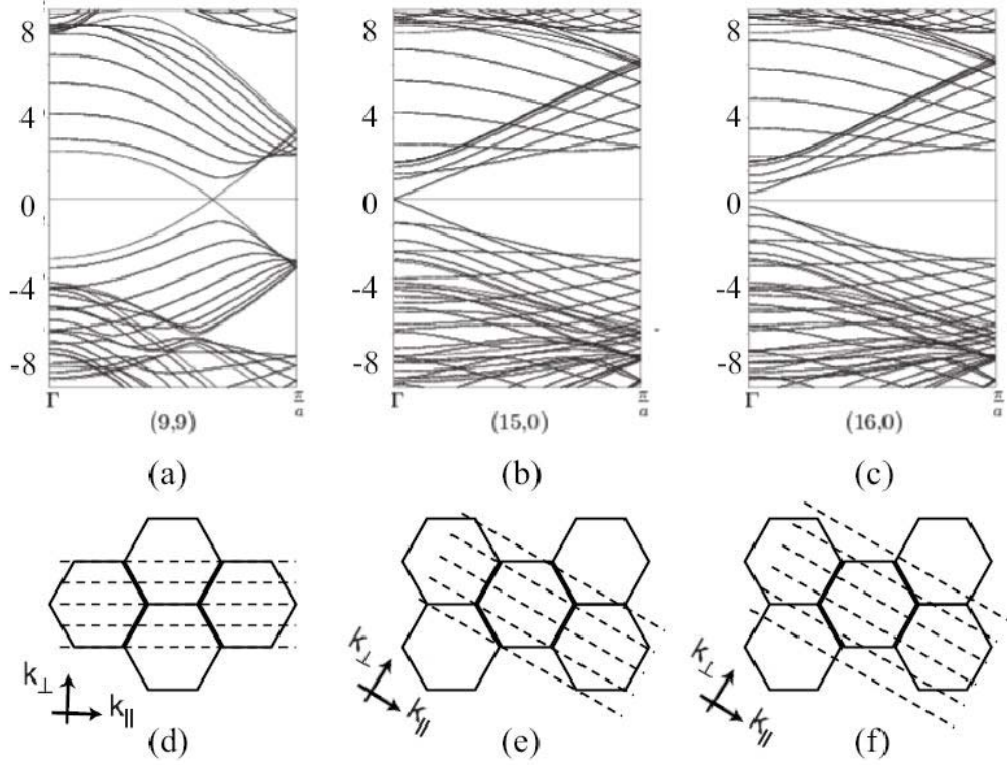


Figure 2.6. Band Gap energy and its relation to conduction properties in CNTs. For a, b and c, the y axis is the energy and the x axis is the band structure [5]

as well as the dotted lines in (d-f) that go through the corner of the hexagonal bonds (K points) representing the CNT carbon structure. Of the three samples shown, (a) the armchair and (b) the metallic zigzag cross the Fermi line, indicating that the corresponding CNT will behave as a metal. In the armchair configuration (a) it is clear where the lines cross the origin, just slightly right of center and the dotted lines in (d) go right through the corners and along the bond on the side of the hexagon. These factors signal a strong ability to act as a conductor. In the zig-zag configuration (b) the lines cross right at the beginning of the phase, and then will diverge to go back in opposite directions. The dotted lines in (e) are off axis and only go through the corners of the bonds and not the bond boundaries. Since the energy bands did not cross the origin line by only just coming into contact with it and only go through the corners, the zig-zag will have conduction properties but not as pronounced as seen in

the arm chair configuration. In the final picture, another zig-zag form (c) there is no contact with the origin line and in (f) no energy bands go through any corners, which means that the corresponding zig-zag CNT will not have any conduction properties. Just as in the mechanical properties, these values represent those for perfect single strands of SWNTs. In bulk or arrays forms, the values are lower since they are made up of all three variations of CNTs, armchair, zig-zag, and chiral. A single CNT strand has been found to carry up to 25 A [51]. When taking into account its size, CNT yarns doped with iodine have been found to have a maximum conductivity of approximately 10^7 S/M, compared to the current density of copper of 5.96×10^7 S/M, makes CNTs a close competitor as a conductor. [49]. The band gap energy of the CNT is closely related to the diameter of the tube. While band gap energy does not have an effect on the tensile properties of CNT, CNTs that are used to conduct electricity could see changes if tensile loads are applied. Understanding these principles would be crucial when calculating their conduction ability. The bandgap energy of a semiconductor CNT can be seen by Equation 2.2 [52]

$$Eg = (|t|a_{cc})/D = .84eV/D \quad (2.2)$$

Where

$|t|$ = overlap energy of carbon to carbon bond

a_{cc} = bond length (for carbon to carbon $a_{cc}=1.42$ Å)

D = diameter of the tube

The applications of space and aerospace for CNTs will expose them to varying thermal environments. As with the other properties previously mentioned, the chirality and size of the tubes have an effect on the thermal characteristics as well. Due to the strong sp^2 bond in the CNT, a large phonon, or lattice vibration, mean-free

path exists [53]. This, coupled with its low density, gives CNTs a high theoretical value of thermal conductivity with some predictions of values of 10,000 W/m-K [54]. Experimental data, however, illustrates that the thermal properties of an individual SWNT have found to be less than the predicted value, around 3,000 W/m-K. CNT strands are even lower at 1000 W/m-K. [55] This is compared to the thermal conductivities of copper at 400 W/m-K and diamond at 1,000 W/m-K [56]. The range of values for the CNT materials are accounted for by the defects introduced through the manufacturing process, gathering of the single tubes, and the winding of the tubes into strand form [57]. Even with these variances, the specific thermal conductivity of CNT fibers has been found to be $1931 \pm 488 \text{ mW}^2/\text{kgK}$, which is about 10 times the value for metals. [57] These properties make CNT fiber an attractive choice as a light weight metal wire replacement in planes and space systems.

2.3 Past Work and Relevant Research

2.3.1 CNT Textiles-Yarn

From the seemingly incredible properties and potential that CNTs possess, scientist and engineers have been trying to put CNTs in useful forms so that their potential could be maximized. The two main textile products made from CNTs are yarns and sheets. Early on, CNTs were used to enhance composites strength by being integrated into them; however, the CNTs were seen to be crushed while integrating them into the composite. The crushed CNTs resulted in a massive reduction of their strength and electrical conductivity. Through the process of discovering ways new approaches for using CNTs while minimize strand crushing, CNT yarn was created. Yarns can be formed in two ways. The first is by taking the CNT forest created through the CVD method and sending it through a specialized spinner [58]. The yarns created in this way have been found to have low packing densities and poor alignment, and has

been shown to affect the mechanical properties. Even so, CVD creates long strands of CNTs which enhance electrical properties through decreased junctions between tubes [59]. Advancements have been made to work toward the advantages of longer strands to help increase the overall strength of the CVD yarn. The second method is through a wet spinning process [60]. Here the CNTs are submerged in a liquid dispersant and then forced out through a spinneret creating long cylinders of CNT. The cylinders are then pressed into a solid fiber by getting rid of the liquid dispersant. This method has more potential to be scalable in the long term and is seen as a better alternative compared to the spinning process. The yarns' mechanical, thermal and electrical properties have been tested to determine how they compare to individual CNT tubes, as well as to understand how they could be integrated into other technology, without losing their properties. Tension tests on CNT yarn have shown that it does not behave in a similar fashion compared to the testing individual strands or based on how more common materials behave [6]. Tests were conducted on yarns made of 1, 30, 60, and 100 strands. The tension response of the 1-strand yarn resulted in a familiar stress vs strain curve. The curve was initially sharp and strain increased linearly with increased stress, changing to a non-linear stress/strain relationship as the fiber reached failure. The yarns made of 30, 60, and 100 strands had an abnormal curve shape and an unexpected response to the tensile load. The strands started to strain at a low stress until a certain point, where the strands would then regain strength to resist the strain as stress increased as seen in Figure 2.7. The application of these results is that the mechanical and physical characteristic of the yarn changes, when it is braided, as opposed to when it is a single strand. The response could be attributed to defects and kinks in the strands, which were created during manufacturing or the sliding and compression of the strands during tension, which would result in lower strength properties.

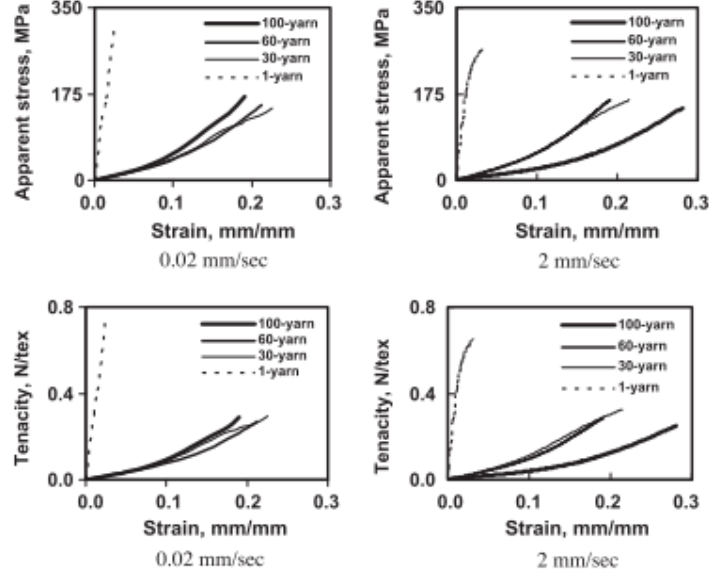


Figure 2.7. Tensions results of yarns with increasing strand amounts [6].

CNT yarn has also been tested in creep. Similar to the tension test, three different types of yarn, 1, 30, and 100 strand yarn, were put under various loads lasting from as long as 14 days [7]. These tests showed that the strain rate for the 200 hour test was smallest for 1-strand yarn and greatest for the 100 strand, but the strain rate profiles for both where the strain rate would increase as the stress increased is a typical response of a material in creep. They also showed the three distinct regions in the monotonic tensile load with strand slipping occurring in the second stage followed by stretching and tightening in the third stage. The slipping could lead to damaging of the tube and reduction of the helix angle. Based on these two tests, significant differences in response to tensile force were noticed when the CNT was put into a bulk item like yarn and sheets. The test demonstrates that the CNTs are highly susceptible to damage, as proven in failure analysis test [6]. Yarns with different strand counts were tested in tension and the failure mode changed based on the number of strands in each yarn and the load type that was applied as seen in Figure 2.7. For example, when the 30-strand yarn was tested for fatigue, the common failure mode was bending

and twisting, a mode seen in other materials tested this way. During tension testing however, multiple modes of failure were seen and no pattern could be found. The researchers believed these failures were the result of unaligned CNTs on part of the strands the experienced compressive forces. From the failures, cracks propagated and weaknesses. The 60 and 100 strand yarns had similar results, with the failure modes being different for both the tension and the fatigue testing [7].

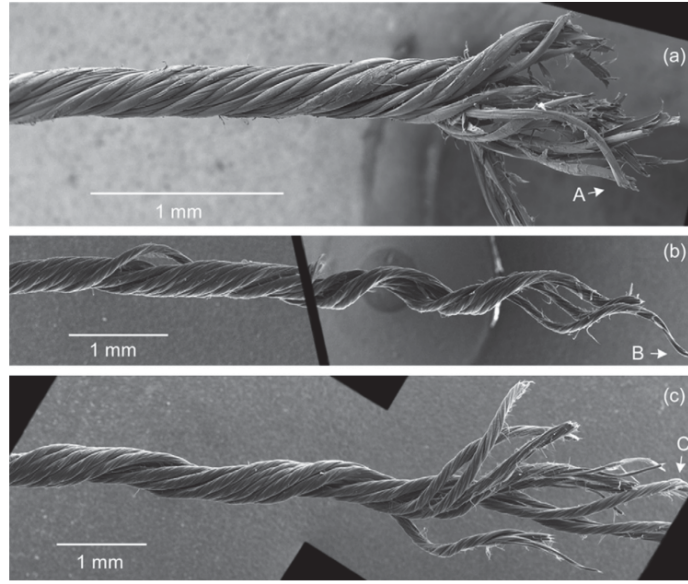


Figure 2.8. Yarns failures with decreasing number of strands from a to c [7].

2.3.2 CNT Textiles-Yarns in Creep

Creep can be conducted in constant force and constant strain mode to find creep and stress relaxation. CNT yarns have been tested at constant strain by Zhang et al. The test consisted of holding a CNT yarn at a constant strain of 6% increase from the yarns initial length for 20 hours. During this time the yarn saw some stress relaxation but it only occurred in the first 20 minutes of the test and was no more than 15%. [61]. CNT yarn's response to creep and recovery has been described as viscoelastic where it behaves similar to both in an elastic and viscoelastic form, similar to silicon

rubber [62]. Just as in the previous studies, the number of strand per yarn was key in the performance of the tensile test. It was shown that the larger and more dense the bundle is, the larger the creep rate would be [63].

2.3.3 CNT Sheets

Carbon nanotube sheets are another material that has been manufactured using CNTs. First created at Rice University in 1998, CNT sheets are still relatively new and are less understood. Studies discussing their mechanical properties or potential uses are scarce. Formed almost like paper, small bundles of interconnected tubes go through a purification process and were deposited on a film. Tensile tests of CNT sheets have shown strengths similar to those of CNT yarn, 6.29 MPa and Youngs modulus of 2.3 GPa. [64]. The thermal conductivity of CNT sheets has been found to be consistently lower than CNT strands and yarn. This comes from the lower density and the effects of phonon scattering from defects in the sheet itself [65]. CNT sheets do have semiconducting behaviors similar to CNT yarns and strand.

2.3.4 Applications and Potential Uses

Based on CNT sheet material properties, research into a number of different practical applications have been explored. A large area is using the natural electromagnetic (EM) properties of the CNT sheet as protection from electromagnetic interference (EMI). EMI can affect an electrical component by interfering and disrupting its flow of electrons and even changing bits of data in a computer which could cause faults or system failures for space vehicles. EMI protection is used on cables to protect the signal running through it from being distorted. It has already been proven that wires could be made from CNTs [57], but researchers are seeing that CNT wires are not only conductive, but they protect themselves from EMI [66]. The largest im-

pact of replacing copper wires, with CNT yarns would be in the space industry. The CNTs would have a better weight to conduction ratio and its dual purpose role that it could play in a space vehicle could have measurable benefits of saved weight to a development team.

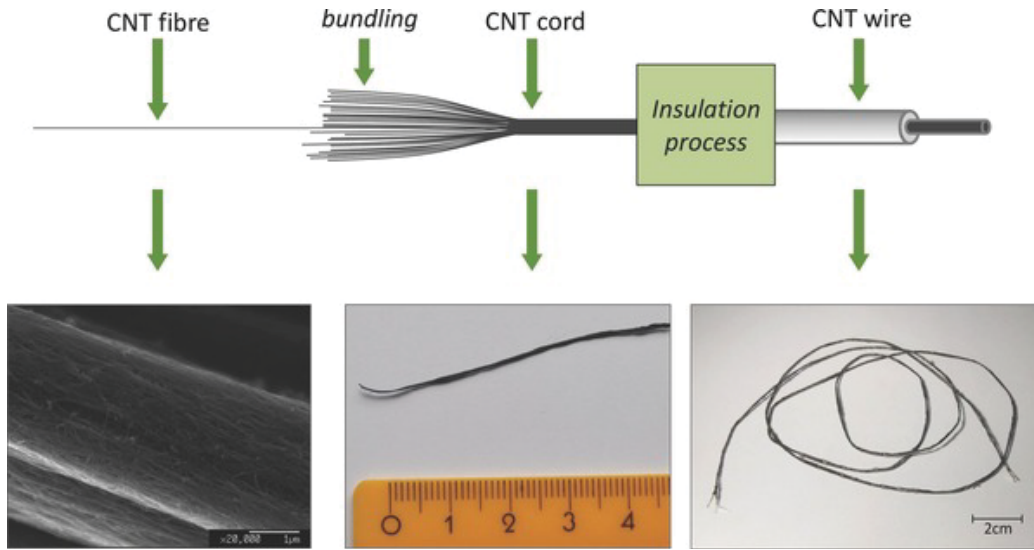


Figure 2.9. Macro- and microscale images of potential CNT wire[8].

If used as a wire material, having a clear understanding of the tensile strength and creep characteristics of the CNT would be vital. A long strand of CNT wires would still need to be capable of supporting any tensile load caused by its own weight and would need to withstand a situation where there is some constant mechanical load placed on it. Knowing the mechanical response of the material would allow engineers and scientist to properly design a wire tether system within the mechanical performance parameters of the CNTs.

The EM properties of CNTs can be applied to other areas as well, such as antennas. By harnessing the inherent electrical properties of CNTs, scientists are able to use the CNTs as conductors that will create an electromagnetic field which can be used to transmit and receive radio signals. Researchers have found that a bundle of CNT sheets perform much better than individual sheets and can match or exceed that of a

conventional antenna [67]. The performance enhancements added with the benefits of low mass and EMI protection make CNT antennas an item researchers find valuable and a property that is currently still being investigated.

With both wires and antennas, there have been tests studying using CNT as a component in composite material [68]. CNTs by themselves don't have much structural rigidity and are expensive to make in large quantities. They also will not, currently support any compressive loading. By combining CNTs with carbon fibers in a resin matrix are cheaper and easier to manufacture to create new composite materials that are able to take advantage of the best properties from the material components it is made from.

One potential composite form is CNT along with metals, specifically copper. Creating metal matrix composites involves mixing the metal with some sort of reinforcement. This addition to the metal matrix provides extra support, through increased strength and stiffness, and also can increase wear resistance [69]. All available research shows that using a powdered form of CNTs and mixing them with copper increases the coefficient of friction and decreases the wear rate proportional to the volume fraction of CNT powder is added. Research have seen not only the coefficient of friction grows based on the increase of percent volume of CNTs added but also improvements in the mechanical, electrical and thermal properties of Cu/CNT composites [70].

A highly researched area of composite is the combination of polymer/CNTs. Polymers are usually light and easy to manufacture, but do not have the mechanical properties to be direct replacements in areas where light weight metals are being used. By mixing CNTs with polymers, it has been shown that the CNTs keep many of their unique properties that can, in many ways, serve as a dual purpose. The CNTs are turned to powder and mixed in with polymers as seen in Figure 2.10. Tests have

studied the effect of creep on epoxies [9] and how the change in CNT mixture percent volume can have a positive affect on mechanical and time dependent properties and the coefficient of friction [71], and its piezoresistive properties under uniaxial cyclic tensile and compressive loading [72]. Engineers have not stopped at just polymers and metals. There have also been tests conducted to understand CNT effects when mixed with concrete [73] which show an increase in the flexural strength, fracture toughness, frost resistance, and overall strength of the concrete mix.

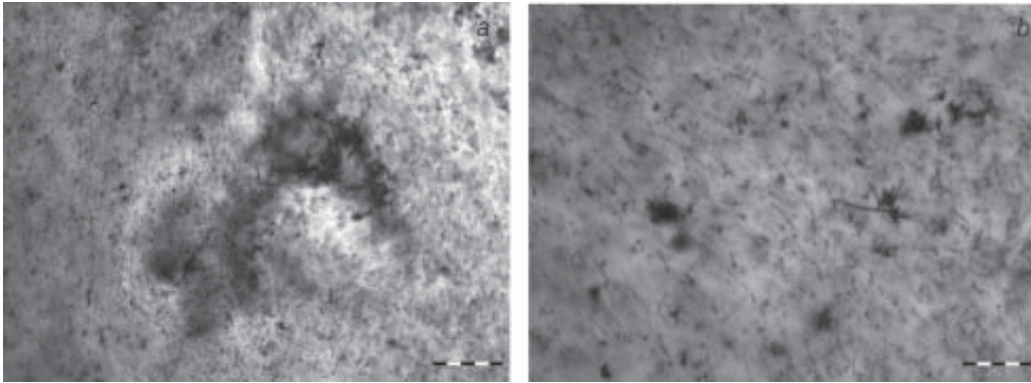


Figure 2.10. Optical micrographs of an epoxy sample with 1 wt.% of CNTs at different magnifications: 200 (a) and 500 (b). [9]

All these previously mentioned studies show that incorporating CNT into other materials increased their performance in strength and wear resistance while retaining some of the CNT's electrical and thermal properties. While there are still some key hurdles to overcome, the process of uniformly incorporating aligned CNTs into a composite material is better understood than integrating whole sheets into a composite as a layer or a key component of a layer. Work has been done with a CNT sheet that is reinforced with polyvinylidene fluoride [74]. This test was able to prove that this kind of composite could be built and using the natural properties of the CNT sheet, the composite material saw an increase in electrical and mechanical properties. Using the sheet as opposed to the powder, scientists did not have to worry about having the proper dispersion rate and a consistent composition in the mix, which is a

common concern with the manufacturing of other CNT composites. They also found it had high dielectric permittivity and low dielectric loss.

An application for CNT sheets that has been previously unexplored is the use of the sheets as a stressed skin structure that could be used to provide EM protection to aerospace vehicles' electrical components [75]. Instead of a heavier copper foil covering everything, a stressed sheet of CNT could be used as a replacement, saving weight and providing improved protection to the satellite potentially increasing its life or range. At this time there is no research looking into this, but after CNTs mechanical properties are better understood and with greater trust in manufacturing processing uses such as this will have less risk associated with them and will increase their chance of being studied.

2.3.5 CNT Textiles-Defects and Improvements

As with all other mechanical systems, finding a way to deal with the material's natural defects as well as the defects created during manufacturing has been an issue. As has been addressed in other papers, micro defects in the tubes decrease the electrical, thermal and mechanical properties from the theoretical potential. Studies have even shown that the space elevator, a favorite future dream amongst CNT researchers that already has several practical flaws that have yet to be overcome, would not be practical because 70% of its predicted strength could be lost to defects [76]. This is a trend that has been noticed when trying to scale up from individual strands of CNT, to a larger bulk item like yarns and sheets.

Scaling up the properties has shown to be a difficult task and it is rooted in the fact that the defects that are created during manufacturing based on the substrate surface or the environment, the physical and chemical modifications that are made to the CNTs after they are made to the CNTs pre- and post-processing, and the natural

disorder that CNTs have based on their compositions of an uncountable number of individual strands.

Research has been conducted to find ways to strengthen CNT yarn and to mitigate some of the failure modes. Studies have shown that how the individual tubes that make up the yarns and sheets are arranged affect the strength properties of those sheets. Inside CNT sheets that have just been created, the orientation nanotubes are random and without order. Through the use of tensile loads, the strands begin to align themselves in the direction of the load and increased effect on strength has been seen from the better alignment of the tubes [12]

The main effort has been finding more effective and non destructive methods to align the carbon nanotubes once they are in the yarn or sheet. One method has been through low-energy electron irradiation. Scientists noted that, after Raman Spectroscopic analysis, CNT samples exhibited greater tensile strength[77]. These irradiated samples showed an increase in D peak in Raman Spectroscopy. D peaks signify the presence of sp^2 bonds, which are the strong bonds that hold the carbon atoms in CNT tubes together. The higher the D peak, the more sp^2 bonds which suggests more CNTs in that specific area. The increase in D peak signifies that the CNT sheets were denser and better aligned, which might have lead to better strength properties. They also showed that low-level irradiation did not damage the samples themselves. The electrons do not have the energy to physically move the misaligned CNT strands so, the explanation of this effect is still unknown. Another way scientist are working to improve CNT sheets and yarn is using an electron beam to untangled and aligned by using electron beam irradiation [78].

Reports have also shown that acid treating the CNT sheets helps decrease impurities. The acid treatment process increases the stress strain properties and overall strength of the sheets[79]. The acid treatment also lowered the density of the sheet

while increasing the strength, showing that, as in yarn, impurities play a large role in the behavior of CNT materials.

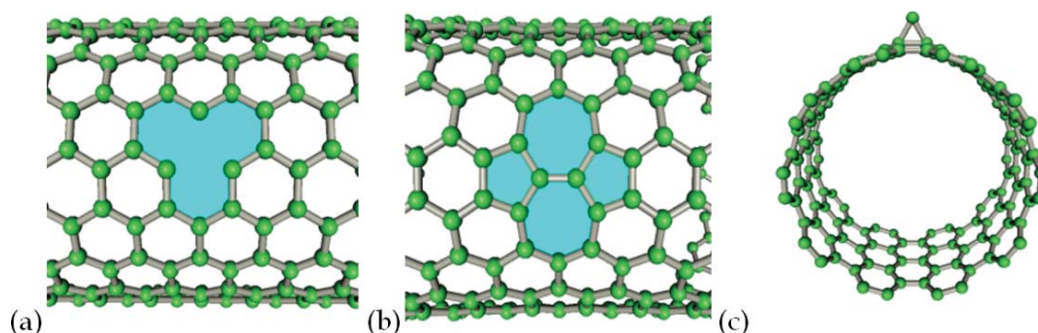


Figure 2.11. Defects found in CNTs: vacancies, stone-Wales defect, and adatom (raised area on crystal surfaces) in SWCNTs [10].

Although there has not been much research done on fixing these defects, some researchers have looked into taking advantage of them for other purposes. As seen in Figure 2.11 one of the common types of defects found in CNTs are Stone-wales defects. These defects are found in carbon nanotubes, graphene, and similar carbon frameworks, where the four adjacent six-membered rings of a pyrene-like region are changed into two five-membered rings and two seven-membered rings when the bond uniting two of the adjacent rings rotates. In these materials, the rearrangement is thought to have important implications for the chemical, electrical, and mechanical properties [80]. These defect areas, when doped with beryllium have been found to be excellent for storing hydrogen. Hydrogen storage at ambient temperature without the need of pressure and temperature control is a key factor to overcome for researchers who want to see hydrogen replace fossil fuels as the main source of energy. When doped with Be, the defect areas of the CNTs are able to exceed the Department of Energy's storage target at near ambient conditions [81]

2.3.6 Space Environment

CNTs have many proposed uses, but its use in aerospace and space applications have by far the greatest implications, especially for the Air Force. Given its mechanical properties space agencies have been studying CNTs in many forms to find ways to maximize efficiencies while also cutting weight. As discussed, using CNTs as electrical wiring or EMI protection has some potential, but all these tests were done on Earth, under ambient atmospheric conditions/in atmosphere. A space environment is going to have different effects on the material and could negatively change its properties as has been seen in space vehicles since the beginning of the space program. Testing in this kind of environment early on can lead to decreased failures for systems when they are eventually deployed. One of the harshest environmental factors of satellites that operate in Low Earth Orbit (LEO) is the amount of Atomic Oxygen (ATOX) and ultraviolet (UV) radiation. On Earth, the atmosphere protects us and all our materials from being hit by UV rays that originate mostly from the sun, but in space there is no natural protection for space craft. The effects have been well documented for polymers and metals but recently there have been studies that show UV rays even affect diamonds [82]. The exposure leads to pits and cracks at the surface and will eventually break down the materials if left untreated in a UV environment for too long. If carbon is susceptible, understanding the effects UV rays would have on CNTs would be important before implementing into space craft design. In the upper atmosphere UV radiation that comes into contact with oxygen creates ATOX. ATOX reacts strongly with many materials, including carbon and sometimes there seems to have an increased effect the longer the material is in a ATOX environment. Understanding how CNT responds to these phenomena early and designing realistic systems that can withstand these harsh environments will only save time and money during further material and system testing.

2.4 Summary

CNTs present engineers and scientist many opportunities for application in the everyday world. The Air Force has seen the potential for CNTs in airplanes, computers, and even in space vehicles. Its thermal, electrical and mechanical properties have been studied and are beginning to be understood. CNTs are making their way into composites and other materials, but their full potential is still unknown. There is still more to do. CNT yarn and sheets are at their infancy of being developed and understanding their basic material response are the building blocks future work can build upon.

III. Research Methodology

3.1 Introduction

This chapter deals with the preparation and the test procedure of the sample CNT sheets. All equipment was located at Wright Patterson Air Force base inside the AFIT Campus to test the tensile strength and creep response of the CNT sheets. The tensile test were performed using a tensile test machine with measurements taken during the tests. The samples were then analyzed using an Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS).

3.2 CNT Test Specimens and Sample Preparation

The CNT sheets used in this experiment were purchased from Nanocomp Technologies, Inc (NTI) Concord, New Hampshire, USA. The sheets were produced from synthetic nano- fibers that were made into a non-woven textile mat from a transitioning drum as shown in Figure 3.1 .

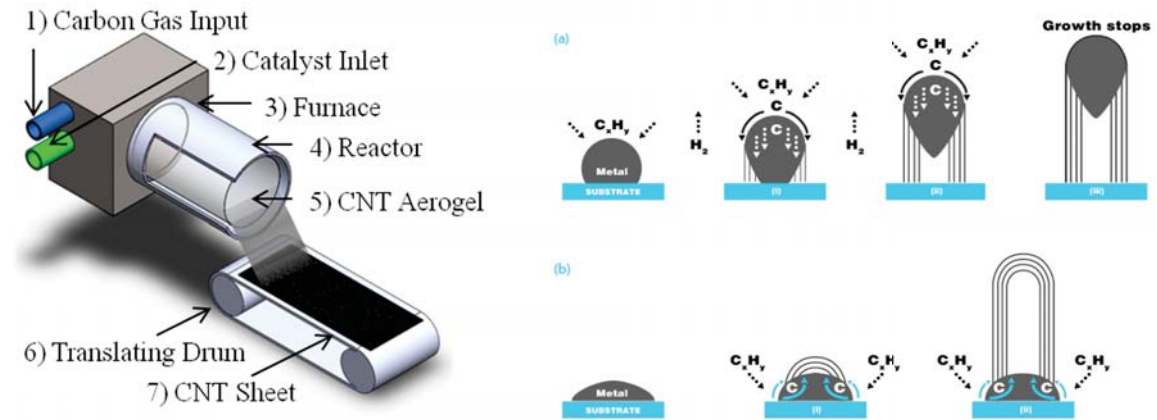


Figure 3.1. CNT sheet production and depiction of growth using CVD. The second photo shows two ways that CNTs grow during the process based on how the metal is impeded into the substrate giving tip or base growth. [11]

The CNT sheets were made from multiwalled CNTs created using a CVD method.

The catalyst Nanocomp uses is iron. After the process, the iron atoms that are still on the CNT sheets are cleaned off using a nitric acid treatment. Through development, Nanocomp has found ways to increase the production rate and quality by depositing large amounts of CNTs at once. Several network layers that the CNTs form are combined to make up the sheet. These layers can be as thin as 50 nm. The process Nanocomp uses is an enhanced production technique that use thicker layers, requiring less of them and decreasing the complexity of the process and the amount of high temperature furnaces and reactors.

For tensile testing, pre deformed dimensions were necessary to calculate area. The thicknesses of several sheets was measured at different locations using a Westward digital caliper with resolution of $2\mu\text{m}$. Because of the varying composition inside of the CNT sheets due to voids, defects, and varying packing densities thickness values were measured between $15\text{-}60\mu\text{m}$. A uniform thickness of $.040\mu\text{m}$ was assumed through average measurement with a micrometer over the sheet that all samples were cut from.

All samples tested in this research came from the same Nanocomp sheet identified by lot number 71385 batch 100154. The CNT samples were into $13 \times 70\text{mm}$ sheets. At the end of the sample sheets, two 0.635 inch thick pieces of GPO-3 sheet fiber glass roughly $15 \times 15\text{ mm}$ were attached using M Bond adhesive to the sheets to give support and protect from premature failure from the grip. The fiber glass was also sanded down at the leading edge, to prevent stress concentration from being applied near the contact area of CNT sheet as seen in Figure 3.2



Figure 3.2. Untested specimens that have been mounted to the fiber glass.

3.3 Equipment

The monotonic tensile and creep sustained loading were performed using a pneumatic tensile testing machine, the Tytron 250. The Tytron was equipped with both a 50 N and a 250 N load cell. The data from the Tytron was compiled using standard MTS software. Imaging software Pixelink was used to take photos and analyze the change in width of the samples during the tests. After the tests were completed they were studied using SEM to understand the change in CNT alignment during the creep tests.



Figure 3.3. Tytron 250, Camera, and Work Station for CNT Sheet Testing

3.4 Tensile Test Method

The CNT sheets were first tensile tested to determine the basic material properties such as Modulus of Elasticity, yield stress and ultimate tensile strength (UTS). The tensile test was performed in order to establish a baseline from which appropriate loads for the creep test could be determined. The monotonic tensile tests were performed in the MTS Tytron 250 bench type test machine with a 250 N load cell shown in Figure 3.4. The tensile test machine provided the ability to test until fracture to find UTS as well as perform creep testing. Below the sample, a green mat was placed to provide a clearer resolution of photos being taken while the tests were conducted. More on this will be discussed in Section 3.5

Using MTS TestStar System Software, a configuration and procedure file was built in Station Builder with the MultiPurpose TestWare (MPT) function. With this function, a test plan was created that would operate the tensile testing machine in

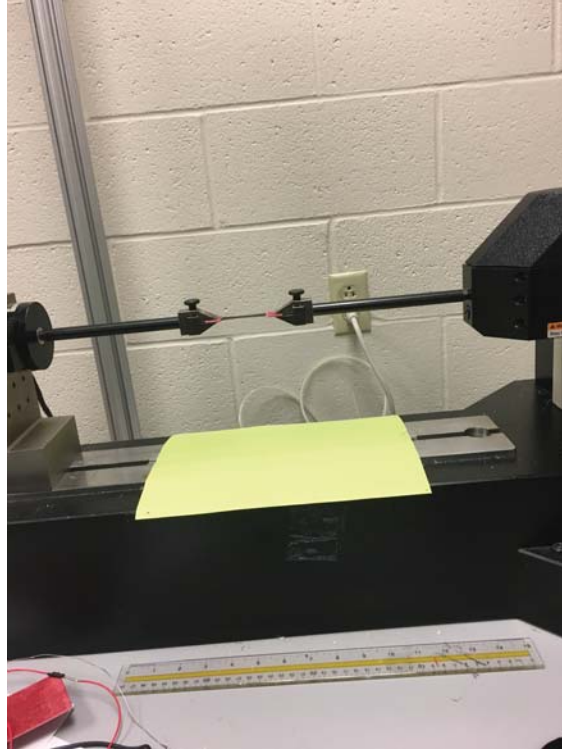


Figure 3.4. A sample being tested in the Tytron 250.

strain controlled mode with a displacement rate of 0.01 mm/s to provide an even and smooth curve. During testing, it was noted that higher strain rates did not provide consistent enough readings and a slower rate provided a more accurate representation of the materials strength. 0.01 mm/s was slow enough to properly characterize the material while still being performed in a responsibly timed manner. This value agrees with and adheres to the displacement rates laid out in ASTM Standard D3039 Test Method for Tensile Properties of Polymer Matrix Composite Materials, the accepted procedure for testing materials with similar properties to CNTs. ASTM D3039 states displacement controlled tests should be done at a rate where the sample will fail between one to ten minutes and the 0.01 mm/s meets these requirements. Monotonic tensile tests were performed on five different samples in order to determine the average UTS. During the test, values of displacement, load, and time were recorded using MPT every 10 seconds. From this data, engineering stress was determined using the

original, undeformed, width and thickness.

3.4.1 Tensile Test Post Analysis

The data that was recorded during the test was analyzed using the following equations.

Equation 3.1 used for engineering stress determination

$$\sigma = \frac{P}{A_0} \quad (3.1)$$

Where

P = Force Measured by MTS

A_0 = Original cross sectional area

Engineering stress bases its values of the original unstressed area and is a standard calculation when conducting any creep or tensile tests. This value assumes that there is no change in area as the test is conducted as seen in most metals and is crucial when calculating the UTS. CNT sheets do deform during testing so engineering stress needs to be accompanied with other values, such as real stress, synonymous with true stress.

Equation 3.2 used for real stress determination

$$\sigma = \frac{P}{A} \quad (3.2)$$

Where

P = Force Measured by MTS

A = Area from the width measurement and the thickness (constant .040)

Real stress is another calculation for stress that allows for a change in area, re-

sulting in most real stress values being greater than engineering stress values. As a materials physical shape changes during tensile loading, which CNT sheets experience, real stress provides a more realistic prediction on performance for when a material. This helps characterize the material as it leaves linear elastic deformation and begins to deform more viscoelasticity. CNT sheets experience this change when stress reaches and then exceeds approximately the 25 MPa which will be discussed more in depth in the following section.

Equation 3.3 used for strain determination

$$\epsilon = \frac{D}{L_0} \quad (3.3)$$

Where

D = Displacement

L_0 = Original length

Engineering strain is another standard calculation for creep and tensile test and was used in this work. Strain is used to quantify the change of length in the load direction based on the original dimensions and is an important value when calculating a Modulus of Elasticity which is the goal of tensile tests. Real strain is another way to represent how much a material deforms but is more for representing the ductility of a material which was not a goal in this work.

Equation 3.4 for Young's Modulus determination

$$E = \frac{P/A}{\Delta L/L_0} \quad (3.4)$$

Where

E = Young's Modulus

ΔL = Change of Length

The Young's Modulus is a representation of elasticity during the elastic deformation rate of the material and is an important material property that is found when conduction tensile test. CNT sheets experience an elastic response in loads less than 25 MPa as seen from the results of the tensile tests shown in the following section. Young's Modulus also provide comparisons to other materials and provide a measure of how much a material will resist to change of length.

Equation 3.5 used for Poisson's Ratio

$$v = \frac{\epsilon_{Lateral}}{\epsilon_{Axial}} \quad (3.5)$$

Where

v = Poisson's Ratio

$\epsilon_{Lateral}$ = Change of Length in lateral direction

ϵ_{Axial} = Change of Length in axial direction

Poisson's ratio is also an important material property calculated from the results of tensile tests and provides another measure of how linear elastic a material. Poisson's ratio along with the modulus of elasticity have long been use to characterize a material.

From these equations and results, test values were compiled into several graphs; real stress vs strain, engineering stress vs strain, stress vs time, and strain vs time. From these graphs, analysis of mechanical performance of the CNT sheets could be made.

3.5 Creep Test Equipment and Method

From the results of the UTS test, creep tests based on ASTM standard D2990 for testing plastics at appropriate range of load values could be conducted to characterize the creep behaviors of the CNT sheets. These loads were 10, 15, and 20 N and

correspond to loads that were approximately 40, 60, and 75% of UTS for the CNT sheets. These load values were chosen to provide a clear understanding of creep response based on the results of the tension test and the observed consistent change of strain rate. The creep tests were also performed with the in the MTS Tytron 250 bench type test machine with a 250 N load cell as seen in Figure 3.5.

Using MTS TestStar System Software, a configuration file was built in Station Builder with the MultiPurpose TestWare (MPT) function. With this function, a test plan was built that would operate the tensile testing machine in a load controlled setting. The functions step included a ramp up to the desired load that was five minutes. A five minute load up time would be standardized between test and would be consistent with the load rate during the tensile test and the MPT recorded displacement and load values every 10 seconds. The collection rate of every 10 seconds was necessary to properly characterize the deformation and response during load up. After the machine had reached the proper testing load, the next step in the procedure was for it to hold the load constant for 48 hours, taking readings every 10 minutes during that time also recording displacement and load measurements. Since the limits of the CNT sheet were unknown at the time of testing, the 48 hour point was set using engineering judgment based off tensile test results as a conservative mark to begin to understand the materials response. Using the Nikon Micro-Nikkor af 200mm f/4d ed camera, photos were also taken to coincide with the data recordings. The camera would take photos every 10 seconds during load and every 10 minutes during the creep phase, syncing the images to the recorded values from the test. A green mat was placed below the sample to provide better contrast for photos so that width measurements could be obtained throughout the test.

From the photos taken during the test, width measurements were able to be recorded to compare real and engineering stress values. Through the use of the digital

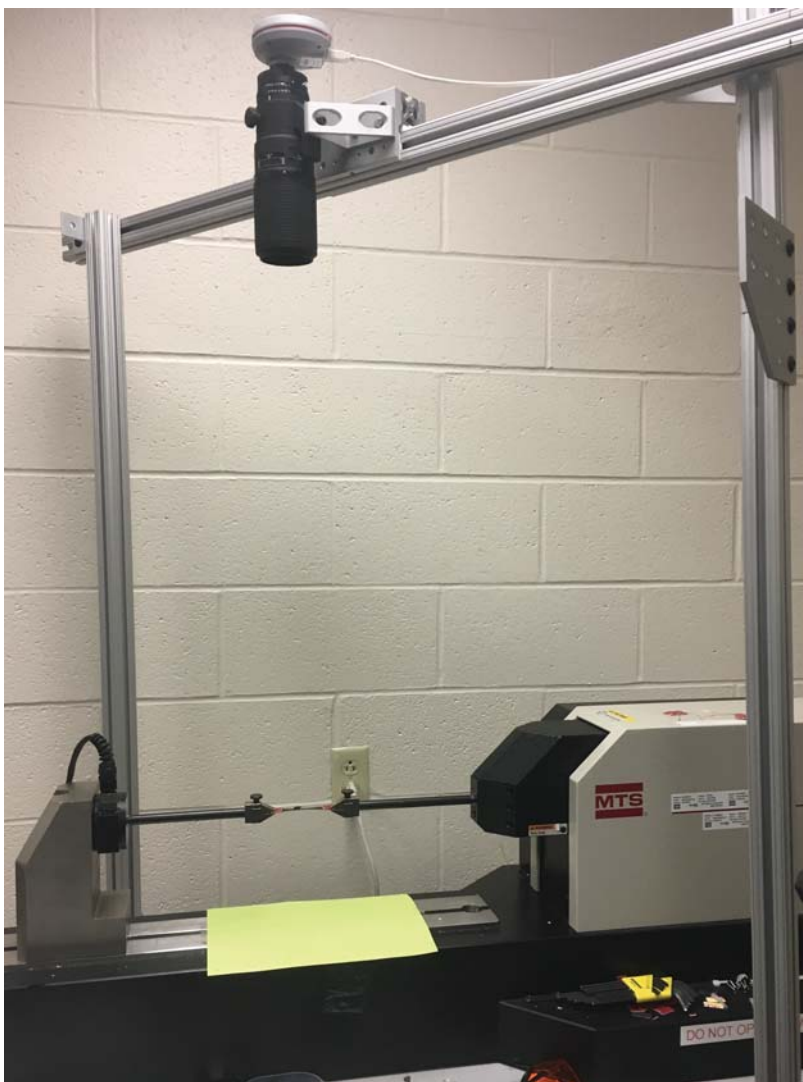


Figure 3.5. The Tytron with the camera set up.

photograph software Pixelink Scope, the photos were able to be analyzed digitally and accurate width measurements from photos of the CNT sheets being tested could be found through the use of the measurement tool. The Pixelink software was calibrated by taking a photo of a specialty micro ruler was placed into the tensile testing machine grips in the same location and distance from the camera that the CNT sheets would be tested at. With the Nikon camera in a fixed place and measuring 10 mm on the micro ruler the software was able to calibrate to the specific distance and measure the CNT sheets during testing in a reliable fashion. The camera set up is shown in Figure

3.5.1 Creep Test Post Analysis

The metamathematical methods and Equations for engineering stress (Eq. 3.1), real stress (Eq. 3.2), and strain (Eq. 3.3) were used to analyze the data and results from the creep test were identical to those used to calculate values during tensile testing.

From these equations and results, test values were compiled into several graphs; real stress vs strain, eng Stress vs strain, stress vs time, strain vs time, and change of width vs time. From these graphs, analysis of the mechanical performance of the CNT sheets could be made.

The tested specimens were analyzed using a SEM. This was done to better understand how the test load level affected the CNT sheets, and more specifically, to see how applying load changed the alignment of individual CNT strands inside of the sheet. The EDS analysis results were used for better characterization the material's chemical composition and make up.

3.6 Ultra Violet Exposure

CNT sheets were tested after being exposed to ultraviolet (UV) rays to provide a realistic assessment on performance in a space like environment. The samples were held under vacuum at 10×10^{-6} Torr and exposed to UV rays. The UV light had a peak intensity of 245 nm wavelength, classifying it in the UV-C wavelength range. UV-C are the most damaging UV rays, found only in the upper atmosphere and space environments. The average intensity inside the chamber was measured. The CNT samples were taped to a wire and hung approximately 1 cm away from the UV source. The CNT sheets were only exposed on one side and were not rotated so that

a constant vacuum could be kept on the samples. The specimens were placed in the chamber for 200 hours to assess the effects of the UV radiation. The CNT sheets were cut into 35 mm by 5 mm sheets so that more samples could be fit into the vacuum chamber. After the CNT sheets were cut, they were weighed using an Ohaus Voyager Pro milligram balance with reliability of 1 milligram before being placed in a vacuum chamber with UV rays from a specialty lamp. After 200 hours, the sheets were then weighed using the same scale to record weight change.

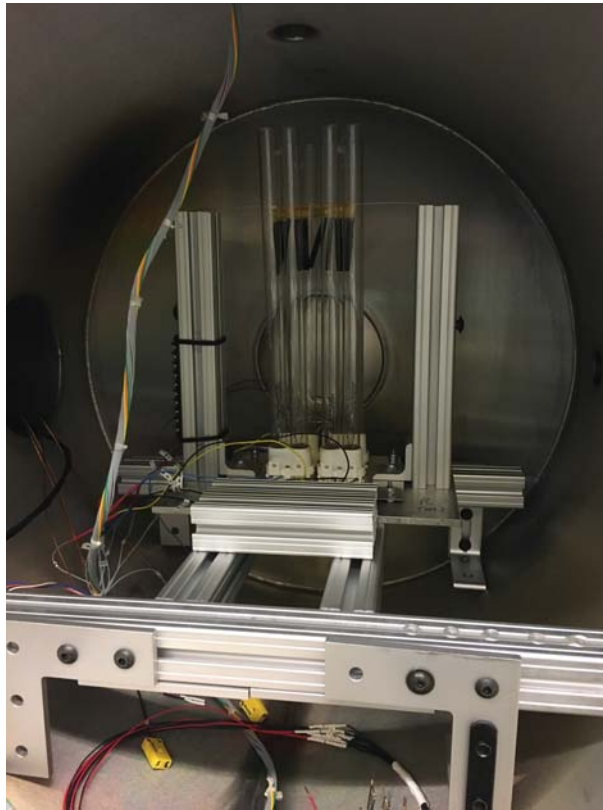


Figure 3.6. CNT sheets inside the vacuum chamber prior to UV exposure.

3.7 Ultra Violet-Tensile Test

The CNT sheets were removed from UV exposure and tested for tensile strength. The monotonic tensile tests were performed in the MTS Tytron 250 bench type test machine with a 250 N load cell shown in Figure 3.4. The samples were smaller in size

but were prepared as described in Section 3.2.

Using MTS TestStar System Software, a configuration file was built in Station Builder with the MultiPurpose TestWare (MPT) function. With this function, a test plan was constructed to operate the tensile testing machine in strain controlled mode at a rate of 0.01 mm/s to provide an even and smooth curve. During testing, it was seen that higher strain rates did not provide consistent enough readings. Monotonic tensile tests were performed on two different samples in order to determine the average UTS. This test was done on an exploratory basis and as a result of just five samples being exposed to UV, only two tensile tests could be done so creep tests could also be performed. During the test, values of displacement, load, and time were recorded using MPT every 10 seconds. From this data, stress was determined using the original, undeformed, width.

3.8 Ultraviolet-Creep Test Test

The CNT sheets were removed from UV exposure and tested in creep. The monotonic tensile tests were performed in the MTS Tytron 250 bench type test machine with a 100 N load cell. The samples were smaller in size but were prepared as described in Section 3.2.

The creep testing procedure of the CNT sheets was identical to Section 3.5 using the same tension testing machine, testing software, test procedure files, camera, and digital photograph software. The UV exposed CNT sheets were smaller than previously tested sheets so the load of the creep test had to be modified. This test was conducted to explore the future possibility of study and was restricted from the limited amount of exposed samples. Based on the results from the tensile tested CNT sheets, 40 MPa was chosen as a conservative goal creep stress that would provide a comparison to the 15N test previously performed and would provide usable test data

and minimize the risk of a sample rupturing during the test.

3.9 Post Analysis Ultra Violet

After completion of the tensile and creep tests, untested, tensile tested, and creep tested samples were imaged using an SEM. This was done to compare exposed vs unexposed sheets and to begin to better understand the change in performance from the CNT sheets. EDS was also done to see if there were any chemical changes to the CNT sheets.

3.10 Summary

This chapter laid out the process for evaluation of CNT sheets in creep. Considerations and thought processes for preparing, conducting, and analyzing the tests were outlined. The experimental results from tension and creep test of the CNT sheets will also be included in the the following chapter.

IV. Results

4.1 Chapter Overview

This chapter will present the results from the tensile and creep tests performed on the CNT sheets. Five tensile tests were performed to determine the UTS, as described in Chapter 3. Creep tests were performed to determine the creep response at different levels of stress. There were 16 tests in total, five 10 N tests, five 15 N tests, and six 20 N tests.

4.2 Tensile Test results

The tensile test was performed to find a UTS for the CNT sheet. The test used the Tytron 250 and the 250 N load cell. Force control was used during the tests, making sure the the load was applied in constant and controlled. After conducting five tensile tests and calculating the engineering stress, an average ultimate tensile strength (UTS) was found to be at approximately 52 MPA. This translates to a load of 27N.

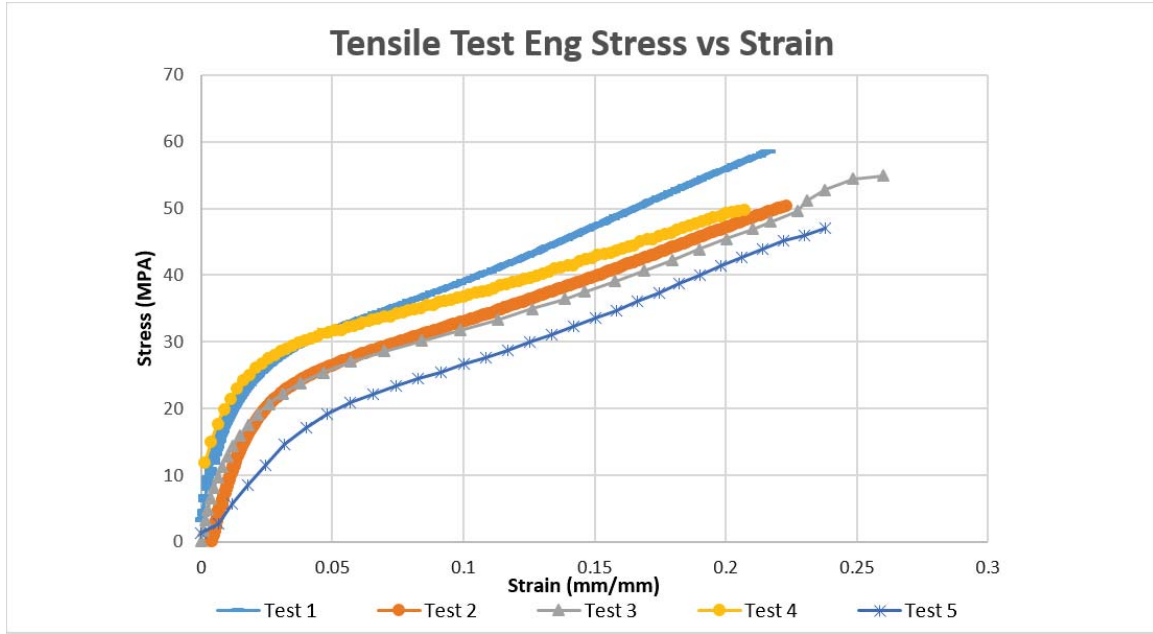


Figure 4.1. Tensile Test Eng Stress vs Strain results.

From the Figure 4.1, there was a consistent overall shape of the Stress/Strain curve for all samples. There is a distinct bend in curve breaking each line into two distinct, almost linear segments. This would begin when the load reaches approximately 12 N and the stress is 23 MPa. At this point the samples would start to show visible necking and deformation would begin. After the necking began, the plastic response portion of the Stress/Strain curve for the CNT sheets were nearly parallel and stayed that way until failure occurred. Based on the different initial responses of the CNT sheets while in the elastic, there were a range of responses for the Modulus of Elasticity from 0.8 and 1.4 GPa. Poisson's Ratio was calculated as being 0.40. Axial strain was calculated using the width measurements obtained by the camera and can be seen in the Appendix. These values are in line with what previous research and literature reviews have found of 1.2 GPa [64] and 1.1 GPa[83]. Although there was a wider range of values for UTS and the elasticity modulus, all values were tested for normalcy and compared to each other and found to be within a 95% confidence interval for being considered normal. Table 4.1. provides the averages and standard deviations for the

tests.

Table 4.1. Averages and Standard Deviations of Material values from the five tensile tests

Material Values	Average	STD
UTS	52 MPa	4.3
Yield Stress	23 MPa	3
Modulus of Elasticity	1.1 GPa	483
Poisson's Ratio	.40	.001

As the CNT sheet failed, each CNT layer that makes up the sheet was drawn apart. Shown in Figure 4.2 is a close up examination of the failure mode. Several wisps of CNT strands were drawn out from the sheet as it was separated from the other side. Failure in the CNT sheets is not as complicated as noted in CNT yarns as was discussed in chapter two. CNT sheets all failed in similar fashions, having the layers spread apart from itself as the failure from one leads to the failure of the next.

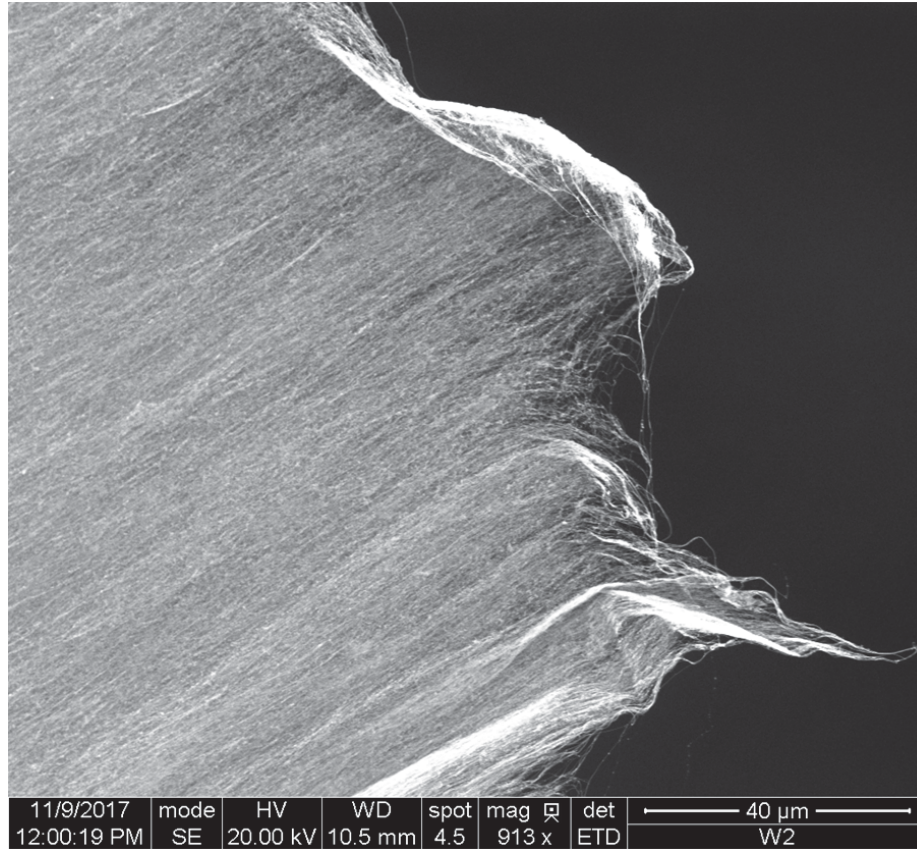


Figure 4.2. CNT Sheets after Tensile Testing

Displayed in Figure 4.3 are the samples post tensile test and there is clearly a pattern of breaking away from the center. The most common failure point was near the ends where the original width was being maintained by the grips. This has been attributed to the more random alignment that still exist toward the end of the sample as opposed to the load induced higher aligned segments found toward the center. Literature has shown that having the highest alignment also gives this area the highest strength [77].



Figure 4.3. CNT Sheets after Tensile Testing

The highest alignment of the CNTs is found in the thinnest portion of the samples where it is experiencing the highest stress which, during tensile testing, occurs in the center of the sample. As depicted in Figure 4.4, the alignment of the tubes becomes increasingly random as the distance from the center increases. The random alignment leads to the CNTs not being able to withstand the force and fracturing near the grips. More analysis on the alignment will be done when discussing the SEM images of the stressed CNT sheets.

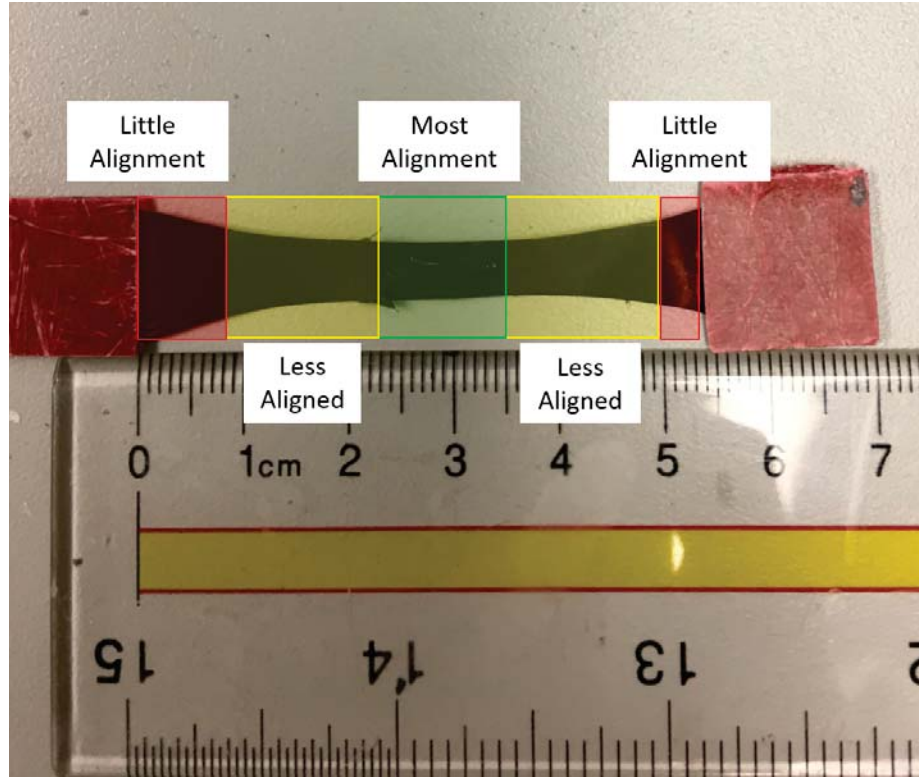


Figure 4.4. A depiction of alignment of strands in a CNT sheet after experiencing stress with higher alignment being towards the center and then getting less aligned the closer the tubes are to the grips based on quantitative results and is in agreement with other works [12].

4.3 Creep Testing

4.3.1 Creep Results

After the tensile testing was conducted and the results were analyzed, the loads for creep testing were able to be determined based on the shape of the stress strain curve. On all the tensile test results, there was a distinct change in strain rate as it goes from an elastic to more plastic response when the stress reaches approximately 23 MPa. This change of strain rate is the yield stress of the material. The loads for the creep test were chosen to understand the response of the CNT sheet at and around this change of strain rate. 10 N was the lowest load and at 10 N the stress applied would be close to 20 MPa (40% UTS) which is below the yield stress point,

so only elastic deformation was expected with no yielding. The next load was 15 N which would result in a load of roughly 30 MPa (60% UTS), which is slightly above yield stress. At 30 MPa the material begins to deform in a plastic manner, showing signs of yielding through necking and the CNT sheet begins to have a different strain rate. The final load was 20 N which would result in a stress near 40 MPa (75% UTS). This is shown in Figure 4.5. Figure 4.6 provides an example of how CNT sheets looked during testing.

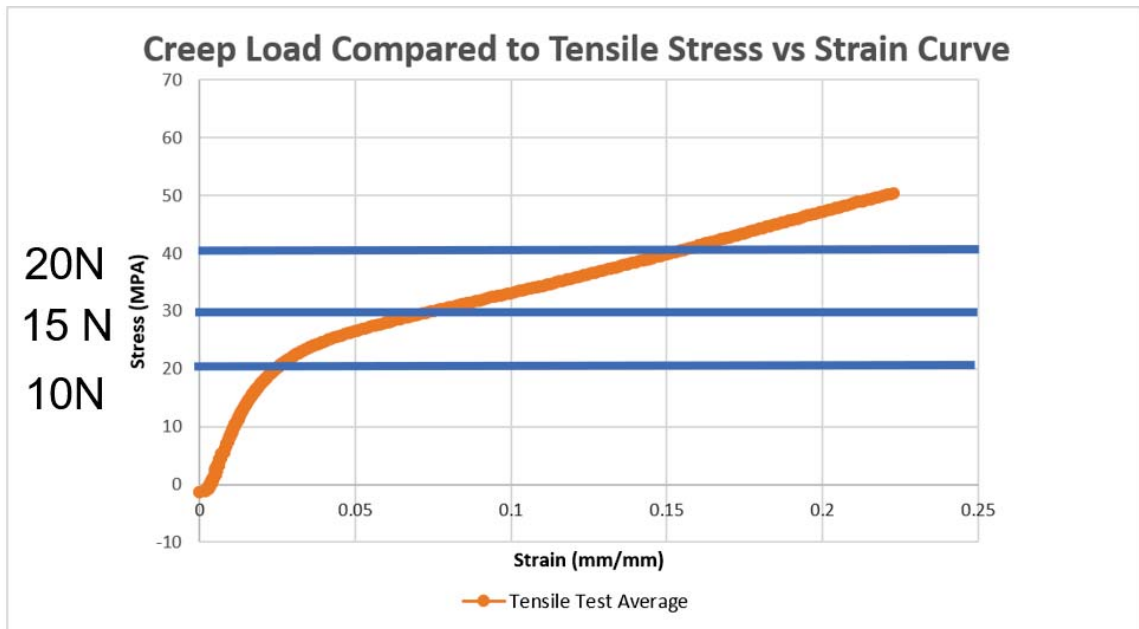


Figure 4.5. Depiction of the loads used during the creep test and how they relate to the UTS and the stress strain curve created using results from the tension test



Figure 4.6. An example of a CNT sheet during creep testing at 15 N

One overall trend between each sample tested was that the strain rate for each sample went almost to zero once the final load had been achieved and varied only slightly the remainder of the 48 hours. This is most evident strain vs time curves, where once the final load was achieved the final strain was seen to increase just slightly. The strain rate was calculated for each test and through these calculations, strain rate averages were determined and plots were created of the strain rate vs time, found in the appendix.

Each average strain rate for all tests could be considered zero, and this minimal strain rate accounted for the small amount of strain the samples experienced during the creep portion. For all the tests the largest increase during the 48 hours of creep was only 0.02 mm/mm. Also, it can be seen that no sample reached a third stage of creep. At these loads, the time needed to get to a third stage of creep would have to be measured in weeks or months, if it ever even got there at all.

In the 10 N test, once the final load was reached the sample experienced a constant

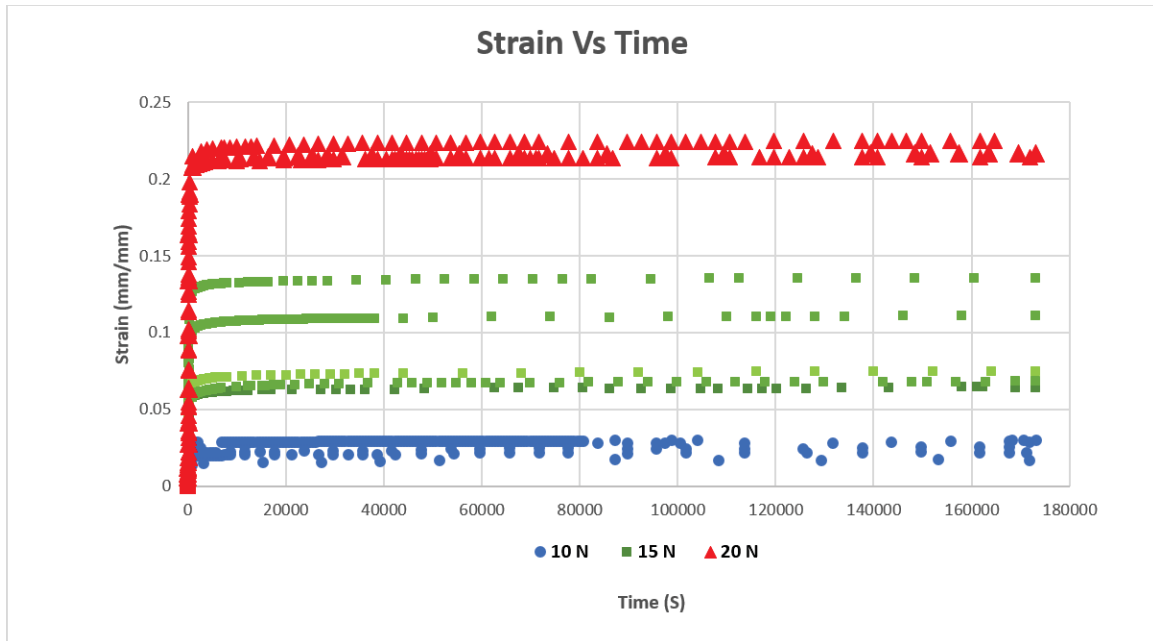


Figure 4.7. Strain vs Time for all 10, 15, and 20 N tests

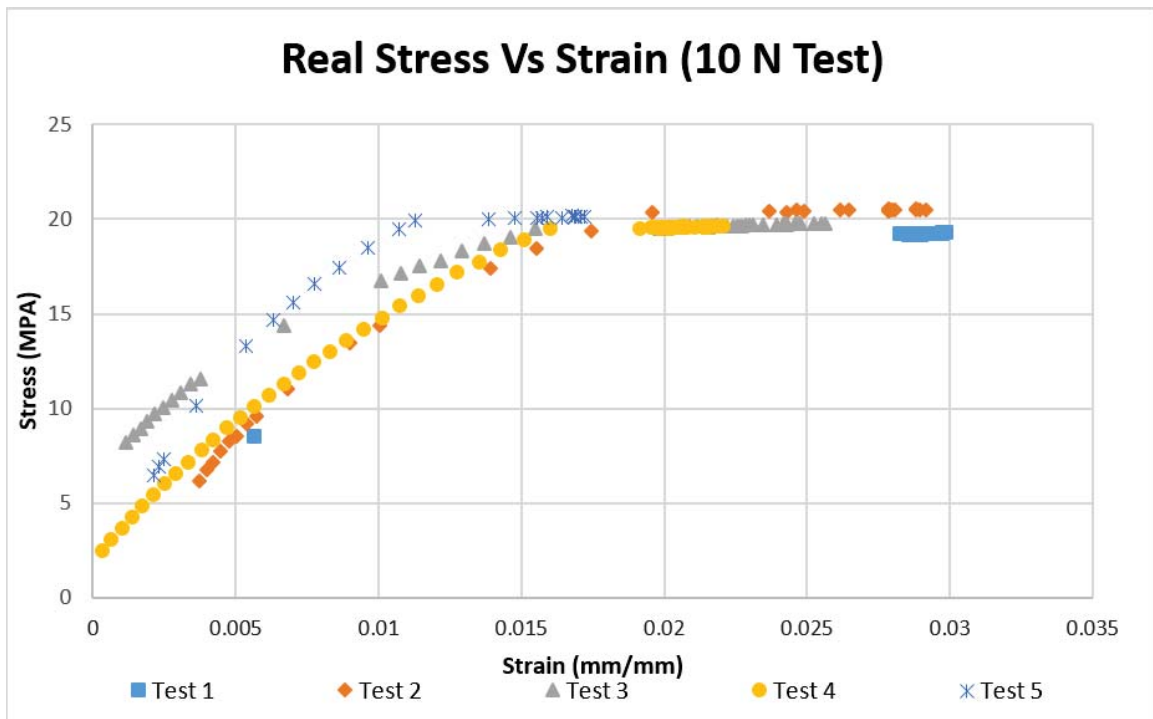


Figure 4.8. Real Stress Vs Strain at 10 N Creep.

strain rate of near zero as seen in Figure 4.7. The sample's cross sectional width did not see a large change since the CNT sample did not yield and kept its original shape,

minimizing the difference between the actual and pre-stressed areas. This was not observed in the 15 and 20 N test which saw larger differences between the real and engineering stress vs strain plots.

When comparing the Real Stress vs Strain graphs, both the 15 N tests and 20 N test show that the strain rate for the sample after it reached a yield stress of approximately 25 MPa, decreased and changed direction. This new strain rate is nearly identical to the strain rate the sample continues to experience in creep.

This shows that the plastic deformation and the change in dimensions at the end of the ramp up, after the yield stress is exceeded, and during the creep portion, once the final load was achieved, were almost equal, even though both occurred over different time spans. This response is very different in the 10 N tests where the creep stress did not reach this yield stress.

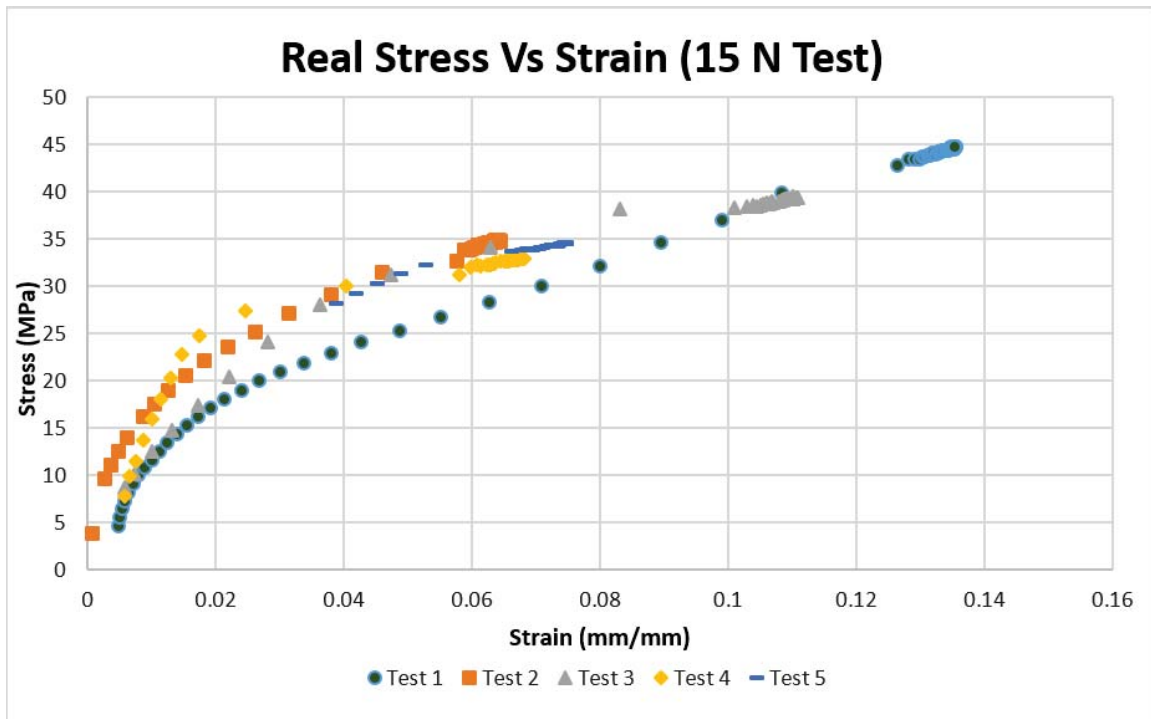


Figure 4.9. Real Stress Vs Strain at 15 N Creep.

In Figure 4.11, it would appear that the slope of the stress vs strain curve varies

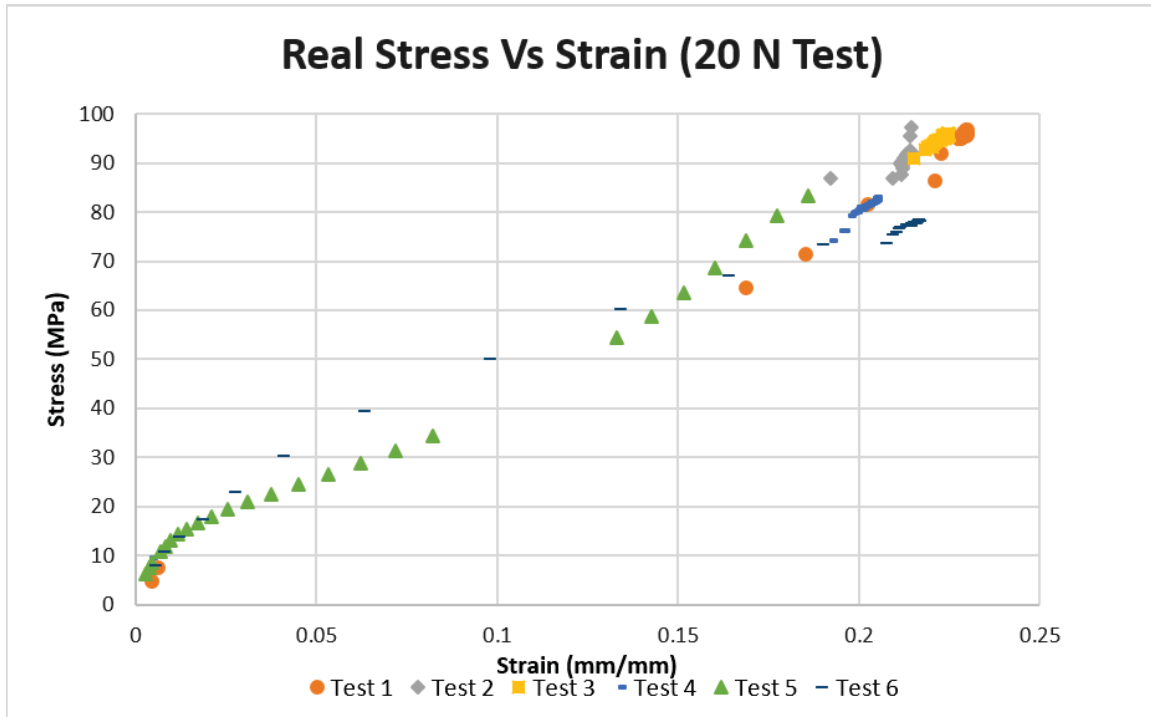


Figure 4.10. Real Stress Vs Strain at 20N Creep.

between tests. This varied strain rate is the result of the ramp up time being kept at a constant five minutes for each test. The ramp up time was kept constant to keep consistency in the test times.

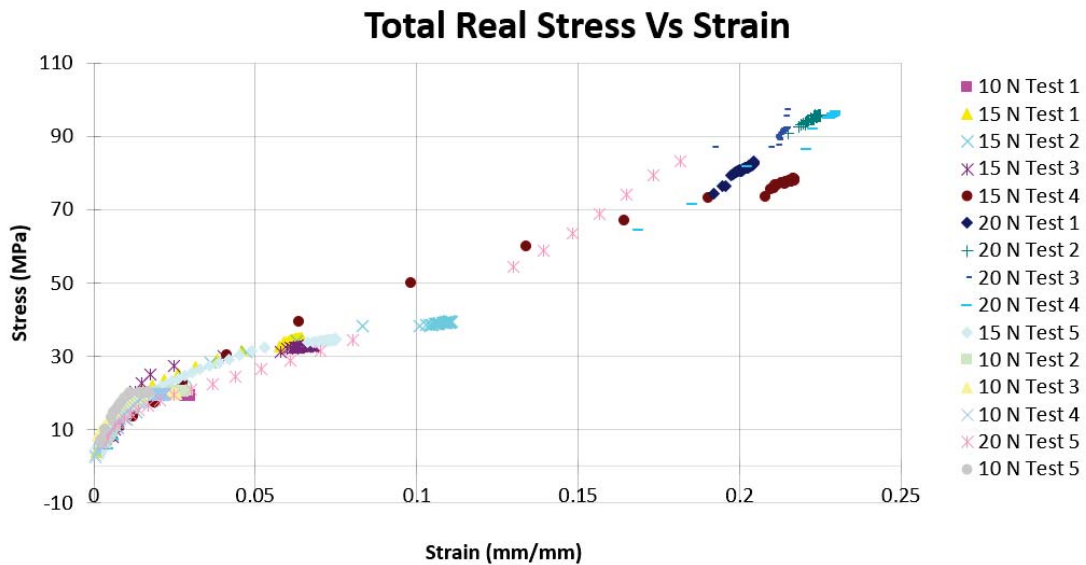


Figure 4.11. Combined Real Stress vs Strain Graph In Creep.

The goal of this research was not to study the CNT sheets under loading but how they responded to creep so small variations during the ramp up time were chosen to be accepted. The constant ramp up time to various final loads resulted in a slightly higher strain rate for the 20 N (0.03mm/sec) and 15 N (0.015mm/sec) tests compared to the 10 N test (0.0025mm/sec).



Figure 4.12. 3 Samples after creep tests at 10, 15, and 20 N applied load.

From Figure 4.12 there was a noticeable increase in final strain for each of the three samples. It was also noted the change in width for the 15 N and especially the 20 N sample was dramatic, decreasing as much as 7mm. The change of width measurements for each sample taking before and after testing can be seen in table 4.2 In every test 15 and 20 N test, the sample would experience necking that would begin and end at the grips and would be thinnest near the center of the sample. For the 10 N test, the load was only large enough to extend the CNT sample and the width did decrease throughout the test but no samples experienced visible necking. This necking does lead to a more pronounced alignment of the CNTs which will be

discussed in Section 4.3.4 and seen in Figure 4.15.

Table 4.2. The change of width was more uniform for the 10 and 20 N tests as opposed to the 15 N test which saw a large variations of width change

		Width Before (mm)	Width After (mm)	Change (mm)
10 N	1	12.498	12.166	.332
	2	13.037	12.641	.396
	3	13.017	12.73	.287
	4	12.731	12.413	.318
	5	13.235	12.957	.278
15 N	1	13.018	10.761	2.257
	2	12.519	9.508	3.011
	3	12.433	8.385	4.048
	4	13.166	10.84	2.326
	5	13.061	11.387	1.674
20 N	1	12.037	5.141	6.869
	2	12.997	5.236	7.761
	3	12.949	6.018	6.931
	4	12.879	6.375	6.504
	5	12.74	5.168	7.572

Comparing each individual tests, there was more variability in the results of the 15 N compared to the 10 N and 20 N tests. Seen in the the strain rates of Figure 4.7 and the Real Stress vs Strain Curves for 10, 15, and 20N see in Figures 4.8, 4.9, and 4.10, the 10 N and 20 N tests were more consistent with each other compared the the samples tested at 15 N. This is more clearly seen in the difference in final stress and strain values as shown in Table 4.3. These results can be explained by understanding what is occurring in the material when this load is applied.

Table 4.3. Final Stress vs Strain values for Creep Tests

	Difference in Final Stress (MPa)	Difference in Final Strain (mm/mm)
10 N	2	0.04
15 N	12	0.75
20 N	18	0.05

As a material is being loaded under creep, its response will be characterized as being in one of the three creep regions seen in Figure 1.2. The primary region is

characterized by a decreasing strain rate. This occurs as the material is reacting to being loaded. The strain rate will decrease for a period of time after it has reached its final load and reaches an internal equilibrium. Once it has stabilized, the material transitions to the secondary creep region where it experiences a more constant strain rate. This stage is dependent on the load the sample is being held at and the duration of the test. If the test is too short, the sample might not move past this region. This region could also continue for a prolonged period of time if the load is too low. After a certain time and under certain loads, the material may begin to rupture, causing it to progress into the third creep regions. Here the sample will see an increase in strain rate until failure. For this CNT sheets, the transition from the first to second stage of creep can be seen in Figure 4.13.

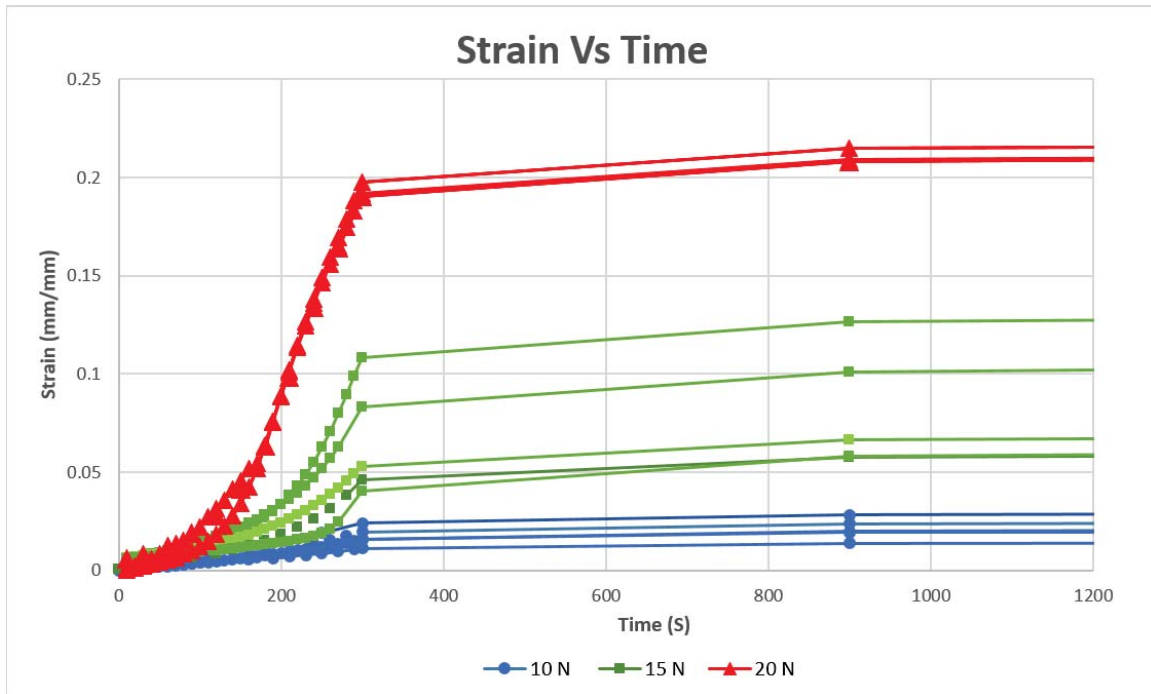


Figure 4.13. A close up of Figure 4.7 as the strain rate decreases and becomes constant

The creep response and the corresponding strain rates are dependent on the material and load that is being tested. The strain rates once each of the samples reached their final loads all went to near 0 mm/sec, which is an expected response when a

material enters the second stage of creep. As previously discussed, these creep regions have to be considered along side the elastic and plastic response of a material. From the tests that were conducted, the CNT was expected to respond in an elastic way when tested at 10 N and behave in more of a plastic way when tested at 15 N and 20 N. At each of these loads the stress vs strain rate will be determined based on whether the CNT sheet is in an elastic or plastic region and this was seen. The stress vs strain rate for the 10 N test was nearly linear, which is what an elastic material would experience. The stress vs strain rate for the 15 N and 20 N test were not as uniform and featured a change in rate at the yield stress point. At 15 N, the CNT sheet will just be passing the stress needed to start yielding and the material will begin the change over from elastic to plastic. Depending on how far the sample would transition into the plastic phase had the largest impact on the final load and strain results since the strain increased only slightly once the final load was reached as stated above.

The effect of being so close to this transition point of the 15 N test was seen in the Real Stress vs Strain Curve. The variability caused by the amount of necking that occurred had a large impact on the final Real Stress vs Strain values. These inconsistencies are not the result of poor samples or bad tests, but just highlight the large area of response in terms of deformation that can be expected when testing this material near its yield point. This inconsistency was not seen as much in the 20 N tests. At 20 N, each of the samples exceeded the yield stress during load up, giving the samples more time to respond and resulting in more consistent final strain values near the maximum of the material's performance level. Even when testing the material so close to its maximum stress though there was still variability in the 20 N final real stress values which is dependent on how much necking occurs. No sample ever made it to the third region of creep. For creep testing, the timescale that tests

could be conducted could go on for 1 month per test to get a material to fail during the test. Given how little was known about the material and the limited time frame to conduct testing for this research, the two day test period was decided on in order to ensure useful results.

4.3.2 Statistical Analysis

Given the variability in the responses from the different tests, it was necessary to determine if these results could be considered a fair representative of the CNT sheets as a whole. Statistical analysis through the calculation of averages and standard deviations was done and a normality test was performed to verify if the samples fell within an accepted level of normality. For each test, real stress, engineering stress, and strain values were chosen at specified times during the test to determine the consistency of the results found. A collection of that data can be seen below.

Table 4.4. 10 N Average and Standard Deviation of Real Stress vs Strain

Time (S)	10 N Real Stress		10 N Strain	
	Average (MPa)	STD	Average (mm/mm)	STD
30	6.77	2.23	0.002	0.001
90	9.53	1.72	0.004	0.001
180	13.95	1.007	0.008	0.002
300	19.84	0.41	0.02	0.003
900	19.72	0.46	0.02	0.005
173100	19.88	0.50	0.02	0.005

Table 4.5. 15 N Average and Standard Deviation of Real Stress vs Strain

Time (S)	15 N Real Stress		15 N Strain	
	Average (MPa)	STD	Average (mm/mm)	STD
30	8.08	4.36	0.005	0.003
90	11.67	5.89	0.008	0.005
180	17.80	8.85	0.017	0.010
300	28.67	14.58	0.05	0.037
900	29.80	15.20	0.068	0.043
173100	31.10	15.84	0.075	0.046

Table 4.6. 20 N Average and Standard Deviation of Real Stress vs Strain

Time (S)	20 N Real Stress		20 N Strain	
	Average (MPa)	STD	Average (mm/mm)	STD
30	6.73	4.049	0.004	0.002
90	12.41	1.93	0.013	0.004
180	28.68	3.82	0.052	0.006
300	68.63255	5.61	0.16	0.01
900	68.65	7.92	0.17	0.01
173100	75.16	8.82	0.18	0.010

These values were then processed into probability charts to validate if they are normal and could accurately represent the CNT sheet's material characteristics. Each set has a 95% confidence rate of being normal.

From the charts and the values presented it confirms that the consistency of the data for the 10 N and 20 N test can be seen since they both have a smaller standard deviation. The values for the 15 N show that there is a wide range of response that the material saw at this stress level. This was to be expected given the results of the tensile test, since at this point the material stops behaving elastically and begins to deform in a plastic manner. The values for the 10 N and 20 N were much closer. This could be that since 10 N is in the region where the material has an elastic response its performance is more predictable. At 20 N the material is so close to its stress limit that the CNT sheet is almost "maxing" itself out.

4.3.3 Power Law Fit

Each test was also graphed on a Stress Log vs Strain Log plot. This was done to determine if the data could have a power law relationship. This relationship does attempt to characterize the power law curves based on the engineering stress vs Strain data. After the data was graphed a trend line was able to run through each set of data, 10 N, 15 N, and 20 N as well as a trend line that would go through all the points graphed together. This is a method historically used for metals but it will provide a

baseline assessment of the results and allow them to be compared to other knowns values. In the power curve equation,

Power Law Equation

$$\sigma_t = K \times e^n \quad (4.1)$$

Where

σ_t = Stress at a certain time

K = Strength coefficient

n = Strain hardening exponent

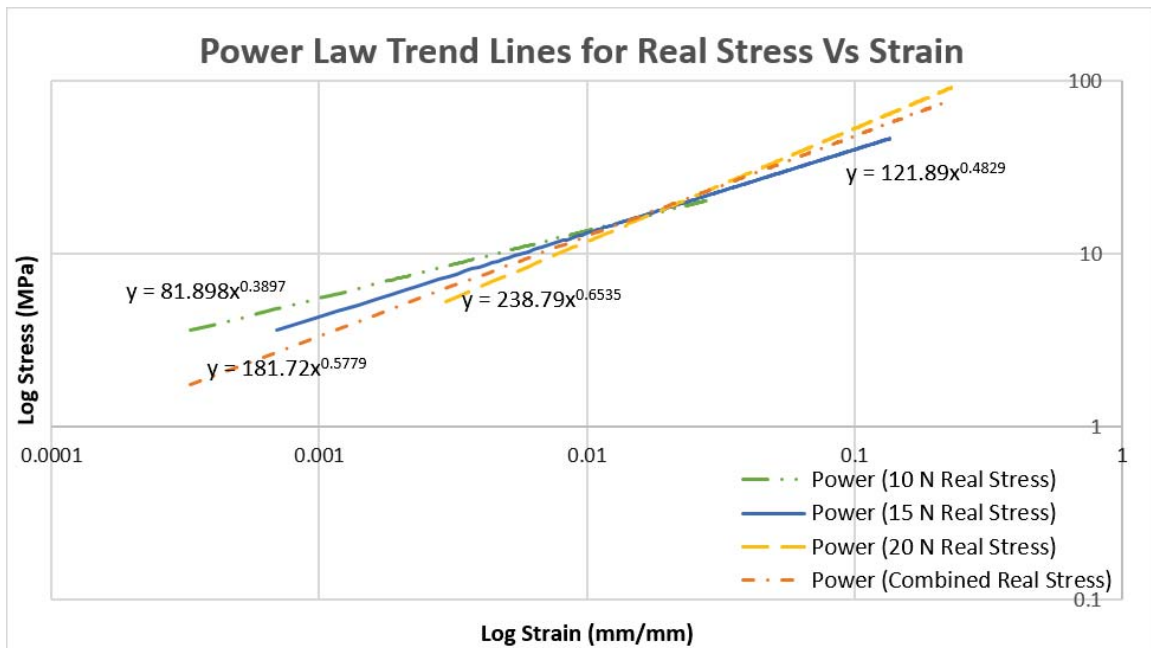


Figure 4.14. Power law trend lines for real Stress Vs strain.

Table 4.7. Power Law Equations by Variables

Power Law Equations		
	K	n
10	81.898	.39
15	121.89	.48
20	238.79	.65
Combined	181.72	.58

These values of strength coefficient, K , and strain hardening, n , can be used to help predict the response of CNT sheets. As can be seen in Table 4.14 the values for the 10 N, 15 N, 20 N, and get increasingly larger with the Combined values being an average of the three. This would again confirm the strain hardening characteristics for the material that are described in section 4.3.4. The 10 N test has a slightly less pronounced slope compared to the other tests which were all similar. An explanation could come from understanding where this model works best. Since this model was constructed with metals in mind it is most reliable when the material that is being modeled has already started to yield. At 10 N the material sees little to no yielding which is seen from the strain response never getting more than 0.03 mm/mm for the entire test. From the tension test, this strain corresponds to right at or before the change in direction of the stress vs strain line indicating a change from elastic to plastic regions. At 10 N the CNT sheet is still in an elastic region and will not yield, so it will not best be represented by this model.

4.3.4 SEM and EDS Imaging

After the tests were complete, 4 samples were taken for SEM imaging. These samples were an untested sheet, and sheets that were tested at 10, 15 and 20 N. The images taken can be seen in Figure 4.15

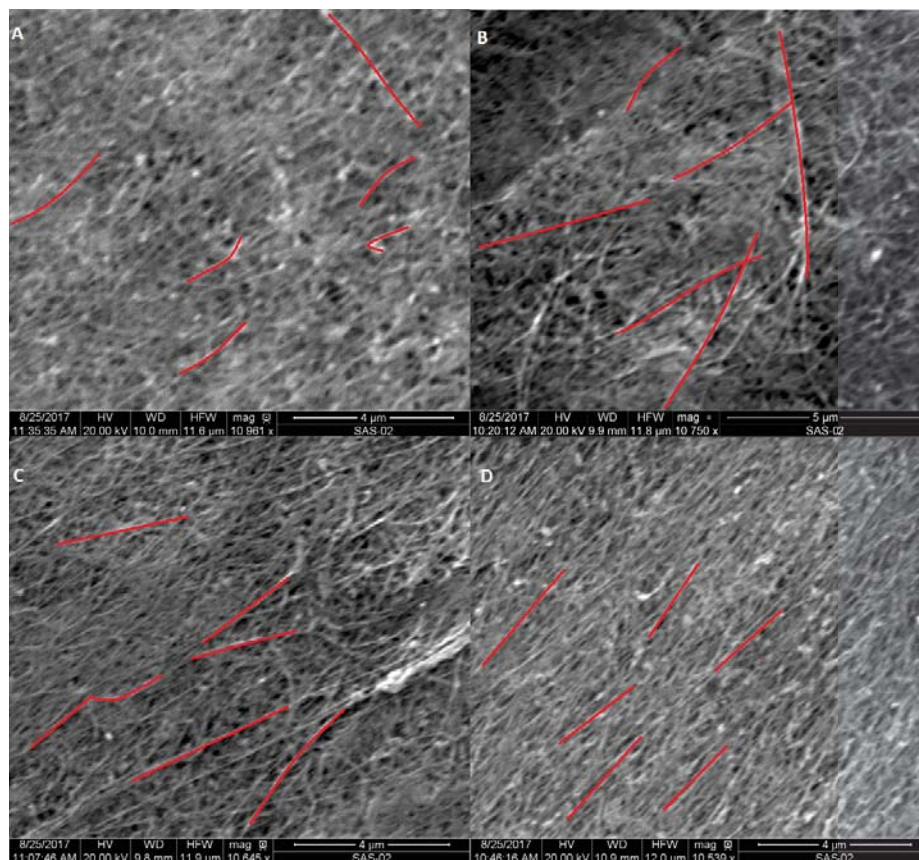


Figure 4.15. SEM images. Starting from the top left; A. 0N, B. 10 N, C. 15 N, and D. 20 N. The red lines provide a representation of the orientations of the tubes. As the sheet experiences more stress, the individual tubes all begin to orient themselves in the same direction while also becoming straighter and more densely packed.

The SEM images show that the alignment of the CNT inside the sheets was more pronounced the higher the load the CNT sheet was exposed to. As the stress increases, the direction of the individual fibers becomes more aligned in the direction of the stress. As such, the CNT alignment is an area that researchers are focusing on to increase strength in the CNT sheet as well as several of other properties during the tensile tests, it was observed that the samples would usually break, not in the center, but would be closer to the ends close to the fiberglass grips. The CNT fails here because the alignment is best in the center and decreases as it moves closer to the ends. So it would follow that the sheet would not fail at the center, where it is stronger, but more towards the ends where it would be weaker.

Another way the material responded as expected is with its recovery. Recovery is defined as how much a material will revert back to its original shape after being deformed. After the CNT sheet experienced any bit of strain and once the horizontal width began to decrease there was no recovery. Even at the lowest load of 10 N there was still no recovery from the small amount of alignment that had taken place. This signifies that once the CNT is aligned it is irreversible and will hold that form indefinitely.

The samples were also analyzed using the Energy-dispersive X-ray spectroscopy (EDS) to confirm the CNT sheets had an elemental composition consistent with what the manufacture claims as well as used to establish a baseline to compare with CNT sheets exposed to UV radiation. All four samples that were tested contained over 94% carbon with small traces of iron (4.7%) silicon(.62%) then small traces of ambient elements such as oxygen and nitrogen. The larger amount of iron and silicon were expected since both materials are used in the CVD process.

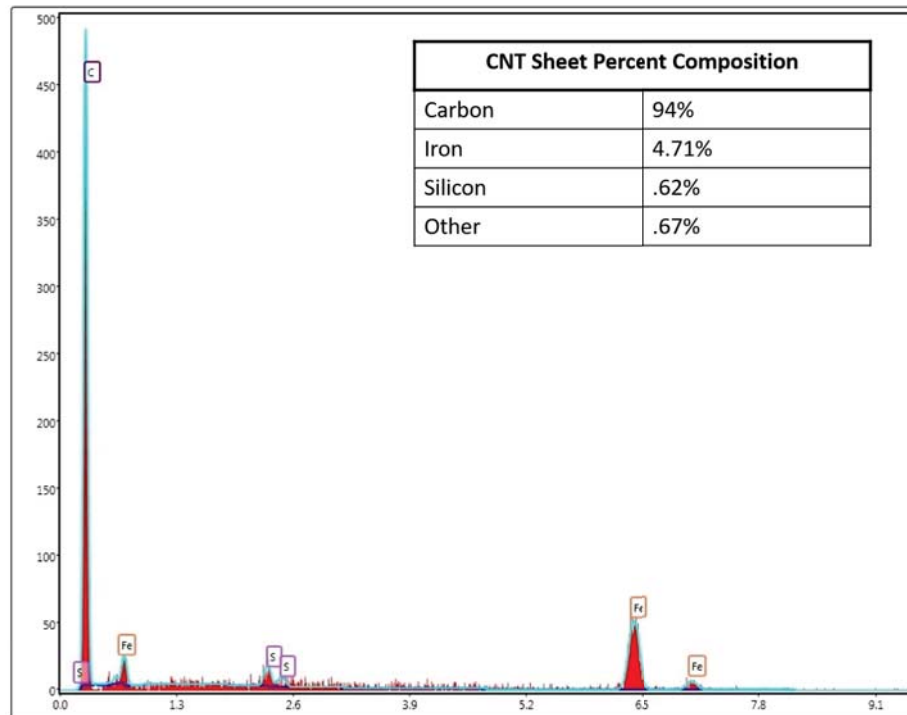


Figure 4.16. EDS image from a CNT sheet sample.

Based on these results, it has been shown that the CNT sheets produced by Nanocomp are consistent in both mechanical properties and chemical make up as these results match the values found in other work using Nanocomp CNT sheets [83]. The material production has proven to provide a uniform product that has in family behavior throughout the specimen and provides results that are in line with accepted characteristics of CNTs.

4.4 Ultra Violet Exposure

4.4.1 Change of Weight and UV Exposure

The UV rays the sample was exposed to were measured at 254 nm which registers as UV-c radiation. Inside the vacuum chamber the exposure measured was approximately $3 \text{ mW}/\text{cm}^2$. Referencing NASA Technical Memo 4527, it specifies an intensity at 254 nm as $0.0227 \text{ W}/\text{m}^2$. Dividing the intensity measured by the NASA provided amount expected gives a ratio of intensity. Multiplying this ratio by the length of the test (200 hrs) and dividing to convert to days than years provides a value of space equivalent dosage of 3.02 years worth of space radiation.

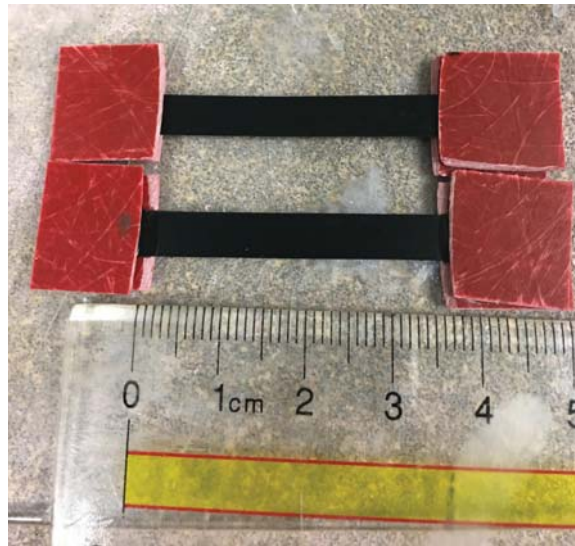


Figure 4.17. Samples after UV exposure

The tensile tests were used to find the UTS of the CNT sheets after exposure to 200 hours of UV rays. This time period was chosen to guarantee enough exposure and to explore the possibility for this to be an area of further study. The test was performed on two separate samples which were first measured to see how much mass loss was experienced.

Table 4.8. CNT Weights Before and After UV Exposure

	Wight Before (g)	Weight After (g)	Change (g)
1	0.0031	0.0029	-0.0002
2	0.0026	0.0025	-0.0001
3	0.0031	0.0033	+0.0002
4	0.0026	0.0027	+0.0001
5	0.0026	0.0033	+0.0007
1	0.0040	0.0046	+0.0006
2	0.0039	0.0036	-0.0003
3	0.0044	0.0047	+0.0003

As can be seen from the table 4.8, there was not a real measurable amount of mass loss or gain with all changes being in the realm of error for the Voyager Pro scale which has readability of 1 milligram. This shows that after 200 hours, there is very little physical effect on on the CNT sheets, which will be confirmed in the SEM and EDS discussion in the following sections.

4.4.2 Tensile Tests

The results of the two samples that were tested can be seen in Figure 4.18 as compared to the average of the tensile test of unexposed CNT sheets as well as three other unexposed samples of the same 5 x 50 mm size to better directly compare results

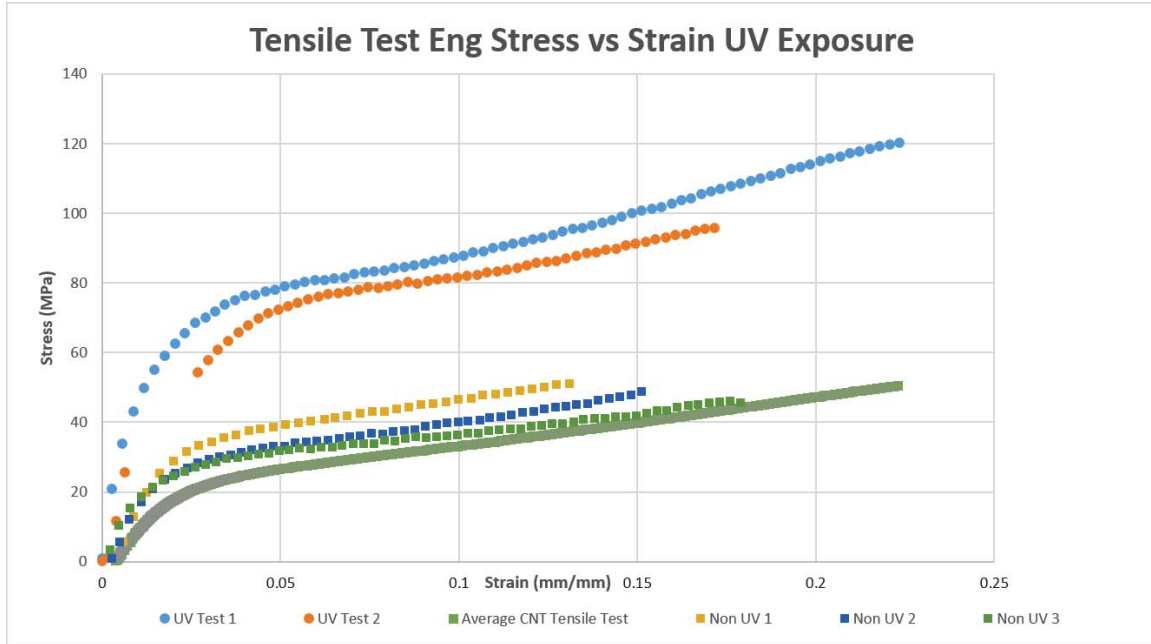


Figure 4.18. Engineering stress vs strain tensile test of UV exposed CNT sheets.

The UTS determined from the engineering stress of the tested two samples were 120 MPa and 96 MPa, noticeably higher than the results from the unexposed UV samples that were between 50-60 MPa. The yield stress was also higher, at approximate 70 MPa compared to the 23 MPa yield stress seen in the unexposed samples. The Young's Modulus for these samples is 4.01 GPa, a close to four times increase. This was not expected given the typical response to UV rays from materials as discussed in Chapter 2 is to weaken and break apart. The SEM images of the samples are also below

Possible explanations from the increase in strength could have something to do with the alignment of the CNTs from the UV rays.

4.4.3 UV Creep Tests

The results of the creep tests as compared to the average creep stress for the 15 N tests are seen in Figure 4.19. From the higher Young's Modulus, the amount of strain the UV exposed sample experienced was less at corresponding stress levels than

the unexposed samples. Of the two sheets that were tested, the samples behaved differently during the creep portion of the tests. For the first sample, the CNT sheet responded similarly to all the other tests, with very little change in final strain once the load up was complete and the final load was applied. The second sample, however, saw an increase in strain during the creep portion, more than any of samples tested as a part of this research. Based on the limited data there is not enough information to form a conclusion as to why this occurred and it certainly warrants further testing. All unexposed samples tested at the 15 N tests experienced yielding, which was determined by its visible necking, and also the strain rate was nearly identical once sample had yielded and during the time in twas in creep. The exposed samples were tested at a comparable stress level (40 MPa) but did not see hardly any necking.

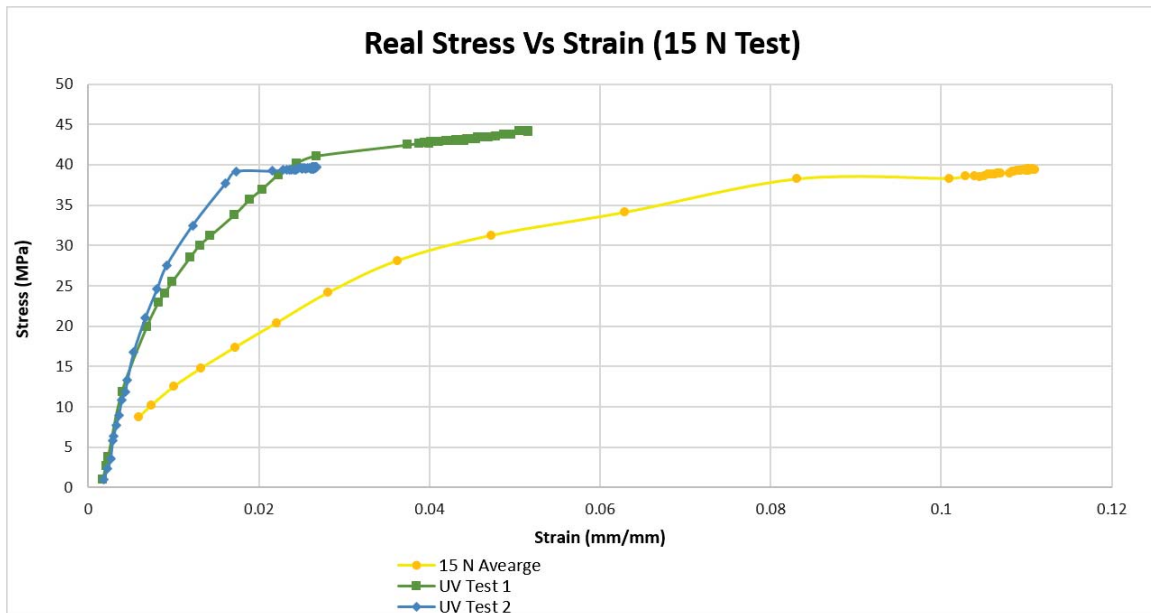


Figure 4.19. Real Stress Vs Strain of UV and Non UV Exposed CNT Samples in creep

The shape of stress vs strain curve from the UV exposed sheets is most similar to the the creep results of the 10 N unexposed tests. For both samples, neither was tested at a load that was above its yield stress point, so the stress vs strain rate would

be nearly linear throughout the loading. There is still some variations between the curves, so based on the limited amount of data it is difficult to infer or classify the materials response. What can be said is that the unexposed sheets have an increased performance at similar loads as compared to unexposed sheets.

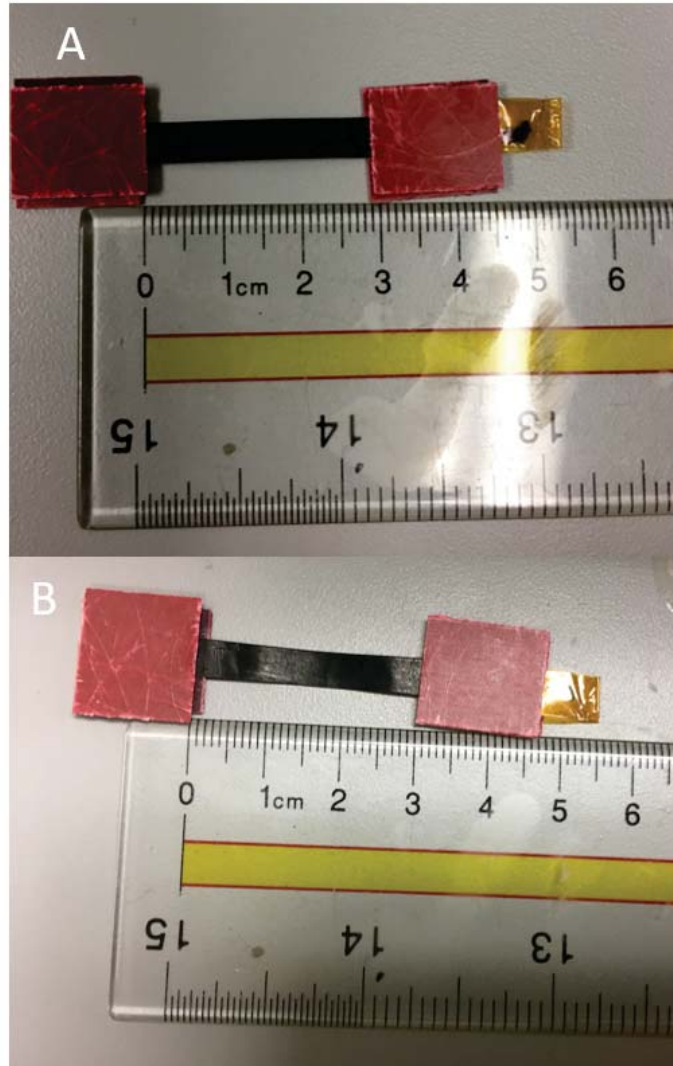


Figure 4.20. (A) UV exposed CNT sheet before creep test. (B) UV exposed CNT sheet after test. Almost no visible necking and only a slight increase in length was seen after testing

As stated above, the samples did not yield or show any deformation during testing as seen in Figure 4.22. Even though the UV exposed samples were originally thinner than the non exposed samples and the stress that were applied were similar, there

was no visible necking at stresses where other CNT samples did experience it. During research it was pointed out that CNTs are stronger when they are in less of a bulk form. Because the samples were cut in a smaller sheet, this could account for some of the increased strength properties but this alone could not explain the trend of 2-4 times increase in performance.

4.4.4 SEM and EDS Imaging

SEM imaging was taken to look for potential changes to the structure after UV exposure in untested samples as well as samples that had experienced creep.

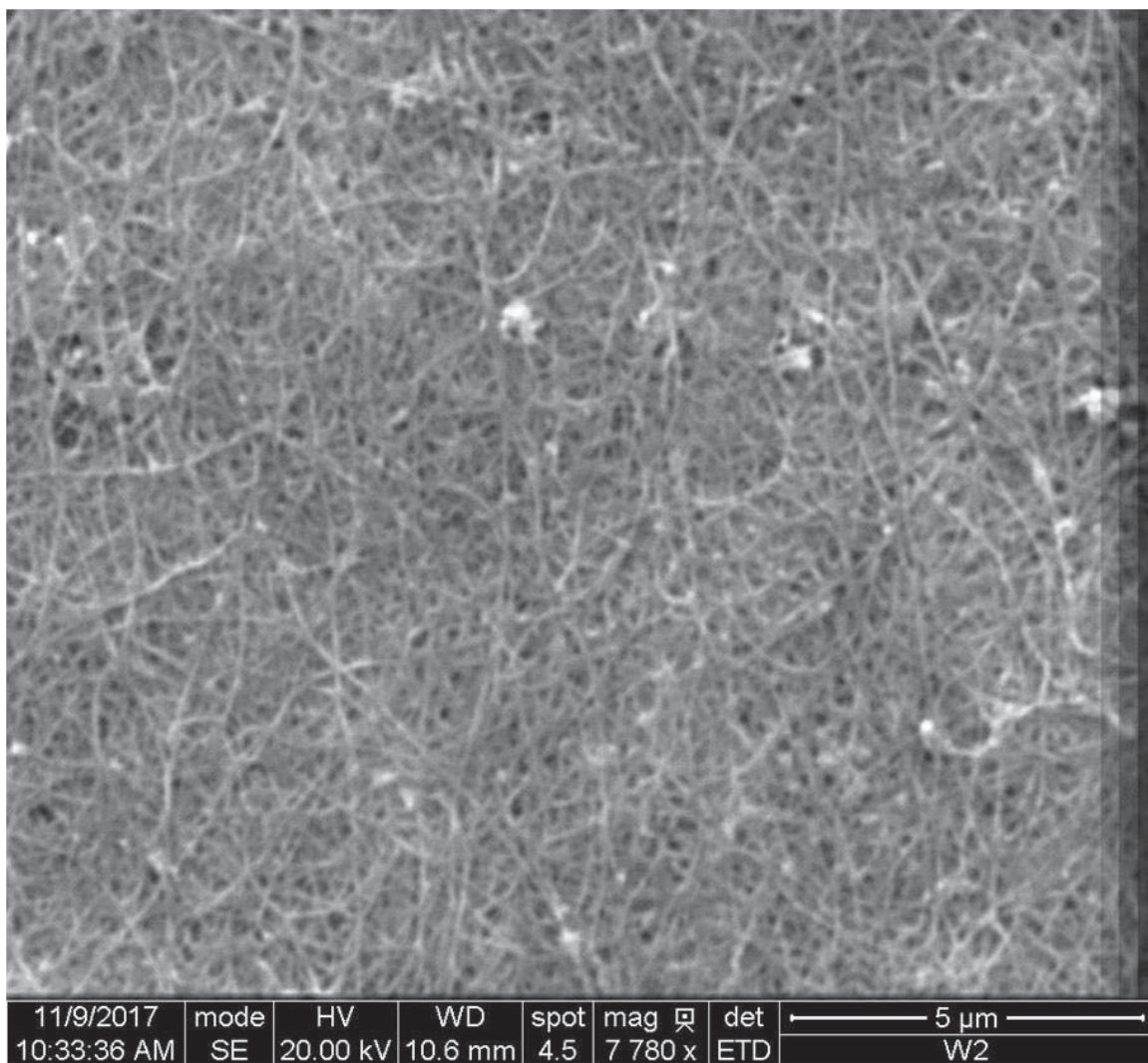


Figure 4.21. CNT sheet sample after exposure to UV conditions

From Figure 4.21 the individual CNTs appear early identical to what is seen in unexposed CNT sheets. There is no noticeable alignment between the tubes nor is there any damage, decay, or separation that occurred from the UV rays. To understand if there were any chemical changes or changes in proportions or atoms present, EDS was performed.

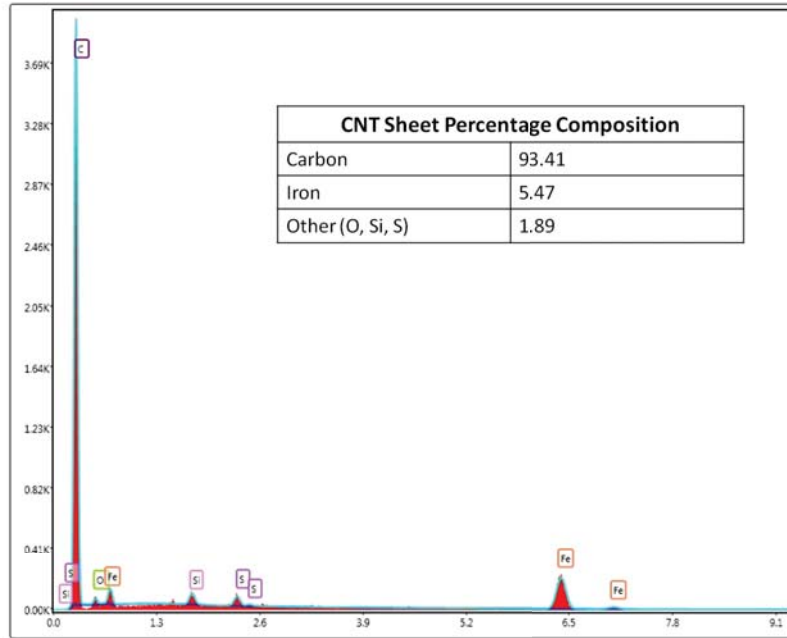


Figure 4.22. Elemental composition is nearly the same, with this sample having just a slightly larger composition of Iron which is deposited into the material during the manufacturing process and within expected limits

There was not any noticeable change in the elements that were present in the sample after exposure to UV. The carbon amounts still accounted for over 93% of the CNT sheets elements. The weight percentages did not see any changes showing that there was no loss of material which is consistent to the weight measurements taken before and after UV exposure.

CNT sheets after creep testing were also analyzed using SEM. Since the samples did not yield and did not pass their yield stress there was hardly any alignment so photos will be posted in the appendix.

4.5 Summary

This chapter discussed the results from tensile test and creep test of CNT sheets as well as the tensile test of UV exposed CNT sheets and provided discussion based on the findings. The material was tested for tensile strength and its response to

three different creep loads. The CNT sheets behavior of stress and strain response at different loads was found to be statistically normal and the material properties found were agreeable to other published results. During the creep tests, CNT sheets all showed varying degrees of strain based on final load. When the final load had been achieved for each test the strain grew only by slight amounts never more than .01 mm/mm. None of the samples ever showed strain recovery once the load had been removed. Samples analyzed using SEM showed an increased strain alignment based on increased load as expected based on literature [12]. From the tests, an average Modulus of Elasticity of 1.1 GPa, Poisson's Ratio of 0.40, strain hardening exponent of .58, and strength coefficient of 181.72. CNT sheets exposed to UV rays were tensile tested to and found to have an increase in UTS of two to three times and corresponding Young's Modulus of 2.1 GPa .

V. Conclusions and Recommendations

5.1 Chapter Overview

The goal of this research was to understand the creep behavior of CNT sheets through tensile and creep testing as well as exposing CNT sheets to UV rays and begin to understand their behavior after exposure. This chapter will review the work that was done to answer those questions as well as discuss the results that were found. Recommendations for future work with CNT sheets will also be made.

5.2 Summary of Work

This research focused on the mechanical behavior of CNT sheet. The CNT sheets were obtained by Nanocomp and tested uniaxially in tension by tensile testing methods.

To begin, an ultimate tensile strength had to be found for the material. This was done through a tensile test. The samples were cut into 13 mm x 70 mm strips and then attached by glue to four 15 mm x 15 mm pieces of fiberglass to provide extra grip during loading. During the tests, a camera was placed above the specimen to record width measurements so that real stress and engineering stress could be calculated as well as a Poisson's ratio.

The results of the test were in congruence with findings of other researchers and were presented. Each sample yielded closer to the edge and not in the center as to be expected based on the poor alignment in areas that do not see changes in alignment due to load [12], the Modulus of Elasticity was found to be 1.1 GPA, and the Poisson's ratio was 0.40 over the range of the samples tested. These values are within accepted limits of what is expected of the CNT sheets based on work done on other forms of CNTs, theoretical values, and the limited work done on CNT sheets from other

researchers which validates the consistency and reliability of manufacturing methods. Since these values are lower than the theoretical strengths of individual CNT strands, researchers have arrived at several explanations that mostly revolve around alignment of individual strands and defects in the CNT tubes that could explain the performance gap.

The primary study, however, was on the response of the sheets undergoing a sustained load. In creep testing, the sheets were held at several loads based on the UTS for a period of 48 hours. There were five samples tested at each load level and then the engineering and real stress was calculated and graphed. The real stress could be calculated based on width measurements taken during each test by a camera that was mounted above the samples.

Each test would take five minutes to reach its final stress level and then hold a constant load for 48 hours. Data from the test was collected and graphed on several stress strain curves. The data that was gathered was checked for normalcy and all were found to be within a 95% confidence interval. From these graphs, it was shown that once the CNT sheets reached their target stress level, the change of strain over the next 48 hours was minimal not exceeding 0.01 mm/mm. The largest change was seen during the 20 N tests and it was only a 5% increase of strain from the beginning to end of the test. The samples all behaved similarly when they were loaded, the width thinning at the middle and the edges curving inward, however no sample no sample tested experienced an increase in the strain rate, therefore, no sample entered the third range of creep or failed during the 48 hour tests. From the graphs, power law curves were generated showing that there was some power law relationship between engineering stress and strain as was predicted. Using the SEM, the CNTs inside the sheets were shown to become more aligned as the load increased. The length of loading did not seem to have an effect on the alignment of the individual CNTs, since

there was little change in strain once the load was kept constant.

CNT sheets were preliminary tested after UV exposure to determine the validity for future studies on the effect of UV exposure on strength properties. CNT sheets were tensile tested after being subjected to UV rays for a period of one month. Typical material responses after being in a UV environment are weight loss and degradation of material properties. The CNT did not see a significant change of weight during this time . During tensile test the UV exposed CNT sheets had a higher engineering stress at failure then the unexposed sheets. This could be from the difference in sheet dimensions since the UV exposed sheets were 35 mm x 5 mm where the original sheets were 70 mm x 12mm. During creep test the sheets also saw less strain at the same stress level as compared to the unexposed sheets. Only two samples were tested in tensile and creep but these initial results certainly justify a more thorough and focused research effort.

5.3 Future Work

Since CNTs are still a relatively new material and CNT sheets are just now beginning to be reliably manufactured and studied, there are many material properties that require characterization and potential applications that can still be tested. Increasing the time of the tests so that a full creep curve with all three regions can be created would be the next step. Fatigue testing and cyclic load testing usually follows a creep test to understand the wear resistance of a material. Electrical and thermal properties were not studied in this work so observing those changes as the CNT sheets undergo a sustained load would provide a better understanding of how the alignment effects conductance. Since alignment has shown to strengthen the CNT sheets, tensile testing pre-stressed sheets to see if there is an increase in UTS could be valuable as a way to increase material properties. The effects of in increased or decreased load

rate on alignment or total strain could also begin to help find a relationship between these two parameters.

Post failure examination of creep tested samples were not fully performed in this work. Studying the failure modes during tensile tests and creep tests would provide some insight into what is occurring on a molecular level inside and around the tubes that make up the sheet. SEM images of the failed samples could be taken and analyzed to find commonalities among samples and might highlight what weaknesses or defects are most often the cause of yielding and fracture. Other post examinations that could be studied would be the quantifying of the CNT alignment after stress and how that relates to increased strength properties. By using Raman spectroscopy and analyzing the intensity of the D-peak, which signifies the amount of sp^2 bonds in an area which can be related to the concentration of CNT tubes, a prediction of performance could be formed.

Removing defects and aligning CNTs has been found to be a crucial factor to overcome for mechanical performance limitations of CNTs. Because these defects have such a detrimental effect on material properties and because of how expensive CNTs currently are to produce, large scale use of CNTs has not been practical or feasible. Work has been done to minimize these defects during production, but giving the random nature of the individual carbon tubes and the vast number of defects in even a small strand of yarn, there is a low probability of removing all the defects within the CNT sheets. With this in mind post, production processes should be examined to minimize these defects. Thermal treating has been used to correct minor defects in carbon nanofibers so there is a potential that some defects could be corrected after they are formed as a way to strengthen the material.

Future studies involving space environment and its effect on CNT sheets will need to be conducted before any material or system using CNT sheets is ever developed.

Every test that was previously listed would need to be replicated after UV exposure. Based on the results, UV exposure results in an increase in material properties. This increase needs to be quantified and reason why needs to be explained. This research only did a small amount of samples and for, what was determined by analyzing the results, not enough time. The tests need to be conducted on the time scale of weeks and months to see what the limits of the material are. Seeing how UV rays effect CNT's other material proprieties will provide a developers and engineers better guidelines on how CNTs could respond in space and if they are a material that is worth using.

5.4 Conclusion

Carbon Nanotubes and their applications have only begun to be studied. Work on understanding this unique material must continue to realize the full potential of this material system. There must also be continued growth to improve the production process so a stronger and more reliable product can be made at a reasonable price. Only when those two things happen will there ever be the widespread application of carbon nanotubes where scientists can maximize their potential and take advantage of CNT's properties to make materials to be used for space to everyday life.

Appendix A. Test Data

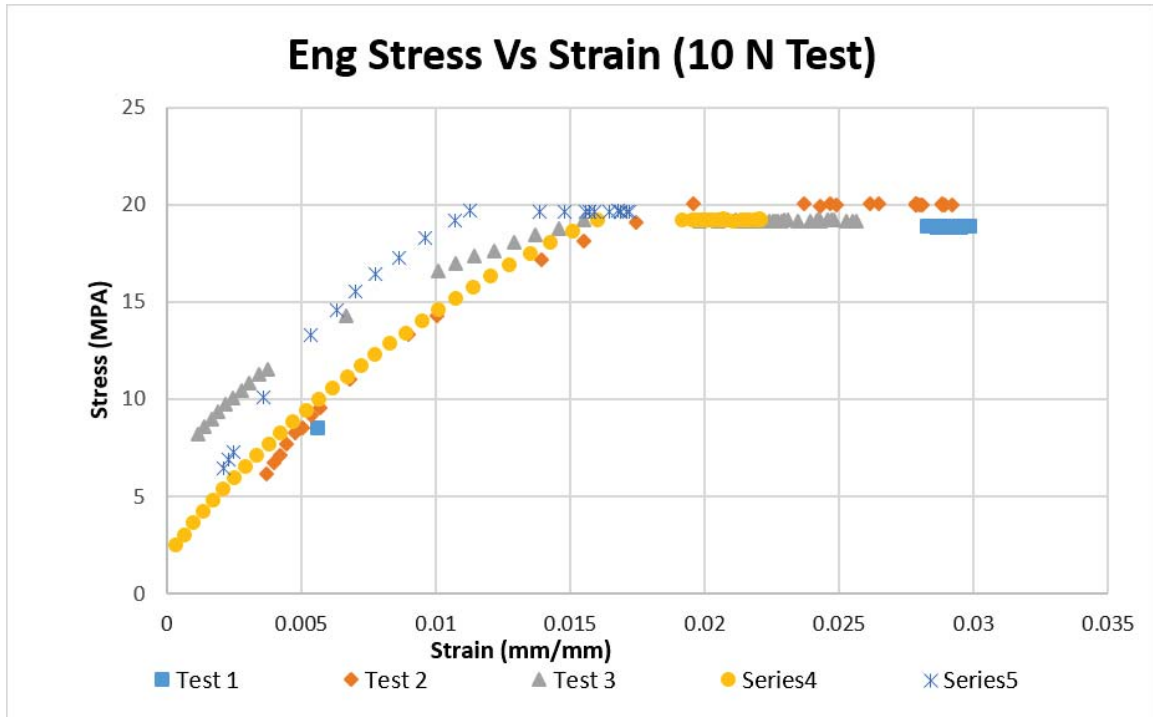


Figure A.1. 10 N Eng Stress vs Strain

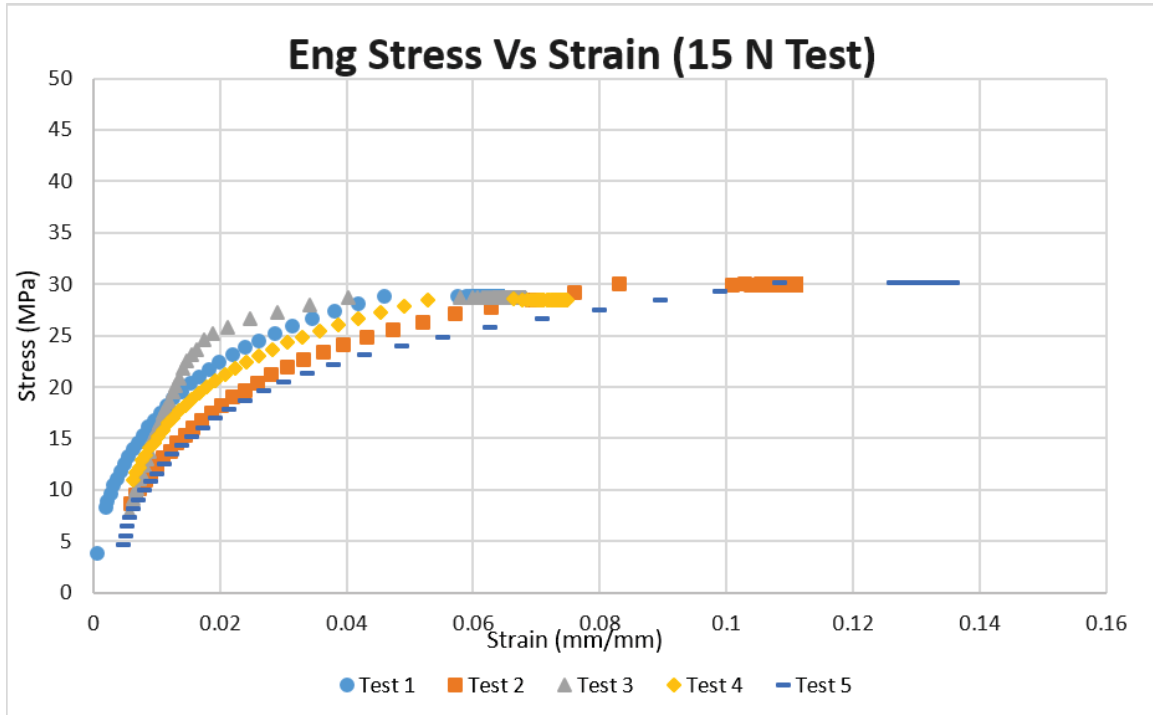


Figure A.2. 15 N Eng Stress vs Strain

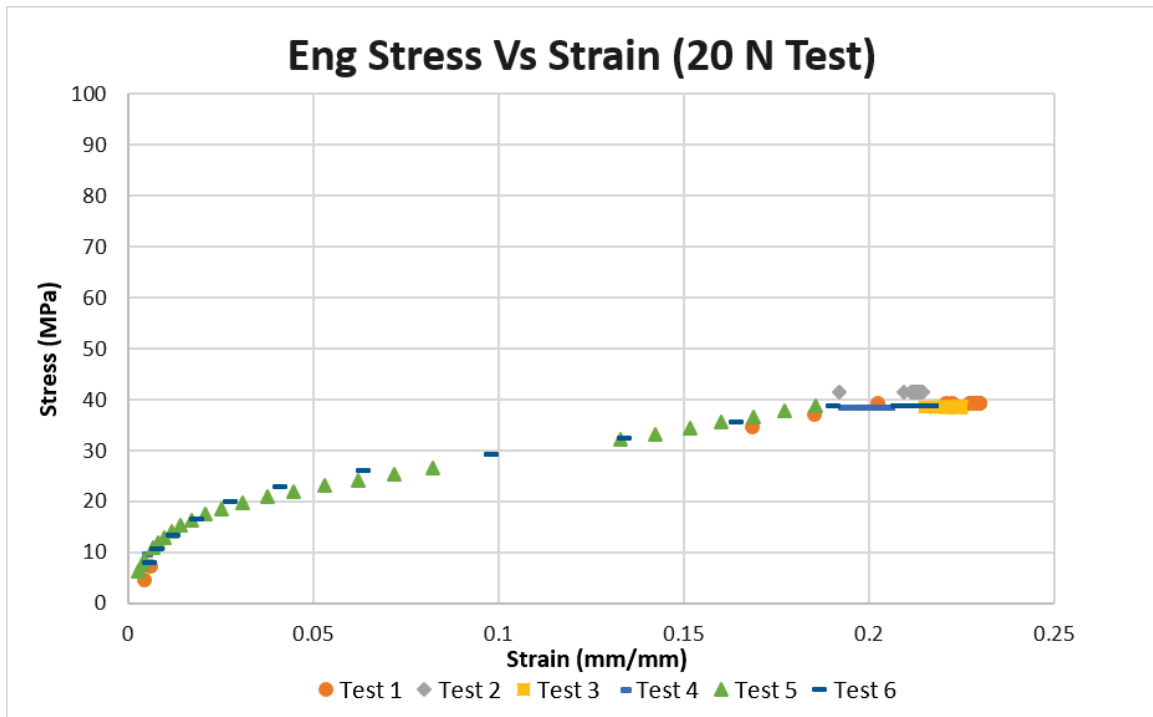


Figure A.3. 20 N Eng Stress vs Strain

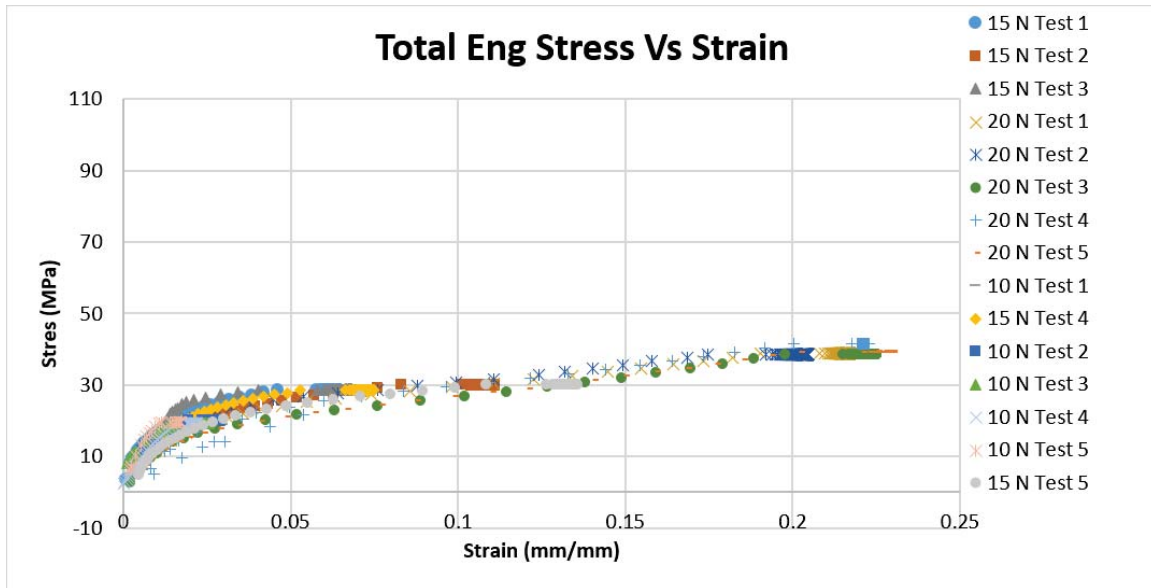


Figure A.4. Combined Eng Stress vs Strain

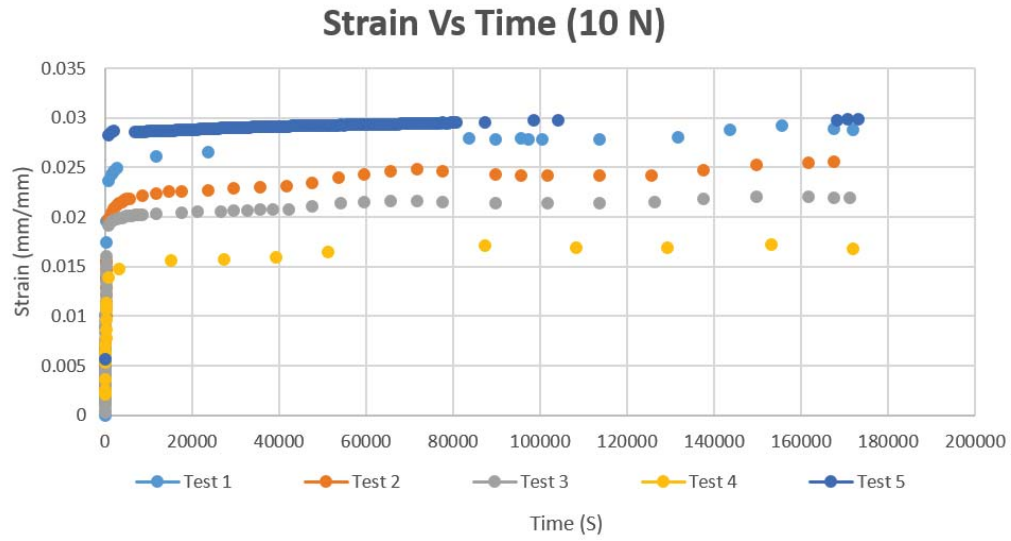


Figure A.5. 10 N Strain vs Time

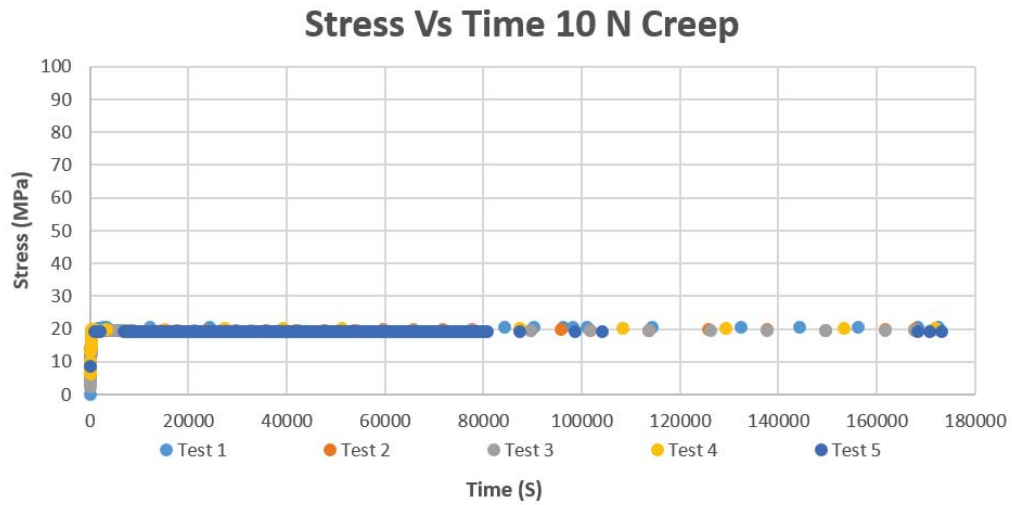


Figure A.6. 10 N Stress vs Time

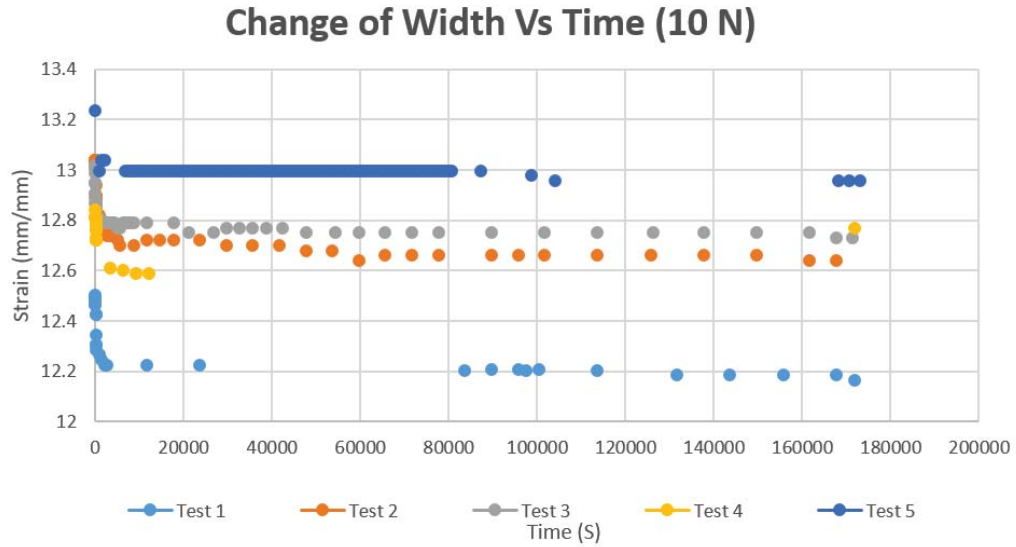


Figure A.7. 10 N Change of Width Vs Time

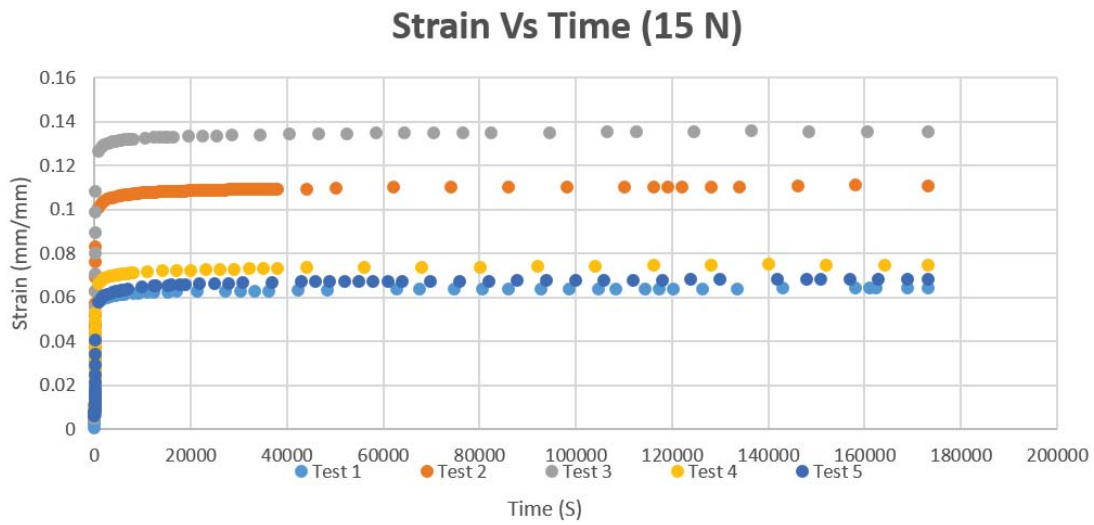


Figure A.8. 15 N Strain vs Time

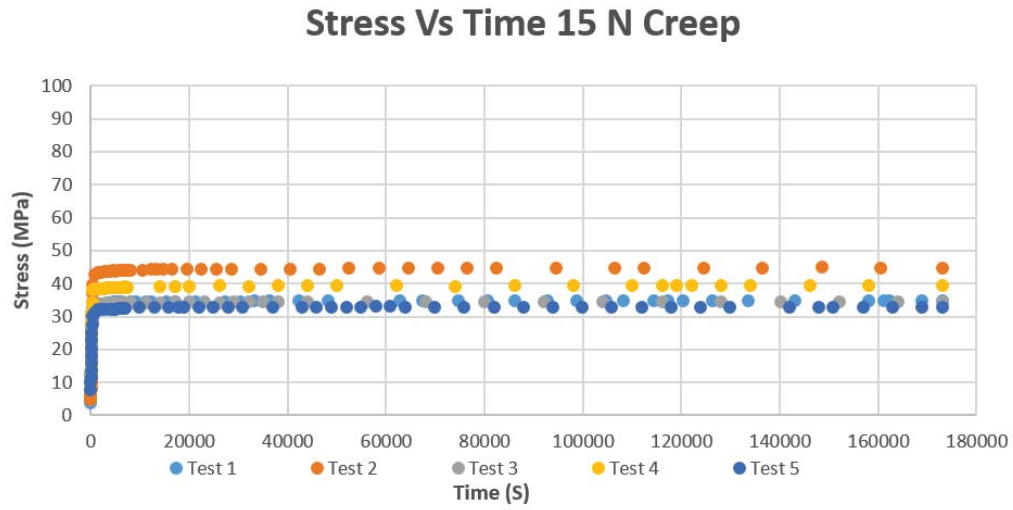


Figure A.9. 15 N Stress vs Time

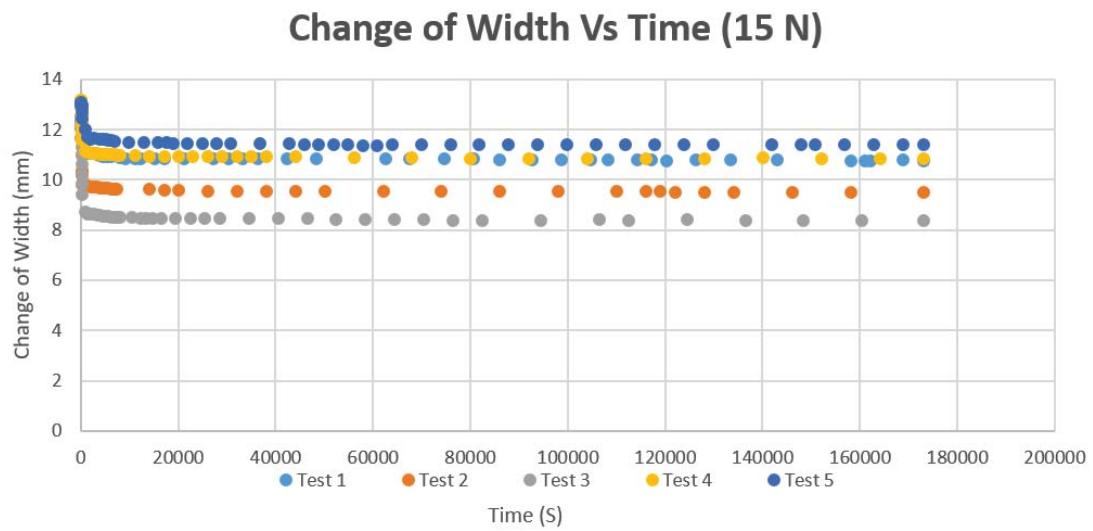


Figure A.10. 15 N Change of Width Vs Time

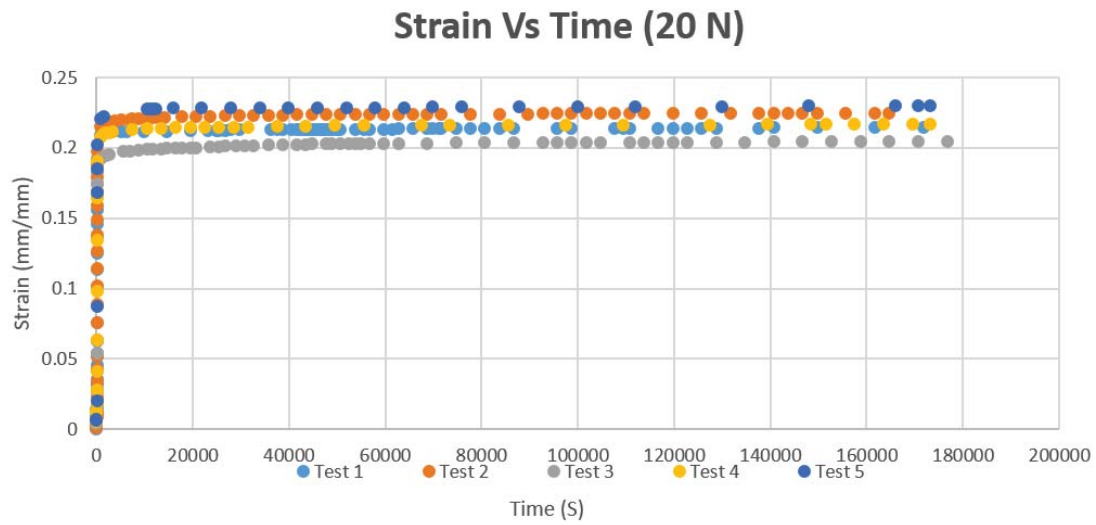


Figure A.11. 20 N Strain vs Time

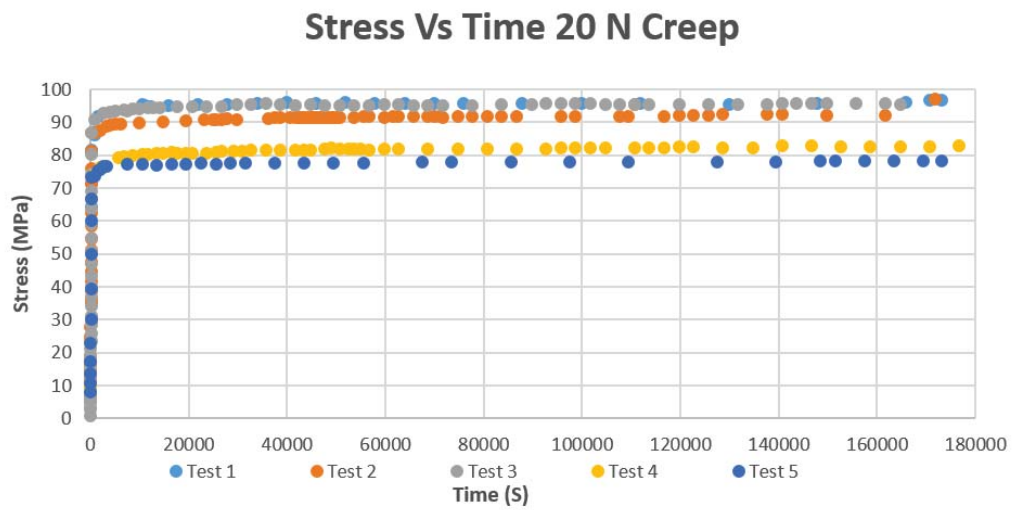


Figure A.12. 20 N Stress vs Time

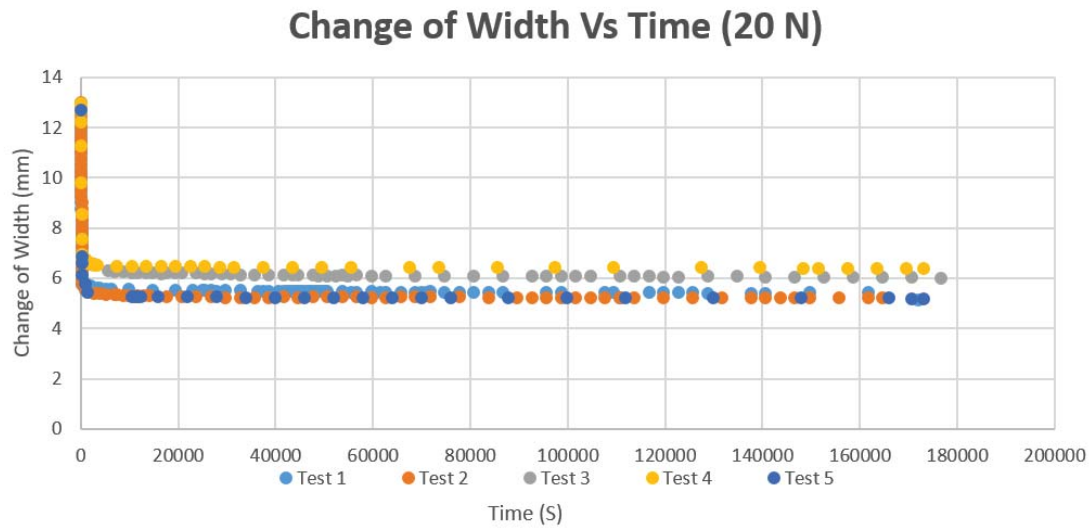


Figure A.13. 20 N Change of Width Vs Time

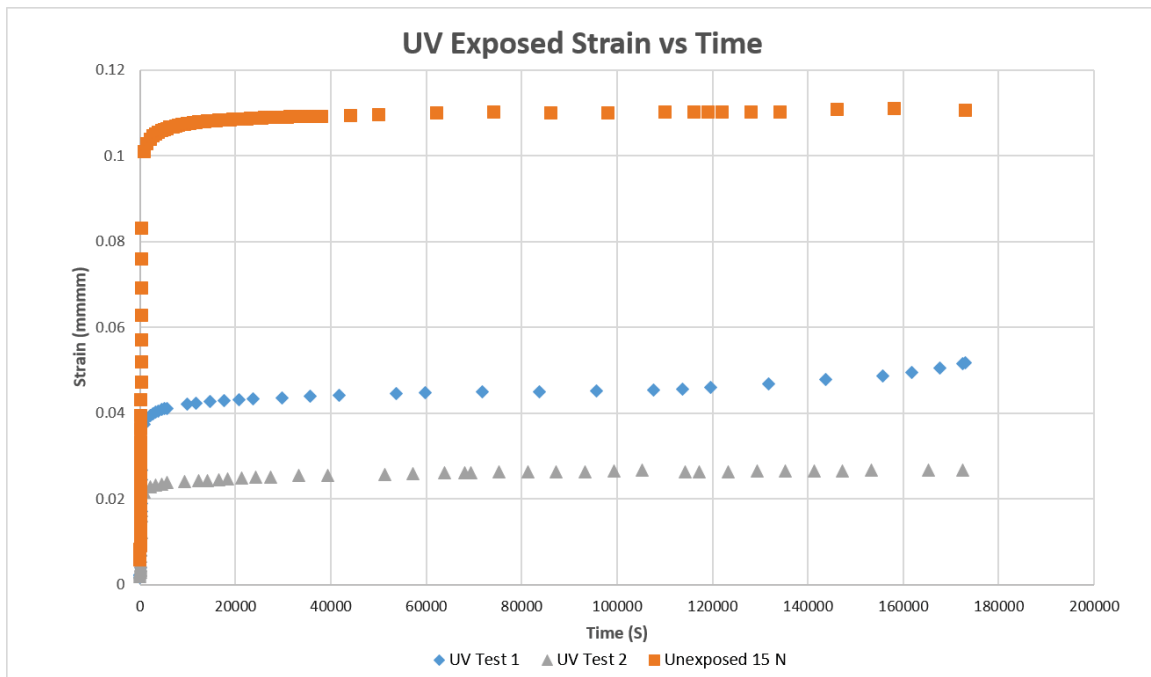


Figure A.14. UV Strain vs Time

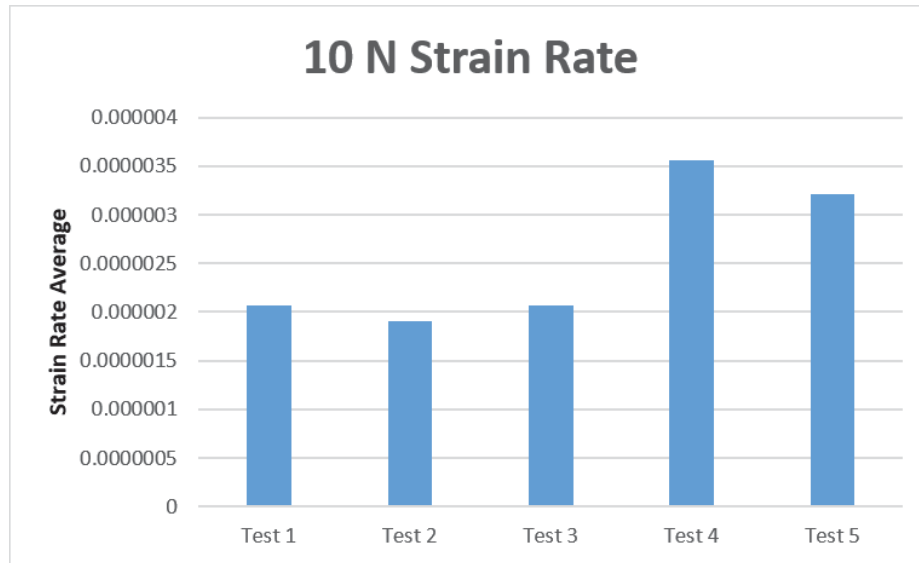


Figure A.15. Bar graph showing the average strain rate for the five samples tested at 10N

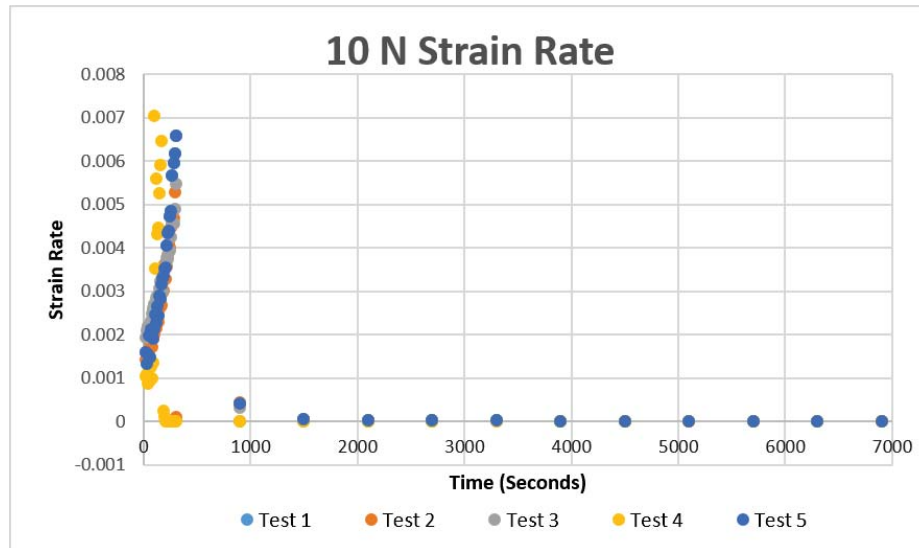


Figure A.16. Strain Rate vs Time for 10N tests

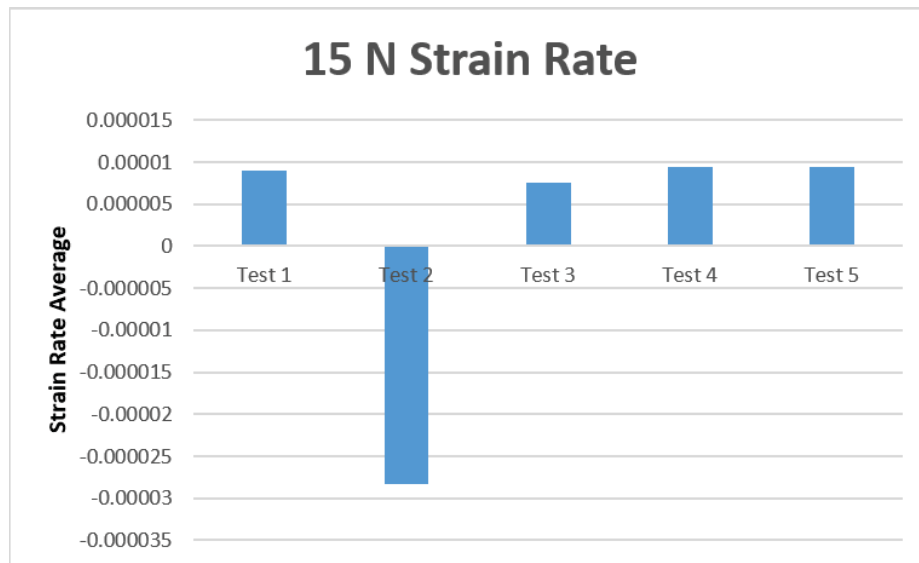


Figure A.17. Bar graph showing the average strain rate for the five samples tested at 15N

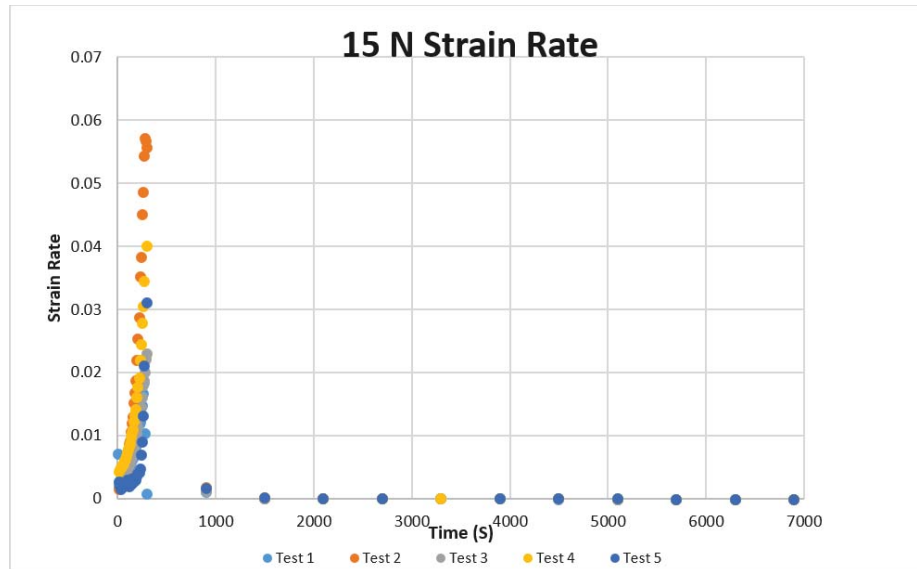


Figure A.18. Strain Rate vs Time for 15N tests

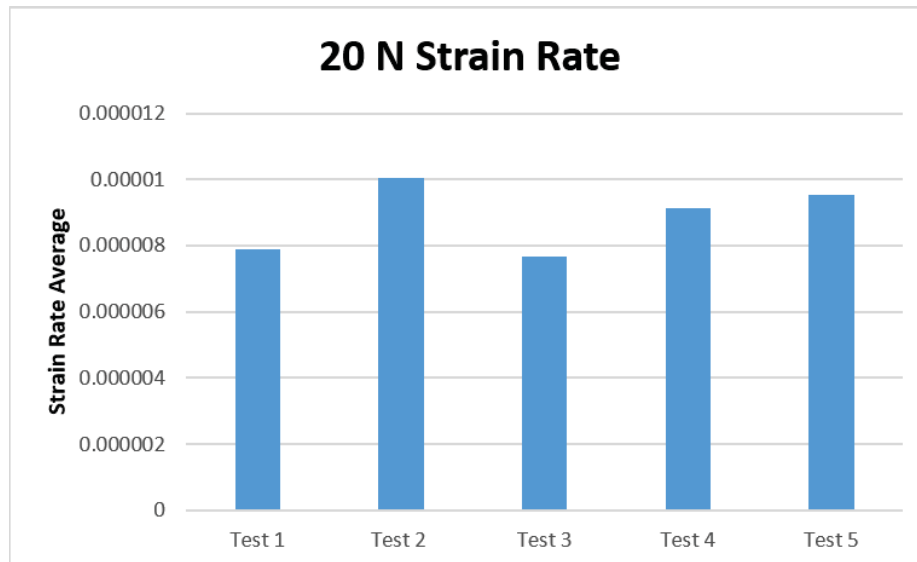


Figure A.19. Bar graph showing the average strain rate for the five samples tested at 20N

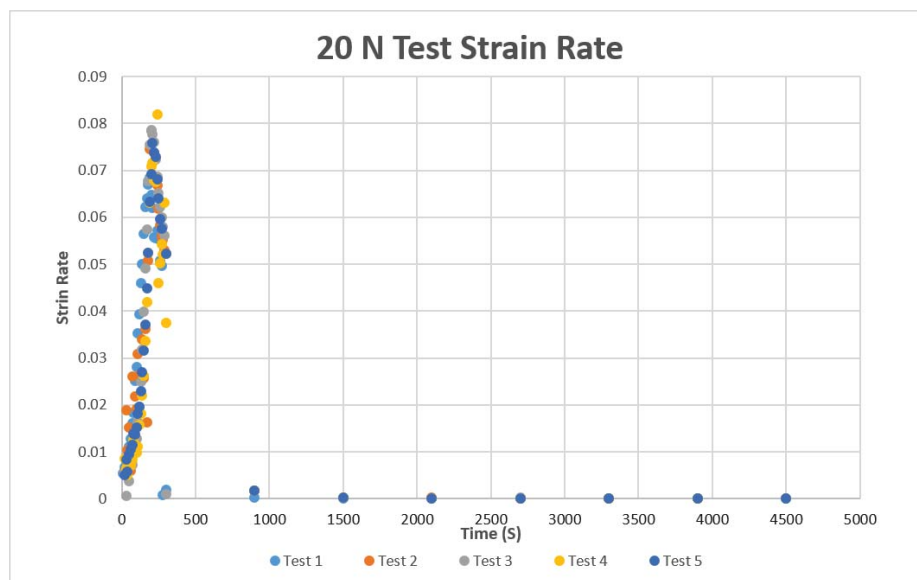


Figure A.20. Strain Rate vs Time for 20N tests

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14. ABSTRACT Carbon nanotube sheets are a new and promising material with properties such as high tensile strength and low density that are ideal for future applications in the aerospace industry. Before those materials can be implemented in future air- and spacecraft, their mechanical properties must be fully understood. Tensile and creep tests are the first and necessary steps to being able to better understand the properties and failure mechanics of any new material. This research is to understand the long term effects and performance of CNT sheets under tensile load, specifically through tensile tests, creep, and tensile tests after exposure in a space like environment. The data was used to create stress vs strain plots in order to mathematically quantify the tensile and creep behavior of the CNT sheets. The sheets were also exposed to Ultra Violet radiation in order to understand how the strength properties changes under relevant space like conditions.						
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