ABSTRACT

BRADFORD, PHILIP DAVID. Mechanical Characterization and Morphology Study of a Novel Class of Carbon Nanotube Textiles and Composites. (Under the direction of Sam Hudson and Russell Gorga.)

Carbon nanotube yarns are an emerging class of carbon nanotube materials that show great promise in composite applications. This research study was conducted to gain insight into the morphological structure of the yarns and to correlate their structure to the mechanical properties of both dry yarns and composites. Complex 3-D braided nanotube yarn structures were provided to determine the mechanical properties of macroscopic samples and to determine the effect of processing on the yarns. To accomplish these goals, baseline samples of carbon fiber were tested, a microscopical study was conducted, the cross sectional area of the samples were properly determined, composites were fabricated, and samples of the dry nanotube yarn structures as well as their composites were tested in tension.

The results of this study showed that in composite structures with low viscosity resin, the nanotube yarns did not act as the constituent reinforcement. Due to resin penetration through the yarns structures, the individual nanotubes that make up the yarns acted as the constituent reinforcement. In addition, the testing of the 3-D braided yarn structures showed that this process did not significantly weaken the structure and could be useful in making macroscopic preforms of carbon nanotube yarns.
MECHANICAL CHARACTERIZATION AND MORPHOLOGY
STUDY OF A NOVEL CLASS OF CARBON NANOTUBE TEXTILES AND
COMPOSITES

by

PHILIP DAVID BRADFORD

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Approved by:

________________________________  ________________________________
Dr. Samuel Hudson           Dr. Russell Gorga
Co-Chair of Advisory Committee        Co-Chair of Advisory Committee

________________________________  ________________________________
Dr. Ronald Scattergood            Dr. Alexander Bogdanovich
Committee Member       Committee Member
BIOGRAPHY

Philip Bradford was born in Columbus, Ohio, November 3rd 1982. His family moved to Wake Forest, North Carolina, where he attended elementary, and middle school. He graduated from Wake Forest–Rolesville High School in 2001 and started his college career at the College of Textiles at North Carolina State University the following fall. As a Centennial Scholar, Philip was involved with many activities within the college and met his future wife at a Professional Textile Fraternity conference. He graduated in 2005 with a Bachelor of Science degree in Textile Engineering. His interest in composite materials led him to pursue both Master of Science in Textile Engineering and Master of Material Science and Engineering degrees simultaneously at NCSU.
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Additionally, I would like to thank my mother and my father for their belief in me. I thank them for instilling in me the values that every researcher must possess: determination, patience, motivation, and creativity.

Finally, I would like to thank my fiancé Jenni for the continuous support, motivation and love that she has given me every step of the way.
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1 Introduction

Carbon nanotubes are interesting and versatile materials that have been the subject of thousands of research studies due to their unique electrical, thermal and mechanical properties. The use of carbon nanotubes in electronic circuits, biomedical scaffolds, energy storage and field emission devices are just some of the areas that have been investigated. Perhaps the most intensely researched area has been that of carbon nanotube polymer matrix composites. This thesis examines the mechanical properties and morphology of a new class of nanotube composites produced from carbon nanotube yarns and epoxy resin.

The covalently bonded structure of carbon nanotubes make them one of the strongest and stiffest materials yet discovered. Even though diameters of carbon nanotubes are extremely small, they can have extremely long aspect ratios that make them the ideal structure for the reinforcement of polymer matrix materials. Under the ideal conditions of defect free nanotubes, excellent nanotube orientation, high volume fraction and good interfacial bonding, carbon nanotube composites could achieve modulus and strength values greater than the best performing commercial carbon fiber composites.

To date, the production of carbon nanotubes in a powder form has limited their usage in composites. Polymer matrix composites have consisted of low volume fractions of randomly aligned, short to medium length nanotubes. While these nanotube filled polymer materials can be useful for improving existing polymer products, they will never reach the extreme mechanical properties that have been suggested for nanotube composites. Recently, the development of pure, continuous nanotube yarns has opened a new avenue for carbon
nanotube composite development. Now, through the use of these yarns, nanotubes can be manipulated on a macroscopic scale, to direct their reinforcement in polymer matrix composites. This work details the first study of the mechanical characterization of nanotube yarns, nanotube yarn preforms and their epoxy composites.

The overall objective of this study was to determine the mechanical properties of different dry nanotube yarn materials and their composites with increasing size from 5-ply yarn to 3-D braided preforms. However, to achieve this objective, many other important steps were utilized to validate the findings. These steps included:

- Baseline testing of PAN based carbon fiber filaments
- Cross section area determination of yarns, plied yarns and 3-D braids
- Mechanical characterization of 5-ply nanotube yarns, 25-ply nanotube yarns and 3-D braids (the latter consisting of 180 single nanotube yarns)
- Fabrication of nanotube yarn epoxy composites
- Mechanical characterization of 3-D braided nanotube yarn composites

1.1 Motivation and Objectives

The development of any new technology requires extensive investigation of the fundamental mechanisms that govern the properties of the material. With this knowledge, the properties of the material can be optimized to their fullest potential. Many past research studies have explained and characterized the properties of single carbon nanotubes and composites fabricated from nanotubes dispersed in a matrix. The development of carbon nanotube yarns has incited claims of this material being the ideal candidate for the reinforcement of the
composite materials; however, thus far, no studies of their behavior as a fibrous reinforcing material have been conducted. The research presented in this paper will provide insight into the morphology, mechanical properties and load transfer mechanisms in these complex structures. The study of these structures will help to answer the following fundamental questions:

- Are the 3-D braids produced on 3TEX’s manually operated device damaged and weakened in comparison with the constituent yarns?
- Do the mechanical properties and failure mechanisms of the yarn translate to the composite?
- Do the yarns, or the nanotubes that comprise the yarns, act as the constituent reinforcing materials in the composite structures?
- How do the mechanical properties of these novel composite materials compare to respective properties of commercially available composite materials?
2 Literature review

2.1 Nanotube Properties

Carbon’s ability to covalently bond with itself provides the foundation for materials with truly remarkable properties. Diamonds and graphite are the most recognizable forms of pure carbon and have been used in industrial and engineering applications for many years. In 1991, a new carbon structure, the carbon nanotube, was identified by Sumio Iijima of the NEC Corporation [1]. His discovery of the sp$^2$ bonded carbon tube structure spawned thousands of research studies to explore the production, structure and properties of these materials.

Carbon nanotubes make three covalent bonds with adjacent carbons, similar to the structure of graphite found in commercial carbon fibers. However, bonds in the carbon nanotube structure are rotated slightly so that a seamless tubular structure results instead of a flat graphitic sheet. Different processing methods create nanotubes with a single wall (SWNT) as well as nanotubes with multiple walls of concentric tubes (MWNT). The length of carbon nanotubes is also dictated by the processing method and varies greatly, from hundreds of nanometers up to millimeters. The uniformity of the seamless carbon lattice, lack of impurity atoms, and the absence of defects in their structure give nanotubes their outstanding predicted properties. It is not uncommon for a material to possess one or two advantageous properties simultaneously; however, carbon nanotubes are in a class by themselves. For example, it has been predicted that they exhibit ballistic electric conduction while their thermal and mechanical properties are superior to any other known material.
This study was focused on the mechanical properties of carbon nanotube composites. However, it is important to briefly address the electrical and thermal properties of nanotubes, keeping in mind their potential as reinforcements for multifunctional nanocomposites.

The electrical conductivity of carbon nanotubes depends on the wrapping structure of the graphite sheet. A nanotube’s chirality can be expressed by two vectors, $n$ and $m$, that describe the orientation of the graphite sheet. If the vectors are equal to each other ($n=m$), the nanotube retains its symmetry and is electrically conductive. Nanotubes in which the vectors are not equal are considered semi-conducting [2]. MWNTs can contain both tube chiralities making their electrical characterization more complex. A wide range of electrical property data has been collected for carbon nanotubes, which is related to the differences between nanotube samples and testing methods used in different studies. Even when examining tubes from the same batch, it has been shown that differences in the structure provides for a wide range of tube conductivities [3]. Due to their tubular shape, once an electron enters the structure, it travels down the tube until it encounters a defect. Conductive carbon nanotubes have shown to exhibit ballistic conduction of electrons along their length [4,5]. Due to this conduction mechanism, extremely high current densities, up to $1 \times 10^6$ A/cm$^2$, have been measured at the point of nanotube failure [6]. Nanotubes dispersed in polymers can be used to dramatically increase the electrical conductivity of the insulating matrix to the point where the composite can be used for applications such as static discharge.

Carbon nanotubes exhibit exceptionally high thermal conductivity in one dimension, along their length. The lack of free electrons in the nanotube structure means the thermal
conduction is dominated by atomic vibrations (phonons). The regularity and stiffness of the structure ensures that the phonons are propagated quickly down the tube with few phonon collisions and little phonon scattering [7]. Thermal conductivity values of up to 6000 W·m$^{-1}$·K$^{-1}$ have been calculated based on the optimal tube structure for phonon transport. In [8], a thermal conductivity of 3000 W·m$^{-1}$·K$^{-1}$ was measured across a single MWNT, which was very close to the predicted value for that structure.

To meet the objectives of this study, understanding the mechanical properties of carbon nanotubes is essential and will help to explain the behavior seen in the carbon nanotube yarns and composites. The extreme strength and stiffness of carbon nanotubes arises from the covalent sp$^2$ bonding and the stability provided by the tube structure. The seamless nanotube structure is stronger than graphite planes that contain the same chemical repeat units. The stiffness of a nanotube is not dependent on the chiral structure, but is dependent on the diameter and number of walls in the nanotube [2]. As the ratio of the wall area to core area is increased, the modulus is increased due to the increased number of graphene sheets loaded per unit area. However, at the same time, the specific modulus is decreased as the density approaches that of pure graphite (2.1 g/cm$^3$). Modulus values for ideal nanotube structures are less than twice that of commercial pitch based carbon fibers, yet their strength could be up to 10 times greater. Values from 13-52 GPa were obtained in a study by Yu et. al. [9]; they provide a range in which the values from many other studies are included. Due to the perfect bonding of the structure, dislocation movement and crack propagation do not occur in carbon nanotubes. Thus, these mechanisms do not contribute to the failure, as they do in many other engineering materials, which allow carbon nanotubes to fail at very high strain, in
the range of 6-12% [10]. However, the presence of defects in the carbon lattice has shown to reduce the strength of the tube [11]. As the length of the nanotube increases, the strength decreases due to the higher probability of defects present in the structure. The size, structure and presence of defects are dependent on the processing techniques used to produce the nanotubes.

2.2 Nanotube Production

Three principle methods are currently used to produce carbon nanotubes: electric-arc discharge, laser ablation, and chemical vapor deposition (CVD). The oldest and most commonly used method is electric-arc discharge. In this process, an extremely high current produces an electric arc between two carbon electrodes. The carbon on the surface of the anode sublimates, and a portion of the carbon plasma self assembles into nanotubes on the way to the cathode. Laser ablation works in a similar fashion, but the carbon is vaporized by a pulsing laser in a high temperature chamber. The nanotubes form as the gaseous carbon condenses on cooler parts of the chamber. These two methods generally produce the straightest and most defect free nanotubes because the extremely high processing temperatures ensures that all carbons contain only sp² bonds. The disadvantages of these two processes are that the length of the nanotubes is very limited and a large amount of amorphous carbon is left behind and has to be removed in subsequent processing steps.

The carbon nanotubes used in this study were produced by chemical vapor deposition. This process uses both metal catalyst particles and hydrocarbons to grow nanotubes in an oven. In the presence of catalyst nano-particles, the hydrocarbons break down and the carbon atoms
self assemble on the surface of the catalyst. If the particles are injected into the gas mixture in the furnace, the nanotubes can grow as an aerogel [12]. If the particles are dispersed on a substrate such as silicon, the nanotubes will grow attached to the surface. Catalyst particles that are spaced closely together will often grow nanotubes in vertical arrays because the close proximity of the tubes allows them to support each other through Van der Waals forces. The nanotube arrays used to spin yarns for this study were grown to a height of 300 μm [13], while recent advances in this technology have produced 3 mm high forest [14]. Nanotubes grown using this method have shown that the nanotubes are not perfectly straight and contain more defects than nanotubes produced by arc discharge or laser ablation. This is caused by the low temperatures at which CVD growth takes place [2]. The quality of the nanotubes produced by CVD may play an important role in the future discussion of nanotube yarn and composite properties.

2.3 Nanotube Yarn Formation

Three formation methods are currently used to create carbon nanotube yarns. Only one yarn formation method was used to make the yarns in this study; however, it is important to briefly examine the others to gain an understanding of the positive and negative attributes of each.

The earliest method of nanotube yarn formation was developed by Vigolo et. al. in [15]. In this process, SWNT or MWNT are dispersed in an aqueous solution of sodium dodecyl sulfate (SDS) using sonication. This solution was injected into a flowing polyvinyl alcohol (PVA) solution. The PVA destabilized the nanotube dispersion so that the nanotube solution
coagulated into a ribbon structure. This ribbon was then extracted from solution, washed with water to remove the SDS and PVA, and then dried. The resulting yarns showed orientation of the nanotubes along the fiber axis when studied with x-ray diffraction and the nanotubes became even more aligned when the yarns were stretched and dried under a tensile load [16]. These yarns inherently contain trapped PVA and had to be annealed at high temperatures to remove remaining polymer to make a “pure” yarn. Although many research papers have been written on this process, the authors have yet to publicize the quantity of fibers they have been able to make.

A less published, but equally interesting method for spinning carbon nanotube yarns, was developed by Kinloch et al. [17]. This method is the most direct method for producing yarns because it is a one step process. In a CVD furnace, hydrocarbon gas and iron particles react to form a free floating nanotube aerogel, which can be collected, twisted, and taken up onto a roll inside the furnace. The authors mentioned that the yarns varied greatly in diameter and, therefore, a large range of strength values were recorded for these yarns. The length of the individual nanotubes in the yarn was estimated to be tens of nanometers long. A large amount of residual metal catalyst could be seen in the yarns due to the fact that they were spun directly from the mixture of catalyst and hydrocarbon gasses. Successive washings removed some, but not all of, the iron. The authors of [17] have had a follow up study to examine the type of hydrocarbon gases used [18], but have not published the quantities of this fiber that can be produced.
The third and most publicized method for making continuous carbon nanotube yarns was the one used for to supply the yarns used in this thesis. The basis for this method was accidentally discovered by the Jiang et al. in [19], who pulled a strand of connected nanotubes from an array of vertically aligned nanotubes grown on a substrate. Vertical arrays of carbon nanotubes are often referred to as nanotube “forest” because of their resemblance to a bamboo forest. With some modifications, research teams from the University of Texas at Dallas and CSIRO Textile & Fiber Technology (Australia), were able to create continuous yarns using a similar process, but added twist to the strands drawn out of the array [13]. Figure 2.1 shows a picture of this spinning process.

![Figure 2.1 Nanotube Yarn Formation [19]](image-url)

Finding the right packing density of the nanotubes on the surface of the substrate was the main challenge to producing spinnable arrays. If the nanotubes are spaced too far apart, the
Van der Waals bonding between the tubes will be weak so that they will pull off individually and not in succession. If the spacing between the tubes is too close, “clumps” of nanotubes will be pulled from the array. The yarn produced in the study above is uniform along its length, has good electrical conductivity (300 S/cm), and has unique flexibility, high strain to failure and high knot strength. The nanotubes within the yarns were MWNT with an average length of approximately 150 μm.

The nanotube yarns produced by the three different methods discussed above, have shown an extremely wide range of mechanical properties considering that they have the same basic building blocks. These mechanical properties can be used as a point of comparison for the work conducted in this study.

### 2.4 Nanotube Yarn Spinning

The nanotube yarns studied here were produced by the NanoTech Institute at the University of Texas at Dallas mentioned in the previous section. A variable speed yarn spinning apparatus was used to draw and twist the nanotubes from the forest while continuously taking up the finished yarn onto a bobbin. A schematic diagram of this apparatus is illustrated in Figure 2.2.

![Figure 2.2 Schematic diagram of Yarn Spinning Apparatus [46]](image)
The CVD grown MWNTs in the forest were approximately 300 μm long with average inner and outer diameters of 5 nm and 10 nm respectively. The process was optimized to produce yarns with a diameter of approximately 10 μm and twist level of approximately 25 turns/mm in the counter-clockwise direction. Five single yarns were then plied together with a twist of 4 turns/mm in the clockwise direction to produce the 5-ply yarns used in this study. Additionally, five 5-ply yarns were twisted to obtain 25-ply yarns. For the purpose of this study, 38 one-meter long 5-ply yarns were provided to 3TEX. All but two of these pieces were used for producing a 3-D braided structure. One meter of 25-ply yarn was also supplied.

2.5 3-D Braided Nanotube Yarns

The industrial rotary 3-D braiding process developed by Mungalov and Bogdanovich [20] was scaled down to accommodate the braiding of continuous carbon nanotube yarns and can be seen in Figure 2.3. This braiding device and the 3-D braided nanotube yarn structures produced for this study were manufactured by 3TEX, Inc. whose methods were published in [21].

Figure 2.3 3TEX Apparatus for 3-D Braiding [48]
This hand operated braiding mechanism was mounted on top of a plexi-glass box to prevent accidental contact with the very small yarns. The braiding device contains 36 carriers to which the 5-ply nanotube yarns were attached. A microscope mounted to a movable track on the box allowed the operator to view the braiding point during operation. One meter of the 3-D braided structure consisting of 36 5-ply nanotube yarns was provided for mechanical characterization in this study.

2.6 Nanotube Yarn Mechanical Properties

The published data for the mechanical properties of carbon nanotube yarns is far from complete. The data from four different research groups using three different yarn formation techniques is presented in Table 2.1.

Table 2.1 Mechanical Properties of Carbon Nanotube Yarns

<table>
<thead>
<tr>
<th>Study</th>
<th>Strength (MPa)</th>
<th>Ultimate Strain (%)</th>
<th>Load vs. Extension Curve</th>
<th>Nanotube length (μm)</th>
<th>Source</th>
</tr>
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<tbody>
<tr>
<td>1. Furnace Spun</td>
<td>1460</td>
<td>13.5</td>
<td>n/a</td>
<td>20-30</td>
<td>[18]</td>
</tr>
<tr>
<td>2. Solution Spun</td>
<td>230</td>
<td>1</td>
<td>n/a</td>
<td>n/a</td>
<td>[16]</td>
</tr>
<tr>
<td>3. Forest Spun</td>
<td>300</td>
<td>7.5</td>
<td>n/a</td>
<td>150</td>
<td>[13]</td>
</tr>
<tr>
<td>4. Forest Spun</td>
<td>3300</td>
<td>n/a</td>
<td>n/a</td>
<td>1000</td>
<td>[14]</td>
</tr>
</tbody>
</table>

Study of the literature revealed that none of the aforementioned studies provided details of the testing method, load vs. extension curves or breaking load values for their given tests. With the addition of the breaking load data and cross sectional area for the tested specimens, the reader could draw their own conclusions about the strength values reported. Study [14]
did not mention how the cross sectional area of the yarns was determined, while studies [16] and [13] made the assumption that the yarns were circular so that diameter measurements could be made with a scanning electron microscope (SEM). Study [18] shows a disproportionately high strength based on the length of the nanotubes in the yarn as compared to the other three studies. The cross sectional area obtained in that example were obtained by dividing the linear density (Tex) of the yarn by the volumetric density of the graphite (2.1 g·cm$^{-3}$). However, nanotube yarns do not have the volumetric density of graphite, as they contain a large fraction of empty space as seen in [13] and [16]. Hence, the cross sectional area they calculated was much smaller than the actual area. This discrepancy is seen in the paper, as the authors calculate a range of diameters from 2-19 μm, yet the microscopic pictures show yarns that appear to have diameters from 30-100 μm. The calculated stress is then lower than reported.

In this thesis, the parameters for the mechanical testing of the plied nanotube yarns and 3-D braids are well defined to ensure the validity of the testing data presented.

2.7 Standards for Mechanical Testing

The four example studies mentioned previously, all presented mechanical data but did not give the reader any details about how the materials were tested. However, it was apparent that some of the studies used textile based standards, while others used composite based standards. The uniqueness of carbon nanotube yarns and their similarity to both traditional textile yarns and continuous fibers used in composite materials, could have led to this discrepancy. To gain a better understanding of the properties of nanotube yarn structures,
appropriate standards must be used to allow the comparison of results across the scientific community. Three different ASTM standards could apply to the nanotube yarns and composites being tested in this study:

1. ASTM D2256 – Tensile Properties of Yarns by the Single Strand Method [22]
2. ASTM C1557 – Tensile Strength and Young’s Modulus of Fibers [23]

The first standard [22] is associated with staple yarns made by traditional textile spinning methods. The types of yarns tested with this method are usually yarns for weaving apparel and industrial fabrics. Fabrics and preforms for composites are usually woven exclusively out of continuous fiber tows. The textile industry characterizes yarns using a direct yarn numbering system that describes the linear density (mass/unit length) of the material. Processes and applications utilizing these yarns rarely require the cross section of the yarns to be known, while the cross sectional area value (A) is the basis for stress calculations (\(\sigma = \frac{F}{A}\)) used in many engineering disciplines. The textile industry has adapted the term “tenacity” to describe the strength of yarns which is calculated as: Tenacity = Force/Linear density. Standard D2256 is also different from the other two mentioned above in that the samples do not have to be tabbed to prevent slippage. The large yarn diameters and relatively low strength of the yarns ensure that yarn slipping in the grips is not an issue. This standard also requires a larger gauge length than the other two due to the fact that the staple fibers in yarns can be long and should not be held by both grips at once.
The second standard [23] is used to test extremely fine continuous carbon and ceramic fibers that make up much larger tows that are utilized in composite materials. These fibers range in diameter from 5-10 \( \mu \text{m} \) which incurs the need for a tensile tester with a very sensitive load cell. These samples must be fixed in tabs to allow for proper fiber alignment in the testing fixture and to prevent slippage. Figure 2.4 shows the schematic diagram for tabbing a single fiber using standard ASTM C1557.

![Figure 2.4 Tabbed Single Fiber Tensile Sample [21]](image)

The inherent high modulus of the fibers, paired with their small size, will cause them to slip through even rubberized grips. Epoxy, superglue or another suitable adhesive should be used to affix the fibers to cardboard or heavy paper. Relatively short gauge lengths can be used because of the small diameter and monofilament nature of the test specimen.
The third standard [24] uses the complete bundle of fibers that makes up a carbon tow to obtain the average mechanical characteristics of the individual fibers. This standard is commonly used by producers of carbon fiber to quickly obtain the average strength of the fibers within the tow. In this method, the tow is dipped in an epoxy resin to consolidate the fibers and then squeezed through rollers to eliminate excess resin. The tow is dried under tension so that all of the fibers are parallel to each other. The epoxy resin allows for stress transfer between fibers, which is essential when testing bundles of fibers in tension. If a resin matrix is not used, many of the thousands of fibers that make up the tow will not receive equal stress under tension; the specimen will not fail catastrophically, but rather will fail by “fraying”.

2.8 Nanotube Composites

Fiber reinforced composites capitalize on the desirable properties of the fiber and the matrix material. The anisotropic fibers bear the load while the matrix defines the shape of the material and provides load transfer, shear stiffness and compressive stability to the fibrous reinforcement. Composites have been around for thousands of years, but only in the last two decades has the study of nanocomposites emerged. Naturally, carbon nanotubes are the ideal reinforcing material, thus numerous studies have been conducted to capitalize on their remarkable mechanical properties. Polymer matrix nanotube composites are grouped into the following four major groups based on their processing method and matrix type: solution processed composites, melt processed thermoplastic composites, mixed thermosetting composites and matrix infiltrated composites.
Solution processing of carbon nanotube composites is a simple method to evenly disperse nanotubes in a polymer matrix. With the aid of a surfactant, nanotubes can be dispersed in a solvent using sonication. If polymer is present in solution, the nanotubes will be entrained in the polymer left behind as the solvent is evaporated away. The most simple form of this method, with water as the solvent, was used by Shaffer et. al. in [25] to disperse nanotubes in a poly(vinyl alcohol) solution to create composite films. A more complicated method was used in [26] to integrate nanotubes into polystyrene. Here the MWNT were sonicated in toluene and then added to a solution of polystyrene and toluene. Adding 1% weight fraction of nanotubes to the polystyrene increased the modulus and breaking stress by 36% and 25% respectively. This method is limited to the production of thin films where the solvent can be completely evaporated away.

Melt processed carbon nanotube composites have a great potential for large-scale production of nano-composites. Traditional extrusion [27], injection molding [28] and compression molding [29] processes have been modified to incorporate carbon nanotubes in the bulk polymer. Distributing nanotubes in viscous polymer melts is accomplished through shear mixing, which can result in good nanotube dispersions at low volume fractions. At higher volume fractions, the nanotubes can change the viscosity of the melted polymer. Most studies have shown that at low volume fractions of nanotubes, the strength and modulus of the polymer increases. At a certain point, the addition of more nanotubes decreases the strength of the composite. This point signifies the transition where the nanotubes can no longer be fully dispersed in the matrix.
In melt spun extruded fibers, the high shear stress at the spinneret has been shown to align the nanotubes in the direction of the fiber. These fibers have shown the most impressive increases in mechanical properties. In [30], the modulus of polypropylene fibers was tripled, increasing from 0.4 GPa to 1.4 GPa with the addition of 5 wt. % SWNT.

Thermosetting polymers such as epoxy are more widely used in consolidating fiber reinforced composites than thermoplastic materials. The low viscosity of uncured resin allows it to easily penetrate tight bundles of fibers found in composite preforms. Once the thermoset resin is fully cured, it is very thermally stable. Thermosetting polymers have a keep their structural integrity up to the point of their thermal degradation [31]. Thermosetting resins are primarily used in the composites industry due to their initial low viscosity.

Thermosetting polymers used in composites are generally brittle materials. Matrix cracking is a major source for composite failure. To help reduce the tendency of cracking, it is desirable to increase the toughness of the matrix material without reducing the modulus. With the addition of nanotubes to epoxy and other thermosets, researchers have increased both the modulus and the strength of these materials. Bai increased the strength and modulus of epoxy with low nanotube loading [32]. The modulus of the epoxy doubled from 1.2 GPa to 2.4 GPa with the addition of 1 wt % MWNT, while the strength increased from 30 to 41 MPa.

In the three previous processes for producing nanotube composites, the nanotubes are added to the matrix material in the form of a powder. In a matrix infiltrated nanotube composite, the matrix is added to a “preformed” nanotube structure. This method is especially intriguing, as
this is the method that was utilized during the course of this research to infuse nanotube yarns
and braids with epoxy resin.

Carbon nanotube arrays have been infiltrated with a polymer to create a composite. Lahiff et
al. spin coated polystyrene-b-polydimethyl-siloxane (PDMS) onto a MWNT array to produce
a thin film that was peeled away from the substrate. The modulus of the composite was twice
that of pure PDMS, but the strength was also reduced by 25% [33].

The infiltration method has been used primarily to increase the mechanical properties of
“buckypaper”. Buckypaper can be created by dispersing nanotubes in a solvent and removing
the solvent through a filter and evaporation. The remaining nanotubes create a non-woven
mat that has no preferential nanotube orientation and a large amount of free volume.
Thermoplastic polymers in solution such as poly (vinyl alcohol) and polystyrene were used
to infiltrate buckypaper by Coleman et al. in [34]. They achieved up to 30 wt. % polymer into
the structure which increased the modulus, strength and toughness values by 3, 9 and 28
times respectively. Epoxy has also been used to produce buckypaper composites in [35]. In
this method, the epoxy was thinned with acetone to reduce the viscosity to facilitate resin
flow through the nano-porous nanotube structure. The authors experienced complete
penetration of the resin and as a result, the modulus of the composite was six times greater
than that of the neat epoxy.
2.9 Mechanical Behavior of Carbon Nanotube Composites

2.9.1 Load transfer

The transfer of load from matrix to fiber is essential and defines the fibers contribution to the mechanical properties of a composite material. The strength of the interface is governed by the morphology and bonding between the two materials. If the surface of the fiber is rough, mechanical interlocking of the two materials will create a strong interface. Most common reinforcing fibers have a smooth surface, which means that bonding interactions at the interface will dominate. The strength of the interface increases with increasing bond strength. Thus, van der Waals bonding provides the weakest interface, while covalent bonding provides the strongest. The strength of the interface is quantified by the interfacial shear strength (IFSS), which has been can be calculated using fiber pull out or push out tests [36].

The strength of the interface is especially important for composites that utilize discontinuous fibers as their reinforcement. When loading short fibers, the load increases from the ends to the mid-point of the fiber. The critical length of a fiber corresponds to minimum fiber length where the maximum load transfer from matrix to fiber can be reached. However, at this point only a small fraction of the fiber carries the maximum load. As the length of the fiber increases, a greater fraction of the fiber length carries the maximum load. This can be characterized by the load transfer efficiency. For example, a fiber that carries the maximum load across 80% of its length has a load transfer efficiency of 80%. To obtain excellent mechanical properties in short fiber composites, the fibers must be long enough so that they carry the maximum load along most of their length.
Carbon nanotube’s perfectly cylindrical structure and lack of free bonds or functional groups does not encourage interlocking or strong interfacial bonding. A wide range of interfacial shear strengths have been calculated for nanotube composites. Values as low as 2.7 MPa were calculated by Frankland et al. with the use of molecular simulations of carbon nanotubes and polyethylene [37]. Liao et al. calculated a much higher value of 160 MPa for the IFSS between polystyrene and nanotubes [38]. Simulations considering the bonding between carbon nanotubes and epoxy fell between these values at 138 MPa [39].

Mechanical testing of the IFSS of nanotubes and polymers has shown a much wider range of values. This can be attributed to the difficulty in manipulating and testing a single nanotube. Cooper et al. used a modified fiber pullout test to measure the load needed to pull a nanotube out of epoxy. In their test, a nanotube spanning across a micro-crack in the epoxy was pulled out when an atomic force microscope (AFM) tip was dragged across the crack. The difficulty in measuring the initial imbedded length of the carbon nanotubes resulted in a range of 35-375 MPa for the six samples tested. [40]. A traditional pull out test was accomplished by Barber et al. to pull MWNT out of a polyethylene-butene matrix. A MWNT was secured to an AFM tip and then dipped into softened polymer. When the polymer solidified, the nanotube was pulled from the matrix and the pull-out force was measured. They obtained an average value of 47 MPa for the IFSS [41]. Values much greater have been recorded from nanotubes that have been modified with functional groups to facilitate covalent bonding. This effect was modeled in [42] and produced an IFSS value of 500 MPa between nanotube and polymer in [43]. The IFSS in traditional carbon fiber-epoxy composites ranges from 50-90 MPa [44]. The range for carbon nanotubes overlaps the range for carbon fibers. It is thought
that the nano size scale of the tubes, huge surface area and occasional defects along their length create more interactions per unit area with polymers molecules than traditional fibers in a polymer matrix do.

With known values of the IFSS of nanotube and polymer, the critical length and the load transfer efficiency have been calculated. A comprehensive study by Haque et al. [45] used an analytical model and a Finite Element Analysis (FEA) model to predict the stress transfer length of carbon nanotubes. The models showed that nanotubes could reach the stress saturation point with a length to diameter (l/d) ratio of 10. However, at this point, the average stress along the nanotube was very low. To reach the highest load transfer efficiency, it was recommended that the l/d ratio be 1000 or greater [45]. For nanotubes with a diameter of 10 nm, the tube length would need to be around 10 μm for efficient load transfer. This ratio assumes that each nanotube is separate from others and has no flaws in the interface along the length of the tube. It is reasonable to assume that nanotube bundling could dramatically increase the l/d ratio needed for efficient load transfer.

### 2.9.2 Nanotube Composite Modulus Prediction

Generally, the mechanical properties of nanotube composites have not reached the theoretical limits based on the stiffness and strength of individual carbon nanotubes. The two most common methods used to predict the modulus of nanotube composites are the rule of mixtures and the Halpin-Tsai equations.

The rule of mixtures is the most simple of all composite mechanical property models and is commonly used to predict the modulus of unidirectional composites. It describes a fiber
architecture in which all of the fibers run the complete length of the composite parallel to the
direction of loading. This model assumes that there is perfect interfacial bonding; therefore
the strain of the matrix will be equal to the strain in the fiber. The composite modulus is
given by:

\[ E_c = E_f V_f + E_m (1 - V_f) \]  

(1)

Where \( E_f \) and \( E_m \) are the modulus of the fiber and matrix respectively and \( V_f \) is the volume
fraction of fiber. The rule of mixtures calculates the upper limit of the composite modulus in
the fiber direction. Factors such as fiber disorientation, fiber discontinuity and an imperfect
interface will reduce the modulus. Nanotube composites do not meet the fiber architecture
requirements for this model; however, using this model to describe the theoretical upper limit
of nanotube reinforcement provides researchers the motivation to continue to strive to reach
this value.

The Halpin-Tsai model is much better suited for predicting the modulus of nanotube
composites. In this method, the length and the diameter of the fiber are factored into the
model to account for load transfer efficiency. These equations were developed as a semi-
empirical model applied to unidirectional composites. However, with modifications, this
model has shown to correctly predict the stiffness of short fiber composites. Longitudinal and
transverse modulus values are calculated as follows:

\[ E_{11} = \frac{1 + 2(l_f / d_f)\eta \cdot V_f}{1 - \eta \cdot V_f} E_m \]  

(2)
\[ E_{22} = \frac{1 + 2\eta V_f}{1 - \eta V_f} E_m \] (3)

\[ \eta_u = \frac{E_f / E_m - 1}{E_f / E_m + 2(l_f / d_f)} \] (4)

\[ \eta_r = \frac{E_f / E_m - 1}{E_f / E_m + 2} \] (5)

where

- \( E_{11} \) = modulus in the longitudinal direction
- \( E_{22} \) = modulus in the transverse direction
- \( V_f \) = fiber volume fraction
- \( E_f \) = fiber modulus
- \( E_m \) = matrix modulus
- \( l_f \) = fiber length
- \( d_f \) = fiber diameter

For a composite with random fiber orientation in two dimensions (ex. a non-woven mat of fiber) the modulus is calculated as:

\[ E_r = \frac{3}{8} E_{11} + \frac{5}{8} E_{22} \] (6)

For a composite with random fiber orientation in three dimensions (ex. short fibers randomly dispersed in bulk resin) the modulus is calculated as:

\[ E_r = \frac{1}{5} E_{11} + \frac{4}{5} E_{22} \] (7)

As the fibers become less oriented, the modulus of the composite drops substantially. This
factor plays a large role in the mechanical properties observed for nanotube composites.

### 2.10 Proposed Composite Applications

There is a possibility that carbon nanotube yarns could someday replace carbon fibers in traditional composites due to their potential strength and weight savings. This switch would certainly be many decades away. The first applications for carbon nanotube yarns would be specialty applications where the cost is no object or where only a small quantity of yarn is needed. Bogdanovich has suggested that the first application for carbon nanotube yarns could be through thickness reinforcement of three dimensionally textiles such as 3-D woven fabrics [46].

Composites produced from 3-D woven fabrics are known for suppression of delamination, damage tolerance, impact energy absorption, improved fatigue resistance, and ballistic performance. Z-yarns run through the thickness of the fabric to tie the multiple fabric layers together which makes them superior to laminates in the properties mentioned above. As the size of the z-yarns increases (and the through thickness properties increase) the mechanical properties in the plane of the composite are affected by the reduced volume fraction of yarns in plane. Typical 3-D woven fabrics have an in-plane $V_f$ of 45-55% compared to 70% for laminated structures.

One way to minimize this problem is to develop a textile fiber that is much stronger than currently available carbon fiber. The increased strength would allow the size of the z-yarn to be reduced. Thus, the smaller yarns would still provide the desired through thickness
properties while the in plane stiffness and strength would increase. This concept was shown by the model developed in [46] and can be seen in Figure 2.5

![Figure 2.5 3-D weave with Varying Z-yarn Size](image)

Carbon nanotube yarns would be the perfect candidates for this application if their mechanical properties are greatly increased. As seen from the figure above, the yarn would provide the desired through thickness enhancements while only using a small amount material. In the same paper there are some concepts of 3-D braided composites that utilized carbon nanotube yarns in the same manner. It was proposed that small nanotube yarns could be 3-D braided around much larger axial tows to improve the damage tolerance of the
structure without significantly altering the in-plane mechanical properties of the unidirectional axial tows.

The mechanical characterization of nanotube yarn composites concurrently with further development of the yarns is necessary to make progress in both fields and to make applications, like the ones suggested above, a reality.
3 Baseline Tensile Testing

The inconsistency of the mechanical testing methods and results given in previous research of carbon nanotube yarns has shown the need for consistent testing methods. One of the goals of this research was to provide a thorough investigation of the mechanical properties of the materials being tested, while presenting the methods of testing as a platform for consistent future research.

The carbon nanotube yarns of interest are only microns in diameter and thus the breaking load is very small. Tensile testing load cells have a lower limit of accurate measurement, which is around 1%. At fractions of their load limit below 1%, error in the load measurements goes up dramatically. The experiments conducted using plied nanotube yarns require that extremely low load measurements be taken. A special load cell with a maximum loading of 5 Newtons (N) was used, so loads down to 0.05 N could be accurately measured. The tensile tester was an Instron model 5544, shown in Figure 3.1. The Instron was controlled electronically through a personal computer loaded with Blue Hill Instron control software. The displacement and strain of the samples throughout the study were determined by the displacement of the grips as calculated by the Blue Hill software. Strain gauges could not be used, due to the small size of all of the samples.

To verify the accuracy of the load cell, and to determine the validity of the sample mounting procedures, single filaments from commercial carbon fibers were mounted and tested on the Instron with the 5 N load cell. Carbon fibers were chosen because of their similarity to the nanotube yarns in their small diameter and breaking load. Hexcel AS4 carbon fibers from a
12k tow were chosen to obtain the baseline data.

A 50 mm length of 12K AS4 carbon fiber tow was cut off from a large package. This piece was then soaked in a bath of water for two hours to remove as much sizing as possible. This allowed the individual fibers to be separated from the tow much easier. After the tow was air dried, single fibers were carefully extracted using fine tweezers. They were mounted and tested according to the ASTM C1557-03 standard [23]. Tabs for securing the fibers were made by printing out the pattern on a piece of cardstock paper using a desktop publishing program. The holes in the tabs were exactly 10 mm wide and were cut out using a sharp razor.
blade. The tabs were secured to a piece of white foam core board with tape for stability when mounting the carbon fibers. A 10x magnifying glass was needed to make sure that only one single fiber was mounted on each tab. The carbon fibers were placed perpendicular to the hole in the center of the tab and the ends of the fiber were secured using tape. Epoxy was used to fix the fiber in place on the tab so that it would not slip during testing.

The epoxy system used for securing the fibers was an Epon 9504 and Epi-Cure 9554 mixture. The mix ratio was 100:25 parts by weight for the epoxy and hardener. Small drops of the mixed resin were applied to the tabs making sure that it covered the fiber up to the edge of the cut out hole. This ensured that the gauge length of 10 mm would be consistent for each sample. The epoxy was allowed to cure for 16 hours at room temperature and then was post cured at 90 °C for one hour.

The cross section of the round filaments was calculated from the diameter (7.1 μm) published by the manufacturer. The results for 15 tensile test specimens can be seen in Figure 3.2. The average strength of the samples was 4034 MPa and the average modulus was 205 GPa. The samples showed a wide variation of strength values, which is not uncommon for fibers within a single carbon fiber tow. In [47], carbon filament tensile testing showed a breaking strength range of 1940 MPa, which is greater than the range seen here. The average values obtained in this study were in good agreement with the manufacturer’s data of 4278 MPa and 228 GPa, see [48].
The data in Figure 3.2 show typical curves for carbon fiber. The entire curve is in the elastic loading region and the samples failed in a brittle manner at around 2% strain. None of the samples slipped out of the epoxy tabs. Slippage for most samples is characterized by a leveling in the stress value and excessive strain to failure. It was deemed that the load cell was working properly and that the tensile tester measured the strain correctly. These mounting procedures were used for subsequent tensile testing of carbon nanotube yarn samples.
4 Tensile Testing of Plied Yarn and Braided Structures

4.1 Microscopical Study

The yarns tested in this study were much smaller than traditional textile yarns. In fact, to the naked eye, the yarns appeared to be a single fiber instead of five plied yarns. To understand the morphology of the 5-ply yarns better, optical and scanning electron microscopes (SEM) were employed.

It was perceived that the 20 different 5-ply nanotube yarns studied had visibly different diameters when viewed with the naked eye. Before 3-D braiding took place, 3TEX supplied a small sample of each to be viewed under the microscope to see these differences. This was confirmed by the optical microscope picture shown in Figure 4.1 - one can clearly see that there is significant variation in the yarn diameters when they are viewed at 63x magnification.

![Figure 4.1 Yarns From 18 Different Spools, 63x Magnification](image)

It was difficult to determine whether the twist level was the only factor that significantly influenced the 5-ply yarn diameter. Figure 4.2 further shows a close-up of the first six yarns
from Figure 4.1, obtained with a JEOL 6400F Field Emission SEM. This micrograph shows that even those yarns that have a similar level of twist vary significantly in diameter. This effect of the yarn geometry variation has significant meaning when comparing breaking loads of yarns taken from different spools.

![Figure 4.2 Comparison of 5-ply Yarns From Different Spools](image)

The fine structure of the 5-ply nanotube yarns was studied more closely using the SEM. This allowed for extremely high magnifications where single nanotubes could easily be distinguished. Figures 4.3-4.5 show a series of pictures taken at successively increasing magnifications. A preferred orientation of the nanotubes and nanotube bundles can be seen in Figure 4.3. The nanotube orientation angle was measured using Scion Image software and was found to be 33°.
Figure 4.3  5-ply Nanotube Yarn, 5000x Magnification

Figure 4.4 provides a closer view of the same yarn. Large bundles with a preferred orientation can be seen, but there are many individual nanotubes and small bundles thereof that are not in line with the aforementioned orientation angle. The bundles of nanotubes ranged in size but were as large as 100 nm. Figure 4.5 further details the nanotube yarn morphology, and individual 10 nm diameter nanotubes can be distinguished. This close-up shows a much more disordered nanotube arrangement, and it becomes more difficult to determine the direction of preferred alignment. It was suggested by the yarn manufacture that this misalignment was a surface effect caused by spooling and handling the yarns and does not continue into the core of the yarn. These pictures show that the yarns contain a significant amount of void space that could be filled with a matrix material.
Figure 4.4 5-ply Nanotube Yarn, 20000x Magnification

Figure 4.5 5-ply Nanotube Yarn, 150000x Magnification
Clearly, in order to better utilize unique mechanical properties of carbon nanotubes, the yarn manufacture should try to significantly improve alignment of the nanotubes and their bundles within the yarn and also reduce the angle between their preferred orientation and longitudinal axis of the yarn. Improving the orientation of the nanotubes would simultaneously increase their packing density.

4.2 5-Ply Yarn Tensile Testing

To correctly predict the mechanical properties of a composite material, the mechanical properties of the two constituent materials (fiber and matrix) must be known. It was hypothesized that the dry yarns would behave much differently than the same yarns impregnated with epoxy. The yarns and the braid were tested on the Instron machine with the 5 N load cell that was used for the tests described in Section 3. This testing gave load vs. extension results. Stress vs. strain data are presented in future sections after the cross-sectional area of the yarn structures was properly determined.

All samples had a gage length of ten millimeters and were secured to cardstock tabs using an Epon 9504 and Epi-Cure 9554 epoxy mixture. The yarns were tabbed in the same manner as the carbon fibers. The first samples produced were viewed with an optical microscope, and it could be seen that resin was coating the nanotube yarn about 1 mm away from the edge of the tab. It was thought that the epoxy had a viscosity low enough that it was being pulled down the surface of the yarn by small capillaries in the nanotube structure between the plies. When mixing the epoxy for the next set of samples, the mixture was allowed to react for 30 minutes to become more viscous before application on the tabs. When these samples were
viewed under optical microscope, no epoxy was seen on the nanotube yarns. Figure 4.6 shows a 5-ply nanotube yarn that has been tabbed with epoxy.

![Figure 4.6 Tabbed 5-ply Nanotube Yarn Sample](image)

All of the 5-ply yarn samples for the tensile tests reported below were taken from the same spool containing approximately 1 meter of yarn, so that tensile property variation between the yarns taken from different spools (and, likely, having different cross sections) would not be compared. The spool of yarn chosen was one that appeared to represent the average size for the group of 20. The rest of the yarns were used in the 3-D braiding process. Due to the limited amount of yarn, some tests were conducted with only a few repetitions.

The first test conducted with the tabbed 5-ply samples was conducted to determine if there was any viscoelastic behavior in the yarns. In normal polymeric materials, testing the sample at slow extension and fast extension rates produces different curves. During slow testing the polymer chains have time to disentangle, straighten and move past each other. At high rate of
extension, the chains become mutually trapped and do not have sufficient time to untangle. Polymeric material tested at a higher loading rate usually shows a higher modulus and lower strain to failure than if it is tested very slowly. This test investigated whether the slipping and untangling of nanotubes in the yarns were similar to the case of polymer chains. Figures 4.6 and 4.7 show that there was almost no difference between the 5-ply yarns tested at 10 mm/min and 0.1 mm/min loading rates. The observed minor difference among the curves was rather attributed to the natural scatter of the yarn sample properties than to the difference in extension rate.

Figure 4.6 5-ply Nanotube Yarn Tested at 0.1 mm/min

Figure 4.7 5-ply Nanotube Yarn Tested at 10 mm/min
Five samples of the 5-ply yarn were then tested to determine the uniformity of the sample. Gage length was 10 mm while the loading rate was 1 mm/min. The load vs. extension curves for these five tests are presented in Figure 4.8. All of the yarns failed within a small range of tensile load, between 0.22 and 0.25 N, and the failure strain varied from 8.4 to 9.5%.

The next test was conducted for 5-ply nanotube yarns with a gauge length significantly larger than the previous samples. Previous samples were tested at 10 mm gage length, while in this test two yarns of 50 mm gage length were tested. Figure 4.9 shows results of these tests. Notice that strain measurements were used to compare the different length samples. Some difference between the group of five black curves (10 mm gage length) and two red curves (50 mm gage length) is seen, however the failure stress for the longer gage length is comparable to the shorter gage length, meaning that the defect frequency at 50 mm was
similar to the defect frequency at 10 mm. Therefore, it was concluded that there was no gage length effect.

**Nanotube Yarn Gage Length Comparison**

![Graph showing stress-strain relationship for nanotube yarns](image)

Figure 4.9 5-Ply Gage Length Comparison

**4.3 Tensile Testing of 25-Ply Yarn and 3-D Braid**

A sample of the 25-ply nanotube yarns and one sample of 3-D braid made of 5-ply nanotube yarns were tested on the Instron machine. Load vs. extension curves for these samples are shown in Figure 4.10. For comparison, one curve that well represents the behavior of the previously tested 5-ply yarns is also included in the figure.
Not surprisingly, the braid containing 180 single yarns was able to withstand a much greater force than both the 25-ply and 5-ply yarns before failing. Therefore, it was more informative to determine what the difference was in the load per single yarn in each of these structures. Such load values were calculated and are presented in Table 4.1. It is seen that the single yarn in the 3-D braid holds 83% of the load that the single yarn holds in the 5-ply yarn (recall that the latter one was the raw material for braiding). This high value indicates that very little damage was imparted on the yarn during 3TEX’s 3-D braiding process. Additionally, optical microscope and SEM observations of the surface of the braid confirmed that damage was practically non-existent. It is further seen from Table 4.1 that the 25-ply yarn holds only 58% of the load that the single yarn holds in the 5-ply yarn. The single yarns in the 25-ply yarns could be seen fraying during the testing, causing the jagged downward slope on the load-
extension curve. The fraying was caused in part by uneven load distribution across the single yarns. The large number of single yarns in 25-ply yarn allowed them to break gradually, without causing the entire 25-ply yarn to fail catastrophically. At the same time, this effect has substantially lowered the load bearing capability of the 25-ply yarn. Keeping the discussed effects in mind, one could speculate that substantial reduction of the load bearing capability between the bundle of 5 parallel single yarns and the twisted 5-ply yarn could take place. It is apparent that it is desirable to minimize the twist rate and apply as even tension as possible to the single yarns when processing multi-ply nanotube yarns.

Table 4.1. Comparison of Breaking Load per Single Yarn

<table>
<thead>
<tr>
<th>Plied Yarn/3-D Braid</th>
<th>Number of single yarns</th>
<th>Breaking load (N)</th>
<th>Breaking load per single (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-ply yarn</td>
<td>5</td>
<td>0.233</td>
<td>0.0466 (100%)</td>
</tr>
<tr>
<td>25-ply yarn</td>
<td>25</td>
<td>0.674</td>
<td>0.0270 (58%)</td>
</tr>
<tr>
<td>3-D braid</td>
<td>180</td>
<td>6.95</td>
<td>0.0386 (83%)</td>
</tr>
</tbody>
</table>

4.4 Determination of Cross-Sectional Areas

To determine the stress and strength of each one of the tested yarns and braids, their cross-sectional areas had to be defined. For traditional textile plied yarns such as cotton or wool, the cross sections are not usually measured and used for strength measurements. The strength of such yarns is measured in tenacity, which is derived from the linear density and the breaking force. However, the stress values for fibers and yarns used in composites are usually measured by dividing the force over the fiber/yarn cross-sectional area, which is quite easy to determine for sufficiently rigid carbon, glass or ceramic fibers. For example, each kind of
carbon fiber has well documented diameter value, which allows one to determine the cross section of 1K, 3K, 6K, 12K, etc. yarns with high certainty. Contrary to that, carbon nanotube yarns, especially twisted multi-ply ones, pose a challenge in cross-sectional area measurement. Once twisted, they loose their circular shape. This leads to three optional approaches to measuring their cross-sectional area, which are described next.

The first approach used consisted of measuring the cross section of one single yarn and then multiplying the result by the total number of singles in the multi-ply yarn, with account for some idealized packing model. This method is prone to error if the yarns are compressible, if they do not pack “perfectly” (in accordance with the model adopted), or if they vary in diameter. When using SEM measurements, what is assumed to be the “yarn diameter” may be just a randomly taken measurement of some dimension in the plane perpendicular to the yarn axis. For a single nanotube yarn such “diameter” measurement varied between 10 and 20 µm. Such a huge scatter of this geometric parameter ruled out this approach as the means of yarn cross-sectional area measurement.

The second, direct approach was based on SEM images obtained for the actual plied yarn or braid using Scion Image software. This allows for calculating an average diameter along the yarn length, as illustrated in Figure 4.11. A representative sample from the group of 5-ply yarns that were used in braiding was chosen, and its “diameter” was measured at 36 points along the length. An average value of 46 µm was obtained with corresponding cross-sectional area of 1662 µm². The irregular (non-circular) cross section of a plied yarn may impart significant error on the cross-sectional area determination by this method, because it
implies that all yarn cross sections are perfectly circular. In the case of elliptical cross section, for example, the observed “diameter” variation along the yarn length would be simply due to rotation of the same ellipse in the plane perpendicular to the yarn axis, while the whole ellipse is not recognizable on SEM images.

![Figure 4.11 Application of the Scion Image Method to Measure Diameter](image)

Measurements of the 3-D braid cross-sectional dimensions using this approach should be more accurate due to the use of thirty six 5-ply yarns results in kind of “smearing” their geometric non-uniformities along the yarn length. In addition, the braid had a square cross section, so the side length is very easily distinguishable from SEM pictures. The braid’s average side length was determined as 211 µm from 17 measurements taken along its length.

The third method, which was more complex and time consuming, consisted of taking measurements on the fracture surface of a composite made from the yarn of interest. Areas of irregular shapes in the broken composite cross section were directly measured using Scion
Image software. With this type of software, a reference length is produced from the scale bar on the SEM picture and an outline of the structure is traced on the image using the freehand tool. Using the reference length, the software provided the total area within any closed contour line.

Figure 4.12 illustrates application of this method. The measurements were taken for five different 5-ply yarns inside the 25-ply yarn composite. The dark areas are nanotube-epoxy yarn regions, while the bright outlines are pure epoxy resin areas which were charging in the SEM because of the lack of conductive nanotubes in them. This method was more accurate for determining the cross-sectional area of the plied yarns than the other two methods described above, because the actual shape and packing of single nanotube yarns can be easily viewed and quantified, rather than being arbitrarily assumed or determined by fitting to some geometrical model. As Figure 4.12 illustrates, single yarn cross sections in each of the 5-ply yarns are far from circular; each of them changes its shape to pack more tightly in the twisted plied yarn than cylinders would. The following cross-sectional areas were obtained from the cross section SEM pictures: 1,137 µm² for 5-ply yarn, 5,685 µm² for 25-ply yarn, and 39,212 µm² for 3-D braid. This technique of determining the cross section was adopted for the plied yarn and 3-D braid in the stress-strain plotting and strength evaluation.
4.5 Comparison of Stress-Strain Curves

After calculating the cross sectional area for each carbon nanotube yarn structure, this data was input into the tensile testing software to convert the load vs. extension curves to stress vs. strain curves. The tensile stress vs. strain curves for the 5-ply yarn, 25-ply yarn, and 3-D braid are shown in Figure 4.13. It is seen from the figure that the highest strength (~200 MPa) is reached for the 5-ply yarn; the braid has ~155 MPa strength (78% of the 5-ply yarn strength), and the 25-ply yarn has ~125 MPa strength (62%). These values are in a good agreement with the failure load ratios from Table 5.1 (83% and 58%, respectively), which confirms the accuracy of cross-sectional area determination.
Though the ultimate failure strain of the 25-ply yarn had the highest value (~10%), the load bearing capability of this material dropped by more than a half at ~6.5% strain, which is even lower than the ultimate failure strain of the braid. The 5-ply yarn had the highest ultimate failure strain, above 8%, and broke catastrophically.

Figure 4.14 further illustrates the failure surfaces of the nanotube yarns in the braid. Each surface shows a necking effect caused by so-called “drafting”, and a close-up shows bundles of nanotubes being pulled away at the very tip of the failure zone. All of the nanotube yarn structures failed in this manner and it is assumed that this is the main source for the high strain seen.
The ultimate failure strain values, as well as related flexibility of the studied carbon nanotube yarns and 3-D braid are much higher than those of conventional carbon fibers and yarns used in high performance composites. Of course, this is due to the complex hierarchical structural organization of the novel textile materials fabricated and studied here. The nanotube yarns are held together primarily by van der Waals forces and mechanical friction. The yarns also contain free interstitial spaces that originate mainly from the nanotube bundle misalignment in the vertical nanotube array and from various manufacturing artifacts in the drawing and twisting process from the array. Different obstacles do not allow for perfect packing and alignment of the nanotubes in the spun yarns. Further loss of alignment and packing density is due to the secondary twist, which is applied when processing plied yarns from the singles.

Although mechanical characterization of the single nanotube yarns was not performed in this study, one can anticipate from experimental results presented in Figure 3.16 that such yarns would probably have strength in the range of 350-400 MPa and would break catastrophically at about 10% strain.
5 Composite Fabrication and Tensile Testing

5.1 Fabrication

The resin system selected was Epon 9504 epoxy with Epikure 9554 curing agent. This low viscosity resin system is often used for Vacuum Assisted Resin Transfer Molding (VARTM) applications. The manufacturer recommends mixing the resin at a 100:25 parts by weight ratio of epoxy to hardener and this combination produces a resin with initial viscosity of 300 cp at room temperature. Heating the resin to 60°C lowers the viscosity to around 90 cp. The pot life of the resin at 60°C is approximately 45 minutes. Heloxy 116 modifier was also used in some samples to decrease the viscosity of the resin system. Heloxy 116 is a monoepoxide modifier, which can be added in large amounts without extreme changes in the hardened epoxy’s properties. Unlike other solvents often used to lower the viscosity of epoxy resin systems, Heloxy 116 is bonded into the cross-linked network.

The purpose of modifying the epoxy was to gauge the effect of epoxy viscosity on resin penetration and to view the impact of the resin mechanical properties on the mechanical properties of the composites. If the epoxy is too viscous it would only fill the spaces in between the yarns. As the viscosity decreased it should be able to penetrate into smaller and smaller voids in the structure. Obviously, composites with epoxy completely filling all free spaces among the nanotubes in the nanotube yarn structure should have superior mechanical properties than those composites which have only partial epoxy penetration. The addition of the modifier to epoxy had the effect of lowering the viscosity and greatly decreasing the modulus. Unmodified epoxy has a lower strain to failure than individual nanotubes. Modified epoxy can have a much greater strain to failure than individual nanotubes. By testing
composites with epoxy having different modifier content, the differences between matrix dominated composite failure and fiber dominated composite failure should be apparent.

As the amount of modifier was increased and the viscosity of the resin was decreased, the mechanical properties of the matrix material were also affected. To quantify this effect of the modifier on pure matrix properties, several samples were made with varying amount of the modifier. Samples of resin were mixed where modifier accounted for 0, 20, 30, and 40% of the epoxy’s weight. As the amount of modifier increased, the amount of hardener had to be reduced accordingly. The mix ratios for the four samples fabricated and tested were 100:0:25, 80:20:22, 70:30:21 and 60:40:20 parts by weight of epoxy to modifier to hardener.

The resin was mixed thoroughly and then cast with a thickness of one millimeter on a level and polished aluminum plate. The resin was contained on the plate by “tacky tape”, a thick rubbery sticky material used for sealing in VARTM processes. The plate was put in a vacuum oven for 15 minutes at 60°C to remove all the air bubbles. The viscosity was low enough to allow release of the bubbles within the first five minutes. The samples were then allowed to cure for 16 hours at room temperature and after that were post-cured at 90°C for one hour. The resin sheet was then removed from the plate and cut with a razor blade and a guide into 12 mm wide strips. Five strips of each kind were tested under tension on the same Instron machine described in Section 3.1.

Test results for the four different epoxy matrix materials are presented in Table 5.1. It is clearly seen that the increase of modifier fraction resulted in a sharp reduction of modulus and strength, with a sharp increase of strain-to-failure. Of course, only the first recipe,
without modifier, would be considered for practical structural composites, however the intent was to investigate how these four very different matrix materials would affect mechanical properties of the nanotube yarn and braid composites.

Table 5.1 Mechanical Properties of Epon 9504 Epoxy with Modifier

<table>
<thead>
<tr>
<th>Epoxy:Modifier:Hardner Ratio</th>
<th>Modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:00:25</td>
<td>2.43</td>
<td>64.71</td>
<td>3.6</td>
</tr>
<tr>
<td>80:20:22</td>
<td>0.48</td>
<td>33.8</td>
<td>22.5</td>
</tr>
<tr>
<td>70:30:21</td>
<td>0.19</td>
<td>11.61</td>
<td>62</td>
</tr>
<tr>
<td>60:40:20</td>
<td>0.03</td>
<td>6.58</td>
<td>89.3</td>
</tr>
</tbody>
</table>

The first composite samples were produced with the 5-ply and 25-ply yarns and with the lowest viscosity epoxy formulation, 60:40:20 to provide the most favorable conditions to the epoxy for penetrating inside the multi-ply and single yarns, to wet the nanotubes/nanotube bundles as well as possible, and to easily remove excess resin from the surface of the small yarn structures. Five centimeter lengths of the nanotube yarns were placed in the epoxy bath and then heated and evacuated in a vacuum oven for 20 minutes at 60°C. Heating the resin further reduced the viscosity. Vacuum pressure evacuated the microscopic air bubbles trapped between groups of nanotubes and allowed the low viscosity resin to replace them. The samples were removed from the bath, placed on a paper towel to soak up any excess resin and then were mounted on tabs under slight tension to prevent them from sagging. The lowest viscosity formula also ensured that no excess resin beaded on the surface of the yarn and thus a very uniform composite was produced. After 16 hours, the mounted samples were
post cured at 90°C.

To produce the 3-D braided nanotube composite samples, a 7.5 cm long piece of braid was placed into a bath of the mixed resin system. This was heated and evacuated in a vacuum oven for 20 minutes at 60°C. The infused braided samples were removed from the resin bath and attached to a spring loaded curing fixture shown in Figure 5.1.

![Figure 5.1 Curing Apparatus](image)

The springs provided approximately 25 g of tension onto the curing sample. The curing fixture was placed in the oven at 60°C while the excess resin dripped off of the braid. After 10 minutes, any excess resin was blotted off of the braid and the fixture was set in a stable place for curing. The samples were allowed to cure for 16 hours at room temperature and
then were post cured at 90°C in the oven. The first sample produced had a larger than expected cross section and showed excess pockets of resin when the fracture surface was studied with a SEM. It was thought that the tension was too low during curing. The spring tension was increased to 100 g for subsequent samples, and this eliminated the problem. Braided composite samples were fabricated with all four of the resin formulas listed in Table 5.1. Figure 5.2 shows the size scale of the braided composite sample next to a ruler in inches.

![Figure 5.2 Scale of Braided Composite in Inches](image)

### 5.2 Density Measurements

Density of the 3-D braided structures and their composites were determined using the cross-sectional area measurements, the length of the samples measured with a digital micrometer, and the measured weight of each sample found using a microgram balance. The plied yarn samples were too light, even for the microgram balance to measure, so density data was not collected for those samples.
The density of a composite ($\rho_c$) can be determined through the rule of mixtures using the density ($\rho_f, \rho_m$) and the volume fraction ($f$) of each constituent material in the following equation:

$$\rho_c = \rho_f f + \rho_m (1-f) \quad (8)$$

The density of MWNTs depends on the inside and outside wall diameters. In [49], it was shown that density of nanotubes can range from 1.3-2.1 g·cm$^{-3}$. The density of the nanotubes within the nanotube yarns was calculated to be 1.58 g·cm$^{-3}$ from the inner wall diameter of 5 nm, outer wall diameter of 10 nm, interplanar wall spacing of 0.34 nm and the density of graphite planes as 2.1 g·cm$^{-3}$.

Density of the resin used in this study was calculated from a specimen of known dimensions. Mixed epoxy resin was poured into a glass tube, evacuated in a vacuum oven and allowed to cure for 16 hours at room temperature. The sample was then post cured at 90°C in the oven for one hour. The tube was broken away and the rounded ends were cut off with a diamond saw to produce a perfectly cylindrical sample. The dimensions were measured using a micrometer and the density was calculated as 1.153 g·cm$^{-3}$.

The average measured density of the four dry nanotube yarn braids was 0.676 g·cm$^{-3}$. Using equation (8), and setting the density of air equal to zero, the volume fraction of nanotubes was calculated to be 42.8%.

Taking the density of nanotubes as 1.58 g·cm$^{-3}$, the density of the resin as 1.153 g·cm$^{-3}$ and the volume fraction of nanotubes to be 42.8%, the calculated theoretical density of the composite was 1.336 g·cm$^{-3}$. However, the four 3-D braided composite samples had an
average density of 1.244 g·cm$^{-3}$. By manipulating equation (8), it was found that the composite structure contained approximately 8% void space. The void space consisted of areas where resin did not penetrate and the void space created by close packed bundles of nanotubes. Nanotubes within bundles, with perfect hexagonal close packing along their length, have a density which is 91% of the density of a single MWNT. As can be seen in Figure 4.5, large bundles are present, thus some of the discrepancy can be attributed to the lower density bundles.

5.3 Tensile Testing

The composite samples made with the 5-ply nanotube yarn, 25-ply nanotube yarn, and 3-D nanotube braid reinforcements, were all tested on the aforementioned Instron tensile tester. To ensure that the samples were properly aligned in the grips and to eliminate stress concentrations on the composites during testing, the samples were tabbed using epoxy as shown in Figure 5.3.

![Figure 5.3 Tabbed 3-D Braided Composite](image)
The gage length was 10 mm for the 5-ply and 25-ply yarn composite samples, while it was 20 mm for the braided composite samples. All of the samples failed outside the gripping zone. To calculate stress values, cross-sectional area of each sample was experimentally determined. These values were determined by measuring the cross section of the fractured composites, as seen in Section 4.4. The following cross-sectional area values were obtained and used for the stress calculation: 1,137 µm² for 5-ply yarn composite, 6,609 µm² for 25-ply yarn composite, and 39,212 µm² for 3-D braid composite.

Due to small braid quantities, the 5-ply and 25-ply composite curves are representative samples, while the braided composite curves are single sample measurements. The curves presented in Figure 5.4 show that the highest strength value (320 MPa) was achieved for the 5-ply yarn composite, similarly to what was observed in the dry yarn testing (see Figure 4.13). The 3-D braid composites and the 25-ply yarn composite showed similar strength values in the range of 240 and 314 MPa.

![Nanotube Composites Stress vs. Strain](image)

**Figure 5.4 Stress vs. Strain Curves for Nanotube Yarn Composites**
There was only a small difference in strength and ultimate failure strain between the four 3-D braid composite samples made with very different viscosity resin and characterized by very different mechanical properties of the matrix material (see Table 5.1).

Further, Figure 5.4 shows that there was a substantial drop of strain-to failure values for all six composite samples compared to the dry nanotube yarns and braid (compare to Figure 4.13). The highest ultimate failure strain, just above 2%, was observed for the 25-PLY nanotube yarn composite. The plied yarns and the four 3-D braid composites showed ultimate strains in the range of 1.6-1.8%.
6 Discussion

All obtained tensile test data for the dry reinforcements and their composites are summarized in Table 6.1. The results show that the modulus values of all tested composites are from four to seven times higher than the modulus values for respective dry yarns and braids. The largest increase in modulus was observed for the 5-ply yarn composite. At the same time, the strength values have increased by 35-100%. The largest increase in strength was seen for the 25-ply yarn composite. It can be assumed that in this case, the matrix material bonded all single yarns together, which provided more uniform load transfer across the 25 plies, and thus prevented gradual single-by-single yarn failure discussed in Chapter 4.

<table>
<thead>
<tr>
<th>Material</th>
<th>Modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Strain-to-failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-ply dry yarn</td>
<td>3.04</td>
<td>190.44</td>
<td>8.95</td>
</tr>
<tr>
<td>5-ply yarn composite</td>
<td>21.07</td>
<td>319.78</td>
<td>1.7</td>
</tr>
<tr>
<td>25-ply dry yarn</td>
<td>2.35</td>
<td>127.47</td>
<td>4.62</td>
</tr>
<tr>
<td>25-ply yarn composite</td>
<td>14.18</td>
<td>261.42</td>
<td>2.02</td>
</tr>
<tr>
<td>3-D braid dry</td>
<td>3.98</td>
<td>173.63</td>
<td>6.52</td>
</tr>
<tr>
<td>3-D braid composite 100:0:25</td>
<td>23.91</td>
<td>314.77</td>
<td>1.63</td>
</tr>
<tr>
<td>3-D braid composite 80:20:22</td>
<td>19.74</td>
<td>274.16</td>
<td>1.8</td>
</tr>
<tr>
<td>3-D braid composite 70:30:21</td>
<td>16.07</td>
<td>232.01</td>
<td>1.72</td>
</tr>
<tr>
<td>3-D braid composite 60:40:20</td>
<td>18.87</td>
<td>255.43</td>
<td>1.61</td>
</tr>
</tbody>
</table>

The failure surfaces of the composites reinforced with the nanotube yarns/nanotube braids are much different than those observed for the respective dry yarns/braids. Figure 6.1 shows the fracture surface of the 3-D nanotube braid infused with epoxy (recall that the braid was
made of thirty six 5-ply nanotube yarns). These pictures show an increasing level of detail in the morphology of this 3-D braided composite failure. Specifically, the twist of the nanotube yarns can be seen as the swirl on the surface of each failed yarn. It appeared that there was no significant pullout of the nanotubes and nanotube bundles; the length of the nanotubes in the composites was 300 µm, while the protruding nanotubes were well below 1 µm in length. The close-up images clearly show that nanotubes are surrounded by epoxy resin. The dark spots seen in the picture are due to the extremely high zoom level and the roughness of the fracture surface, which made it hard to focus on the whole surface.

Figure 6.1  Cross Section of 3-D Braided Composite
All of the composite fracture surfaces, no matter what their resin formulation, appeared to be very similar in SEM pictures. It was not apparent that reducing the viscosity of the resin helped to achieve better resin penetration. However, it is possible that none of the samples had excellent resin penetration. The zoom level in Figure 6.1 clearly shows resin penetration into the interior regions of the structure through voids that range in the tens of nanometers, but it was not clear whether the resin consumed the smallest of voids. Calculations described in Section 5.2 confirm that some nano-scale voids must have remained in all of the structures. Any remaining void space could have been detrimental to the mechanical properties.

The failure mode for these studied composite materials changed from a gradual slipping of nanotubes, or nanotube bundles, past one another, to a rather catastrophic failure of the composites. This explains the dramatic decrease of strain-to-failure values in all composites compared to the dry yarns and braids. Low ultimate failure strain values have been reported in other studies of carbon nanotube composites, in which nanotubes were added in high volume fractions to bulk epoxy, see for example [50].

It was interesting to find that the four different 3-D braided composite samples did not vary much in their strain to failure values. This was unexpected, considering that the strain of carbon nanotubes is between 6-12% [10], the matrix failure strain for the unmodified epoxy was 3.6% and the most highly modified epoxy failed at 89.3% strain. In the first case, the low strain to failure of the epoxy should have been the limiting strain for the composite. In the second case, the nanotubes should have provided the limiting strain. Therefore, the
composite with high strain to failure epoxy should have had a failure strain closer to 6-12%.
It was thought that if a significant volume fraction of nano-voids were present, they could have nucleated cracks and which then coalesced and propagated through the structure. This could have contributed to the low strain to failure values for all of the composite samples. The failure strain of carbon nanotubes is also dramatically reduced if there are any atomic defects present in the tube structure. It is possible that the nanotubes in the supplied nanotube yarns contained structural defects. If this is true, it could also help to explain the low failure strain of the composites.

One of the most interesting results following from the performed tests is that the rule of mixtures does not apply to the studied nanotube composites in the conventional way, namely if the nanotube yarn/braid and epoxy matrix are viewed as the composite constituents. The rule of mixtures predicts the modulus of a composite as a weighted average of the moduli of its individual constituents. For example, this rule well applies to predicting modulus of unidirectional carbon fiber composites in the fiber direction, considering that the constituents are a homogeneous carbon fiber and a homogeneous polymeric matrix. Contrary to that, in our case it was seen from the modulus values given in Tables 6.1 and 5.1 that the reinforcing constituent and the matrix have much lower moduli than the final composites they make up. The explanation of this highly synergistic effect is quite obvious: the effective elastic modulus of this kind of composites is not determined by the modulus of nanotube yarn or nanotube braid, but by the modulus of individual carbon nanotubes or nanotube bundles. This further confirms that epoxy resin penetrated significantly into the nanotube yarn to facilitate load transfer.
Predicting the modulus of these composites is not as easy as using the rule of mixtures. Even more complex composite models are not sufficient due to the hierarchal nanotube structure. Only advanced 3-D composite mechanical modeling software could be used to predict the strength and modulus of these materials with high accuracy. However, simple models can be applied to determine if the experimental modulus is closer to the highest calculated possible value (rule of mixtures) or the minimum value (Halpin-Tsai equations for a random composite).

A rule of mixtures modulus calculation would give the highest possible modulus value for the nanotube composites because it assumes all of the nanotubes are parallel and in the direction of loading. According to the literature data, the modulus of individual nanotubes can be as high as 1.2 TPa, however it has been shown that the weak association between nanotubes in nanotube bundles lowers the modulus of the bundles considerably [51]. The assumption was made here that 300 GPa was a reasonable modulus value for the bundles that make up the nanotube yarns based on the size of the bundles seen in Figure 4.5 and the trends given in [51]. By substituting the appropriate modulus values for the nanotube bundles, epoxy with 40% modifier and 42.8% nanotube volume fraction into equation 1, the composite modulus was calculated as 128 GPa.

When the variables above, along with the length and diameter of the nanotubes was substituted into the random fiber composite Haplin-Tsai equations (2-7), the modulus of the composite was computed to be 23.5 GPa.
Now we have the estimate that the experimental modulus values should fall between 128 GPa and 23.5 GPa. Surprisingly, only one of the experimental values obtained for the 3-D braided composite was higher than 23.5 GPa.

One may ask: why do the high theoretical stiffness and strength values of carbon nanotubes were not transferred to the properties of the composite materials? The average modulus of the baseline carbon fibers exceeded the experimental values for the nanotube composites by a factor of 10. Clearly, some additional factors must be taken into account to explain the low modulus values obtained. Two hypothesized factors are explained in the following paragraphs.

First, bundling of nanotubes within the yarns can make it hard for the resin to penetrate inside the bundles, which inhibits their load transfer efficiency. The approach of using less and less viscous resins, which was applied here, did not make a significant effect on either stiffness or strength of the fabricated nanotube composites. It is possible that the bundling within the interior of the yarns was much more extensive than the bundling seen at the surface. That would have a dramatic impact on the modulus of those much larger bundles. Perhaps, the assumed nanotube bundle modulus of 300 GPa was too high, and in reality, could be much lower. A lower nanotube modulus value would substantially change the predicted composite modulus values.

Second, the single nanotube yarns used in this study show an apparent nanotube orientation angle of 33° with respect to the longitudinal yarn axis, as measured with the use of Scion Image software. However, it was seen in Figure 4.5 that not all of the nanotubes follow this
preferred orientation. It is possible that the average nanotube orientation angle is higher, coming closer to the case of randomly oriented nanotubes. It was also seen that the nanotubes were further disoriented away from the tensile loading axis when five single yarns were plied together with twist, and disoriented even more when 5-ply yarns were again plied together with twist or braided. These types of additional disorientation in the structure would effect the experimental values and move them closer to the Halpin-Tsai theory prediction.
7 Conclusions

- Individual carbon fibers were selected as a baseline material based on their geometry and their strength. Their tested values confirmed the validity of the standard test technique and equipment set up.

- Dry nanotube yarns vary in size from sample to sample but the consistent mechanical properties of yarn from a single sample show consistency along the length.

- Dry yarns fail by nanotube slippage, which is seen as drafting or necking of the structure at the failure surface.

- The most accurate cross-sectional area measurements for the nanotube structures were calculated from the fracture surfaces of composite samples.

- Low viscosity epoxy resins in four different formulations penetrated deep into the nanotube yarn structure during infusion.

- Failure of the nanotube yarn composite structures was brittle in nature and occurred at lower strains than that of the dry yarn specimens.

- The epoxy matrix provided load transfer between nanotubes to increase the strength of the yarn structures by 35-100% and modulus values by 4 to 7 times.

- Strength and modulus values of the 3-D braided composites was comparable to the values for the plied yarn composites, indicating that 3-D braiding did not induce considerable damage.

- The experimentally determined modulus of the nanotube yarn and braid composite structures can not be adequately predicted, because the true modulus values of the nanotube bundles within the yarns are not known.
8 Recommendations for Future Work

Much of the future work needed to improve the properties of these materials will be done by the producers of the nanotube yarns. Longer nanotubes must be grown so that less twist is needed to hold together the structure allowing for better orientation of the nanotubes along the yarn axis. In addition, the quality of the nanotubes should be studied and the amount of defects should be quantified. Nanotube processing techniques should be optimized to produce nanotubes which are perfectly straight and defect free.

To improve the nanotube yarn composites, better resin penetration should be achieved while the nanotube bundle size should be reduced. This could be accomplished by the methods normally used to disperse short nanotubes in solution. Sonication has shown to break apart bundles in solution; this method could be applied to nanotube yarns as they are being infiltrated with epoxy resin. Functionalizing the surface of nanotubes with chemical groups that repel each other could also be a possible solution. Copolymers with lyophilic and lyophobic blocks have also shown to separate nanotubes. Separating the nanotube bundles into individual tubes would allow resin to come in contact with every tube. Therefore, the composite modulus would be controlled more by the modulus of the individual MWNT and less by the modulus of nanotube bundles.

Carbon nanotubes exhibit outstanding electrical and thermal conductivity which might be transferred to composites made from nanotube yarns. Multifunctional properties of composites are highly desired; therefore, these properties should be characterized and optimized in parallel with the mechanical properties.
References


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23. ASTM Standard C1557. Tensile Strength and Young’s Modulus of Fibers


