STUDYING THE EFFECTS OF ACID TREATMENTS ON THE ELECTRICAL BEHAVIORS OF CNT WIRES

A Thesis by

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Submitted to the Department of Mechanical Engineering
and the faculty of the Graduate School of
Wichita State University
in partial fulfillment of
the requirements for the degree of
Master of Science

May 2014

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The following faculty members have examined the final copy of this thesis for form and content, and recommend that it be accepted in partial fulfillment of the requirement for the degree of Master of Science with a major in Mechanical Engineering.

Ramazan Asmatulu, Committee Chair

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DEDICATION

To my wife, Sarah, and Dr. Ramazan Asmatulu who were instrumental in maintaining my motivation to formally complete this task.

ACKNOWLEDGMENTS

I would like to thank my wife, Sarah, for giving me the challenge and chance to earn another degree. Without her leading by example, I would have become an intellectual hermit. I would also add Dr. George Talia and Dr. Ramazan Asmatulu to the list of folks who offered intellectual challenges and motivational inspiration in the pursuit of this degree. Both have proven to me that age is no barrier to intellectual discipline.

ABSTRACT

This thesis presents the results of chemically treated carbon nanotube (CNT) yarn in a non-stretched or non-compressed condition. Chemical treatment has been proven to increase the tensile strength and conductivity of CNT wire while under tensile load. In this study, chemical treatment was administered to the CNT wire by emersion without stretching it and simultaneously measuring conductivity. Chemical treatment significantly changed the physical dimensions of the CNT wire, including an increase in diameter and a decrease in length. Physical dimensional changes were not measured, but they did result in changes to conductivity, which were recorded as they occurred. It is obvious that after a period of time, the acid treatment caused separation of individual CNT fibers, which resulted in an overall decrease in conductivity. The acid bath created covalent bonds between the carbon nanotubes and oxides and hydroxyls, while ionic bonds, which presented as increased conductivity, were established. In most test cases, the original conductivity was regained, but then appeared as if the CNT wire lost conductivity to the point of an open circuit. While this study seemingly yielded inconsistent conductivity results between different plies tested, it could be assumed that the inconsistent conductivity is the result of varying tension in the test specimen. One conclusion of this study is that in order to make a direct conductivity comparison between different sized CNT yarns there needs to be a definable consistent tension applied to the CNT wire being tested. Another conclusion is that once a higher-ply CNT wire has begun to un-wind, hand spinning the wire will not recover the conductivity. The final conclusion of this study is that the current spinning technology coupled with acid treating will not permit CNT wire to be used as a direct replacement for copper wire.

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LIST OF ABREVIATIONS / NOMENCLATURE

ATR spectroscopy	Attenuated Total Reflection
CNT	Carbon Nanotube
DI	Deionized
EDS	Energy-Dispersive X-Ray Spectroscopy
FTIR	Fourier Transform Infrared
MWCNT	Multi Walled Carbon Nanotube
SEM	Scanning Electron Microscope
SWCNT	Single Wall Carbon Nanotube
UTS	Ultimate Tensile Strength

CHAPTER 1

INTRODUCTION

Early studies have shown that individual carbon nanotubes (CNTs) tested very high for mechanical strength, thermal conductivity, and electrical conductivity [1]. These early studies also developed may uses for nano-sized material. Then the question became how to transmit the advantages of the nanotubes to macro uses. One of the first developments was the ability to grow individual tube lengths in the 300 to 400 μm range, but this was not generally considered useful by itself in a macro world. However, it was found that by using already-existing spinning technologies, the short fibers could be joined to make a continuous long fiber. Two methods most commonly used for this purpose are an ancient technology called wet spinning and, later on, dry spinning.

Characterization testing of the spun CNT wire has shown that electrical conductivity increases with increased density [2]. Spinning CNT fibers provides a portion of the compaction (conductivity) or density for individual CNT tubes. The question arises: Can chemical treatment cause the same increase in uniform density without having to increase tension in the CNT yarn or otherwise manipulate its mechanical properties? These two areas of research are important because of the method currently used to install copper wire in aircraft.

Today, wire bundles are built in a form approximate to the installed shape. Then connectors are installed, and a final conductivity test is performed to check continuity. In aviation, it is considered bad practice to install a wire bundle that produces a strain on it since that strain will be transferred to the connector. Once that occurs, two likely failure modes will happen: the connector pin will be pulled through the connector, thus breaking contact, or the wire will be physically separated from the pin shroud. In either case, strain on the wire would be relieved as part of the repair procedure. The concept of conductivity without strain applied to the CNT wire will be explored in this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Wet Spinning

Xiao et al. studied a method to change the chemical properties of the CNTs by coating multi-walled carbon nanotubes (MWCNTs) in a custom-designed chemical process [3]. This study was based on the large surface area and conductivity of CNTs, which could be used to produce thermionic emitters that would work at low applied voltages (4.5 to 4.6 eV) with the final objective being a low thermal electron sources such as vacuum fluorescent displays, x-ray tubes, and electro guns.

The yarn was drawn from a MWCNT forest (collected fibers) using a low-pressure chemical vapor deposition growth process and wet spun through droplets of barium salt. The droplet solution was composed of 9.2 g of barium nitrate, 7.4 g of strontium nitrate, 0.3 g of calcium nitrate in a 50 ml volume of ethanol, and 50 ml volume of de-ionized (DI) water. The solvent was dried at 100 ºC in air before heating it to a temperature of 1,100 to 1,200 K for several minutes. The wire was placed in a vacuum and exposed to a direct current to cause the nitrates to change to oxides. The final chemical composition was tested using energy-dispersive x-ray spectroscopy (EDS) which showed the presence of barium and strontium but no nitrates and no measureable calcium.

The outcome of testing was that even after drying at 1,150 K it took about 20 minutes for a steady state emission to occur. That study concluded that Ba-MWCNT was relativity easy to process and yields low resistance at high temperatures (making good thermionic components), but the tensile strength is compromised by the high process temperatures.

2.2 Dry Spinning

Zhang, et al. has summarized some of the new ancient technology advances and advantages applied to spinning CNTs, which occur in both wet spinning of single-walled carbon nanotubes (SWCNTs) and dry spinning of MWCNTs [4]. The concept here is to determine the desired outcome and custom build a process around the CNT to yield the desired results. Zhang et al. investigated CNT fibers harvested from a wafer. While on the wafer, these fibers are collectively referred to as a "forest." This paper was able to substantiate the production of a strand of yarn approximately 50 m long and 2 μm in diameter. The 50 m of yarn was produced from an approximately 1 cm^2 wafer with a 200 μm forest width that was harvested and spun. The twist ratio for the CNTs was about 80,000 turns per meter, compared to much larger diameter cotton fibers, about 80 times larger than CNTs, which can only be twisted about 1000 turns per meter.

The yield of a single ply CNT yarn produced better strength results than typical wet spinning. The thickness of the yarn could be increased by taking two single ply strands of CNT yarn and twisting them together to form a two ply yarn. To further increase the ply, an additional single or two ply strands could be spun together until the desired diameter and /or ply was reached.

The main concept that needs to be retained from this is that spun CNTs are being harvested from a wafer that is uniform in height and pulled into a triangular shape called a web. The web is then rotated to form yarn, which can be further spun to from multi-count yarns. Finally, the tensile strength is better in both improved processes of wet-spun and dry-spun CNT yarn than can be achieved from the original spinning process. Two-ply CNT yarn used in this study tends to stay spun, but multi-ply CNT yarn has a natural tendency to unwind.

Tran; et al. also worked with dry spinning as a method of increasing tensile strength [5]. In that study, the increase in CNT yarn properties was obtained by longer CNTs on an ultra-aligned wafer and improving the spinning performance. The better spinning process may have been the result of a better understanding of how CNTs are spun into yarn.

Until the paper of Tran et al. was published, it was assumed that individual CNT fibers were pulled from the wafer and passed through the web before spinning. The authors identified a web fiber as being up to 100 nano fibers thick and multidirectional. Using modeling and the theory that showed that breaking the yarn was not breaking individual CNT fibers, they concluded that breakage was the result of loss of ionic contact between individual CNT fibers. Tran et al. were able to quantify the strength of the bond as a relationship defined as the length of contact between adjacent CNT fibers that utilizes the sliding force between fibers and corrugation.

Tran et al. postulated that the degree of compression of bundles and degree of condensation (packing) would contribute to the influence of the mechanical properties. It was further postulated that additional packing could be achieved by either increasing the twist or addition of a chemical treatment or both. The experiment in this paper used CNT forests created by chemical vapor deposition (CVD) that were approximately 300-400 µm long with diameters ranging between 7.5 to 8.5 nm.

To achieve denser packing, Tran et al. proposed a change to the original spinning method of drawing CNTs from the wafer along a wall through the web and then onto the bobbin. By passing the web through a set of rollers the CNTs could be drawn out a little further for better alignment before the web was allowed to spin. The as the web was being drawn out further through the rollers, chemical treatment could be applied in order to modify the properties.

Misak; et al. performed a study on CNT wire supplied by Nanocomp Technologies, Inc., Concord, New Hampshire, USA which is the same manufacturer supplier for the samples used in this thesis study [2]. Their study characterized the tension-tension fatigue behavior for three-ply yarn with five tensions, and their results yielded fatigue life data. While under various percents of tension the conduciveness was measured using a four point probe. Failure mechanisms of the CNT wire and damage due to tensioning were characterized and identified as the relative sliding of the yarn, formation of kink bands, and plastic deformation before breakage. Density measurements supported the conclusion of Tran et al. that the increase in conductivity was due to a more uniform density as a result of constriction of voids [5].

The conformation of the CNT wire was demonstrated by a detailed investigation of the mechanical behavior and measurement of electrical conductivity of the CNT wire under cyclic loading. The loading and conductivity was recorded for either 30-, 60-, or 100-yarn wires in the as received condition without chemical or spinning modification. Data for the stress vs. number of cycles to failure (S-N) curves was generated by placing the specimens in an MTS Tytron 250 machine for tensioning. At predetermined tensions, the machine was halted and a four point resistivity unit was used to measure the conductivity.

It was observed that as the tension passing through the CNT wire increased, the angle of the spun fibers also increased, from 37º to 25º. Conductivity measurements also increased from 800 to 1,300 S/cm because the CNT wire tension increased by a factor of 10 (5% to 50% UTS). The increasing tension reduced the cross-sectional area by compressing the CNT fibers. This was confirmed through MicroCT density measurements, which indicated there was a correlation between tension, diameter, and conductivity of the CNT wire.

2.3 Chemical Treatments

Min, et al. reported on a chemical treatment that improved covalent linking of compressed carbon nanotubes and inter-bundle spaces that improved the mechanical properties [6]. This work was preformed after the work of Tran et al. in 2009. Min's work addressed both wet and dry spinning methods, and would be classified as a hybrid method incorporating steps from both methods. It began as dry spinning by harvesting a wafer of uniform aligned CNTs. The CNT web was treated with 4-carbonxybenzenediazonium tetrafluoroborate to form carboxyphenyl groups. The carboxyphenyl groups were reacted with hexa(methoxymethyl)melamine, a cross-linking agent. The yarn was then drawn through another set of rollers to stretch and dry the yarn before winding onto a bobbin.

Details of this chemical reaction are complex and involve the formation of aryldiazonium salt on the yarn during the spinning process. The spun yarn was then passed through a second multifunctional amino cross-linker and cured in the presence of an acid catalyst. The cross-linker was polymerize in situ, forming a 3D polymeric network that fills inter-tube spaces and improves coupling between the CNT fibers. Covalent bonding occurs in the cross-linked chemicals, which strengthen the structure's bonding of CNT fiber to fiber.

Miao et al. explored a method to dramatically change the electrical conductivity of MWCNT yarn by adjusting construction of the yarn [7]. This study explains that the greatest need for conductivity is in a direction parallel to the base plane. Typical SWCNTs will have a conductivity of approximately $3X10^{-3}$ Ω m while the conductivity of MWCNTs can range from $5X10^{-8}$ to $6X10^{-2}\Omega$m. Generally, conductivity, which is parallel to the long axis, can be several times lower than the measured conductivity around the perimeter of an individual nanotube. When the individual CNT fibers are spun together, they end up as yarn, in which the cross section contains individual CNTs that number in the thousands of individual nanotubes, which leads to a non-uniform cross section. Conductivity within the collective bundles depends on the cross-sectional area or structure density and the number of contact points between individual CNTs fibers in the bundles. Just as individual CNT structure density and contact area influences conductivity, bundle structure and bundle contact area influences the overall conductivity of the yarn. One way to control structure density is to regulate the number of turns/m applied during the spinning process.

If the spinning process results in irregularities in the construction of the yarn structure, then there will be variances in conductivity. Miao et al. concludes that increasing the porosity in a yarn structure decreased the conductivity [7]. If bundles could be spun together to have a similar structural density as individual bundles. then the resultant wire conductivity would also be higher. Joining the nanotubes through the spinning process allows a combination of CNT lengths to grow much like individual cotton fibers. Also, it should be noted that in the cotton spinning process a uniform density in the form of compactness of individual cotton fibers significantly influence the final strength of the cotton yarn.

One of the first processes developed to increase the length of CNT fibers was by combining individual fibers in a continuous composited fiber using a wet spinning process. The medium used to suspend the CNTs was usually an alcohol in which the CNT fibers were floated as the entire stream was rotated. In a similar fashion to dry spinning, the CNT fibers were drawn and twisted together or rotated to keep them together. Two major issues with the wet spinning process are that it reduces conductivity and tensile strength of the spun fibers to non-functional levels. The reduction in properties has been attributed to the coating of the CNTs within the transport medium [8]. The reduction in conductivity could further be attributed to minute voids at the end of individual fibers that force the electron path to change fibers, which requires a point of contact with a neighboring fiber to continue the path.

Another CNT spinning method that has been does not use a chemical transport medium was developed. This spinning method is referred to as dry spinning, this method is very similar to traditional cotton spinning, whereby individual CNTs are pulled from a highly aligned source and wrapped around each other to increase the density and the tensile strength [5]. In the case of CNTs, the aligned source was the growth wafer from which the forest of individual CNT was harvested. The highly aligned cotton fibers are of various lengths, even those from the same cotton bloom. In order to produce the strongest cotton yarn the fiber lengths are allowed to mix in a process referred to as "blooming," which allows a wide array of lengths of cotton to be spun together in order to produce the most yarn.

The maximum length of CNT growth has been measured as 1,000 μm [5]. The longest cotton fibers have been measured to be longer than that by 20 to 30 times. During the spinning process the longer cotton fibers are able to wrap around shorter fibers, thus providing a more uniform fiber density, which results in increased tensile strength and length for the resultant yarn.[9]. However, unlike cotton fibers, the spinning of CNTs does not improve the tensile strength of the final fiber when compared to the initial CNT strength. Various spinning methods (wet vs. dry) have been utilized, and methods to improve the mechanical properties of the CNT wire have been developed, but there seems to be a physical limit in the ability to improve the mechanical properties of CNT fibers utilizing currently technology. CNT fibers are simply too short, stiff, and uniform to be able to wrap around each other like the cotton fibers do. Jia et al. concluded in a study that longer, thinner CNTs would provide better mechanical properties after spinning [10]. This could be attributed to the individual longer CNT fiber providing additional contact points between adjacent CNTs (more ionic bonding) and greater flexibility, which would allow the individual CNTs to twist around each other. However, the properties achieved with longer CNTs being spun together would still remain significantly less than that of individual CNTs. Some post-spinning chemical processes would most likely be required to improve the bonding properties either by somehow securing covalent bonding between CNT fibers or by providing even more contact points to enhance the ionic bonding.

An additional vital point to be made about individual CNT fibers is that once formed, the graphite tube has a uniform exterior that could be considered smooth. This uniform exterior does not provide a varied surface on the atomic level, so CNTs need to remain in physical contact to produce any ionic bonding from which tensile strength is developed. Shown in Figure 2.1 is a scanning electron microscope (SEM) images of both unstrained and strained 30-ply CNT wires.

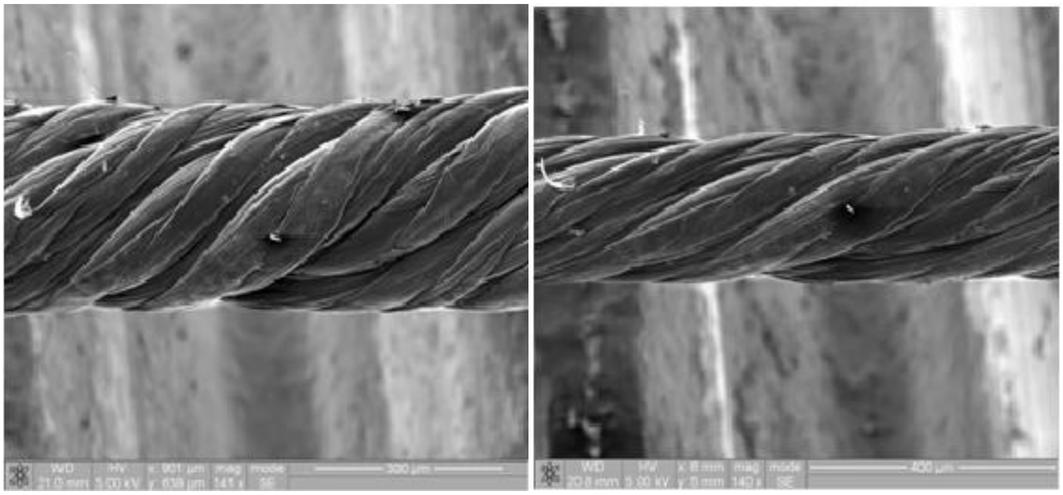

(a) (b)

Figure 2.1: SEM images of 30 ply CNT wire (a) before straining and (b) after straining (18%UTS)[2]

The drawing process allows individual CNTs that are being drawn from the wafer to be arranged head to head and then tail to tail, in order to further align and, in some cases, separate at the attached point (either the CNT head, tail, or both) during the drawing and spinning process. During the harvesting process, small gaps may occur among the CNTs. These gaps can widen slightly as the fibers are further drawn and spun. Any gaps between CNTs cause a reduction in transmission of electrons or a decrease of conductivity. Gaps in the fiber continuity also contribute to the low tensile strength, since the wire is depending upon ionic or van der Waals forces to remain together and the number of points of contact are reduced. Another In other words, the only mechanism available to transfer the tensile force from one CNT to another is the ionic bonding between individual CNT fiber contact points. Likewise, the electrical conductivity in spun yarn is increased when the number of contact points between CNTs increases [1]. The decrease in strength and conductivity of the spun wire could be identified as lacking covalent and ionic bonding between individual CNTs [5, 8]. A more succinct way to summarize the bonding reaction is that van der Waals forces or ionic bonding is the only source of tensile strength in the spun CNT wire, and ionic bonds do not have the strength of covalent bonds. Therefore, covalent bonds between CNT fibers would be most desirable if they could be created. As mentioned earlier, CNTs are grown as smooth cylinders as show in Figure 2.2:

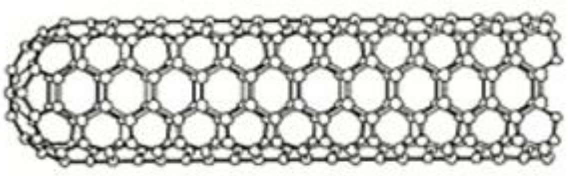


Figure 2.2: Typical single wall nano tube [2]

The double-carbon bond of the CNT needs to be replaced with additional molecules that are covalently bonded in order to provide additional contact points with other CNTs. This could be accomplished by rearranging the C=C bond so that each carbon atom bonds with –OH or –OO molecules to become a C-O-H or C-O-O covalently bonded molecule on the CNT. In the spun state, the additional covalently bonded molecules would provide a “rough surface” that would hinder the CNTs from sliding along its axis, thereby increasing the tensile load between the spun CNTs.

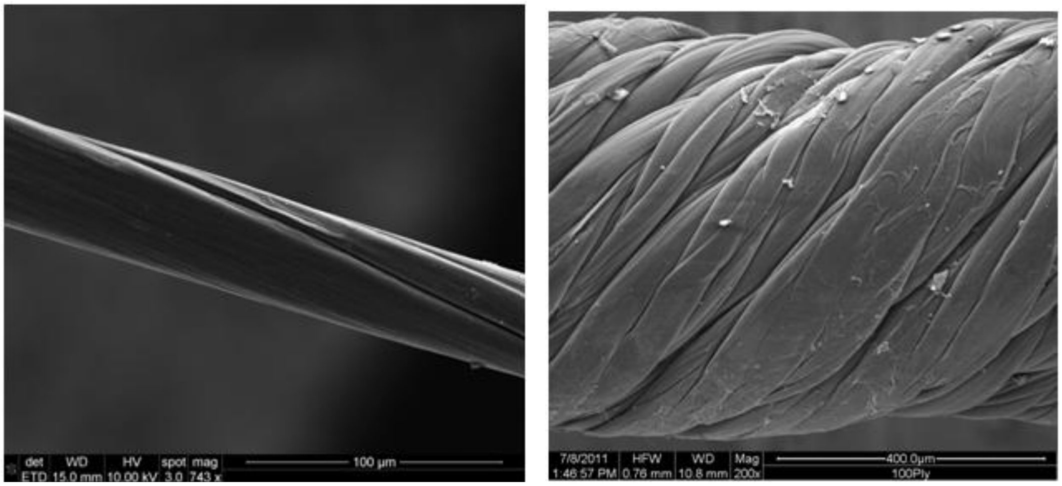
This paper demonstrates a post-spinning chemical treatment method of creating alternate carbon bonds on the CNTs involving -OH and -OO groups. Others have demonstrated similar methods of custom chemical processes to improve specific properties such as tensile strength, conductivity, and temperature resistance through creation of covalent bonding. Xiao et al. demonstrated that barium nitrate may be utilized to make yarns that hold up well in high temperature (1,317 K) cathodes[3] . Trakakis et al. functionalized buckypaper, which improved the mechanical and electrical properties by oxidation and epoxidation reactions in composites [11].

CHAPTER 3

EXPERIMENTATION

3.1 Materials

CNT yarn was procured from Nanocomp Technologies, Inc., Concord, New Hampshire, USA. The CNT 1-yarn has a linear density of 0.98 ± 0.10 tex. Acid treatment of the as-received CNT yarn was performed by submerging 98 cm yarn segments into a 3:1 volumetric solution of sulfuric acid and nitric acid for 35 minutes. Following acid treatment, the yarn was dipped in DI water multiple times to remove acidic residue. Figure 3.1 shows SEM images of the 1-yarn and 100-yarn CNT wires used for the experimentation in this study.



(a) (b)

Figure 3.1: SEM images of a) the one and b) 100 yarns of CNT Wires used for the experimentation [2]

3.2 Methods

Post-dry spinning, the CNT wire was bathed in a 9M solution of H_2SO_4 and HNO_3 in a 3:1 ratio. The wire was immersed for 135 minutes while taking a conductivity reading every 5 minutes. Conductivity measurements were made with an Extech multimeter. The collected data was then plotted as conductivity vs. time to determine the optimum time required in the acid bath to produce the maximum conductivity. Note: In a separate study, the same acid bath with minor chemical variations was used to address changes in tensile strength. Changes in tensile strength due to cross-linking were not addressed in this study.

The length of the wire tested was chosen to be approximately 87 cm, as measured with a ruler. This length corresponded to the diameter of the container used for the acid bath so that probes could rest on the sides of the beaker without placing any tension on the CNT wire. The CNT yarn was cut using either a blade or shop scissors. Each end of the CNT wire was held by a single mini test clip adapter (Radio Shack Model 270-334) or adapter. This adapter kept the CNT wire from further un-spinning during testing and provided a conductive path for the conductivity reading. A lead from each multimeter's probe was plugged into one Radio Shack adapter. A typical set up is shown in Figure 3.2. A CNT wire is captured in each adapter, but this is difficult to see because the 1-yarn wire is the width of about a human hair.

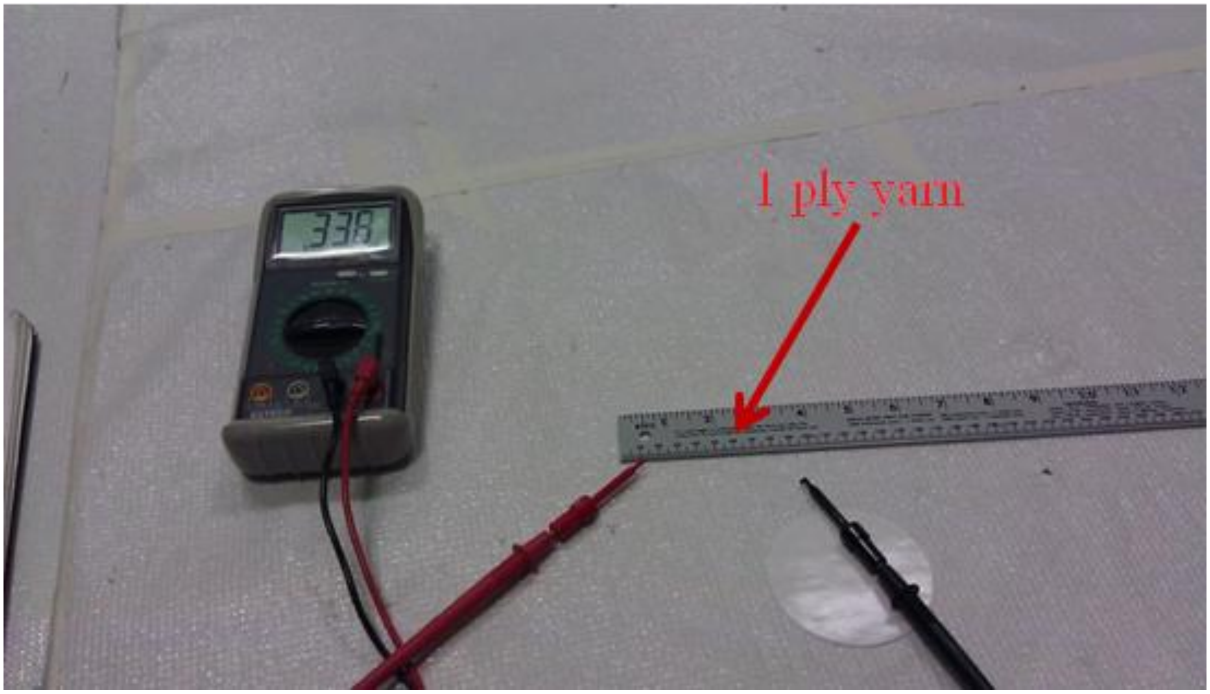


Figure 3.2: Adapter holding 1- yarn CNT wire and multimeter for measuring resistances.

The arrangement allows the conduciveness of the CNT wire to be continuously monitored for recording. After connecting the adapters to the CNT wire the wire was placed into the acid bath. The adapters were placed against the outer portion of the container to keep the wire wound and relativity un-tensioned since it was observed that deviations in tension resulted in corresponding changes to conductivity and the wire tended to unwind if not restrained. Figure 3.3 shows the typical technique for emersion of an un-tensioned CNT wire in the acid bath.

Figure 3.3: Typical emersion of CNT wire in acid bath.

At the end of the time in the acid bath, the leads were disconnected from the multimeter, and the adapters and CNT wire rinsed in DI water to neutralize/remove any residual acid. Some test specimens were returned to the Air Force Institute of Technology, Department of Aeronautics and Astronautics for additional testing and characterizations while a select few underwent additional characterization testing at Wichita State University (WSU) laboratories.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared Data Discussion

In addition to verifying that an acid bath would increase conductivity, the expected formulation of additional (–OH and –OO) molecules was estimated by calculation. It was assumed that the number of carbon atoms in either a single-wall or multiwall carbon nanotube wire remained constant for the length of the CNT wire. Thus, the total number of carbon atoms was calculated using a measured density per length of the CNT wire. The "as- received" density and the "after-chemical treatment" density per unit length of the CNT yarn were utilized for this comparison. For simplicity, it was assumed that the CNT wire had a uniform or constant diameter which allowed the weight of a given length to be used without analyzing the specific structure. The weight was utilized to determine the number of carbon atoms in a specified volume of material or a virtual molar concentration. The number of carbon atoms was then considered the number of donor sites for attachment of –OH and –OO molecules. The weight of the post-acid bath CNT wire was utilized to devise a molecules ratio for the chemical formula. The final formula was identified as simplified because of the limited information available from the attenuated total reflection (ATR) spectroscopy or Fourier transform infrared spectroscopy (FTIR), and the measured sample weight. The calculations also assume that no carbon was removed from the CNT structure during or after the chemical treatment. The reason why the chemical concentration was calculated relates to the optimum goal of obtaining CNT wire with the lowest treated density and maximum electrical functionalization. The chemical treatment used in this testing to increase the conductivity did increase the ultimate tensile strength when compared to the "as-received" condition, but this was not the central issue of this study and is mentioned here only because tensile data was gathered via a previous study. Using Table 4.1 as a guide, the presence of –OH and –OO bonding can be observed through spikes in the 2,500 to 3,300 cm^{-1} range of FTIR data as show in Figure 4.1.

Table 4.1: FTIR Frequency To Bonding Guide

Frequency Range	**Bond**	**Comment**
1100	C-O	Check for OH and C=O bonding
1650	C=C	
1715	C=O	Depends on type of carbonyl
2150	C≅C	Most obvious in terminal alkynes
2250	C≅N	Characteristic since little else around it
3000	C-H	As hybridization of C changes sp3-sp2-sp, the frequency increases
3500	N-H	Can tell primary from secondary
3600	O-H	Broad due to H bonding

The spikes show that –OH and –OO attaches to the CNT wire. It should be noted that the graph labeled “as-received” had not been tested in either DI water or an acid bath, but had been exposed to atmospheric conditions between the time the original spinning process had been completed and when testing was performed. Unprotected CNTs exposed to atmospheric conditions could likely lead to an oxidized surface coating, which can be seen in the graph of the as-received FTIR frequency response (spikes) in the 1,100 to 1,750 cm^{-1} range.

Figure 4.2 shows the method used to store and transport the specimen wires. Also, note that the wire appears to spontaneously unravel on the 100-yarn spool just beyond the taped end.

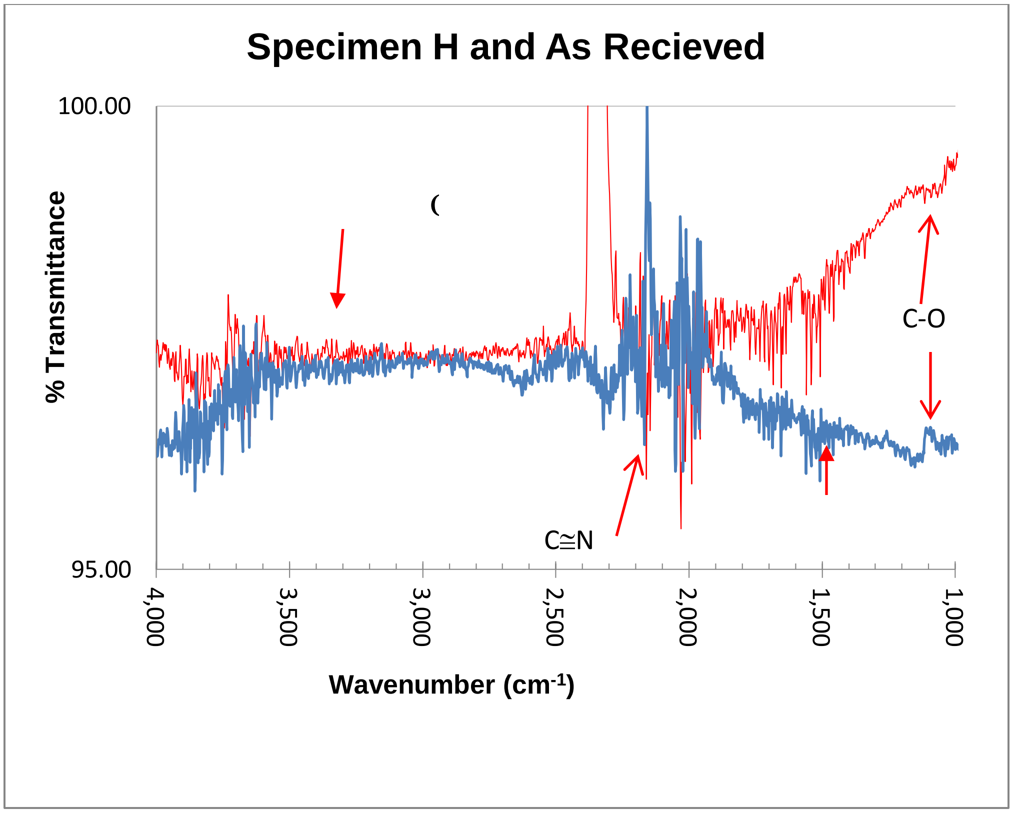


Figure 4.1: FTIR data as- received (blue) vs. specimen H (red)

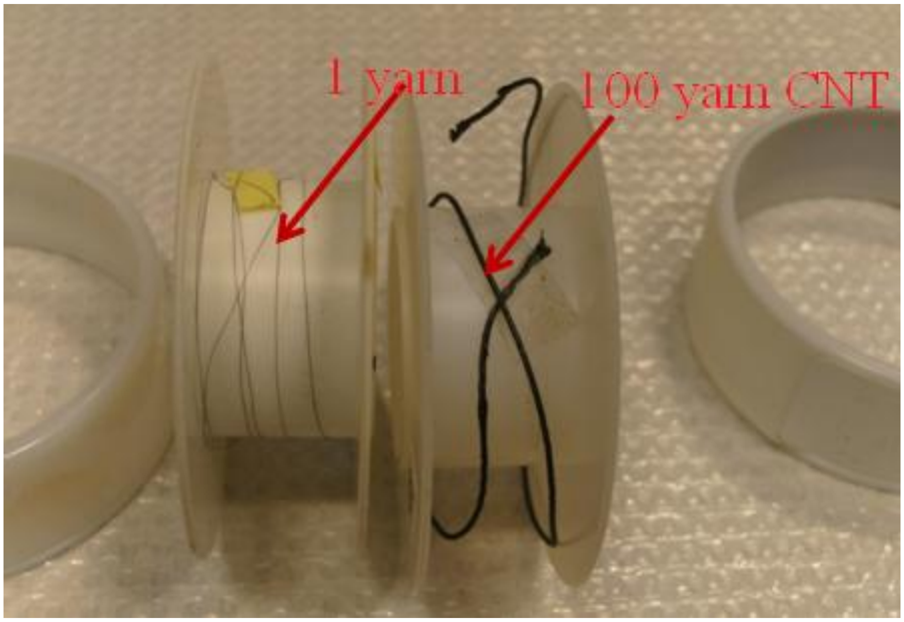


Figure 4.2: Storage Spools, 1 Yarn Left 100 Yarn Right

Continuing the calculation of the molar content of the CNT wire, the weight measured by Misak et al. of the as-received and treated CNT wire was the basis used [12]. The as-received wire was measured to be 0.98 tex (or g/km) and the after treatment CNT wire was measured to be 3.04 g/km [12]. Assuming dry spinning of the CNT wire, there should not be any other chemicals/molecules included in the CNT structure, even though Figure 4.1 shows some frequency responses other than carbon, hydrogen, and oxygen. This assumption would allow the calculation of the number of carbon atoms in the CNT wire for an average density and fixed length without attempting to calculate the as-received ratio. The molar content (M) of the non-treated wire would be calculated as[13]:

$$M = \frac{measured\ weight}{Carbon\ molar\ weight} \tag{4.1}$$

Placing the measured average density/km in the equation as measured weight and molar weight of carbon, the equation would be:

$$\mathrm{M} \approx \frac{\mathbf{.98}\ \ \boldsymbol{g/km}}{\mathbf{12.01}\ \ \boldsymbol{g/M}} \tag{4.2}$$

Therefore, the molar content would be 0.08 M/km for the carbon in the CNT wire. The calculated linear density stated as a concentration would yield 0.4816 x10^{23} carbon donor atoms that could be utilized to form either –OH or –OO covalent bonds. The additional peaks indicate that additional bonds are present, but the FTIR does not give ratios or exact compounds. However, using just the compounds –OH and –OO along with the linear density after treatment (measured as 3.04 g/km), a simple chemical ratio could be calculated, which would lead to the formula in Equation 4.3. Although mathematically accurate for the molar content of carbon, the formula is not in standard form and does not reflect the exact pattern for –OH and –OO attachment.

$$C + 4\ OH + 6\ OO \tag{4.3}$$

Detailed calculations of atomic displacement due to the addition of atoms on the outer diameter would show that there is an expected increase in the fiber diameter. This can be observed in Figure 4.18 (b) which will be discussed later on. The only point being discussed now is the almost doubling of the diameter after immersion in the acid bath. The actual increase in diameter could be calculated or measured, as shown in Figure 4.18. Atomic expansion is beyond the intended scope of this paper and the result would not have any effect on the conductivity of the individual CNT but could minutely influence the compactness of the CNT wire. The –OH and –OO molecules would also explain some of the observed physical dimensional changes and alignment of individual CNTs. The observable shortening of axial length of the 100–count CNT wire could be explained using the rationale of atomic addition to the diameter.

The complete FTIR data obtained for Specimens E, F, G, and H is shown in Table 4.2, captured using an Avatar 360 FT-IR platform, as shown in Figure 4.3. Test specimens A, B, C, and D were returned without FTIR testing. Specimens were placed under a stylus that pressed the specimen against the light source and receptors.

Figure 4.3: Photograph showing the Avatar 360 FT-IT used in the present study.

Table 4.2: FTIR Sample Source used in the present study.

Sample ID	**Yarn**	**Time in Treatment**	**Treatment**	**Reference Figure**
E	1	30 min	DI Water	Figure **4.4**
F	1	30 min	DI Water	Figure **4.5**
G	100	30 min 4:1	Acid Bath	Figure **4.6**
H	100	30 min 4:1	Acid Bath	Figure **4.7**
As-Received	1	N/A	None	Figure **4.8**

The FTIR data shows that –OH and –OO bonds were formed in all specimens. Peaks in the 1,000 cm^{-1} to 1,700 cm^{-1} range correspond to C—O and C—O—C bonding, while peaks in the 3,400 cm^{-1} range correspond to –OH bonding. Specimen E, as shown in Figure 4.4, is one of the flattest or non-peaked cures obtained. Peaks in the 3,500 to 3,600 cm^{-1} range would indicate that the DI water was able to contribute to ionic –OH molecules, which would then form covalent bonds with the carbon with very little energy input. The region of the curve that exceeds 100% transmittance indicates the presence of a strong C–C or C—N bond.

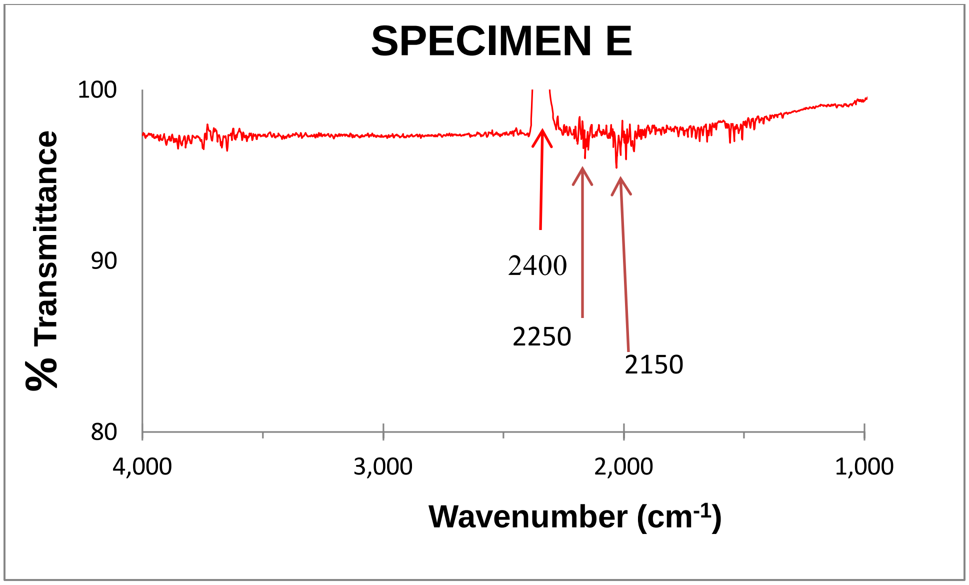


Figure 4.4: Specimen E – 1–yarn thread

Specimen F as seen in Figure 4.5 is very similar to Specimen E and was also submerged in DI water. Again there are peaks in the 3,500 to 3,600 cm^{-1} range which would indicate that the DI water was able to break into ionic –OH molecules which would then form covalent bonds with the carbon with very little input. While again the region of the curve that exceeds 100% transmittance indicates a strong C-to-C or C-to-N bond.

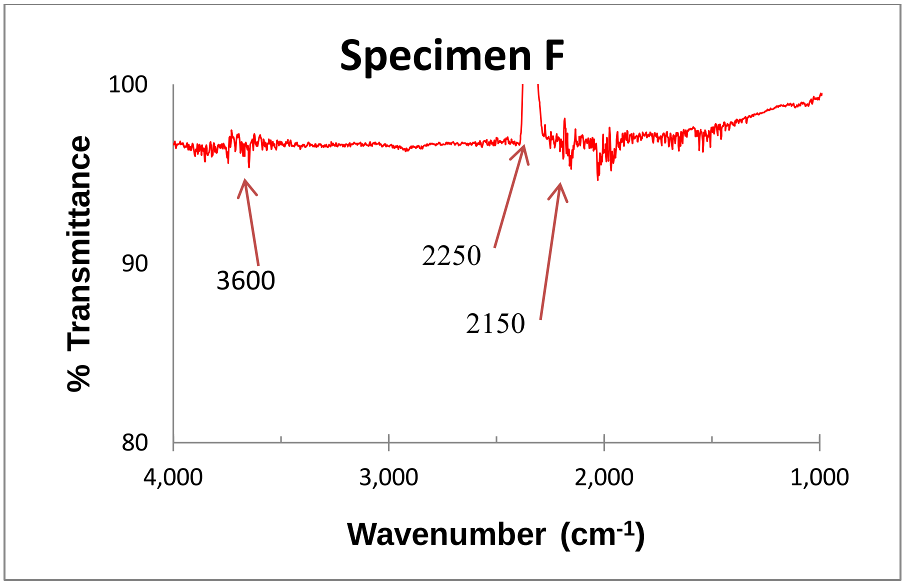


Figure 4.5: Specimen F - 1 yarn Di water

Specimen G (shown in Figure 4.6) is 100 times larger in diameter than Specimen E or F and shows as less reflective (less percent Transmittance) than Specimen E and F due to the increased diameter of the CNT. The size difference is strictly a result of the number of yarn used to make the sample. Specimen G FTIR data is similar to Specimen E and F in peaks and frequency, thus implying that soaking the CNT wire in H_2SO_4 and HNO_3 does not yield stronger bonds or effect the results.

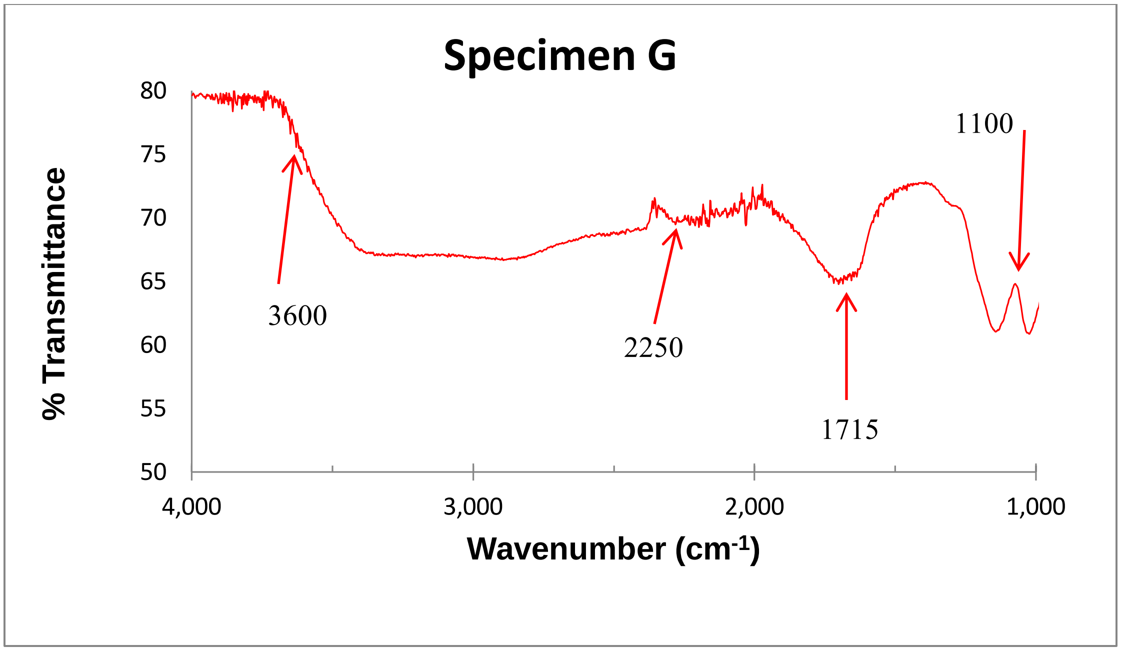


Figure 4.6: Specimen G - 100 yarn post acid bath

It can be seen that the results for Specimen H, shown in Figure 4.7, are not much different than the results for Specimen G, shown in Figure 4.6. The change in percent transmittance is likely due to a minute change in procedure between the two samples. During testing, Specimen G physically contracted while in the acid bath.

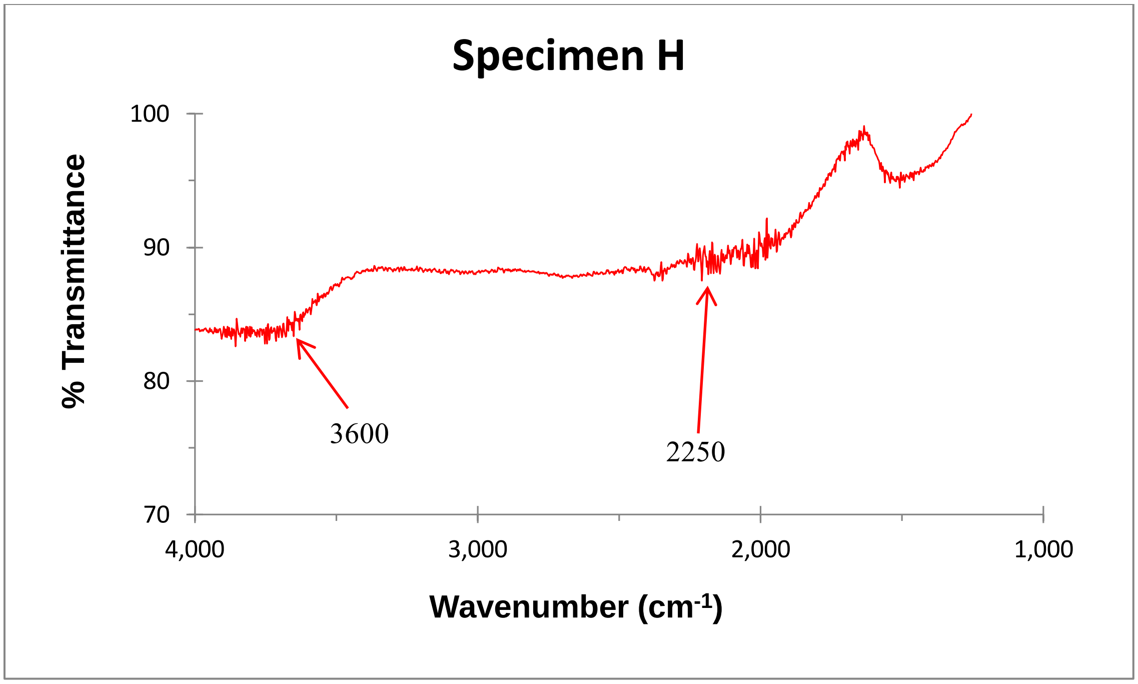


Figure 4.7: Specimen H - 100 yarn

The last FTIR graph, presented in Figure 4.8, shows the results of the as–received specimen. Like Specimens G and H, this is a 100–yarn specimen. Also, like the other specimens the presence of –OH and –OO bonding is evident from the frequency response.

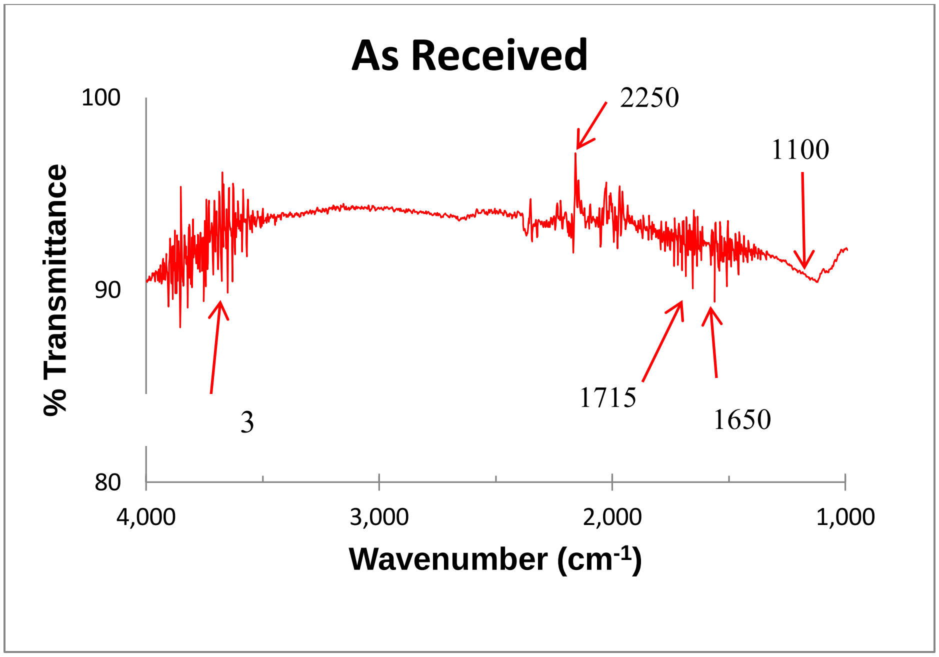


Figure 4.8: As-received - 100- yarn CNT specimen

The FTIR did not have the issues with tension and unwinding like the conductivity testing. The only problem was that carbon does not reflect infrared (IR) light as well as other materials/chemicals, and testing needs to be accomplished on relatively uncrushed sections. Once the number of scanning cycles was established there were no issues in obtaining data.

4.2 Conductive Test Results

The resistance readings were made with the Extech multimeter, as shown in

Figure . The ohms were hand recorded for conversion into conductivity at each recorded time. Equation (4.4) was used for the actual conversion [13].

$$= {}^{l}\!/_{\ * a} \tag{4.4}$$

where is conductivity, *l* is length between probes, Ω is measured resistance, and *a* is the cross–sectional area of the CNT wire. For all samples, the value was calculated for the air resistance value before placing the sample in the acid bath for functionalization. The air resistance value for each specimen was used to normalize the conductivity readings for each specimen's acid bath conductivity readings. Areas for the 1–yarn and 100–yarn specimen were calculated based on provided diameters of as–received specimens and no actual pre-testing or post testing measured diameters were obtained.

Conductivity measurements are presented in Figure 4.9, as well as Figure 4.11 to Figure 4.16 and discussed separately. These measurements were normalized using the pre–bath conductivity or air conductivity. Data from the first test, Specimen A, is presented in graphic form in Figure 4.9, the long immersion time was an investigation to establish a relationship between time immersed vs. conductivity of the CNT wire. The issue being investigated was whether there would be multiple conductivity peaks for extended immersion time or if the conductivity of the CNT wire continued to increase with additional immersion time. The specimens were immersed in the bath with the conductivity monitor connected and readings were recorded every five minutes. After 95 minutes, little change in conductivity was observed. The CNT wire was left an additional 45 minutes (total of 135 minutes) in the acid before the specimen was removed and rinsed in DI water. The first 20 minutes of results have been broken into segments and discussed.

4.3 Conductivity Measurement Segment 0 to 10 Minutes

The initial drop in conductivity from 1 to -0.1 can be explained by the theory that either a protective oxide layer was removed by the acid before the –OH and –OO molecules covalently bonded or the acid bath caused the CNT wire diameter to expanded. Simultaneously to the oxide removal was a mixing of copper from the probes, carbon from the CNT wire, and sulfuric acid, which may have resulted in generation of free electrons which resulted in the negative conductivity readings, but negative conductivity or resistance measurement can exist. The negative resistance readings did end after a short period. Possibly the negative readings were the result of copper continuing reaction with the nitrogen in the corrosive nitric acid solution which built up an insulation layer around the copper that stopped the generation of electrons, but did not interfere the flow of electrons along the CNT wire. The decrease in conductivity followed by an increase is graphically demonstrated in Figure 4.9. As the time increased beyond 30 minutes there was a decline in conductivity until 95 minutes when conductivity asymptotically approached an open circuit condition.

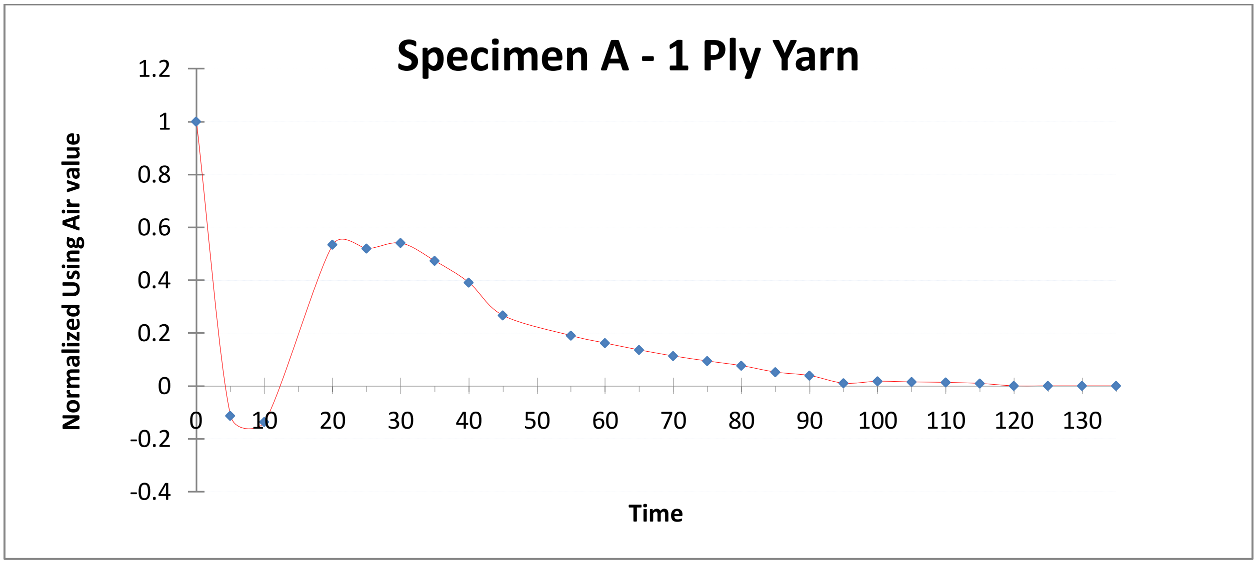


Figure 4.9: Specimen A 135 minute test

4.4 Conductivity Measurement Segment 10 to 30 Minutes

As the nitrogen layer grew on the copper probe, the potential between the copper and carbon decreased due to the increased inefficiency of the probes maintaining proper contact with the CNT wire. As time continued, the copper-to-nitrogen layer reacted with the H_2S0_4 and

HNO_3 to reestablish the contact between the probe and the CNT wire, which resulted in an increase in conductivity in the CNT wire for a relatively short time period. The longer the CNT wire was exposed to the acid bath, the lower the conductivity became. This trend can be observed as the drop in conductivity with the increase in time.

The above explanation is sufficient for Figure 4.9, Figure 4.11, and Figure 4.12. The difference in curve shapes may be partly attributed to the delay between each test and a new acid bath that was prepared for each test. The time periods between mixing the H_2SO_4 and the HNO_3 and testing were not consistent which could have resulted in differences in temperature of the acid mixture at the time of testing. A second reason for some the differences could be attributed to corrosion of the probes. At the start of data collection for Specimen B, the adaptors were sanded using a P1000 emery paper. The connection between the multimeter probes and the Radio Shack adaptors, shown in Figure 4.10, was not broken and therefore not cleaned. A continuity check of the test equipment showed a meter reading of 0.2 ohms when connected to each other. The graph of Specimen B has not been included due to the probe's resistance reading.

The differences in energy levels between the baths could be due to the length of time the acid bath was allowed to stand between mixing and testing which could have allowed the temperature of the bath to cool to room temperature before running the test. An exothermic reaction occurs when H_2SO_4 and HNO_3 are mix. The closer to the time of mixing, the more elevated the temperature of the mixture. An elevated acid temperature will produce a slightly more aggressive reaction due to the higher energy state. However, the temperature was not recorded for any acid solution mixing or prior to testing. Moving to Specimen C, (Figure 4.11) and Specimen D (Figure 4.12), there were some minor changes in procedures that could explain the differences in the results. Specimen C had both the adapters and multimeter probes cleaned before testing (see Figure 4.10). There was zero resistance before starting the test on Specimen C. The adapters and probes were not cleaned before testing Specimen D. The 9M H_2SO_4 was mixed with 9M HNO_3 but was not deliberately allowed to cool to room temperature before testing was started. The acid ratio of 3:1 was used. There may have been some ionic exchanges occurring between the copper adapter and CNT wire as the acids completed mixing and began to cool to room temperature.

Figure 4.10: Multimeter probe after cleaning

Specimen C (Figure 4.11) and D (Figure 4.12) did show a major decline in conductivity followed by an increase to the original value. The trend shown in Specimen C and Specimen D graphs generally agrees with the original test specimen. The removal of the corrosion caused a decrease in tensile strength of the adaptor and compromised internal spring tension in the probes.

These factors could create an increase in resistance that would be measured as no or little change.

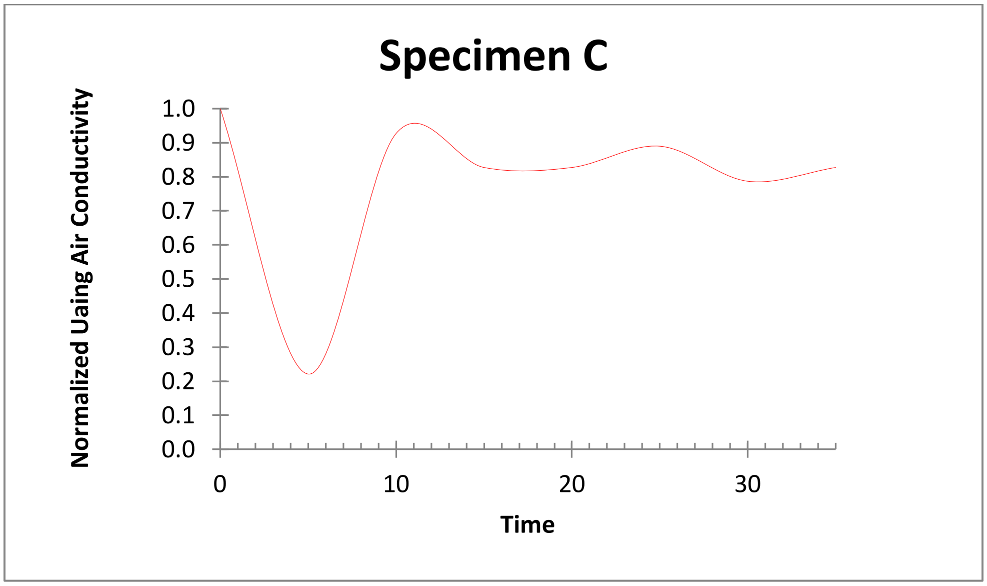


Figure 4.11: Specimen C, 1 yarn in acid bath

Specimen D (Figure 4.12) generated a normalized continuity graph similar to specimen A (Figure 4.9). After the peak at 10 minutes, the specimen D conductivity dropped until reaching no conductivity at 35 minutes. Events that may have contributed to the differences seen between the results for specimen C and D are that the acid bath was not changed between testing, the probes were not cleaned, and the clamping force was increased by manipulating the adaptor.

There is no data for one specimen because the wire spontaneously un-spun and disengaged from the adaptor. Testing was stopped and attempts to remedy the issues were unsuccessful. However, the second attempt resulted in the spontaneous disintegration of the CNT wires between the adaptors. One segment was approximately 25 cm while the other was 64 cm. In an attempt to capture the longer segment with the adaptors, one probe was pulled through the adaptor housing, as shown in Figure 4.13.

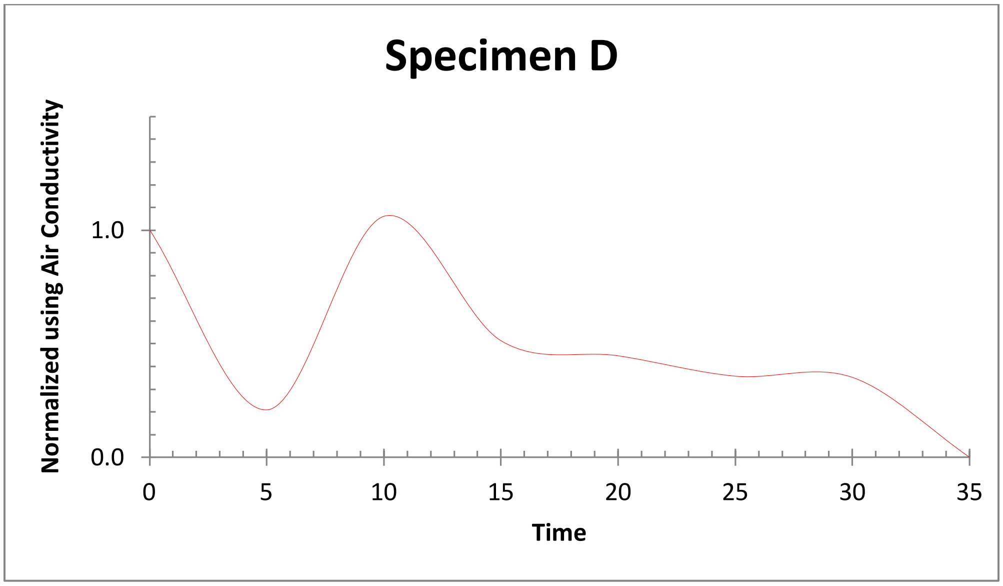
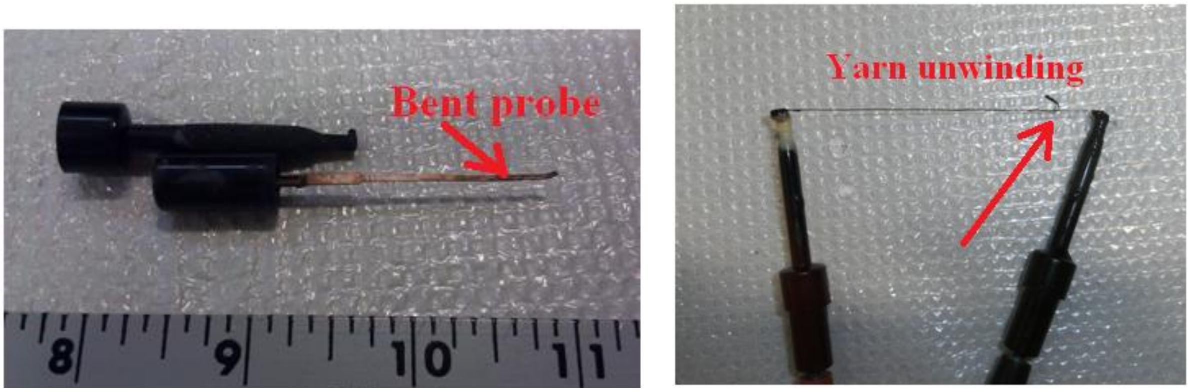


Figure 4.12: Specimen D -1 yarn specimen



(a) (b)

Figure 4.13: (a) bent mini probe and (b) unwinding CNT wire

For Specimen E, shown in Figure 4.14, the test medium was changed from the acid combination of H_2SO_4 and HNO_3 to DI water. The hypothesis was that DI water may provide the covalent bonds for functionalization without the destruction of the CNT wire, as was seen with the acid. The covalent and ionic bonding of water could easily provide the addition of –OH and even –OO to the carbon in the CNTs, just like the acid.

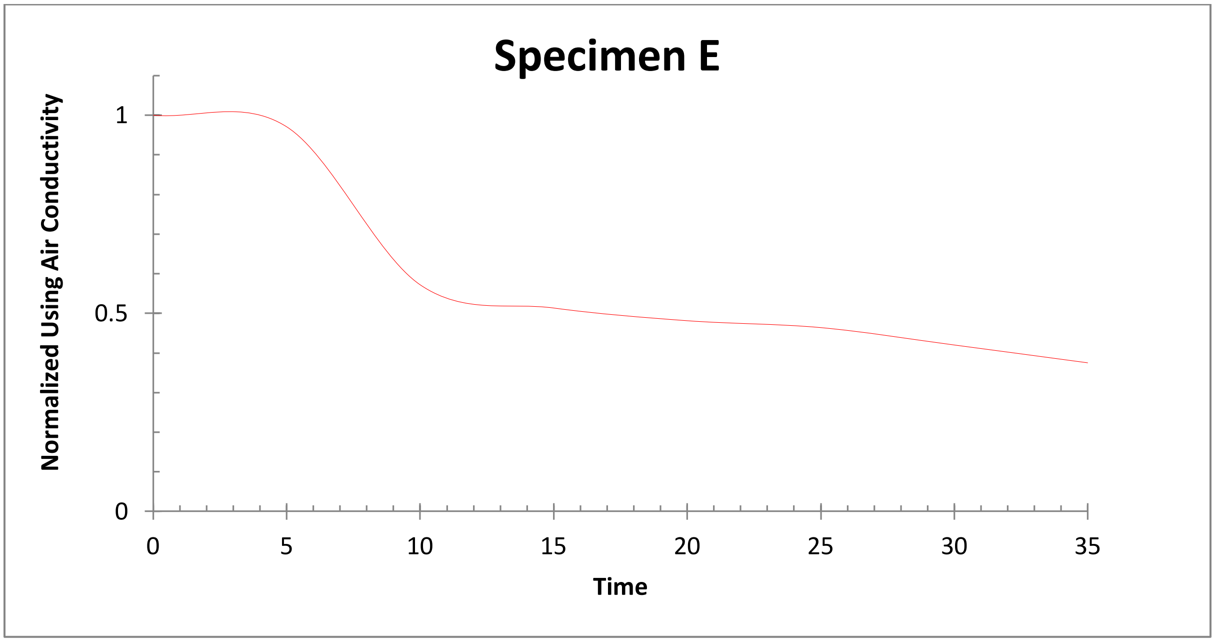


Figure 4.14: Specimen E – 1 ply yarn in DI

Specimen F, as shown in Figure 4.15, was also tested in DI water. The results are similar to those of specimen G, with an anomalous reading at 30 minutes. The specimen was observed to be contracting in the container. The contraction and swelling of the diameter should have generated different conductivity results, but neither the contracted length nor the diameter of the specimen was accurately measured. Stretching would have resulted in increased tension, which would have increased the conductivity and in turn produce a manipulated peak, similar to what is shown in Figure 4.15 at the 30 minute time mark.

The negative slope observed after the peak on both graphs in Figure 4.14 and Figure 4.15 point to the possibility that an expensive acid or wetting agent is not required as a treatment for increased conductivity. It appears that the CNT wire immersed in DI water provided an economical increase in conductivity.

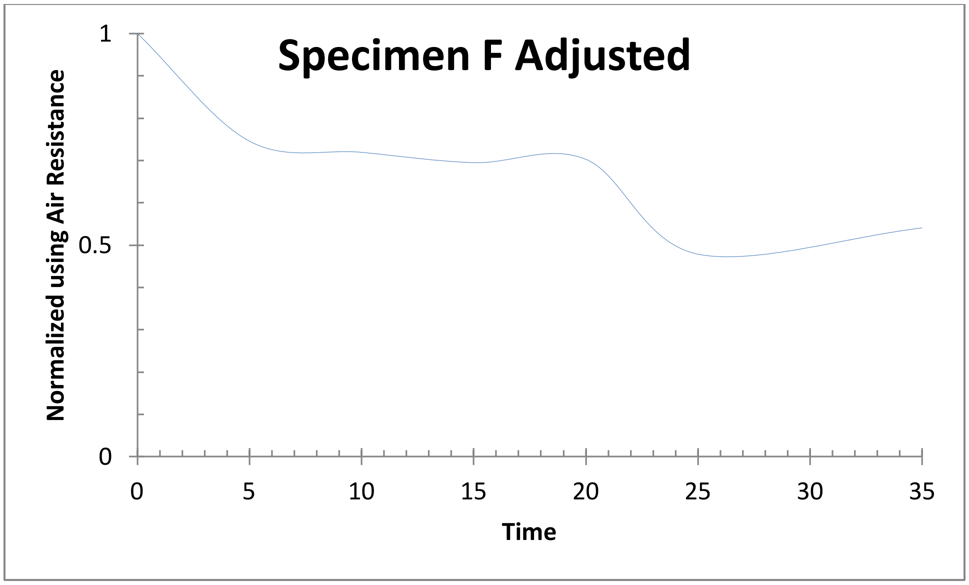


Figure 4.15: Specimen F adjusted data

The last two specimens tested were 100-ply yarn. They both were immersed in a mixture of H_2SO_4 and HNO_3. The ratio of the acid mix was changed from 3:1 to 4:1, and conductivity was again normalized using the conductivity readings measured in the air before submersion. The graphs were not consistent with the 1-yarn specimens and are not shown. A review of the methodology used in preparing the 100-yarn specimens reveals that the ends of the CNT wire were not secured during removal and seizing. The lack of sufficient security would allow the CNT wire to lose the twist which would allow the CNT wire to decompress to the point that the wire could become an open circuit.

The last 100 yarn specimen tested, Specimen H, exhibited a similar increase in conductivity in the beginning, but has a more rapid decline to zero conductivity. The cause of the significant differences in the graphs for conductivity between the 1-yarn and 100-yarn specimens has not been fully resolved. It has been theorized that the increases in conductivity were the results of the covalent bonding of –OH and –OO, which occurred on the decompressing wire. Simultaneously, as the covalent bonds formed, ionic bonding forced the rearrangement of nanotubes so that the molecules were atomically interspaced with equal gaps. In the decompressed or relaxed state, the atoms were not providing sufficient force to maintain contact points for conductivity. It may be theorized that the 100-yarn data is suspect due to a greater compromised diameter than the 1-yarn data. A graph of normalized conductance vs. time was created for the single- ply yarns and is shown in Figure 4.16. The graphs of each yarn in the same test medium seem to show similar curves.

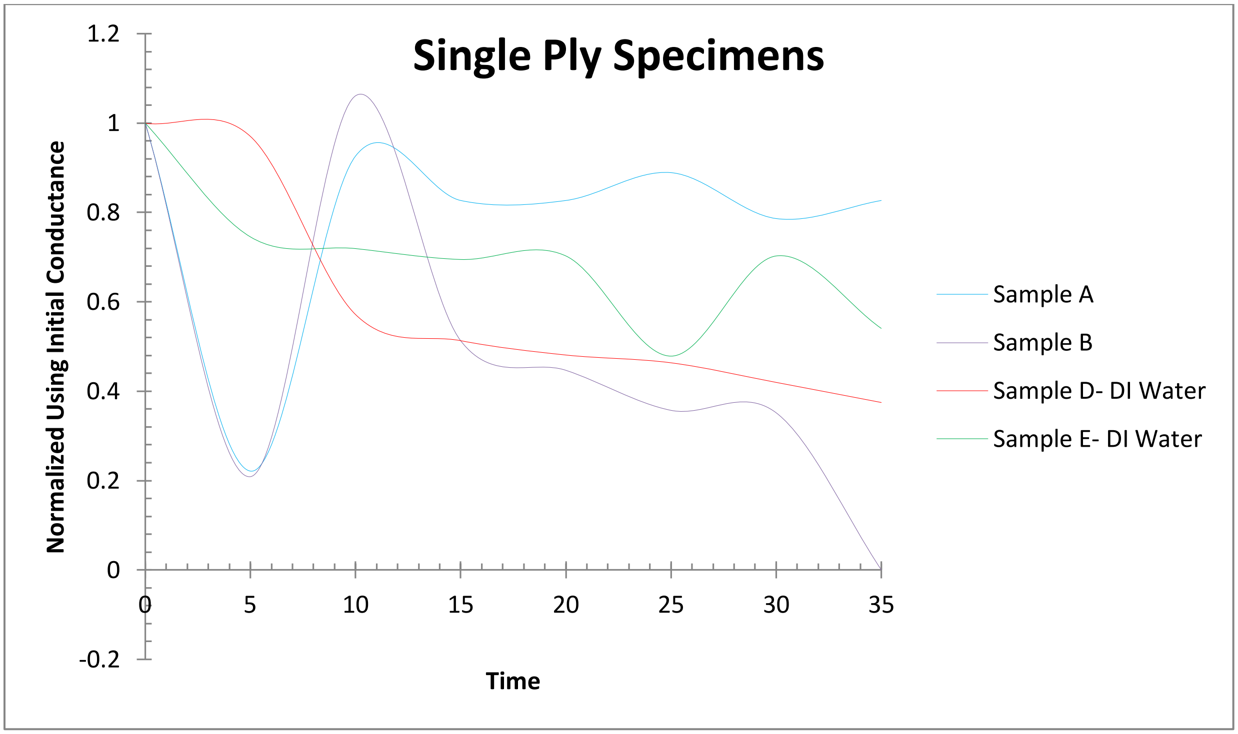


Figure 4.16: Single ply yarns

3 lists the run number, specimen description, test time, and maximum conductivity recorded for each test performed. The graph shown in Figure 4.17 gives the peak conductivity for each test run.

Table 4.3: Peak conductivity

Run	**Sample Description**	**Time**	**Peak Conductivity value**
1	Long Soak	30	20876
2	30 Minute Soak	0	2224
3	Sample A	0	330
4	Sample B	10	39043
5	Sample D	0	24746
6	Sample E	0	246
7	Sample F	5	906
8	Sample G	5	28990

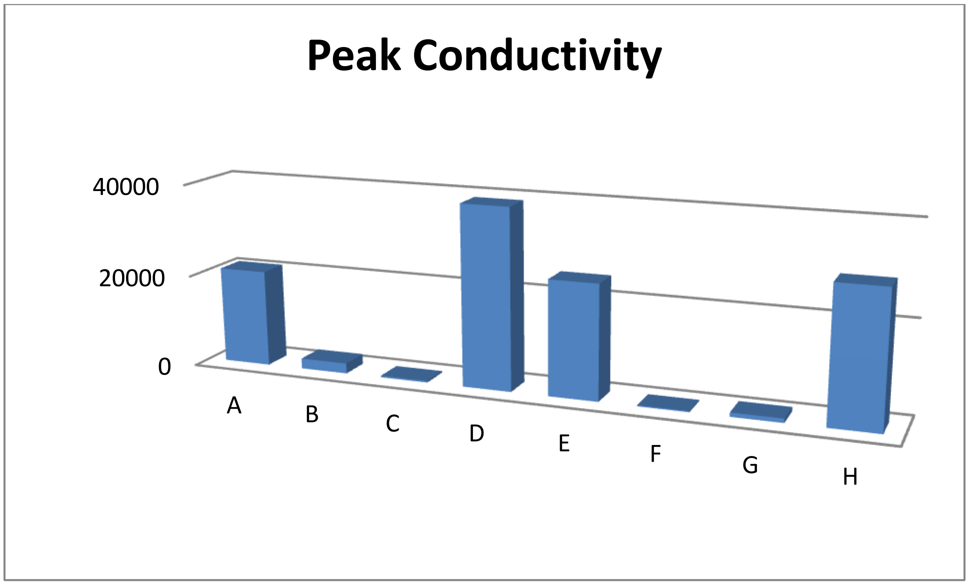
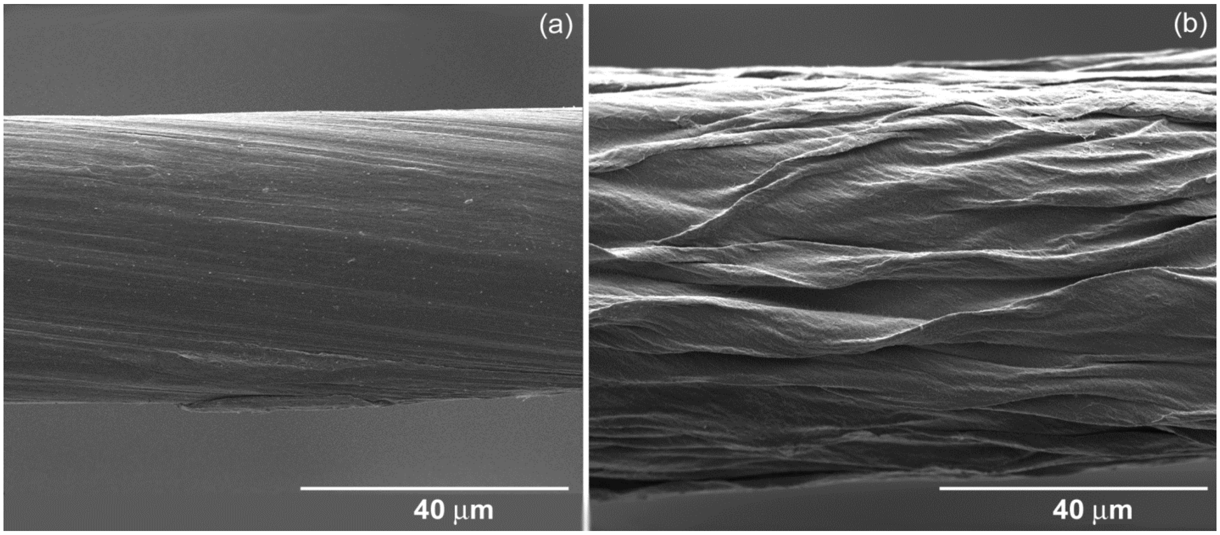


Figure 4.17: Peak Conductivity for each Sample.

The lack of consistency in peak conductivity is confusing until it is considered that the tension of each sample was not held to a fix value. The inconsistent tension would, in turn, allow for inconsistent conductance rates for the same specimen of CNT wire in or out of a bath of acid, as was observed and recorded in a video clip early in the testing. The variable tension could affect the infusion rates of the ionic compounds –OH and –OO. As recorded in the video, higher tension in the CNT wire would result in increased conductivity. The increased tension would also provide increased compressed, which should slow the infusion rate of the ionic materials to the interior of the specimen while improving conductivity. The end result is that the combination of higher tension on the CNT wire with the effects on the exterior ionic bonding of –OH and –OO to the CNT wire was not fully investigated in this series of tests.

Along with the corrosion seen on the probes after immersion in the acid bath or DI water, the CNT wire or yarn seems to have increased in diameter, as shown in Figure 4.18, and developed an uneven appearance as a result of the acid bath. For lack of a better description, the uneven appearance is called "corrosion" in this paper. This corrosion is not easily observed on the single-ply yarn, but with an estimated 30 μm increase in diameter and a roughening of the surface, it can be clearly seen in the 100-ply yarn. The wire count or ply doesn't necessarily affect the surface roughness. Single-ply wires may suffer from surface roughness to the same degree as the 100- ply yarn, but no SEM photographs were taken. Figure 4.18 shows a wire before and after functionalization (functionalization is equivalent to immersion in the acid bath to increase conductivity), in order to increase the cross-linking, which has been hypothesized to produce the secondary benefit of increased conductivity.



(a) (b)

Figure 4.18: SEM of 100 yarn (a) as received, and (b) Functionalized [2]

Shown in Figure 4.19 is a photograph of the results of corrosion and contraction that occurs in a beaker of acid during testing. Part of the yarn has escaped confinement and started to unwind.

Figure 4.19: Sample being tested- rough surface

4.5 X-Ray Refraction

An attempt was made to use the Wichita State University X-ray refraction machine, as shown in Figure 4.20, to confirm the addition of the –OH and –OO groups. Two major obstacles prevented the successful gathering of data: specimen size and insufficient intrusion of CNT wire into the x-ray path. An 87 cm by 688 μm section of a CNT 100 ply wire was folded multiple times along the long axis and placed on translucent tape, as shown in Figure 4.21, in order to increase the profile of the specimen for testing. The resulting CNT profile offered a wider target, but was still only about 688 μm high. The tape was then placed on the objective table. The table and X-ray emitter were aligned per standard machine procedures. No useful data was generated because the CNT wire did not present sufficiently intrude into or interrupt the path of the x-rays as they passed across the objective platform to the receiver. To increase the specimen to a height that would scatter the x-rays, the CNT wire was removed from the tape and mounted in a specimen holder. Still no useful x-ray data could be obtained, so the entire line of testing was abandoned.

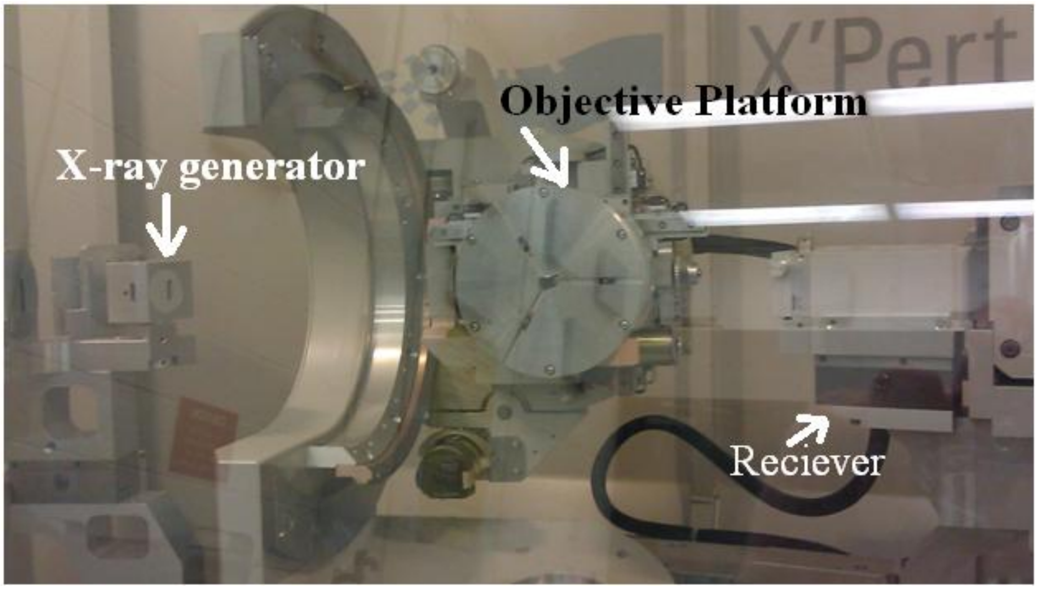


Figure 4.20: X-ray refraction machine used for the testing.

Figure 4.21: Specimen ready to mount on objective platform

4.6 Contribution to Conductivity

The goal of this research was to design a custom treatment for CNT wire that is lighter, stronger, and at least as conductive as copper wire. The final customized design also needs to be at least as robust as copper wire. In addition to the basic wire, the method of joining sections of CNT wire needs to be considered as part its development and testing. To obtain a preliminary look at the robustness of the current CNT wire, observations from this test matrix and additional separate tests would be in order.

If it is assumed that CNT-centered wire would need to be produced with at least the same safety issues in mind as copper-centered wire, then there should be an insulating coating to contain the core. To make electrical contact with the copper core wire, the wire must be exposed in the cross-section, or the insulation would need to be penetrated. The same is true for CNT-spun wire, but several other limitations need to be resolved. The penetration of the insulating material would work with either core wire material, however, the method that involves removal of insulation before termination would prove to be problematic since the CNT wire is not a solid wire.

AS shown previously in Figure 4.2, the spool on the right shows that even a minute length of 100-ply yarn stored on a spool can begin to unwind spontaneously. This unwinding may have been the result of manipulation during the last time a specimen was cut from the spool, but there is no direct evidence to support this theory. In a series of test involving 100-ply yarn that was not directly measuring the conductivity in this study, an 85 cm section was attached to the end of aluminum rod by means of copper wire is shown in Figure 4.22. Before attaching the CNT wire to the probe, additional twists in the direction of wire spin, was added to compact the wire more than just the amount due to the spinning process. The probe was wrapped in Teflon tape to insulate it from the electrolyte. The probes was then placed in an electrolyte composed of a salt water solution, or 2 molar H_2SO_4, or 2 molar H_2SO_4 plus percent weight of carbon black. Results of the experiment showed that the cathode probe (right most probe in Figure 4.22) lasted through more testing that the anode probe.

Figure 4.22: 100 Yarn CNT attached to probe

It was not determined exactly what was occurring at the anode, but the following theory was advanced:

The ions passing through the anode forced the individual CNTs to repel each other and they began to oxidize. The repulsion was obvious when a current passed through the anode and the CNTs became uniformly separated. The repulsion appeared to weaken the van der Waal forces, which allowed the residual tension stored in the twisted CNT wire to dislocate or separate the individual nanotubes along their long axis. As the number of contact points was reduced, the van der Waal forces could not keep the CNT fibers wound together, even after the current was removed from the CNT wire. It was unknown if the positive DC current was causing the rapid disintegration or if any form of current would cause loss of van der Weal forces. In either case, disintegration could be an issue if the CNT wire is exposed to energy in an oxidizing environment.

For a couple decades, a number of different nanotechnology products have been utilized to increase the efficiencies of novel nanomaterials, systems and devices. However, these developments also bring some risks, uncertainty and danger to the environmental health and safety of individuals. Therefore, the future of nanomaterials and devices mainly depends on public acceptance of the benefits and risks associated with nanotechnology applications. Supplementary research will be needed to identify the nanosafety concerns of this new classes of materials and devices[14].

Because of the coating that remains on the CNT yarn after wet spinning, this process may not be the optimal choice to increase conductivity. It is not clear either if wet spinning provides an optimal technique to increase structural density. Cleaning the CNT wire with an oxidation process, as discussed in this study. may provide some improvement in conductivity, but could also cause damage to the CNT yarn after such a short exposure to an oxidizing bath.

While Zhang et al. was investigating downsizing ancient technologies to produce functional carbon nanotubes, investigation and analysis of late 19th and 20th century techniques for spinning cotton fibers, which produce a stronger cotton yarn as a group compared to individual fibers, was not as compete as one could hope [4]. A cotton ball that is picked from a plant has a variety of lengths, which can be processed into highly aligned individual fibers and then spun into an almost uniform dense yarn. Sui; et al. performed a study that was able to electronically identify the quality level of cotton fiber samples [9]. The reason that quality level of cotton fiber samples needed to be identified is because cotton growth in the same field and from the same seed groups does not remain consistent from year to year due to a multitude of variants. In the late 1800's and early 1900's, the cotton industry would open bales of cotton from different geographic areas and let the fibers mix in an area called the "bloom room" in order to reduce fiber length variations and thus obtain a more consistent cotton yarn density. The lesson from cotton spinning is that varied lengths appear to make it easier to obtain uniform density and increased strength.

Dry spinning of CNTs does provide a modest increase in strength when compared to wet spinning. It also provides a modest increase in conductivity compared to wet spinning. Both the conductivity and increase in ultimate tensile strength result from the compression of the bundles which seems to occur with greater frequency in dry-spun CNT yarn than with wet spun CNT yarn. Neither wet nor dry spinning processes provide an increase in the conductivity that is close to achieving the conductivity of copper, which is the reason for custom modification processes. The ultimate goal would be to achieve a conductivity of CNT wire similar to copper wire without tension with a much smaller density per unit length than copper, thus allowing CNT wire to replace copper wire as the primary electrical conductor in aircraft.

Increased conductivity can be achieved through chemical treatment. FTIR data shows that carbon atoms take either an -OH or -OO molecule. In addition, the weight gain confirms that these molecules have attached themselves to the CNT yarn. Based on the linear average density, it is apparent that each carbon atom takes on one or the other. It is expected that the exterior of each single-wall CNT would look like that in Figure 4.23. If it were a multiwalled

CNT, it would not look much different since each nested CNT would rotate to provide maximum atomic clearance.

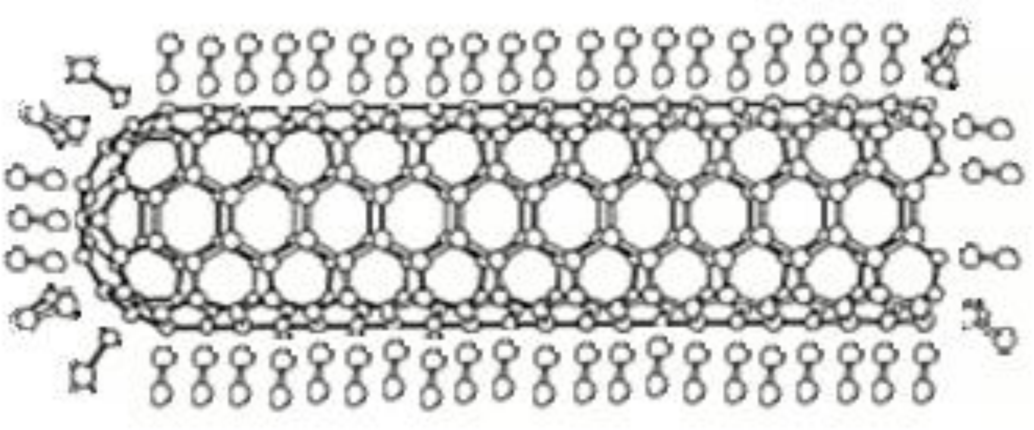


Figure 4.23: Projected CNT with -OH and -OO

The –OH and -OO molecules would arrange themselves in such a way that there would be additional points for ionic bonding between CNTs in contact with each other. The increased ionic bonding sites would also have a positive impact on tensile strength. If the methodology of dry spinning cotton could be applied with equal results to CNTs, then the need for chemical treatment of the CNT yarn to achieve greater tensile strength or increased conductivity could possibly be eliminated. Uniform density of spun cotton is achieved through the blending of different fiber lengths and diameters, which provide maximum contact points and minimum gaps between fibers. Part of the individual fiber characteristic is the flexibility, which is due in part to the atomic alignment that makes up the fiber and the ratio of length to. diameter. In copper wire, that flexibility is intuitively called the minimum bend radius. In reviews of literature on CNTs, the characteristic of flexibility has not been considered a material property worth investigating.

An additional way that fiber flexibility affects the ability to spin fibers is that if the flexibility is exceeded during the spinning, fibers would have a tendency to unwind if unrestrained. The reason for this is that the side of the individual CNT where the atoms are compressed would create repulsive forces (compressed atoms) within the atomic structure and separate until atomic distances are satisfied or the force is neutralized. Relying on observations in place of calculation, it can be concluded that the 100-yarn CNT wire used in this testing was highly over spun. This theory would include MWCNTs which are not as flexible as a CNT of the same length.

It is theorized that a more rigorous scientific approach to spinning could result in a process for producing CNT wire which would make it possible to reproduce the most desirable properties of solid metal wire in the CNT wire without chemical treatment. This could be accomplished by investigating the flexibility characteristic in various CNTs. Characterizing desirable traits are in the spinning process, as well as building a web using a process that will allow the incorporation of those most desirable characteristics in the spun CNT yarn is needed. A major anomaly with the data obtained in this study is the inconsistency of the peak conductivity as shown previously in Figure 4.17. It can be shown that the conductivity varies with changing tension of the CNT wire. As the tension increases the conductivity appears to unpredictability increase. Over all, this changing conductivity is an undesirable feature that could be a major hurdle for using the CNT wire as a direct replacement for conventional copper wire. If the conductivity routinely varies as much as the data suggests, current production methods may not be able to provide the predictable conductive product sought. If it is further confirmed that the variation in conductivity is the result of inconsistent compression, then the current procedure of draping wire between terminals will ensure constant compression and uniform density, the method of spinning needs to be revisited.

CHAPTER 5

CONCLUSIONS

The current state of spinning technology for CNT wire is insufficient to produce it as a direct replacement for copper wire without some modification like stretching or chemical treatment. Results indicate that chemical treatment alone is not a suitable substitute for tension-induced compaction in order to increase the conductivity of CNT wire plies. The initial reduction in conductivity followed by an increase has been thought of as removing oxidization followed by an increase in covalent and ionic bonding. However, from the result of work in this investigation, it is believed that the initial decrease is caused by individual fibers moving apart to make room for molecules that created the covalent bonding. The increase in conductivity is occurring because the ends of the molecules exhibit a van der Waals connection or touch points between fibers. The atoms continue to align themselves, which creates a second decline in conductivity as the ionic bond atoms adjust their space to achieve the lowest energy level. Without tension on the spun fibers, the chemically induced conductivity is lost as atoms achieve a lower energy state.

This study also indicated that once the spinning of the CNT wire is compromised, there is no chance of regaining the spun level of conductivity. Stated in terms of the basic hypothesis of using CNT wire as a direct replacement for copper wire, CNT wire does not seem to be currently capable of becoming a direct replacement for copper wire. Again, on the atomic level, the atoms would tend to arrange themselves to achieve the lowest energy state possible. A nanotube in a bundle of nanotubes would have one side compressed and the opposite side stretched, and would attempt to equalize the two forces along each side so as to lower the overall energy state.

CHAPTER 6

FUTURE WORK

Conductivity of spun CNT wire appears to be greatly influenced by the compression of fibers. One method to improve compression is through selection of a variety of CNT fiber lengths and diameters to feed the web for spinning. As in cotton spinning, the variety of CNT fibers should provide a more uniform structural density with minimum twist per length, which in turn should improve conductivity by eliminating gaps between fibers. Also, the variety of lengths and diameters should better resist spontaneous untwisting. As an alternative to compressing the CNT fiber through tension, an exterior coating that would maintain the compression of twist could be developed. If the coating were stiff enough, it would maintain compression of any coated length without additional tension on the CNT wire segment.

REFERENCES

REFERENCES

[1] M. Mial, "Electrical conductivity of pure carbon nanotube yarns," *Carbon*, vol. 49, no12, pp. 3755–3761, October 2011.

[2] H. E. Misak, R. Asmatulu, V. Sabelkin, S. Mall, and P. E. Kladitis, "Tension-tension fatigue behavior of carbon nanotube wires," *Carbon*, vol. 52, pp. 225–231, February 2013.

[3] L. Xiao, P. Liu, L. Liu, K. Jiang, X. Feng, Y. Wei, L. Qian, S. Fan, and T. Zhang, "Barium functionalized multiwalled carbon nanotube yarns as low work function thermionic cathodes," *Applied Physics Letters*, vol. 92, pp. 3755-3761, 2008.

[4] M. Zhang, K. R. Atkinson, and R. H. Baughman, "Multifunctional carbon nanotube yarns by downsizing an ancient technology," Science, vol 306, no 5700, pp. 1358–1361, November 19, 2004.

[5] C. D. Tran, W. Humphries, S. M. Smith, C. Huynh, and C. Lucan, "Improving the tensile strength of carbon nanotube spun yarns using a modified spinning process," Carbon, vol. 47, pp. 2662–2670, 2009.

[6] J. Min, J. Y. Cai, M. Sridhar, C. D. Easton, T. R. Gengenbach, J. McDonnell, W. Humphries, and S. Lucas, "High performance carbon nanotube spun yarns from a crosslinked network," Carbon, vol. 52, pp. 520–527, February 2013.

[7] M. Miao, J. McDonnell, L. Vuckovic, and S. C. Hawkins, "Poisson's ratio and porosity of carbon nanotube dry-spun yarns," Carbon, vol. 48, p. 2802–2811, 2010.

[8] X. Zhang, K. Jiang, C. Feng, P. Liu, L. Zhang, J. Kong, T. Zhang, Q. Li, and S. Fan, "Spinning and processing continuous yarns from 4-inch wafer scale super-aligned carbon nanotube arrays," Advanced Material, vol. 18, pp. 1505–1510, 2006.

[9] R. Sui, A. J. Thomasson, Y. Ge, and C. Morgan, "Multispectral sensor for in-situ cotton fiber quality measurement," Transactions of the ASABE, vol. 51, no. 6, pp. 2201–2208, 2008.

[10] J. Jia, Z. Jingna, X. Geng, D. Jiangtao, Y. Zhenzhong, T. Yuyu, F. Chao, Z. Zhang, X. Zhang, L. Zheng, and Q. Li, "A comparison of the mechanical properties of fibers spun from different carbon nanotubes," Carbon, vol. 49, pp. 13333–1339, 2010.

[11] G. Trakakis, D. Tasis, C. Aggelopoulos, C. Galiotis and K. Papagelis, "Open structured in comparison with dense multi-walled carbon nanotube buckey paper and their composites," Composites Science and Technology, vol. 77, pp. 52-59, date March 22, 2013

[12] H. Misak, R. Asmatulu, M. O. O'Mally, E. Jurak, and S. Mall, "Functionalization of carbon nanotube yarn by acid treatment," International Journal of Smart and Nano Materials, vol. 5, no 1, pp 34-43, Feburary 17, 2014.

[13] T. Baumeister, E. A. Avallone, and T. Baumeister III, Marks' Standard Handbook for Mechanical Engineers, New York: McGraw-Hill, 1978.

[14] R. Asmatulu, Nanotechnology Safety, Nederland: Elsevier, 2013.

[15] M. F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, "Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load," Science, vol. 287, pp. 637–640, Jan 28, 2000.

[16] B. Peng, M. Locascio, P. Zapol, S. Li, S. L. Mielke, and G. C. Schatz, "Measurements of near-ultimate strength for multiwalled carbon nanotubes and irradiation-induced crosslinking improvements," Nature Nanotechnology, vol. 3, issue 10, pp. 626–631, 2008.

[17] J. Wang, H. Xie, Z. Xin, and Y. Li, "Increasing the thermal conductivity of palmitic acid by the addition of carbon nanotubes," Carbon, vol. 48, issue 14, pp. 3979–3986, Nov 2010.

[18] K. White, M. Shuai, X. Zhang, H.-J. Sue, and R. Nishimura, "Electrical conductivity of well-exfoliated single walled carbon nanotubes," Carbon, vol. 49, pp. 5124–5131, July 14, 2011.

[19] P. Bradfore, D .Bogdanovich, and E. Alexander, "Electrical conductivity study of carbon nanotube yarns, 3-D hybrid braids and their composites," Journal of Composite Materials, vol. 42, n 15, pp. 1533–1545, August 2008.

[20] M. B. Jakubinek, M. B. Johnson, M. A. White, C. Jayasinghe, G. Li, W. Cho, M. J. Schulz, and V. Shanov, "Thermal and electrical conductivity of array-spun multi-walled carbon nanotube yarns," Carbon, vol. 50, pp. 244–248, August 17, 2012.

[21] A. S. Wu, X. Nie, M. C. Hudspeth, W. W. Chen, T.-W. Chou, D. S. Lashmore, M. W. Schauer, E. Tolle, and J. Roiux, "Strain rate-dependent tensile properties and dynamic electromechanical response of carbon nanotube fibers," Carbon, vol. 50 pp. 3876–3881, April 6, 2012.

[22] F. Deng, W. Lu, H. Zhao, Y. Zhu, B.-S. Kim, and T.-W. Chou, "The properties of dry-spun carbon nanotube fibers and their interfacial shear strength in an epoxy composite," Carbon, vol. 49, pp. 1752–1757, December 23, 2011.

[23] M. Aizawa and M. S. Shaffer, "Silylation of multi-walled carbon nanotubes," Chemical Physics Letters, vol. 368, pp. 121–124, October 30, 2003.

[24] N. Patil, A. Lin, E. R. Myers, K. Ryu, A. Badmaev, C. Zhou, H.-S. P. Wong, and S. Mitra, "Wafer-scale growth and transfer of aligned single-walled carbon nanotubes," IEEE Transactions on Nanotechnology, vol. 8, pp. 498–504, July 2009.

[25] Y. Gao, J. Li, L. Liu, W. Ma, W. Zhou, S. Xie, and Z. Zhang, "Axial compression of hierarchically structured carbon nanotube fiber embedded in epoxy," Adanced Functional Materials, vol. 20, no 21, pp. 3797–3803, Nov 9, 2010.

[26] M. Zu, Q. Li, Y. Zhu, M. Dey, G. Wang, W. Lu, J. M. Deitzel, J. W. Gillespie Jr, J.-H. Byun, and T.-W. Chou, "The effective interfacial shear strength of carbon nanotube fibers in an epoxy matrix characterized by a microdroplet test," Carbon, vol. 50, pp. 1271–1279, November 9, 2012.

[27] J. Y. Cai, J. Min, J. McDonnell, J. S. Church, C. D. Easton, W. Humphries, S. Lucas, and A. L. Woodhead, "An improved method for functionalisation of carbon nanotube spun yarns with aryldiazonium compounds," Carbon, vol. 50, pp. 4655–4662, May 24, 2012.

[28] L. Randeniya, A. Bendavid, P. J. Martin, and C.-D. Tran, "Composite yarns of multiwalled carbon nanotubes with metallic electrical conductivity," Small, vol. 6, issue 16, pp. 1806–1811, August 2010.

[29] M. Miao, S. C. Hawkins, J. Y. Cai, T. R. Gengenbach, R. Knott, and C. P. Huynh, "Effect of gamma-irradiation on the mechanical properties of carbon nanotube yarns," Carbon, vol. 49, pp. 4940–4947, July 23, 2011.

[30] J.-W. Jiang, J.-S. Wang, and B. Li, "Thermal expansion in single-walled carbon nanotubes and graphene: Nonequilibrium Green's function approach," Physical Review B, vol. 80, no 20, pp. 205429-1–205429-7, 2009.

[31] C. Huynh and S. C. Hawkins, "Understanding the synthesis of direct spinnable carbon nanotube forests," Carbon, vol. 48, pp. 1105–1115, November 24, 2010.

[32] K. R. Atkinson, S. C. Hawkins, C. Huynh, C. Skourtis, J. Dai, M. Zhang, S. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, and R. H. Baughman, "Multifunctional carbon nanotube yarns and transparent sheets: Fabrication, properties and applications," Physica B: Condensed Matter, vol. 394, no 2, pp. 339–343, May 15, 2007.