Mechanical Energy Storage in Carbon Nanotube Springs

by

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Submitted to the Department of Mechanical Engineering
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Doctor of Philosophy
at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Abstract

Energy storage in mechanical springs made of carbon nanotubes is a promising new technology. Springs made of dense, ordered arrays of carbon nanotubes have the potential to surpass both the energy density of electrochemical batteries and the power density of capacitors due to the effective Young's modulus of carbon nanotubes of 1 TPa and their high elastic strain limit of up to 20%. The energy density of springs made of carbon nanotubes is predicted to be more than three orders of magnitudes higher than the energy density of conventional springs made of steel. The present work studies the mechanical properties and energy storage capabilities of two types of carbon nanotube arrays: fibers made of continuous, millimeter-long carbon nanotubes prepared from forests, and spun yarn made of carbon nanotubes. The highest recorded strength and stiffness of the fibers are 2 N/tex and 68 N/tex, respectively, and the fibers have demonstrated reversible energy storage of 670 kJ/m³ or 6.9 kJ/kg. The spun yarn has a specific strength of 0.8 N/tex, a specific stiffness of 48 N/tex, a maximum energy density of 7720 kJ/m³ or 6.7 kJ/kg, and a maximum demonstrated power density of 190 MW/m³ or 170 kW/kg. The energy density of the current springs is three orders of magnitude lower than the theoretical limit. Mechanical testing, Raman spectroscopy during loading, scanning electron microscope imaging during loading, and simultaneous stress and electrical resistance measurements have provided valuable insights into the mechanisms governing the mechanical behavior of carbon nanotube fibers and yarn. While elastic loading is optimal for reversible energy storage, the results indicate that disorder in the structure of both materials causes loading to deviate from purely elastic behavior. Densification of carbon nanotubes in fibers using capillary effects is shown to be an effective way to consolidate CNTs and create high performance fibers since the CNTs self-assemble into dense, interacting networks that promote load transfer.

The first demonstrations of carbon nanotube springs that store energy and power small-scale systems are presented. These systems include mechanical watches, escapements, slingshots, and a mechanical energy harvester. Power regulation mechanisms were implemented to control the rate at which energy was released from the springs. Electric batteries were developed that store energy mechanically in carbon nanotube springs and release the energy in the electrical domain. The energy density, power density and efficiency of the springs in each of the systems are characterized to evaluate the performance of the springs as an energy storage medium.

Thesis Supervisor: Dr. Carol Livermore
Title: Associate Professor
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I would like to thank my two collaborators for providing the carbon nanotube materials that made this work possible: John Hart and his team at the University of Michigan for providing carbon nanotube forests, and David Lashmore and his colleagues at Nanocomp Technologies Inc. for supplying carbon nanotube yarn.

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1. Introduction

One of the important technological challenges over the next decade will be developing breakthrough technologies in energy storage. Improvements in energy storage technologies would benefit a wide range of applications, from large-scale grid storage to portable electronics. The electrical grid has a relatively stable energy supply, but it must meet fluctuating demands during different times of the day; currently nearly 2.5% of the energy in the electrical grid in the United States is stored as pumped hydroelectric energy prior to being delivered to help manage supply and demand [1]. Continued development of an optimized smart grid will depend on improving the efficiency, reliability, storage capability, and cost of large-scale energy storage technologies. Vehicles would also benefit from new energy storage technologies. The vast majority of vehicles (96% in the United States) are powered by fuel; the transition from fuel to advanced hybrid vehicles and full electric vehicles depends on development of long-lasting, robust, and high-density energy storage technologies, particularly focusing on improvements in batteries and capacitors [2]. Energy storage is also needed to manage energy from renewable sources such as wind and solar energy to provide a steady supply of energy to end-users and to more easily integrate energy from renewable sources into the electrical grid [3]. A final example is portable electronics, such as smart phones and laptops, which would also benefit from better energy storage technology. These devices require long-lasting and lightweight power supplies that can be recharged and discharged repeatedly without degradation and that operate with little self-discharge. Batteries are most commonly used to power portable electronics, but they are limited by their weight, storage capacities and short lifetimes that create battery waste. Technological developments in energy storage would benefit these and many other applications.

The principal technologies currently employed for energy storage are batteries, capacitors, compressed air storage, flywheels, mechanical springs, pumped hydro, and superconductive magnetic energy storage, although many other storage technologies exist. Energy can additionally be stored densely as fuel. Of these storage technologies, highest energy density is found in batteries and highest power density is provided by capacitors. Neither storage technology offers a combination of both high energy density and power density. Mechanical energy storage (compressed air, flywheels, springs, pumped hydro) offers a robust alternative to electrochemical energy storage, but their energy densities are much lower than those of batteries and fuel. Much of the current high energy density storage research focuses on batteries, but batteries are a mature technology, and improvements in their performance have been modest over the past few years. While battery research is important, it is also worthwhile to explore alternative energy storage technologies.

Of the different types of mechanical energy storage, mechanical springs have the lowest energy density and are used to power few practical devices. Mechanical springs are used to store energy and provide power to specialized, small-scale mechanical systems (mechanical watches, spring-based robotics actuators, latches, and toys), but springs are used to power neither large-scale mechanical systems nor electronics. Conventional mechanical springs are made of steel and offer an energy density of 1080 kJ/m$^3$ or 0.14 kJ/kg [4]. To improve the performance of springs, it is useful to look to new advanced materials with better mechanical properties than steel.

Carbon nanotubes (CNTs) were first reported in 1991; not long after, it was discovered that CNTs had mechanical properties that far surpassed those of conventional engineering structural materials. The carbon-carbon bond found in CNTs is the strongest bond found in nature. Defect-
free CNTs have an effective stiffness of 1 TPa and strength as high as 100 GPa [5]. CNTs are five times stiffer and more than 100 times stronger than structural steel. With these impressive mechanical properties, CNTs offer a considerable advantage over steel as a potential material from which to construct mechanical springs. Initial calculations predicted that the energy density of springs made of CNTs would surpass the energy density of steel springs by several orders of magnitude. Subsequently, continuum models were used to predict that the theoretical energy density upper bound of CNT springs is $7.7 \times 10^6$ kJ/m$^3$ or $5 \times 10^3$ kJ/kg [6, 7]. In comparison, high energy density and rechargeable lithium-ion batteries have an energy density of $2 \times 10^6$ kJ/m$^3$ or 730 kJ/kg, and nickel-metal hydride batteries have an energy density of $1.5 \times 10^6$ kJ/m$^3$ or 320-400 kJ/kg [8], so CNT springs present a viable alternative to electrochemical energy storage. Energy in a mechanical spring is stored by stretching or compressing atomic bonds, so energy can be released from a spring very rapidly; therefore, springs made of CNTs have the potential to offer a unique combination of both high energy density and high power density.

Prior work by the present author focused on developing models to generate estimates of the maximum energy density that can be achieved in CNTs springs [6, 7]. The estimates were compared to the energy density of conventional storage media to determine whether energy storage in CNT springs was a viable way to store energy; the results were promising and the idea warranted further experimental investigation.

The objective of this thesis is to study energy storage in mechanical springs made of carbon nanotubes. The thesis has two main areas of research. The first area of research is an experimental study of CNTs as mechanical springs. At the molecular scale, CNTs can function as ideal mechanical springs that store a great deal of energy for their size, but a single CNT does not store a useful amount of energy. Instead, emphasis in this work was placed on storing macroscopic amounts of energy in large, ordered arrays of CNTs, with the objective of being able to supply power to drive macroscopic systems. The energy storage capabilities of two different types of CNT assemblies were studied: fibers of millimeter-long, ordered, aligned CNTs grown in forests, and spun yarn made of CNTs. The goals of this work were to understand how the composition of a fiber or a yarn, including its structure, size, defects, inter-CNT interactions and packing density, affected its mechanical properties, particularly its strength, stiffness and energy storage capacity. Both fibers from forests and yarns are imperfect assemblies of CNTs, since the CNTs contain atomic defects and the ordering between CNTs is not ideal. As such, the energy density and mechanical properties were not expected to match the theoretically predicted properties. Nonetheless, these materials offered an opportunity to study how structural imperfections in CNT assemblies affect the performance of these materials as mechanical springs. Understanding the mechanisms that limit the mechanical performance of large CNT assemblies is essential to being able to construct CNT assemblies with superior performance.

The second area of research focused on developing practical demonstrations of CNT springs that store energy and power small-scale systems. Mechanical springs are best-suited to drive mechanical loads, so CNT springs were first used to power mechanical systems. The versatility of the springs was demonstrated by using the CNT springs to drive both low power and high power devices. Next, electric batteries were developed that store energy mechanically in CNT springs and release the energy in the electrical domain. The energy stored, the efficiency and the power output from the springs in each of the systems were characterized to evaluate the performance of the springs as an energy storage medium.
Finally, the results from the theoretical models, the mechanical characterization of macroscopic assemblies of CNTs as springs, and the practical implementation of CNT springs were evaluated to ascertain the feasibility of using CNT springs to power real systems. Further work that remains to be done to improve the performance of CNT springs and the outlook for the future adoption of CNT springs as an energy storage medium are both addressed.

1.1. Energy storage technologies

There are many different ways to store energy. The most common energy storage systems include batteries, capacitors, compressed air storage, flywheels, mechanical springs, pumped hydro, and superconductive magnetic energy storage. Energy can additionally be stored as fuel. This section provides an overview of conventional forms of energy storage and discusses their performance metrics, advantages and limitations.

Electrochemical batteries store energy as chemical energy. Batteries output energy by generating a voltage across the battery terminals through chemical reactions to produce electricity. To input energy for storage, an electricity input drives the chemical reaction in reverse and recharges the battery. Losses within batteries lead to less than one hundred percent storage efficiency, calculated as the ratio of electricity output to electricity input. Four of the most common commercial types of rechargeable batteries are nickel-cadmium, nickel-metal hydride, lead-acid, and lithium-ion. Their main applications are uninterruptible and backup power supplies, starting, lighting and ignition in vehicles, electric and hybrid electric vehicles, and portable consumer electronics such as cell phones, laptops and cameras [8]. Table 1-1 lists the energy density, number of lifetime recharging cycles and efficiency of different types of batteries. Batteries can have very high energy densities, but they offer relatively low power densities because the chemical reactions limit the rate at which energy can be discharged. Operating temperatures for batteries are typically in the range of -20°C to about 60°C [8]. In addition to their limited power density and a relatively narrow operating temperature range, a disadvantage of rechargeable batteries is their high level of self-discharge. Losses can be 15% of stored energy per year for lithium-ion batteries, 50% for lead-acid batteries, and 100% for nickel-cadmium and nickel-metal hydride batteries, all at 20°C [8]. This is an important disadvantage of batteries used as backup power supplies or for long-term energy storage.

Supercapacitors store energy in an electrochemical double layer between a pair of high surface area electrodes and an electrolyte. Supercapacitors store energy with a density of about 22 kJ/kg or 20-70 MJ/m³, and can reach an energy storage efficiency greater than 95% [9, 10]. Supercapacitors typically have lower energy density than batteries but much higher power density because the rate of energy discharge does not rely on chemical reactions. A limitation of supercapacitors is energy self-discharge by as much as 5% per day, so supercapacitors are better suited for short-term storage.

Superconducting magnetic energy storage (SMES) stores energy in the magnetic field of a DC current in a superconducting coil at very low temperatures (~270°C) with a density of 36-180 kJ/kg [3, 11, 12]. SMES can provide high power, can store energy with nearly 98% efficiency, and allows an indefinite number of recharging cycles. These systems can be used to store very large amounts of energy, although a drawback is the costly refrigeration system.

In addition to rechargeable energy storage media, energy can also be stored chemically as fuel. The energy density of common fuels is listed in Table 1-2. Fuel can only be used to
generate energy once, but it offers a much higher energy density than batteries. Energy is released from fuel through combustion; engines and power plants use the heat from combustion to produce mechanical and electrical energy. The net energy density of the fuel is much lower than the values listed in Table 1-2 once equipment needed to convert the fuel into a usable form is taken into consideration. There are losses in converting the chemical energy in fuel to mechanical work or electricity; for instance, the fuel-to-wheel efficiency of most vehicles is about 15%, and the efficiency of fossil fuel power plants is about 40% [9]. One of the main drawbacks of fuel for energy storage is the environmentally harmful byproducts of combustion.

Fuel cells convert energy from fuel into electricity. Hydrogen can be used to store energy very densely, and the only byproduct from hydrogen combustion is water. Reversible energy storage in hydrogen is possible by coupling energy from an external source, such as wind energy or solar energy, to an electrolyzer to produce oxygen and hydrogen, which are stored. To recover the energy, oxygen and hydrogen are input to a fuel cell to produce electricity; round trip efficiency of the process of 50% has been reported to date [13]. Batteries offer a higher round trip efficiency above 80%, but battery self-discharge makes hydrogen storage more efficient for long-term storage. The net volumetric and gravimetric energy densities of the total hydrogen storage system (electrolyzer, storage tank, fuel cell, and hydrogen) are much lower than the energy density of hydrogen alone.

Energy can also be stored mechanically. Table 1-3 lists the energy density, life cycles and efficiency of mechanical energy storage technologies. Compressed air energy storage compresses air and pumps it into a reservoir when there is an excess supply of electricity; when electricity demand increases, the compressed air is used to run turbines to obtain electricity. The energy density of this form of storage is 43 200 kJ/m³ or 40-100 kJ/kg, and round trip efficiencies of 18% to 70% are reported [3, 9]. Smaller scale compressed air storage is also used in regenerative braking in trucks, with round trip efficiency of 90% reported, which can be used to capture 70% of the kinetic energy of the vehicle [9]. For small scale applications, lifetime cycles are limited by fatigue in the storage vessel. Long-term storage can be limited by leakage in the storage reservoir.

Flywheels store kinetic energy in a spinning rotor. Typical flywheels have energy storage capacities between 0.9 MJ to 90 MJ, reach energy densities of 36 kJ/kg or 40 MJ/m³, have up to 10⁷ lifetime operating cycles, and an operating temperature range of -20°C to 40°C [14, 15]. The energy stored in a flywheel is given by the kinetic energy of the rotor, \( \frac{1}{2} I \omega^2 \), where \( I \) is rotor’s moment of inertia and \( \omega \) is the rotor’s angular velocity, so the stored energy depends on the density, size and angular velocity of the rotor. The rotor is connected to a motor and generator to input energy to and remove energy from the rotor; the efficiency of the energy transfer can be over 90%. Rotors are commonly made of high strength carbon fiber composites so that the rotor can withstand the forces induced by the rotation. Disadvantages of energy storage in flywheels include high costs, friction and long-term storage losses: flywheels can lose as much as 20% of their stored energy per hour [14]. For this reason, long-term storage with flywheels is impractical and flywheels are primarily used for short-term storage.

Pumped hydro storage is a large-scale energy storage technology that uses excess electricity during times of low demand to pump water from a reservoir at a low elevation to another at a higher elevation. Once electricity demand increases, the water is returned to the low elevation and electricity is generated using turbines. This technology requires high capital costs to build the infrastructure and is designed to store large amounts of energy. For instance, nearly 2.5% of
electricity in the United States passes through pumped hydro storage before being delivered to consumers [1]. The round trip efficiency of this storage technique is 75% [9].

Mechanical springs store energy as elastic energy by compressing or stretching a material. Typical materials for springs are steel or rubber. Springs made of steel store energy with a density of 1080 kJ/m$^3$ or 0.14 kJ/kg, three orders of magnitude lower than the energy density of batteries. For this reason, springs are primarily used to power specialized small-scale mechanical systems, such as mechanical watches, spring-based robotics actuators, latches and toys. Springs are not used for large-scale energy storage, nor are they used to drive electrical systems because of their low energy density. Springs are capable of many charge-discharge cycles, and can store energy over the long-term with little discharge in the absence of creep.

Figure 1-1 plots volumetric energy density as a function of gravimetric energy density for many different energy storage technologies. Highest energy density is found in fuel and batteries. Note however that the energy density of fuel considered in the plot is the energy density of the fuel alone, without considering the reduction of energy density due to equipment needed to convert the fuel into a usable form. Mechanical energy storage is more robust than energy storage in batteries since mechanical energy storage offers many more lifetime recharging cycles, but the energy density of mechanical storage is several orders of magnitude lower than batteries. The Ragone plot in Figure 1-2 plots the power density and energy density of various energy storage technologies. Highest energy density is provided by batteries, while highest power density is found in capacitors.

The theoretical energy density and power density of CNT springs are included in the plots in Figure 1-1 and Figure 1-2. Note that the energy density considered for CNT springs is the energy density of the spring alone, without considering the mass and volume of any supplemental architecture needed to operate the springs. The plots show that vastly superior springs could be made by replacing traditional spring materials with CNTs. The plots also indicate that CNT springs have considerable potential as an energy storage medium, offering a combination of high energy density, high power density, and a potentially infinite number of recharging cycles if energy can be stored in CNTs elastically. CNTs could replace or complement battery storage, particularly for applications in which battery storage is ill-suited, such as for long-term energy storage. These results indicate that CNT springs are a promising new energy storage technology that merits further scientific investigation.

Table 1-1: Energy density, life cycles and efficiency of batteries and supercapacitors [8, 9]

<table>
<thead>
<tr>
<th>Energy storage</th>
<th>Gravimetric energy density (kJ/kg)</th>
<th>Volumetric energy density (MJ/m$^3$)</th>
<th>Life cycles</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel-cadmium battery</td>
<td>160-290</td>
<td>360</td>
<td>1500</td>
<td>55-70%</td>
</tr>
<tr>
<td>Nickel-metal hydride battery</td>
<td>320-400</td>
<td>1550</td>
<td>300–500</td>
<td>65-70%</td>
</tr>
<tr>
<td>Lead-acid battery</td>
<td>110-180</td>
<td>252</td>
<td>200–300</td>
<td>85-95%</td>
</tr>
<tr>
<td>Lithium-ion battery</td>
<td>730</td>
<td>2050</td>
<td>300–500</td>
<td>88%</td>
</tr>
<tr>
<td>Supercapacitor [10]</td>
<td>22</td>
<td>20-70</td>
<td>&gt;100000</td>
<td>95%</td>
</tr>
</tbody>
</table>
Table 1-2: Energy density of different forms of fuel [9]

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Volumetric energy density (MJ/kg)</th>
<th>Gravimetric energy density (MJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>49.7</td>
<td>25 400</td>
</tr>
<tr>
<td>Gasoline</td>
<td>46.8</td>
<td>34 700</td>
</tr>
<tr>
<td>Diesel oil (DERV)</td>
<td>45.7</td>
<td>37 900</td>
</tr>
<tr>
<td>Ethanol</td>
<td>29.5</td>
<td>23 400</td>
</tr>
<tr>
<td>Methanol</td>
<td>19.8</td>
<td>18 000</td>
</tr>
<tr>
<td>Bioethanol</td>
<td>26.9</td>
<td>21 600</td>
</tr>
<tr>
<td>Coal</td>
<td>28.8</td>
<td>24 500</td>
</tr>
<tr>
<td>Firewood</td>
<td>15.8</td>
<td>8 100 - 14 700</td>
</tr>
<tr>
<td>Liquid hydrogen</td>
<td>140</td>
<td>9 500</td>
</tr>
<tr>
<td>Natural gas</td>
<td>53.5</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 1-3: Energy density, life cycles and efficiency of mechanical energy storage technologies

<table>
<thead>
<tr>
<th>Technology</th>
<th>Gravimetric energy density (kJ/kg)</th>
<th>Volumetric energy density (kJ/m³)</th>
<th>Life cycles</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal CNT spring</td>
<td>5000</td>
<td>7 700 000</td>
<td>Many cycles</td>
<td>-</td>
</tr>
<tr>
<td>PDMS spring [16]</td>
<td>5</td>
<td>4900</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Steel spring [4]</td>
<td>0.14</td>
<td>1080</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rubber band</td>
<td>3</td>
<td>3600</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Isoprene spring</td>
<td>220</td>
<td>200 000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>High modulus carbon fiber spring</td>
<td>7.0</td>
<td>15 000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>High strength carbon fiber spring</td>
<td>46.1</td>
<td>83 000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Silicon spring</td>
<td>20.8</td>
<td>48 500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fly wheel [9, 14]</td>
<td>36</td>
<td>40 000</td>
<td>$10^7$</td>
<td>90%</td>
</tr>
<tr>
<td>Pumped water [9]</td>
<td>3.6</td>
<td>3600</td>
<td>50 000</td>
<td>75%</td>
</tr>
<tr>
<td>Compressed air [3, 9]</td>
<td>40-100</td>
<td>43 200</td>
<td>15 000</td>
<td>18%-90%</td>
</tr>
</tbody>
</table>
Figure 1-1: Comparison of gravimetric and volumetric energy density of different energy storage technologies. HMCF stands for high modulus carbon fiber, HSCF stands for high strength carbon fiber, Li-ion refers to a lithium-ion battery, Ni-MH refers to a nickel-metal hydride battery, and Ni-Cd refers to a nickel-cadmium battery. Note that the energy density of fuel considered in this plot is the energy density of the fuel alone, without considering the reduction of energy density due to equipment needed to convert the fuel into a usable form. Similarly, the energy density of ideal CNT springs is the energy density of the spring alone, without considering the mass and volume of any supplemental architecture needed to operate the springs.
1.2. Thesis outline

The objective of this thesis is to study energy storage in mechanical springs made of carbon nanotubes. Chapter 1 provides a short overview of conventional energy storage technologies, motivating the need for new research into energy storage technology alternatives. Chapter 2 presents background material on CNTs and assemblies of CNTs, including details of their structure and mechanical properties. Calculations of the energy density and power density of ideal springs made of CNTs are outlined. Alternative materials for high performance springs, potential applications of CNT springs, and theoretical models of ideal yarn are discussed. Chapter 3 outlines the results of mechanical tests performed on fibers made of millimeter-long CNTs prepared from forests to study their behavior as mechanical springs. Chapter 4 discusses the results of mechanical tests performed on spun yarn made of CNTs to evaluate their behavior as mechanical springs. Chapter 5 examines design considerations involved with using springs as energy sources, and presents the design, operation and performance characteristics of a range of different CNT-powered devices. Chapter 6 summarizes experimental results from Chapter 3 to Chapter 5. The mechanical properties of CNT fibers and CNT yarn are compared to properties of individual CNTs and to mechanical properties of conventional engineering structural materials. The energy density and power density of fibers, yarn, and CNT-powered devices are compared.
to the storage capabilities of conventional energy storage technologies. Finally, Chapter 7 presents concluding remarks and addresses future work and the outlook for CNT springs.
2. Carbon nanotubes: a material for energy storage

2.1. An introduction to carbon nanotubes

Carbon nanotubes were described by Iijima in 1991 [18]. These one-dimensional structures proved to be stable, electrically and thermally conductive, with a higher strength and stiffness than other common structural materials. In the years that have followed since their discovery, a tremendous amount of research has been conducted to study the structure, properties and applications of this material.

2.1.1. Structure

An ideal CNT is a molecule made of carbon atoms, similar to a sheet of graphene rolled into a seamless cylinder and capped at the ends. Both CNTs and graphene have sp2 bonding, a highly stable covalent bond. Single-walled CNTs (SWCNTs) are made of a single shell, and multi-walled CNTs (MWCNTs) are made of two or more concentric shells, as shown in Figure 2-1.

Chirality describes the angle of the carbon graphene bonds with respect to the CNT axis. The structure of each shell of a CNT is uniquely characterized by a diameter \( d \) and a chiral angle \( \theta \), or equivalently by a chiral vector \( C_h \). The chiral vector is perpendicular to the CNT axis and follows the length of the CNT perimeter. The chiral vector is expressed as \( C_h = na_1 + ma_2 = (n, m) \), where \( a_1 \) and \( a_2 \) are unit vectors. Special structures include armchair CNTs when \( n=m \) and zigzag CNTs when \( m=0 \). Chirality affects the electrical conductivity of a CNT, determining whether it is metallic or semiconducting, but has little impact on mechanical stiffness and strength.

Experiments have shown that the diameters of SWCNTs fall in the typical range of 0.6 nm to 2 nm, though diameters as small as 0.4 nm and as large as 3 nm have been observed [19]. SWCNTs can have very high aspect ratios, with lengths as long as several centimeters [20]. The stability of a SWCNT cross-section decreases as diameter size increases. The cross-section of a SWCNT deforms in the radial direction when it comes into close contact with another tube or a substrate because of the van der Waals interactions between them. The deformation becomes more pronounced in tubes with larger diameters [21]. During synthesis, SWCNTs often form bundles [22], densely packed groupings of a few up to several hundred tubes arranged in a hexagonal lattice, because of the attractive van der Waals forces acting between the SWCNTs.

Each concentric shell of a MWCNT has the same structure as a SWCNT, though each shell can have its own chirality. The interactions between neighboring shells are based on van der Waals forces, and these are generally weak. MWCNTs typically have an outer diameter less than 100 nm and inner diameter greater than 2 nm [19], and can have between two to over a hundred shells [23]. The distance between adjacent shells in a MWCNT is measured to be 0.34 nm, the same distance that separates each of the graphene sheets in graphite.
2.1.2. Synthesis

CNTs are currently being fabricated using several different processes, including laser ablation, the arc-discharge method, thermal chemical vapor deposition (CVD) growth of CNTs on a substrate, and CVD growth of CNTs in an aerogel, among many others. Each synthesis process requires a carbon source, a catalyst, and heat. Variations between the processes produce CNTs with different levels of defects, purity, diameters, numbers of shells and lengths.

The arc discharge method applies a voltage between two graphite electrodes spaced about 1 mm apart in a chamber filled with low pressure helium or argon. The temperature of the gas between the electrodes reaches above 3000°C and the carbon in the electrodes sublimates to form a plasma. CNTs deposit on the cathode: MWCNTs form without a catalyst, while SWCNTs form when catalyst particles (iron, nickel, cobalt or yttrium) are added to the graphite anode. The lengths of the produced CNTs are relatively short, generally about 20 μm long [23]. This technique produces CNTs of high quality and with few structural defects, but the CNT products are mixed with graphite, metal clusters and amorphous carbon that must be separated to obtain purified CNTs. Drawbacks of this method include high cost and limited control of CNT lengths and diameters [24].

The laser ablation technique sends laser pulses toward a graphite target located in a quartz tube filled with low pressure argon or helium. The tube passes through a furnace operating near 1200°C. The laser pulses decompose the target into small carbon aggregates which recombine to form CNTs in the vapor phase. These are carried with the surrounding gas toward a cooled collector made of copper at the end of the tube where they deposit in bundles with lengths on the order of tens of microns. Graphite, amorphous carbon and metal catalyst particles also deposit on the collector and these must be removed using purification techniques [23]. A target made of graphite results in the formation of MWCNTs while a target of graphite mixed with catalyst
particles forms SWCNTs. CNTs produced with laser ablation are typically of high quality and contain few structural defects.

Growth of SWCNTs or MWCNTs using thermal chemical vapor deposition (CVD) takes place on a substrate that has been patterned with catalyst particles, often iron, nickel or cobalt. The substrate is placed in a quartz tube inside of a furnace that heats the tube to a temperature between 500 and 1000°C. Hydrocarbon gas mixtures of methane, ethane, ethylene or acetylene flow through the tube during the growth period. The temperature, gas composition and type and size of the catalyst particles determine the number of walls, lengths, diameter distributions, degree of alignment, defect density and growth rate of the CNTs. The result is densely packed, aligned arrays of CNTs which grow vertically from the substrate, mixed with amorphous carbon and catalyst particles. These arrays are often referred to as CNT ‘forests’. Alignment of the CNTs depends on the process parameters, and can range from tangled, poor alignment to relatively good vertical alignment. Forest density is typically in the range of $10^{10} - 10^{13}$ CNTs per cm$^2$ [25]. The lengths of CVD-grown CNTs can be as long as millimeters, and MWCNTs can be grown with more than a hundred shells [23]. An important drawback of CNTs grown using thermal CVD is that the defect density of the CNTs is much higher than with the laser ablation technique or the arc discharge method because of the low temperature used in the process. The main advantages of thermal CVD are that it can be used to grow CNTs with high yield, high purity, long lengths, and with a great degree of control over diameter distribution [26]. The growth of CNTs in aligned arrays makes CVD grown forests suitable for many applications that require macroscopic, aligned arrays of CNTs. For instance, CNTs grown in forests are well-suited as a potential material for macroscopic CNT springs because of their millimeter long lengths and ordered alignment, though their high defect density is a disadvantage.

CNTs can also be grown inside of a CVD reactor in the vapor phase. This process does not require a substrate. Instead, a carbon source and a catalyst (such as ethanol and ferrocene) are injected in the liquid phase into a hydrogen carrier gas, flowing inside of a furnace heated to temperatures between 1050°C to 2000°C [27]. CNTs grow on the catalyst particles inside of the furnace and aggregate to form an aerogel. The diameter and number of shells of the CNTs can be adjusted by changing the concentration of the gases, the composition of the injection liquid including the type of carbon source, the temperature of the furnace, and the gas flow rate in the reactor. The CNTs in the aerogel can be spun together using a rotating spindle to form a dense yarn [27].

### 2.1.3. Mechanical properties of individual carbon nanotubes

The carbon-carbon bond in CNTs is the strongest bond found in nature, so extensive experimental and theoretical studies have been undertaken to measure and model the mechanical properties of CNTs. Since CNTs are essentially a sheet of graphene rolled into a cylinder, the stiffness of a CNT in the axial direction has been found to be 1 TPa, the in-plane stiffness of graphene [28]. Many experimental techniques have been devised to measure the mechanical characteristics of CNTs. The Young’s modulus was measured by finding the amplitude of thermal vibrations of CNTs in a transmission electron microscope (TEM) [29], and embedding CNTs in a polymer and measuring deformations using micro-Raman spectroscopy [30]. Other
techniques, including performing tensile tests by stretching CNTs between atomic force microscope (AFM) tips [28, 31] and deflecting a suspended CNT using an AFM tip [32, 33], have been used to measure both the Young’s modulus and axial strength. A summary of reported values for the Young’s modulus of individual SWCNTs, MWCNTs, and ropes of SWCNTs obtained through experimental and theoretical work are listed in Table 2-1. Assigning a Young’s modulus to a CNT is applicable only within a continuum framework in which each shell is assigned an equivalent thickness. The accepted value for the Young’s modulus of a CNT is 1 TPa with an associated shell thickness of 0.34 nm, which is equal to the spacing between graphene sheets in graphite (Figure 2-2) [34]. Studies have shown that the Young’s modulus is independent of the number of shells in a MWCNT and the van der Waals interactions between the shells [35], so similar stiffness for both SWCNTs and MWCNTs is expected. The elastic properties of CNTs have been shown to be nearly independent of chirality [36, 37].

Studies have shown that CNTs are able to withstand large strains elastically. CNTs are stiff along their axis, but are flexible in the direction normal to their axis [38]. CNTs can undergo large deformations under compression, bending, stretching and twisting reversibly and without the formation permanent atomic defects [32, 39]. Under compression or bending, carbon fiber fractures, but CNTs form kink-like ridges that relax elastically once the load is removed [38, 40]. This behavior is explained by the nanoscale structure of CNTs that doesn’t form the stress concentrators that lead to failure in macroscale materials [41]. Maximum tensile strains as high as 13.7% have been measured experimentally to date [5], though modeling studies predict strains in defect-free CNTs as high as 20-30% [36, 42, 43]. Defects and impurities limit the failure strains measured experimentally.

A Young’s modulus of 1 TPa corresponds to an ideal specific stiffness of 448 N/tex, where tex or mg/m corresponds to linear mass density. Considering a 6% elastic strain limit, the ideal fiber specific strength is 26.9 N/tex. Considering a 15% elastic strain limit, the ideal fiber specific strength is 67.2 N/tex.

In MWCNTs, there are relatively weak van der Waals interactions between the nested shells. Failure of MWCNTs under tension has been described as a ‘sword-in-sheath’ fracture mechanism [31], in which the outer shells fractures and the unaffected inner shells are pulled out. A load applied to the outer shell of a MWCNT is largely carried by the outer shell because of poor load transfer from the outer shell to the inner shells. The effect is a lower tensile strength for MWCNT because the inner shells contribute little to bearing a load. Such behavior limits the usefulness of MWCNTs as structural elements for loading in tension or torsion, though compressing or bending a MWCNT will affect all shells, and indicates that SWCNTs may be the more useful structural material for springs.

A bundle, often also called a rope, is a naturally occurring dense array of SWCNTs arranged in a lattice with hexagonal packing [44], as shown in Figure 2-3. The CNTs are held together with van der Waals forces, and the bundles can be several hundreds of microns to a few millimeters long [45]. Ideally, the intertube spacing approaches 0.34 nm. The CNTs are parallel and highly aligned within the bundle. Bundles of continuous CNTs are expected to maintain the same stiffness as individual CNTs since the hexagonal network of covalent bonds gives CNTs their stiffness in the axial direction, and this structure remains unchanged in a bundle [32]. Salvetat et al. measured a bundle stiffness of 1 TPa by bending a suspended bundle of SWCNTs using an AFM tip [32]. Yu et al. measured the stiffness of SWCNT bundles by stretching SWCNTs bundles in tension [28]. One end of the bundle was attached to the end of an AFM tip
using carbonaceous deposits, and the other end of the bundle was tangled within SWCNT “paper”. They noticed that only the SWCNTs on the perimeter of the bundle were supporting the load, with little load transfer to the inner SWCNTs in the bundle. These observations were a result of their attachment method which gripped only the SWCNTs along the bundle’s perimeter. For energy storage applications, bundles are useful structures only if all CNTs within a bundle are equally loaded. To measure the actual stiffness and strength of a CNT bundle in tension, all CNTs must be gripped at the attachment site because load transfer mechanisms between CNTs by van der Waals forces and shear interactions are weak and do not adequately distribute a load throughout the structure. It should be noted that the condition on the gripping method is relevant only for loading in torsion and tension since compression and bending will load all CNTs within a bundle regardless of the attachment method. The shear modulus of bundles falls short of the shear modulus of individual CNTs also because of weak van der Waals forces acting between CNTs. Salvetat et al. measured a shear modulus in SWCNT bundles of 1 GPa [32] and Lasjaunias et al. reported 1-2 GPa [46], considerably lower than the shear modulus of 450 GPa for a single SWCNT. The authors attributed their results to a shear modulus in bundles that is dominated by interactions between CNTs rather than by the hexagonal lattice of carbon atoms in an individual CNT.

Bundles of discontinuous CNTs are bundles in which the constituent CNTs do not span the entire length of the bundle [34, 47]. The bundle still maintains CNTs arranged in a hexagonal lattice, though vacancies are present at the CNT ends [32]. The intercalated arrangement of CNTs in the bundle requires excellent load transfer between the CNTs for the overall bundle to maintain high strength and stiffness. With weak shear interactions between CNTs at the overlaps, slip between the CNTs would be the principal failure mechanism of a bundle of discontinuous CNTs stretched in tension. Ideally, van der Waals forces between the CNTs could allow the CNTs in the array to be loaded to the maximum loads of individual CNTs [34]. Yakobson et al. modeled SWCNT bundles and concluded that the overlap length of the constituent SWCNTs should greater than 10 μm for the bundle to approach the strength of an individual SWCNT [47]. Qian et al. estimated that contact lengths must be on the order of 10 μm to 120 μm or greater for optimal load transfer [44]. If the results from Yakobson et al. and Qian et al. are correct, then macroscale bundles of discontinuous CNTs with an intercalated structure could be built with long lengths and large diameters and continue to maintain excellent properties as long as the CNTs can be assembled into ideal bundle lattices with tight packing, high crystallinity, good load transfer, and long overlaps.
Chapter 2. Carbon nanotubes: a material for energy storage

Table 2-1: Experimental and theoretical determination of the Young’s modulus of CNTs

<table>
<thead>
<tr>
<th>Structure</th>
<th>Young’s modulus</th>
<th>Thickness</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lu [35]</td>
<td>SWCNT 0.97 TPa</td>
<td>0.34 nm</td>
<td>Empirical force-constant model</td>
</tr>
<tr>
<td>Yakobson et al. [39]</td>
<td>SWCNT 5.5 TPa</td>
<td>0.066 nm</td>
<td>Molecular dynamics</td>
</tr>
<tr>
<td>Mo et al. [42]</td>
<td>SWCNT 0.92 TPa</td>
<td>0.34 nm</td>
<td>Molecular mechanics and finite elements</td>
</tr>
<tr>
<td>Lourie et al. [30]</td>
<td>SWCNT 2.8 - 3.6 TPa</td>
<td>unspecified</td>
<td>Micro-Raman spectroscopy</td>
</tr>
<tr>
<td>Yu et al. [28]</td>
<td>SWCNT ropes 1.0 TPa</td>
<td>0.34 nm</td>
<td>Tension using an AFM probe</td>
</tr>
<tr>
<td>Yu et al. [31]</td>
<td>MWCNT 0.27 - 0.95 TPa</td>
<td>0.34 nm</td>
<td>Tension using an AFM probe</td>
</tr>
<tr>
<td>Wong et al. [48]</td>
<td>MWCNT 1.28 ± 0.59 TPa</td>
<td>0.34 nm</td>
<td>Bending force measurement using an AFM</td>
</tr>
<tr>
<td>Salvetat et al. [32]</td>
<td>SWCNT ropes 1 TPa</td>
<td>0.34 nm</td>
<td>Deflection using an AFM tip</td>
</tr>
<tr>
<td>Treacy et al. [29]</td>
<td>MWCNT 1.8 TPa</td>
<td>0.34 nm</td>
<td>Measurement of thermal vibrations using a TEM</td>
</tr>
</tbody>
</table>

Figure 2-2: Models of a SWCNT and a MWCNT as continuum structures with a shell thickness of 0.34 nm [6, 49].
2.2. Performance of ideal carbon nanotubes as springs

Calculations of the maximum theoretical energy density and power density that can be reached in CNTs are needed to evaluate this proposed energy storage method. The following sections outline calculations of energy density for CNTs under different modes of mechanical deformation, and calculations of power density for ideal springs.

Much of the content in section 2.2.1 was developed as part of the present author's Master's thesis [6]. Subsequently, the work was extended in breadth and in level of detail for publication [7]. The content from [7] includes important background results that are relevant for the present work, so the material is included in this thesis for completeness.

2.2.1. Energy density estimates

Analytical models for CNT mechanics are used to estimate the energy that may be stored in elastically-deformed CNT springs under a broad range of different loading conditions [7]. The analytical models used here employ several approximations. The CNTs are modeled using the continuum assumption [34], in which each CNT is treated as a uniform, hollow, cylindrical beam, and each shell of the CNT is taken to contribute 0.34 nm to the beam's wall thickness. Therefore, each beam has an inner radius $r_i$, a tightly-packed wall thickness of $n \times 0.34$ nm, and an outer radius $r_o = r_i + n \times 0.34$ nm, where $n$ is the number of shells in the CNT. The model does not account for sets of diameters of the internal MWCNT shells other than the tightly-packed structure described above because non-tightly packed MWCNTs would buckle more easily and would in general have lower spring performance than otherwise identical, tightly packed MWCNTs would. The commonly accepted Young's modulus $E$ of 1 TPa is employed [22]. The maximum deformations are assumed to be governed by either the elastic limit or the onset of buckling, depending on which limit is reached first. Treating a CNT as a beam is a simplistic model that does not account for the nested shell structure, van der Waals forces, shear interactions between the layers, or non-linear post-buckling behaviour [21]. However, because the simple analytical models used here employ parameters derived from more advanced analytical models such as molecular dynamics, they provide reasonable strain energy density.

Figure 2-3: Close-packing structure of SWCNTs in an ideal bundle [44]. The equivalent continuum structure is shown on the right.
estimates in the elastic regime and before the onset of buckling. Finally, the maximum gravimetric energy density of a spring comprising a large assembly of CNTs under a given mode of deformation is assumed to be equal to the maximum gravimetric energy density of a single CNT under that deformation. In practice, some modes of deformation are more readily applied to all members of an assembly in a uniform fashion than others, so this assumption will generally produce an upper bound on the maximum energy density that may be stored in the assembly. Using these assumptions, the strain energy density is estimated in CNT springs under loading in axial tension, axial compression, bending, and torsion.

The energy stored in an elastically-deformed object is given by

\[ U = \frac{1}{2} \int \sum_i \sum_j \sigma_{ij} \varepsilon_{ij} dV \]  

(2-1)

where \( V \) is the volume of the body, \( \sigma \) is the stress tensor, and \( \varepsilon \) is the strain tensor. For the case of CNTs loaded below the failure and/or buckling limits in axial tension or axial compression to a linear, elastic strain of \( \varepsilon \), the volumetric energy density \( u^\text{shells}_v \) within the shell walls (i.e. omitting the unfilled space inside the CNT from the volume integral) is given by

\[ u^\text{shells}_v = \frac{1}{2} E \varepsilon^2 \]  

(2-2)

while the gravimetric energy density \( u^\text{shells}_m \) within the shell walls is given by

\[ u^\text{shells}_m = \frac{1}{2} E \varepsilon^2 \frac{1}{\rho} \]  

(2-3)

where \( \rho \) is the density of graphite. The existence of unfilled space inside a CNT (and between the CNTs that comprise a CNT assembly) will not affect gravimetric energy density, so the overall gravimetric energy density \( u_m \) will be equal to the gravimetric energy density \( u^\text{shells}_m \) of the shells alone. However, the unfilled space does impact the volumetric energy density of the overall structure, so that the overall volumetric energy density of the spring \( u_v \) will not be equal to the volumetric energy density \( u^\text{shells}_v \) of the shells. Approximating a CNT as a cylindrical tube, its cross-sectional area is \( A = \pi (r_0^2 - r_i^2) \), and its total enclosed area is \( A_{\text{encl}} = \pi r_0^2 \). Therefore, the overall strain energy density per unit volume of a hollow cylindrical beam loaded to an elastic axial strain of \( \varepsilon \) under axial tension or compression is reduced by a factor of \( A/A_{\text{encl}} \), yielding

\[ u_v = \frac{1}{2} E \varepsilon^2 \frac{A}{A_{\text{encl}}} \]  

(2-4)

For springs composed of large assemblies of CNTs, the overall volumetric energy density \( u_v \) of the spring will be reduced further by the spacing between the CNTs in the assembly. The amount of spacing will depend on the size, uniformity, and packing of the CNTs. For CNTs packed into an ideal close-packed triangular lattice [45, 50], the spacing between adjacent CNTs will be 0.34 nm [22]. This reduces \( u_v \) by an additional fill factor \( f = 0.91 \) [6].

Equation (2-4) assumes effective load transfer through all shells of a tightly packed MWCNT. For ideal MWCNTs (that is, those in which the inter-shell coupling is solely due to van der Waals effects), the assumption that all shells fully share the load is only valid under compressive loading or bending. It is not valid for ideal, tightly packed MWCNTs under tensile or torsional loading because the inner shells slide past one another almost without friction [31, 44]. For an ideal MWCNT under tensile or torsional loading, the outer shell carries most of the load, so that the maximum achievable strain energy density for ideal MWCNTs in tension or torsion will be significantly reduced as compared with the case in which all shells carry the load.
However, previous work has shown that inter-shell interactions in MWCNTs are not necessarily ideal. In particular, the existence of inter-shell sp3 bonds, which may be created using controlled sputtering or irradiation, can significantly improve inter-shell load transfer [51]. In this case, it may be possible to transfer loads to the inner shells of the MWCNT, though the induced defects may decrease the axial strength.

Figure 2-4 plots the calculated volumetric energy density $u_v$ (equation (2-4)) as a function of axial strain for the tensile loading both of SWCNTs and of MWCNTs with either just the outer shell carrying the load (to represent ideal MWCNTs) or all shells carrying the load (as an absolute upper bound on MWCNTs with inter-shell load transfer). The SWCNTs’ diameter is taken to be 1 nm, and the MWCNTs’ outer diameters are taken to be 3 nm, 8 nm, and 20 nm. In the case where all MWCNT shells carry the load, the MWCNTs are assumed to be entirely filled with densely-packed inner shells to determine the upper bound on the energy density; under this assumption, the volumetric energy density of MWCNTs in which all shells carry the load does not depend on the outer diameter. The energy density is maximized by applying high tensile strains to the spring; the strain that can be applied to the spring in tension is limited only by the elastic limit. The ratio $A/A_{encl}$ must be large to achieve high energy density, so assemblies of SWCNTs with small diameters offer higher energy density than do MWCNTs in which only the outer shell carries a tensile load. Defect-free, densely-packed, completely-filled MWCNTs in which all shells carry the load offer a somewhat higher value of maximum energy density than that offered by small diameter SWCNTs. This energy density represents an upper bound on MWCNT performance because it assumes that there is complete load transfer between shells but that the defects that enable this increased load transfer do not reduce the shells’ yield strength. For the purposes of the design and potential performance assessments presented here, the SWCNT results will be considered to represent a reasonable best-case scenario for tensile loading. Although this may slightly underestimate the potential performance of MWCNTs with well-coupled shells, the approximation is justified both by the comparability between the SWCNT and coupled-shell MWCNT results and by the better-characterized set of assumptions that go into the SWCNT calculations. SWCNTs with small diameters also offer the most stability against radial deformation due to van der Waals interactions when in close contact with other SWCNTs [21]. With an applied tensile strain of 15% to 1.02 nm diameter SWCNTs ($A/A_{encl}=0.75$), the achievable energy density $u_v$ for a single tube is $8.4 \times 10^6$ kJ/m$^3$, corresponding to a gravimetric energy density $u_m$ of $5 \times 10^5$ kJ/kg, while for a densely packed bundle of these tubes, the maximum volumetric energy density $u_v$ is 9% less, or $7.7 \times 10^6$ kJ/m$^3$. In comparison, the volumetric energy density of a lithium ion battery is $2 \times 10^6$ kJ/m$^3$, corresponding to a gravimetric energy density of 730 kJ/kg [8], and the energy density of a steel spring is about 1080 kJ/m$^3$ or 0.14 kJ/kg [4].
When sufficiently large loads are applied to CNTs in bending, torsion or compression, they deform into complex buckling patterns. While the buckles remain largely elastic and reversible [52], loading above the buckling point increases the likelihood of permanent defects forming in the lattice to release the localized strain. Beyond the first buckle, the quadratic relations between strain energy and strain for compression, strain energy and bending angle for bending, and strain energy and twist angle for torsion are lost, and these relations become roughly linear [39, 53]. To avoid permanent defects forming in the lattice and to maintain the more favorable quadratic dependence of stored energy on strain, applying loads sufficient to induce buckling should be avoided when using CNT-based springs for energy storage.

The treatment of CNTs loaded in compression mirrors that of CNTs in tension, with two important differences. First, energy storage in CNTs under compression may be limited by buckling rather than by the elastic limit of the material. Second, as mentioned above, a compressive load can be transferred to the inner shells of a MWCNT without the need to grasp the inner shells directly. Therefore, equation (2-4) can be used to calculate the maximum strain energy density in a compressively loaded, MWCNT-based spring without modification.

The critical buckling strain for a CNT depends on its structure and is highly sensitive to the number of shells, the CNT diameter, and for MWCNTs, the type and degree of interaction between adjacent shells. Various analytical models have been created to capture this buckling behavior; two basic models will be used here. In one model, Chang et al. [54] used molecular mechanics to develop an expression for the critical buckling strain of both SWCNTs and thick MWCNTs in compression, where a “thick” MWCNT is defined as a tightly packed one that has a diameter ratio $d_i/d_o$ of less than 0.62. In this model, the critical buckling strain $\varepsilon_{cr}$ for SWCNTs is calculated as
where $d$ is the SWCNT diameter, $h=0.34$ nm is the effective wall thickness, $D_o=0.85$ eV is the bending stiffness and $E_t=360$ J/m$^2$ is the in-plane stiffness of the SWCNT. The critical buckling strain $\varepsilon_{cr}^m$ for thick MWCNTs in compression is found in this model to be insensitive to the inner diameter $d_i$ and depends only on the outer diameter $d_o$ according to

$$\varepsilon_{cr}^m = \frac{0.0985 \times 10^{-9}}{d_o}. \tag{2-6}$$

In another model, Xia et al. created a continuum model to predict the onset of buckling in MWCNTs. This model is supported by molecular dynamics simulations and can be used to describe buckling either in ideal MWCNTs or in MWCNTs with inter-shell sp$^3$ bonding. The critical buckling strain is given in [51] as

$$\varepsilon_{cr}^m = \frac{h}{R \sqrt{3(1-\nu^2)}} + \frac{n-1}{n} \frac{G \delta}{E h}. \tag{2-7}$$

where $R$ is the average radius of the MWCNT, $n$ is the number of shells, $\nu$ is the Poisson’s ratio, $G$ is the shear modulus, and $\delta$ is the spacing between the two walls. Both models yield similar values for the critical buckling strain for ideal MWCNTs.

Calculated maximum strain energy densities for SWCNTs and MWCNTs with various shell structures in compression before the onset of buckling are plotted as a function of diameter in Figure 2-5, using the three models for buckling strain described above. A fraction of inter-shell sp$^3$ bonds of 6% has been used in the buckling strain model from [51]. The calculations assume in all cases that buckling occurs before the elastic limit is reached, which is valid if the elastic strain limit is greater than $\varepsilon_{cr}^s$ in the case of SWCNTs and $\varepsilon_{cr}^m$ in the case of MWCNTs. Independent of the buckling model that is used, energy density decreases rapidly with increasing diameter because of the limit on the applied strain due to buckling. Thick MWCNTs also have higher energy density than thinner MWCNTs and SWCNTs for the same outer diameter because of their dense inner shells and higher buckling strain. Beyond these trends, it can be seen that if CNT deformation is limited only by buckling, the energy density of MWCNTs with inter-shell bonding is higher than the energy density both of SWCNTs and of MWCNTs with only van der Waals interactions between neighboring shells. These results are valid only if the elastic limit exceeds the buckling limit. Given that the buckling limit for the MWCNTs examined here is calculated to be as high as 0.1 for certain geometries, this assumption may not be valid. If a fraction of the atoms in a MWCNT form inter-wall bonds, the resulting defects may lower the elastic limit of the shells, and consequently MWCNTs containing these defects are more likely to reach their elastic limit before buckling. In that case, the calculations accounting for inter-shell bonding will overestimate the achievable energy density in MWCNTs. In general, the maximum achievable energy density of SWCNTs depends on parameters that are known with a greater degree of certainty than those of MWCNTs. SWCNTs are therefore recommended as a better structure than MWCNTs for a spring in compression because their smaller diameters ensure high energy densities, independent of the details of the inter-shell interaction.

To evaluate the validity of the continuum beam model employed here for a single shell, the strain energy per atom of a SWCNT under uniform compressive loading prior to buckling is compared with the results of molecular mechanics and finite element models. Figure 2-6 plots strain energy per atom as a function of strain for a 1.41 nm diameter (18,0) SWCNT modeled by
Arroyo et al. [55], a 1.25 nm diameter (16,0) SWCNT modeled by Sears et al. [56], and a 1 nm diameter (7,7) SWCNT modeled by Yakobson et al. [39]. In general, strain energy is expected to be largely independent of chirality [22]. Strain energy per atom for each modeled SWCNT is plotted up to its respective compressive buckling strain, which varies between models because of the different diameters of the modeled SWCNTs in addition to variations between models. The energy per atom of a SWCNT predicted by the continuum beam model is plotted as a function of strain on the same graph. The energy predicted by the continuum beam model is independent of diameter and chirality, so the curve is plotted up to the maximum strain on the graph since the SWCNT diameter, which determines the buckling strain, is unspecified. Good agreement between the four models indicates that the continuum beam model can be used to obtain reasonable energy density estimates.

Figure 2-5: Maximum volumetric energy density before the onset of buckling in compression plotted as a function of diameter for SWCNTs, and plotted as a function of outer diameter for MWCNTs with 3 shells and for thick MWCNTs [7].
Inter-shell sp3 bonding will be neglected in determining the onset of buckling in MWCNTs subjected to bending or torsional loads, for which the analytical expressions of [51] are not directly applicable; the models from [39, 54, 57] will be used instead. As in the case of compression, inter-shell sp3 bonds are expected to increase the buckling strain of MWCNTs but adversely affect the elastic limit. The range of potential MWCNT inter-shell interactions and the variations among the models that describe the onset of buckling in CNTs add some uncertainty to the maximum predicted strain energy densities. The assumptions used here nonetheless provide a reasonable estimate of the overall maximum strain energy density, with a degree of variation with detailed shell structure that is similar to that observed for compressed CNTs.

The treatment of energy storage in bending requires a different framework because of the spatial variation of strain within a bent CNT. In pure bending, a uniform bending moment is applied to the cylindrical beam so that it develops a maximum strain of \( \pm \varepsilon \) at its outer diameter. The volumetric strain energy density of the beam is

\[
U_v = \frac{1}{8} E \varepsilon^2 \left[ 1 - \left( \frac{r_1}{r_0} \right)^4 \right].
\]

For a given value of \( \varepsilon \), high energy density can be achieved when the ratio \( r_1/r_0 \) of the CNT is small, which implies that the highest energy densities will be achieved in SWCNTs with small outer diameters or in MWCNTs with densely packed shells. The amount of bending that can be applied to a CNT is limited by the strain at which a CNT begins to buckle. Yakobson et al. [39] modeled the critical buckling strain of a SWCNT under bending as

\[
\varepsilon_{cr}^\delta = \frac{0.077 \times 10^{-9}}{d},
\]

where \( d \) is the SWCNT diameter. Chang et al. [54] modeled the critical buckling strain of thick MWCNTs in bending as

\[
\varepsilon_{cr}^m = \frac{0.111 \times 10^{-9}}{d_0 + h},
\]
where $d_o$ is the outer diameter and $h=0.34$ nm. Both expressions contain an inverse relation between buckling strain and diameter. As for the case of compressive loading, deforming a CNT in pure bending has the advantage of deforming all shells of a MWCNT rather than just the outermost shell, leading to higher overall energy density than if only the outermost shell were deformed.

The maximum overall volumetric strain energy density in bending before the onset of buckling is plotted as a function of diameter in Figure 2-7. Energy density decreases rapidly with increasing diameter because of the decrease in buckling strain at higher diameters. For the same outer diameter, MWCNTs store energy with higher density than SWCNTs because of the dense packing of inner shells. However, SWCNTs generally have smaller diameters than MWCNTs, so SWCNTs will tend to store energy with higher density, although modifications to the critical buckling strain of MWCNTs due to strong inter-shell interactions may improve the performance of MWCNTs. Overall, SWCNTs with small diameters would be an excellent structure for a spring deformed in bending. Typical radii of curvature for bent CNTs at the onset of buckling are 6.7 nm and 26 nm for 1.02 nm and 2 nm diameter SWCNTs respectively, which are quite small for implementation in springs at anything above the nanoscale.

To estimate the maximum strain energy density of a CNT under torsion, a torsional moment $M$ is applied to the cylindrical beam. The volumetric strain energy density $u_v$ is given by

$$u_v = \frac{M^2}{2GJ\pi r_o^2},$$

where $G$ is the shear modulus and $J = \frac{\pi}{2} (r_o^4 - r_i^4)$ is the polar moment of inertia of the beam. Wang et al. [57] propose a model for the critical moment at which buckling first occurs in torsionally-loaded long SWCNTs and MWCNTs:
where $\nu$ is the Poisson’s ratio. For ideal MWCNTs, an applied moment affects only the outer shell since grasping the inner shells is difficult [31, 58]. However, previous work has shown that load transfer in torsion may be increased through inter-wall sp3 bonding [59], which would enable inner shells to contribute to supporting a torsional load. Using the critical moment from [57], the maximum volumetric energy density of torsionally-loaded SWCNTs and MWCNTs before the onset of buckling is calculated and plotted against diameter in Figure 2-8, indicating that the maximum energy density decreases rapidly with increasing diameter. In this plot, the inner shells of the MWCNTs are assumed to carry loads. However, if only the outer shell of a MWCNT supported an applied load, then the curve for MWCNTs would coincide with the curve for SWCNTs. Within these approximations, SWCNTs will have a higher volumetric energy density than MWCNTs because of their smaller outer diameters, so that for energy storage in pure torsion, the highest energy densities are achieved in SWCNTs with small diameters. For stronger inter-shell interactions, the energy density stored in MWCNTs will be higher than the MWCNT strain energy density shown here only if the increased critical buckling strain is less than the elastic limit which may be affected by the defects present in the structure. Nonetheless, MWCNTs with inter-shell bonding may once again offer an alternative to SWCNTs as a means of reaching high strain energy density.

Figure 2-8: Maximum volumetric energy density before the onset of buckling in torsion as a function of diameter for SWCNTs and outer diameter for MWCNTs [7].

There are advantages and disadvantages to each deformation mode and type of CNT structure. Deforming MWCNTs in axial tension or torsion comes with the challenge of grasping the inner shells, while compression and bending ensure that loading is applied to all shells. Torsion, bending and compression are limited by critical buckling stresses, while tension is limited only by the stress at the elastic limit. For all loadings, the highest energy density without
strong inter-shell bonding is achieved in SWCNTs with diameters of 2 nm or less, with MWCNTs with strong inter-shell bonding offering a potentially attractive alternative structure.

The strain energy densities of bundles of SWCNTs deformed in each of the four deformation modes as a function of diameter are plotted in Figure 2-9. The plot shows that storing energy in tension is advantageous for SWCNTs with diameters greater than 2 nm since the maximum energy density before the onset of buckling drops off rapidly in compression, bending, and torsion because of the limits on the applied strain due to buckling. For diameters smaller than 2 nm, the energy densities of all deformation modes are in the same range, so any of the deformation modes could be selected for a spring, based on practical considerations of implementation. Nevertheless, if elastic strains of 9% or greater can be applied to SWCNTs in tension before failure, then tension would be the best choice regardless of diameter. These results indicate that a good choice for a spring would be a dense bundle of SWCNTs with diameters less than 2 nm, stretched in tension.

![Figure 2-9: Maximum volumetric energy density of SWCNT bundles as a function of diameter for four deformation modes [7].](image)

A support structure is needed to deform a CNT-based spring and hold it in its maximally deformed configuration until the stored energy is released. The volume and mass of this structure must be included in system-level energy density calculations. For instance, a support structure in compression may be used to maintain a bundle of CNTs in tension, and since there are no materials as strong in compression as CNTs are in tension, the supporting structure must be larger than the CNT-based spring itself. This will reduce the overall system’s energy density considerably.

While the loaded support structure stores energy itself, we conservatively assume that only the energy from the spring can be extracted to perform useful work, and the energy stored in the support structure is neglected when calculating the overall energy density of the combined spring
and support system. In practice, an architecture could be designed in which the energy in the support structure is used to perform work as well, so it may be possible to reach higher energy densities than the ones proposed here.

One type of support structure is a solid cylindrical shaft around which a CNT spring stretched predominantly in tension is wrapped. The maximum volumetric energy density in the combined spring and support structure consisting of a cylindrical shaft about which the CNT is wrapped, as described above, is [6]

\[
U_v = \frac{E \varepsilon^2 A/A_{encl}}{2 + \frac{E}{\sigma_y}},
\]

where \(\sigma_y\) is the compressive yield strength of the support structure material, and all the other symbols are defined as above. The maximum volumetric energy density for a CNT spring in pure tension combined with a support structure loaded axially in compression is [6]

\[
U_v = \frac{E \varepsilon^2 A_{encl}}{A} \frac{E \varepsilon}{\sigma_y}.
\]

A comparison of equations (2-13) and (2-14) indicates that higher energy density in a supported CNT spring can be reached with a circular shaft support than with a support in axial compression, though the difference in performance between the two support structures is relatively small. However, wrapping a spring in tension around a shaft is an impractical structure to implement in practice because of friction (see Chapter 5).

The energy density of a bundle of 1.02 nm diameter SWCNTs \((A/A_{encl}=0.75)\) under tensile loading is plotted as a function of applied strain in Figure 2-10, taking into account a support structure loaded axially in compression. The materials considered for the support structure are single crystal silicon \((\sigma_y=7\ \text{GPa})\), single crystal silicon carbide \((\sigma_y=21\ \text{GPa})\), single crystal diamond \((\sigma_y=53\ \text{GPa})\), and tungsten carbide \((\sigma_y=2.7\ \text{GPa})\), all chosen for their high compressive strength [60, 61]. The choice of material for the support structure is important because its properties have an impact on the resulting energy density. The energy densities of lithium-ion batteries and steel springs are plotted on the same graph for comparison. The maximum achievable overall stored energy density is predicted to be comparable to lithium-ion batteries as long as high elastic strains can be applied to the CNTs and a high quality material is used for the support structure. A CNT spring with its associated support structure can store energy with a density more than two orders of magnitude greater than steel springs, so CNT springs have the potential to significantly improve upon the energy storage capability of currently available mechanical springs.

An ideal support structure for a spring could potentially be a support structure made of MWCNTs loaded in compression, supporting a spring made of SWCNTs loaded in tension. A well-designed system would extract both the strain energy of the SWCNTs in tension and the strain energy of the MWCNTs in compression. With such a design, there would be no reduction in energy density once a support structure is taken into consideration.

To conclude, calculations using the widely accepted Young’s modulus and yield strains for CNTs predict the maximum energy density of CNT springs loaded in tension at the highest applied strains to be 7000 times greater than that of steel springs and three times greater than the energy density of lithium ion batteries. Once practical considerations are taken into account, such as the need for a support structure or additional extraction hardware, the energy density of a power source containing a CNT spring will be lower than the calculations predict for the spring.
element alone. However, even when a support structure is taken into consideration, a CNT spring can still store energy with a density more than two orders of magnitude higher than a steel spring and on the same level as batteries. Groupings of SWCNTs with diameters of 2 nm or smaller stretched in tension are identified as the best structure and loading mechanism for high-performance springs.

![Graph showing energy densities](image)

Figure 2-10: Volumetric energy densities of bundles of SWCNTs under tensile loading with a support structure loaded axially in compression made of single crystal diamond, silicon, silicon carbide and tungsten carbide [7]. The energy densities of lithium-ion batteries and steel springs are also shown on the graph for comparison.

### 2.2.2. Power density estimates

Once upper bounds on the energy density in CNT springs are found, upper bounds on the power density expected from CNTs springs can be calculated. To calculate power density, an estimate is needed for the time it takes for strain energy stored in a CNT to be released. Consider the case of a CNT stretched in tension, and model the CNT as a beam of length $L$, cross-sectional area $A$, and density $\rho$. The beam is fixed at one end, and an axial force $F$ is applied to the other end of the beam, as shown in Figure 2-11.
Due to the axial force, the strain in the beam is
\[ \varepsilon = \frac{F}{EA} \quad (2-15) \]
and the axial displacement along the beam in the x-direction is
\[ u(x) = ex \quad (2-16) \]
where x is the distance measured from the fixed end. Once the force on the beam is released, the beam is assumed to undergo simple harmonic motion, so that the displacement of the beam as a function of position and time is
\[ u(x,t) = u(x) \cos wt = ex \cos wt \quad (2-17) \]
The velocity v of the beam as a function of position and time is given by
\[ v(x,t) = -exw \sin wt \quad (2-18) \]
The kinetic energy \( E_k \) of the beam is
\[ E_k = \frac{1}{2} \int \rho v^2(x,t) dAdx = \frac{\rho A \varepsilon^2 w^2 L^3}{6} \sin wt, \quad (2-19) \]
so that the maximum kinetic energy of the beam is
\[ E_{k,max} = \frac{\rho \varepsilon^2 w^2 A L^3}{6}. \quad (2-20) \]
The maximum potential energy of the beam is
\[ U_{max} = \frac{1}{2} E \varepsilon^2 A L, \quad (2-21) \]
If the beam oscillates at resonance, the maximum kinetic energy must equal the maximum potential energy. Setting these two quantities equal, the resonance frequency of the beam \( w_o \) is
\[ w_o = \frac{3E}{\rho l^2}. \quad (2-22) \]
The time period of the oscillations is
\[ T = 2\pi \sqrt{\frac{\rho l^2}{3E}}. \quad (2-23) \]
In reality, oscillations in such a beam will be damped, and all of the energy from the beam will be released within a few times periods. To a first order, the time for energy to be discharged from the beam is \( T \approx \frac{\rho l^2}{3E} \). Also to a first order, the power output from a CNT spring is therefore expected to be
\[ \text{Power} \sim \frac{U_{max}}{T} \sim \frac{E^{3/2} \varepsilon^2 A}{\rho^{1/2}} \text{ Watts.} \quad (2-24) \]
The volumetric power density of a spring is expected to scale according to
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Power density (volumetric) \( \sim \frac{E^{3/2} \varepsilon^2}{\rho^{1/2} L} \ W/m^3 \) \hspace{1cm} 2-25

and the gravimetric power density of the spring scales as:

Power density (gravimetric) \( \sim \frac{E^{3/2} \varepsilon^2}{\rho^{3/2} L} \ W/kg. \) \hspace{1cm} 2-26

Thus the power density of a spring material increases with its Young’s modulus and with the applied strain, and decreases with the length of the spring and its density. With a high Young’s modulus, a high elastic strain limit, and a relatively low density, CNT springs are expected to provide higher power density than springs made of conventional engineering materials such as steel.

These derivations can be used to estimate the upper bound on the power density that can be reached in CNTs. Consider a Young’s modulus of 1 TPa, a 15% elastic strain limit, and a density of 2230 kg/m^3. For a 100 nm long CNT, an estimate for the power density is \( 2 \times 10^{18} \) W/kg. For a 10 \( \mu \)m long CNT, the estimated power density is \( 2 \times 10^{16} \) W/kg. For a 1 mm long CNT, the estimated power density is \( 2 \times 10^{14} \) W/kg. For a macroscale assembly of CNTs, as discussed in section 2.3, that has the same material properties as individual CNTs but geometry similar to a steel spring, the power density would be \( 2 \times 10^{12} \) W/kg for a 10 cm long spring.

Similar calculations can be made to estimate an order of magnitude upper bound for power density in springs made of steel. Consider a Young’s modulus of 200 GPa, a 0.5% elastic strain limit, and a density of 7800 kg/m^3. For a 1 m long steel spring, the power density is \( 3 \times 10^6 \) W/kg. For a 10 cm long steel spring, the power density is \( 3 \times 10^8 \) W/kg. Comparing the power density of a 10 cm long steel spring to a spring of comparable length made of CNTs, the spring made of CNTs offers the potential for considerably higher power density.

2.3. Macroscopic carbon nanotube assemblies

Ordered groupings of CNTs are created to try to capture the high strength and stiffness of individual CNTs in larger assemblies. If CNTs could be assembled into macroscopic groupings with a stiffness and strength that matched the properties of individual CNTs, these groupings would become an important structural material for many engineering applications. However, the properties of individual CNTs at the nanoscale are often not replicated in larger groupings. Across the literature, the properties of macroscopic CNT assemblies fall short of the properties of individual CNTs because of the difficulties of maintaining low defect densities, good ordering and even loading throughout hundreds of thousands of CNTs or more. This section reviews a number of different types of macroscopic CNT groupings that have been fabricated, lists the mechanical properties of these groupings and outlines reasons why the mechanical properties of the groupings fall short of expectations.

At the smallest scale, CNTs often form bundles during the growth process, which are dense assemblies of CNTs in which the CNTs are grouped into a closest-packed triangular lattice with a spacing of 0.34 nm [22]. At larger scales, CNTs have been assembled into mats, forests, yarns (typically spun from forests or spun from the vapor phase in a chemical vapor deposition reactor), and CNTs are also often used in composites as a reinforcing material. To maximize the strength and stiffness of CNT assemblies, particularly for energy storage applications, these
assemblies should be composed only of CNTs and the CNTs should be aligned along the axis of loading, to maximize load bearing by the strong carbon-carbon bonds. Additives of extra materials into CNT groupings, such as coatings and polymer matrices, should be limited to maximize the volume fraction of CNTs. Indeed, suspending SWCNTs in a polymeric matrix has been shown to substantially lower the modulus of the resulting fiber material compared to the initial SWCNTs [62]. Therefore, focus is placed on macroscopic groupings containing only CNTs.

The stiffness of an ideal CNT is 1 TPa, and strength values as high as 100 GPa have been measured in individual CNTs [5], corresponding to a specific stiffness of 448 N/tex and a specific strength of 44.8 N/tex. The goal is to build macroscopic assemblies with strength and stiffness values that approach these upper bounds.

### 2.3.1. Mechanical properties of macroscopic carbon nanotube assemblies

Thermal chemical vapor deposition is used to grow dense assemblies of vertically aligned CNTs on a substrate. These aligned arrays are called forests. The collective mechanical properties of CNTs in forests are straightforward to test in compression. One of the applications of CNT forests in compression is energy absorbing foams. The compressive stress and stiffness of a forest is typically reported using the area of the forest, not the area occupied by CNTs, so the reported stress and stiffness are low in part because CNTs in forests occupy only a small fraction of the area. Yaglioglu et al. reported a low modulus of CNT pillars tested in compression of 2.2 MPa [63]. Cao et al. measured an initial modulus for forests of 50 MPa; applying repeated cyclic compressive loads to their forests substantially decreased the modulus and produced permanent self-organized folded patterns in the CNTs due to collective buckling [64]. Suhr et al. measured a compressive stiffness in forests of 21 MPa and observed viscoelastic behavior, preconditioning, hysteresis, non-linear elasticity and stress relaxation in the loading behavior of their forests [65], far from ideal CNT behavior. Few reports have been made of the tensile properties of CNTs grown in forests; details of tension tests performed on fibers prepared from forests are outlined in Chapter 3.

One of the earliest types of macroscopic CNT assemblies created were CNT films or mats, also referred to as bucky paper. These two-dimensional assemblies of CNTs are typically made of densely packed, randomly oriented CNTs. The mats are usually fabricated by dispersing CNTs in a liquid and filtering the mixture to produce a mat [66]; work has also been done to produce mats in the presence of a magnetic field to align the CNTs [67]. Zhang et al. produced mats with a tensile strength of 74 MPa and a tensile modulus of 5 GPa by dispersing SWCNTs in nitric acid, filtering the dispersion through a membrane and then drying the resulting mat [68]. With poor CNT alignment, the strength and stiffness of mats are quite low.

A substantial amount of research has been done to study methods of creating spun yarn from CNTs. Scaling arguments suggest that CNTs are an ideal material from which to create spun yarn because of their small diameters [69]. Friction in yarn that causes filaments to resist slip scales with filament surface area, or $2\pi r$, where $r$ is the filament radius; forces that cause slip scale with filament area, or $\pi r^2$. To maximize the effects of friction and minimize forces causing slip, filaments should have as small radius as possible. With diameters as small as 1 nm, it should
be possible to create high quality yarn from CNTs. High strength and stiffness CNT yarn requires long CNT lengths, good inter-CNT load transfer, good ordering, straight CNTs with few defects, no amorphous carbon or impurities, and an optimal amount of twisting to create a self-locking structure with high internal radial pressure while minimizing the effects of obliquity. The advantage of yarn as a macroscopic assembly of CNTs is that it can be made as long as kilometers, using continuous spinning processes. Two-dimensional sheets could be made from yarn by weaving it into fabric-like materials. Using a simplified model [69], the ratio of yarn strength $\sigma_y$ to CNT strength $\sigma_{CNT}$ can be quantified as

$$\frac{\sigma_y}{\sigma_{CNT}} = \cos^2 \alpha [1 - (k \csc \alpha)]$$

(2-27)

$$k = \frac{\sqrt{2}}{3L_f} \left( \frac{Q}{\mu} \right)^{1/2}$$

(2-28)

where $\alpha$ is the angle between the CNTs and the yarn axis at the outer surface of the yarn, $a$ is the CNT radius, $Q$ is the migration period, $L_f$ is the CNT length, and $\mu$ is the coefficient of friction between CNTs. These equations indicate that high friction, long CNT length, small CNT diameter, and short migration period all contribute to producing high quality yarn.

Initial fabrication methods to produce yarn used a wet drawing process. It was suggested that CNTs can align along the direction of a liquid flow, which can produce good alignment within yarn once the liquid is dried. For instance, Vigolo et al. dispersed CNTs with a surfactant and then condensed the CNTs into a yarn by injecting the CNTs into a polymer solution [70]. The resulting yarn was made of disordered CNTs and contained amorphous carbon. Yarn produced in this manner had a stiffness of 9-15 GPa and strength of about 160 MPa. Kozlov et al. developed a similar method of spinning CNTs into yarn, but without using a polymer, and reported a specific strength of 0.77 N/tex and specific stiffness of 8.9 N/tex [71]. Ericson et al. used a similar process and produced yarn with strength of 116 MPa and a modulus of 120 GPa [72].

Dry spinning methods proved to be more successful than wet drawing methods, and were used to produce higher quality yarn. A first way to assemble CNTs into yarn is to spin CNTs together from the side of a forest. The CNTs in such a forest must be sufficiently tangled that they can be continually drawn to form a yarn. Using this technique, Zhang et al. fabricated highly twisted yarn 1-10 µm in diameter, with strength of 150-300 MPa and Young’s modulus of 4 GPa [73]. The mechanical properties of the yarn were not ideal and showed hysteretic behavior under cyclic loading. Tran et al. spun CNTs from forests into yarn, and sought to improve CNT and bundle interactions by increasing the density of the yarn and alignment of the CNTs along the yarn axis by tensioning the yarn during spinning; they measured strength of 970 MPa to 1.4 GPa and a mean stiffness of 1.2 GPa in their yarn [74]. Zhang et al. reported on spun yarn from MWCNT forests with strength of 1.35 to 3.3 GPa and stiffness of 100 to 263 GPa [75]. They explained that scatter in their data was due to variations in the yarn due to the spinning process, such as the helix angle, the CNT quality, and the yarn diameter. Non-idealities in their yarn limited its mechanical behavior: low packing density limited load transfer, and CNT ends tended to cluster together, creating weak points in the yarn. As a result of poor load transfer, fracture occurred by a combination of fracture of CNTs and slip, and the authors postulated that uneven loading of CNTs within the yarn initiated fracture. Liu et al. used a similar process and created yarn with a strength of 0.6-1.1 GPa and a modulus of 10-30 GPa [76]. Zhang et al. spun yarn
from the side of forests and noted that strength and modulus increased with smaller yarn diameter [77]. They had two explanations for this observation: first, strength is controlled by defects, and larger diameter yarn has a high probability of containing defects, and second, yarn with larger diameters may contain more CNTs with lower than optimal twist angles. No reason was given for the relationship between yarn diameter and modulus, suggesting that there may be other factors involved. They also found that a higher degree of twisting produced higher strength and stiffness yarn due to stronger inter-CNT interactions and higher radial compressive stresses. Their best yarn had strength and stiffness of 1.91 GPa and 330 GPa, respectively. Zhang et al. spun 1 mm tall MWCNT forests into yarn, densified the yarn by twisting and passing it through ethanol, and measured strength and stiffness of 0.5 GPa and 8 GPa, respectively [78]. Sears et al. cross-sectioned yarn samples produced by spinning CNTs from forests to study the effect of twist and solvent densification on yarn morphology and strength [79]. Their results showed that the behavior of CNT yarn deviates from the behavior of conventional staple yarn since yarn strength does not approach the strength of the CNTs, even with high twist and packing density; they suggest that this is perhaps not surprising given the large degree of CNT entanglement that locks CNTs into non-ideal arrangements, the much larger number of CNTs in CNT yarn (hundreds of thousands or more) than filaments in conventional staple yarn (on the order of a hundred filaments), and the van der Waals forces that become relevant at the nanoscale that are not present in conventional staple yarn. In all of these publications, yarn is produced by dry spinning CNTs from a forest containing very tangled CNTs; CNTs cannot be drawn continuously from a forest without these tangles. Therefore, the tangling of the CNTs in the forests is carried over into the yarn, producing yarns made of tangled CNTs. It is unlikely that any processing technique of the CNTs between the forest and the yarn removes any significant amount of disorder. Tangling and disorder are deleterious for maintaining high yarn strength and stiffness, therefore there is an inherent flaw in this method of producing yarn.

A second way to use dry spinning to assemble CNTs into yarn is to grow CNTs using chemical vapor deposition (CVD) and to spin the CNTs into yarn directly from the vapor phase. It is postulated that CNTs align along the direction of the gas flow to produce yarn with good CNT alignment. This process can be used to spin yarn with varying diameters and lengths. Koziol et al. [80] created yarn by spinning CNTs from the vapor phase and then running the yarn through an acetone vapor stream. They identified a number of factors that limit the strength and stiffness of their yarn: short CNT lengths, defects in CNTs that produce kinks, weak shear interactions between CNTs that limit inter-CNT load transfer, and poor alignment of CNTs along the yarn axis. They found that poor CNT alignment along the yarn axis limits contact between neighboring CNTs and reduces the effectiveness of inter-CNT load transfer. With yarn diameters of 7 μm to 20 μm, they reported a mean strength of 6 GPa or 6 N/tex, and a mean stiffness of 180 GPa or 200 N/tex. They noted a correlation between the strength and stiffness of their yarn samples, and attributed this relationship to local deficiencies in densification due to inclusion of carbonaceous particles in the yarn, which lead to unequal sharing of load throughout the yarn that lowered both strength and stiffness. A follow-up study on the same yarn revealed that the yarn contains compositional variations of the number of CNT shells and CNT diameters, many of the CNTs are collapsed, and that loading throughout a yarn is non-uniform [81]. Zhong et al. used a similar CVD process but passed their yarn through water and then acetone for densification, and obtained yarn made of multilayer sheets [82]. They reported a strength of 0.4-1.25 GPa or 0.2-0.75 N/tex. Li et al. fabricated 3-20 μm diameter yarn of double-walled CNTs
(DWCNTs) with strength of 0.62-2.6 GPa and modulus of 1.2-16 GPa [83]. They list four reasons why the properties of their yarn fall short of the properties of individual DWCNTs: defects in the CNTs that decrease CNT strength by an order of magnitude, fracture occurring in different bundles at different times, imperfect lattice formation of the CNTs, and direct loading of only the perimeter layer of the yarn during loading because of the testing grips.

To improve inter-CNT load transfer in yarn, methods of producing cross-links between CNTs have been proposed, including irradiation and chemical functionalization. These techniques could improve strength and stiffness of CNT groupings by improving load transfer between CNTs, but only as long as the induced defects do not degrade the CNTs' elastic behavior.

Many of the macroscopic assemblies of CNTs show promise, but their properties still fall short of those of individual CNTs. To date, the best mechanical properties are measured in yarn. Table 2-2 summarizes the properties of CNT yarn reported in the literature. The evolution of the strength and stiffness of CNT yarn reported in the literature is plotted in Figure 2-12. Over the course of the ten years during which CNT yarn research has been conducted, there has been a gradual improvement in the yarn properties. This is a new field of research, and continual improvements in yarn properties are expected over the coming years.

To study the behavior of CNT assemblies as mechanical springs, this work focuses on CNT yarn spun from the vapor phase and fibers made from CNTs from forests tested end-to-end in tension. The non-idealities within these materials are taken into consideration during mechanical testing.
Table 2-2: Strength and stiffness of yarn reported in the literature

<table>
<thead>
<tr>
<th>Publication</th>
<th>Method</th>
<th>Strength</th>
<th>Specific strength</th>
<th>Stiffness</th>
<th>Specific stiffness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vigolo et al. [70]</td>
<td>Wet drawing process</td>
<td>160 MPa</td>
<td></td>
<td></td>
<td>9-15 GPa</td>
</tr>
<tr>
<td>Kozlov et al. [71]</td>
<td>Wet drawing process</td>
<td></td>
<td>0.77 N/tex</td>
<td></td>
<td>8.9 N/tex</td>
</tr>
<tr>
<td>Ericson et al. [72]</td>
<td>Wet drawing process</td>
<td>116 MPa</td>
<td></td>
<td></td>
<td>120 GPa</td>
</tr>
<tr>
<td>Zhang et al. [75]</td>
<td>Yarn drawn from forests</td>
<td>1.35-3.3 GPa</td>
<td></td>
<td></td>
<td>100-263 GPa</td>
</tr>
<tr>
<td>Tran et al. [74]</td>
<td>Yarn drawn from forests</td>
<td>0.97-1.4 GPa</td>
<td></td>
<td></td>
<td>1.2 GPa</td>
</tr>
<tr>
<td>Zhang et al. [73]</td>
<td>Yarn drawn from forests</td>
<td>150-300 MPa</td>
<td></td>
<td></td>
<td>4 GPa</td>
</tr>
<tr>
<td>Liu et al. [76]</td>
<td>Yarn drawn from forests</td>
<td>0.6-1.1 GPa</td>
<td></td>
<td></td>
<td>10-30 GPa</td>
</tr>
<tr>
<td>Zhang et al. [77]</td>
<td>Yarn drawn from forests</td>
<td>1.91 GPa</td>
<td></td>
<td></td>
<td>330 GPa</td>
</tr>
<tr>
<td>Zhang et al. [78]</td>
<td>Yarn drawn from forests</td>
<td>0.5 GPa</td>
<td></td>
<td></td>
<td>8 GPa</td>
</tr>
<tr>
<td>Koziol et al. [80]</td>
<td>Yarn spun from vapor phase</td>
<td>6 GPa</td>
<td>6 N/tex</td>
<td>180 GPa</td>
<td>200 N/tex</td>
</tr>
<tr>
<td>Zhong et al. [82]</td>
<td>Yarn spun from vapor phase</td>
<td>0.4-1.25 GPa</td>
<td>0.2-0.75 N/tex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li et al. [83]</td>
<td>Yarn formed in vapor phase</td>
<td>0.62-2.6 GPa</td>
<td></td>
<td></td>
<td>1.2-16 GPa</td>
</tr>
</tbody>
</table>

Graphical representation of strength and stiffness data over time.
2.4. Previous work on carbon nanotubes as springs

Relatively little research has been done to date to study mechanical springs composed entirely of CNTs for energy storage applications. Estimates of the maximum theoretical energy density of CNTs as springs, and experimental work on practical implementations of CNT springs deformed in tension have been reported by the present author [6, 7, 84, 85]. To date, no other known work has reported purposeful storage of mechanical energy in a spring made of CNTs and release of this energy to power a practical device.

Chesnokov et al. measured the response of SWCNTs as springs in compression [86]. They reported a reversible work done to compress their SWCNTs of 0.18 eV per carbon atom. This reversible energy was reported used a 34 mg sample of 1.36 nm diameter SWCNTs, so 0.18 eV per carbon atom corresponds to $1.44 \times 10^6$ J/kg. In comparison, the theoretical energy density of 1 nm diameter SWCNTs stretched elastically in tension to a 15% strain is $5 \times 10^6$ J/kg, so the energy density reported by Chesnokov et al. is remarkable and approaches the theoretical energy density limit of CNTs.

Torsional springs have been developed from single CNTs [58, 87, 88]. These devices consist of either a SWCNT or MWCNT placed over a trench patterned into a silicon wafer. The CNT is attached to the wafer at the edges of the trench using patterned metal electrodes, and a metal paddle is attached to the CNT at the centre of the trench. Electrostatic actuation deflects the paddle, inducing a torsional deformation in the CNT. The devices display high sensitivity, good precision and control over the angle of rotation, resilience, and no performance degradation over time with repeated actuation. Proposed applications of the torsional springs are sensors, optical modulators and high frequency electronics clocks. While these springs are not designed for energy storage, the devices show that CNTs can successfully be used as elastic springs.

Due to their high compressive strength, low density and high elasticity, CNTs grown in forests are being used as foams that can absorb energy repeatedly in compression [64, 89]. Proposed applications of these foams are for construction purposes, energy dissipation, cushioning, packaging, vibration mitigation, and compliant electric contacts such as motor
brushes. The foam does not behave as an ideal spring, however, since their performance gradually degrades over time, with permanent wavelike folds forming in the forests after several compressive loading cycles.

There are several other better-known applications of CNTs for energy storage applications. CNTs have been extensively investigated for use in electrical energy storage devices, primarily as the electrode material in capacitors [90-92] and lithium batteries [93, 94]. Capacitance is directly related to the surface area of a capacitor’s electrodes; since dense forests of CNTs have very large exposed surface areas and high conductivity, CNT forests as electrodes show great promise for improving the energy storage capacity of capacitors. CNTs have also been proposed as a material that can absorb hydrogen for hydrogen storage in order to run fuel cells [95, 96], though recent results have shown that the hydrogen storage capacity of CNTs may fall short of expectations. These applications make use of CNTs’ conductivity, high surface area, or their ability to be functionalized, but do not make use of CNTs as mechanical energy storage elements.

2.5. Alternative materials for mechanical springs

Material property charts can be used to study how different materials behave as springs. A plot of Young’s modulus as a function of strength for many conventional engineering materials is available in reference [97]. The performance index for choosing a material for a spring is \( \sigma_f^2/E \), a measure of the energy density of a material, where \( \sigma_f \) is the failure strength of the material and \( E \) is the Young’s modulus. Note that strength can refer to yield strength for metals and polymers, compressive strength for ceramics, tear strength for elastomers, and tensile strength for composites. From a plot of Young’s modulus as a function of strength, it can be seen that the best conventional engineering materials for springs are elastomers, high strength steel and glass fiber reinforced polymers (CFRP). Brittle ceramics, in which maximum values of \( \sigma_f^2/E \) are found, are unsuitable materials for springs. With an effective Young’s modulus of 1 TPa and strength potentially as high as 100 GPa, ideal CNTs provide a greater advantage as a material for springs than all conventional engineering materials. In order to choose a material for lightweight springs, a plot of specific modulus (Young’s modulus divided by density) as a function of specific strength (strength divided by density) can be examined. Such a plot is available in [97]. Metals are penalized for their high density, so that elastomers, carbon fiber reinforced polymers and glass fiber reinforced polymers are the best engineering materials for springs once weight is considered. Made only of relatively lightweight carbon atoms, ideal CNTs have a specific modulus of 5900 GPa/(Mg/m³) and a specific strength of 590 000 MPa/(Mg/m³), higher values than all other engineering materials. Therefore, CNTs provide a considerable advantage as a material for lightweight springs.

The properties of many conventional engineering materials are listed in Table 2-3, along with estimates of the energy per unit weight and energy per unit volume that can be reached in each of these materials. The table highlights the energy density advantage of elastomers, although the ideal energy density of CNTs surpasses the energy density of most other conventional engineering materials. CNTs are one of few materials that can offer energy densities that can match those of electrochemical batteries; other potential materials include diamond or boron.
nitride nanotubes. The ideal properties and ideal energy density of CNTs have only been demonstrated at the nanoscale to date, and for now these remain upper bounds that still need to be demonstrated experimentally at the macroscale. With currently available materials, the best springs should be made of natural rubber or carbon fiber. However, springs made of CNTs are the ultimate goal, and more research is needed for macroscopic assemblies of CNTs to reach their full potential for energy storage applications.

**Table 2-3: Mechanical properties of different materials for springs [97-103]**

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg/m³)</th>
<th>Strength (GPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Specific strength (N/tex)</th>
<th>Specific stiffness (N/tex)</th>
<th>Volumetric energy density (kJ/m³)</th>
<th>Gravimetric energy density (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood (oak)</td>
<td>300</td>
<td>0.03</td>
<td>13</td>
<td>0.1</td>
<td>43</td>
<td>35</td>
<td>0.1</td>
</tr>
<tr>
<td>Mild steel</td>
<td>7850</td>
<td>0.25</td>
<td>200</td>
<td>0.03</td>
<td>25.5</td>
<td>156</td>
<td>0.02</td>
</tr>
<tr>
<td>Aluminum</td>
<td>2700</td>
<td>0.3</td>
<td>69</td>
<td>0.11</td>
<td>25.6</td>
<td>652</td>
<td>0.2</td>
</tr>
<tr>
<td>Carbon steel</td>
<td>7850</td>
<td>0.5-0.6</td>
<td>205</td>
<td>0.06-0.08</td>
<td>26.1</td>
<td>610-880</td>
<td>0.08-0.1</td>
</tr>
<tr>
<td>Polyimide</td>
<td>3100</td>
<td>0.1</td>
<td>2-4</td>
<td>0.077</td>
<td>1.5-3</td>
<td>1250-2500</td>
<td>1-1.9</td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>1400</td>
<td>2</td>
<td>430</td>
<td>0.6</td>
<td>136</td>
<td>4650</td>
<td>1.5</td>
</tr>
<tr>
<td>Wool</td>
<td>1300</td>
<td>0.17</td>
<td>2</td>
<td>0.13</td>
<td>1.5</td>
<td>7230</td>
<td>5.6</td>
</tr>
<tr>
<td>Spider silk</td>
<td>1400</td>
<td>0.6</td>
<td>12</td>
<td>0.4</td>
<td>8.5</td>
<td>15 000</td>
<td>10.7</td>
</tr>
<tr>
<td>High modulus carbon fiber</td>
<td>2160</td>
<td>5</td>
<td>830</td>
<td>2.3</td>
<td>384</td>
<td>15 000</td>
<td>7</td>
</tr>
<tr>
<td>Cotton</td>
<td>1540</td>
<td>0.6</td>
<td>8</td>
<td>0.4</td>
<td>5.2</td>
<td>22 500</td>
<td>14.6</td>
</tr>
<tr>
<td>Silicon</td>
<td>2331</td>
<td>4</td>
<td>165</td>
<td>1.7</td>
<td>71</td>
<td>48 500</td>
<td>21</td>
</tr>
<tr>
<td>Kevlar 29</td>
<td>1440</td>
<td>3.6</td>
<td>100</td>
<td>2.5</td>
<td>80</td>
<td>64 800</td>
<td>45</td>
</tr>
<tr>
<td>High strength carbon fiber</td>
<td>1800</td>
<td>7</td>
<td>295</td>
<td>3.9</td>
<td>164</td>
<td>83 000</td>
<td>46</td>
</tr>
<tr>
<td>PDMS</td>
<td>965</td>
<td>0.003-0.0012</td>
<td>0.00075</td>
<td>0.003-0.012</td>
<td>0.0008</td>
<td>6000-96000</td>
<td>6.2-99.5</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>1300</td>
<td>0.04</td>
<td>0.0076</td>
<td>0.03</td>
<td>0.006</td>
<td>105 300</td>
<td>81</td>
</tr>
<tr>
<td>Natural rubber</td>
<td>910</td>
<td>0.02</td>
<td>0.001</td>
<td>0.02</td>
<td>0.001</td>
<td>200 000</td>
<td>220</td>
</tr>
<tr>
<td>Glass</td>
<td>2500</td>
<td>2.5-7</td>
<td>72</td>
<td>1</td>
<td>27.6</td>
<td>43000-340 000</td>
<td>17-136</td>
</tr>
<tr>
<td>Diamond</td>
<td>3500</td>
<td>50</td>
<td>1000</td>
<td>14</td>
<td>284</td>
<td>1 250 000</td>
<td>357</td>
</tr>
<tr>
<td>Carbon nanotube</td>
<td>2230</td>
<td>50-200</td>
<td>1000</td>
<td>224 -</td>
<td>448</td>
<td>850 000</td>
<td>560-9000</td>
</tr>
</tbody>
</table>

### 2.6. Potential applications of carbon nanotube springs

High energy density is just one of several potential benefits of CNT springs as an energy storage medium. Because spring-based energy storage is based on different physics than that which governs electrochemical batteries, the operational characteristics and limitations of such a device will be different from those of batteries. For instance, batteries operate with their best energy density when they are discharged slowly; in contrast, springs can release their energy quickly and without great loss of efficiency. In fact, springs can absorb energy quickly or slowly, as well as release their energy either quickly slowly, so that energy can be supplied to an application at either low power or high power. In addition, because stretching chemical bonds by deforming a macroscale spring is inherently a more controllable and reversible process than most
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chemical reactions, which break and reform bonds, an energy storage medium based on CNT springs offers the potential for a much greater number of charge-discharge cycles, less self-discharge, less sensitivity to temperature and other environmental conditions, and perhaps even safer operation than electrochemical batteries. Self-discharge of batteries, due to electrochemical reactions taking place inside the battery even when not in use, can result in discharge rates as high as 20% per month. Since elastic energy storage relies on stretching bonds rather than on chemical reactions, CNT springs are expected to have little or no self-discharge in the absence of creep and as long as energy storage is elastic. Self-discharge of batteries is particularly detrimental in battery-powered devices that are used infrequently or only in emergency situations; CNT springs may be a better suited power supply for these applications.

With less sensitivity to temperature, CNT springs would be well suited to provide power to devices that operate in extreme temperatures, either in cold or hot conditions that are ill-suited for battery operation. Electrochemical batteries must operate within a specific temperature range for acceptable performance. The typical operating range of lithium-ion batteries is -20°C to 60°C [8], with limited performance at cold temperatures and rapid discharge at high temperatures. CNT springs can have a much wider range of operating temperatures, with structural stability observed in CNTs up to 2000°C [104], so that springs could function as power supplies at temperatures at which batteries cease to be operational. For example, CNT springs could be used as power supplies for sensors for high temperature drilling applications.

CNT springs are particularly well suited for applications in which energy can be both input to the spring and output from the spring mechanically. Energy losses can be substantial when energy is converted back and forth from the electrical domain to the mechanical domain. An example of a useful application for CNT springs is regenerative braking for bicycles and vehicles. During braking, energy from wheels could be used to charge up a spring; during acceleration, that energy is transmitted back to the wheels. If the energy stays in the mechanical domain without being converted to electricity to charge capacitors or batteries, the efficiency of the regenerating breaking system can be high. Using springs to absorb energy during braking may be particularly useful for applications such as heavy machinery, since in this type of equipment energy during braking of different moving parts can be released too quickly to be absorbed by batteries without damaging the batteries. Springs can absorb a lot of energy very quickly and can then transmit that energy to a battery, so springs coupled to batteries could be implemented for regenerative breaking systems instead of more expensive and complex capacitor systems coupled to batteries. Mechanical watches already run on mechanical springs made of steel. The energy density in CNTs is predicted to be several orders of magnitude greater than the energy density of steel springs, so high performance watches could be built that run on CNTs that don’t need rewinding for weeks or months at a time.

2.7. Background on fibers and yarn

Before studying the mechanical properties of macroscopic CNT assemblies such as fibers and yarn, it is useful to review the textile industry literature on the mechanical behavior of yarn. While the textile industry primarily concerns itself with conventional textile materials such as rayon, wool, nylon and cotton, the general structure of traditional textile yarn and CNT yarn are
similar. An excellent reference is “Structural Mechanics of Fibers, Yarns and Fabrics” by Hearle et al. [69], which provides a concise summary of theoretical and experimental research conducted on yarn and fibers from the 1900s until the 1960s.

A filament refers to a single strand of a textile material, and yarn is an assembly of these individual filaments. A continuous filament yarn is defined as an assembly of filaments that span the total yarn length, in which the filaments are either parallel and aligned along the yarn axis, or twisted to assume helical paths around the yarn axis. Spun yarn, also known as staple yarn, is made of filaments that are shorter than the total yarn length, so that spun yarn contains discontinuities at the filament ends [69]. Twisting is necessary in spun yarn to provide structural cohesion to hold the filaments together, but twisting is not necessary in continuous filament yarn. More complex textile structures can be created as well: multifilament yarn is made by twisting together two or more strands of yarn, cabled yarn is made by twisting together multifilament yarn, and fabric is created by weaving together yarn, multifilament yarn or cabled yarn into a two-dimensional material [69]. Continuous filament yarn and spun yarn will be discussed in more detail in the sections that follow.

In the remainder of this thesis, somewhat different terminology will be employed than what is used by Hearle et al. Assemblies of CNTs in which the CNTs span the length of the assembly will be referred to as ‘fibers’. Hearle et al. refer to such assemblies as continuous filament yarn. CNTs spun into yarn, which contain CNTs much shorter than the total yarn length and discontinuities at CNT ends, will be simply referred to as ‘yarn’, rather than spun yarn, the term employed by Hearle et al.

### 2.7.1. Continuous filament yarn

It is useful to begin by studying continuous-filament yarn since this material does not contain discontinuities at filament ends that are found in spun yarn. Consider an ideal continuous filament yarn made of straight filaments aligned parallel to the yarn axis. All filaments within the yarn are assumed to have identical properties. When the yarn is loaded in tension, all filaments are assumed to load uniformly and linear elastically. The stress in the yarn is

\[
\sigma = E_f \varepsilon_y
\]

where \(E_f\) is the Young’s modulus of a filament and \(\varepsilon_y\) is the yarn strain. In such an ideal yarn, the stress and strain are uniform in each filament throughout the yarn, and the overall yarn stress and strain are equal to the stress and strain in each filament.

Applying twists to continuous filament yarn changes its behavior. Consider a continuous filament yarn in which each filament lies on a perfect helix with constant radius, such that each filament has the same number of turns per unit length along the axis of the yarn and the angle between the filament and the yarn axis \(\theta\) is 0 at the center and increases to \(\alpha\) at the outer surface, as shown in Figure 2-13. It is assumed that all filaments load linear elastically and have identical properties. The length of each filament will be a function of its radial position in the yarn. For a yarn of length \(h\), outer radius \(R\), and outer twist angle \(\alpha\), the length \(l\) of a filament at a radial position \(r\) is given by [69]

\[
l = \sqrt{h^2 + 4\pi^2 r^2}.
\]
When the yarn is extended to a yarn strain $\varepsilon_y$, strain in the filaments $\varepsilon_f$ varies with radius, with maximum strain at the center ($r=0, \theta=0$) and minimum strain at the surface ($r=R, \theta=\alpha$), according to

$$\varepsilon_f(\theta) = \varepsilon_y \cos^2 \theta$$

(2-31)

where

$$\cos^2 \theta = \frac{h^2}{h^2 + 4\pi r^2}$$

(2-32)

and

$$h = \frac{2\pi R}{\tan \alpha}.$$

(2-33)

Rearranging terms, filament strain is rewritten as

$$\varepsilon_f(r/R) = \varepsilon_y \frac{1}{1 + \left(\frac{r}{R}\right)^2 \tan^2 \alpha}$$

(2-34)

Relative filament strain $\varepsilon_f/\varepsilon_y$ is plotted as a function of relative radial position $r/R$ for different values of outer twist angle $\alpha$ in Figure 2-14a, showing that strain decreases radially outward faster as the twist angle increases. Using this model, filaments are assumed to experience stress only in the axial direction, and the magnitude varies as a function of radial position, according to

$$\sigma_f(\theta) = E_f \varepsilon_f(\theta) = E_f \varepsilon_y \cos^2 \theta.$$  

(2-35)

Neglecting transverse forces and lateral contraction, the mean stress in a continuous filament yarn is given by [69]

$$\bar{\sigma}(\alpha) = \frac{\int_{r=0}^{R} \sigma_f(\theta) \cos^2 \theta \cdot 2\pi r dr}{\int_{r=0}^{R} 2\pi r dr} = \frac{\int_{r=0}^{R} E_f \varepsilon_y \left(\frac{h^2}{h^2 + 4\pi r^2}\right)^2 \cdot 2\pi r dr}{\int_{r=0}^{R} 2\pi r dr}$$

(2-36)

$$\bar{\sigma}(\alpha) = E_f \varepsilon_y \cos^2 \alpha$$

From the expression for mean stress, the overall Young’s modulus of the yarn is

$$E_y(\alpha) = E_f \cos^2 \alpha.$$  

(2-37)
This result indicates that the Young’s modulus of the yarn decreases with twist angle: highest Young’s modulus is achieved with no twist, when \( \alpha = 0 \).

Fracture will begin in the center filaments where there is no twist, filaments are shortest, and strain is highest. Once the central filaments break, the load carried by the remaining outer filaments increases and failure propagates radially outward until the entire yarn fails [69]. If yarn strength is considered to be the force applied to a yarn per unit area at which the central filaments break, then yarn strength is given by

\[
\sigma_{\text{break}}(\alpha) = E_f \varepsilon_{f,\text{break}} \cos^2 \alpha
\]

where \( \varepsilon_{f,\text{break}} \) is the breaking strain of a single filament when it is loaded axially. Yarn strength is \( E_f \varepsilon_{f,\text{break}} \) when the twist angle is \( \alpha = 0 \), and strength is highest when there is no yarn twist. Relative yarn strength \( \sigma_{\text{break}} / E_f \varepsilon_{f,\text{break}} \) is plotted as a function of outer twist angle \( \alpha \) in Figure 2-15a, showing that strength decreases with twist angle due to the effects of obliquity.

When a twisted continuous filament yarn is stretched in tension, a pressure arises between the filaments because they try to straighten. The simple model described above does not account for the pressure between filaments when strain is applied to twisted yarn. When transverse forces and lateral filament contraction are taken into consideration within an ideal, twisted continuous filament yarn, the strain in a filament varies according to [69]

\[
\varepsilon_f(\theta) = \varepsilon_y \left( \cos^2 \theta - v_y \sin^2 \theta \right)
\]

or

\[
\varepsilon_f(r/R) = \varepsilon_y \left[ \frac{(1 + v_y)}{1 + \left( \frac{L}{R} \right)^2 \tan^2 \alpha} - v_y \right]
\]

where \( v_y \) is lateral contraction ratio of the yarn, given by

\[
v_y = -\frac{\text{yarn radial strain}}{\text{yarn extensional strain}} = -\frac{\delta R/R}{\Delta h/h}
\]

Relative filament strain \( \varepsilon_f / \varepsilon_y \) is plotted as a function of relative radial position \( r/R \) for different values of outer twist angle \( \alpha \) in Figure 2-14b, for the case of \( v_y = 0.5 \), showing that strain decreases radially outward as the twist angle increases.

The stress in each filament as a function of radial position is written as [69]

\[
\sigma_f(\theta) = E_f \varepsilon_y \left[ \frac{3}{4} \left( \cos^2 \theta + \cos^2 \alpha \right) - \frac{1}{2} \left( 1 + \ln \left( \frac{\cos \alpha}{\cos \theta} \right) \right) \right]
\]

The mean stress in the yarn becomes [69]

\[
\bar{\sigma} = \frac{2E_f \varepsilon_y \cos \alpha}{(1 + 2v_f)(1 - \cos^2 \alpha)} \left\{ (1 + v_y) \left[ \ln(\cos \alpha) + \frac{2(1 + v_f)}{1 + 2v_f} (1 - \cos \alpha^{2v_f+1}) \right] - \frac{v_y}{2} \frac{3(1 + 2v_f)}{2v_f - 1} \right\} 4(1 + v_f)2v_f - 1 - \cos 2\alpha
\]

where \( v_f \) is the Poisson’s ratio of filaments. From the expression for mean stress, the overall Young’s modulus of the yarn is

\[
E_y = \frac{2E_f \varepsilon_y \cos \alpha}{(1 + 2v_f)(1 - \cos^2 \alpha)} \left\{ (1 + v_y) \left[ \ln(\cos \alpha) + \frac{2(1 + v_f)}{1 + 2v_f} (1 - \cos \alpha^{2v_f+1}) \right] - \frac{v_y}{2} \frac{3(1 + 2v_f)}{2v_f - 1} \right\} 4(1 + v_f)2v_f - 1 - \cos 2\alpha
\]
\[
\sigma_{\text{break}}(\alpha) = \frac{2E_{\text{f, break}}\cos\alpha}{(1+2\nu_f)(1-\cos^2\alpha)} \left\{ \ln(\cos\alpha) + \frac{2(1+\nu_f)}{1+2\nu_f} (1 - \cos^2\alpha) \right\} - \frac{\nu_y}{2(1+2\nu_f)(1-\cos^2\alpha)^2(1+2\nu_f)(1-\cos^2\alpha)^2(1-4\cos^2\alpha)} - 4(1+\nu_f)\cos^2\alpha - 1\cos 2\alpha. \tag{2-45}
\]

Relative yarn strength \(\sigma_{\text{break}}/E_{\text{f, break}}\) is plotted as a function of outer twist angle \(\alpha\) in Figure 2-15b, showing that strength decreases with twist angle due to the effects of obliquity. A comparison of the plots in Figure 2-15a and Figure 2-15b shows that accounting for radial pressure lowers the predicted yarn strength. Note that the two models that have been described in this section assume that all yarn deformation is linear and elastic. In reality, filament behavior becomes non-linear at high strains and near failure, so the exact strength at failure is more difficult to predict. In addition, filaments have varying strength and stiffness, and real yarn does not have ideal structure. Consequently, the plots in Figure 2-15 should be used as a guide to study trends, rather than to determine exact values.

![Figure 2-14: Relative filament strain \(\varepsilon_f/\varepsilon_y\) as a function of relative radial position \(r/R\) in a continuous filament yarn for different yarn twist angles, considering (a) only axial deformation and (b) axial and lateral filament deformation.](image-url)

50
Chapter 2. Carbon nanotubes: a material for energy storage

Figure 2-15: Relative yarn strength $\sigma_{\text{break}}/E_f \varepsilon_{f,\text{break}}$ as a function of twist angle $\alpha$, considering (a) only axial deformation and (b) axial and lateral filament deformation.

The ideal helix model for yarn does not account for the possibility that filaments may migrate, or change their radial position, inside of a continuous filament yarn. A yarn with ideal migration is made up of filaments that follow a helical path with a varying radius so that each filament has the same overall length [105]. If frictional forces are high, then stress and strain will vary along the length of a filament as its radial position changes. If frictional forces are low, then the stress and strain will equalize to a constant value along the entire length of each filament. In the case of low friction so that equalization occurs, the strain in all filaments in a yarn with outer twist angle of $\alpha$ is given by [105]

$$\varepsilon_f = \varepsilon_y [(1 + u_y) \cos \alpha - u_y]. \tag{2-46}$$

Kilby has shown that in continuous filament yarn with migration, strength and stiffness decrease with increasing twist angle, both in the case of high and low friction [105]. Relative strength $\sigma_{\text{break}}(\alpha)/\sigma_{\text{break}}(\alpha = 0)$ is plotted in Figure 2-16, showing the drop in strength as twist is increased in a continuous filament yarn containing migration.
While twisting does not offer a continuous filament yarn with ideal helical structure advantages in terms of mechanical properties, twisting can provide other advantages. Treloar [106] states that “in continuous-filament yarns, twist is not necessary for the attainment of tensile strength (in fact, it reduces it), but it is necessary for the achievement of satisfactory resistance to abrasion, fatigue, or other types of damage associated with stresses other than a simple tensile stress, and typified by the breakage of individual filaments, leading ultimately to total breakdown of the structure.”

Twisting of filaments in continuous filament yarn can be advantageous because it can compensate for weak filaments [69]. Real yarn contains filaments with non-uniform strength and stiffness. In a yarn with low twist, radial pressure is small, filaments behave independently and fracture occurs in each filament when it reaches its fracture strain. Once the weakest filaments fracture, the stress in the remaining filaments increases and fracture propagates throughout the remaining filaments. In a twisted yarn, once a weak filament fractures, the friction between neighboring filaments due to radial pressure can enable the filament to continue carrying a load away from the fracture point. In this way, fracture of weak filaments can be accommodated and does not immediately initiate overall fracture in yarn, so that variation of filament properties has a greater effect in yarn made of parallel filaments than in yarn containing twists. Twisting can strengthen a yarn, although the yarn will have a lower strength to start with because of the twist angle.

Yarn strength is determined by the weakest filaments that make up the yarn, while modulus is the result of the average modulus of the filaments over the yarn length. As a result, radial pressure can increase yarn strength but it has little effect on modulus.

In practice, many different manufacturing techniques are employed to produce twisted yarn, and yarn structure can vary significantly from the ideal models. Studies have shown that the twisting technique, amount of migration, and the magnitude of the tension applied to the yarn during twisting all affect the overall properties of the yarn.
Twisting can provide one final advantage in continuous filament yarn. The models described in this section assume that all filaments in a yarn are loaded equally, both in the twisted and untwisted configurations, which may not be always true in practice. In an idealized continuous filament yarn, loading would be evenly applied to all filaments of the yarn, and twisting would not be needed because there would be nothing to gain from the frictional forces induced by radial pressure. In practice, particularly when the diameter of the filaments is small compared to the diameter of the yarn, such as in the case of yarn made of parallel CNTs, it is difficult to guarantee uniform tensile loading throughout all of the filaments. For testing real continuous filament yarn, it is possible that the radial pressure induced by twisting may help to increase load bearing participation among all filaments. This idea will be discussed in Chapter 3 in more detail.

2.7.2. Spun yarn

Spun yarn, or staple yarn, differs from continuous filament yarn because spun yarn contains discontinuities at filament ends. Continuous filament yarn fails in fracture, while spun yarn can fail by fracture, slip, or a combination of both. In continuous filament yarn, twisting and migration are optional, depending on the application, but not necessary for the yarn to carry a load. In spun yarn, twisting and migration are essential since these are the mechanisms by which filaments in the yarn are held together in order to transmit a load along the yarn length. According to Treloar [106], the cohesion of a spun yarn is “dependent on the frictional forces brought into play by the lateral pressures between filaments arising from the application of a tensile stress along the yarn axis.” Inside yarn loaded axially in tension, there is a buildup of lateral pressure that is zero at the outer surface and increases quadratically towards the center of the yarn [69]. The pressure at the center of a yarn has been shown to vary linearly with the applied tension on the yarn and as the square of the twist in the yarn. Pressure is important for transferring stress between filaments using friction. When a load is applied to yarn, the load is directly applied only to the filaments close to the ends, and that load must be transferred to all other filaments in the yarn through friction. Without lateral pressure, the filaments in yarn can slip past each other when an axial load is applied. If the friction between filaments as a result of pressure is high, then filaments can fracture before they slip, which creates a high strength yarn.

Migration in spun yarn is important because it ensures that a single filament changes its radial position along its length [69]. In spun yarn, load is transferred through friction due to lateral pressure, and lateral pressure is highest at the center of the yarn and smallest near the outer surface of the yarn. With no migration, filaments at the outer edge would be under no pressure and so they would not carry any load. In turn, these outer filaments would apply no pressure to the filaments in the inner layer adjacent to them, and in this manner there would be no build-up of pressure inside the yarn at all. Migration provides cohesion, ensuring that both filaments on the outer edge and in the center are well-gripped, to create a self-locking structure. In addition, migration helps to create even strain throughout the yarn. Without migration, the filaments at the center would be aligned along the filament axis and the angle of twist in the filaments would increase with the radius, and so that fracture would occur first at the center of the yarn where strain would be highest. Migration ensures that on average the path lengths are
the same for all filaments. The rate of migration is also important. A faster rate of migration ensures that all filaments are gripped in at least one region by the central portion of the yarn where pressure is highest, and reduces the chance of certain filaments having long segments near the surface where they are poorly gripped and carry less load.

In yarn, the strength and failure strain of the constituent filaments varies; the variation is often modeled as a normal distribution [69]. In a yarn with sufficient pressure, filaments can break before they slip. Once a filament with a low failure strain fractures, the force carried at the broken ends of the filament goes to zero. Friction from neighboring filaments can transfer load to the two filament segments until the load that they carry is equal to that of the surrounding filaments. In this way, a filament can continue to contribute to bearing a load even after it has broken one or more times. As such, failure of a single filament does not lead to failure of the entire yarn. As the load in the yarn increases, filaments continue to break and inter-filament pressure drops until the residual filament lengths reach a critical minimum, increased slip occurs and the yarn fails. The critical filament length at which slip occurs depends on the strength of the individual filaments, on the lateral pressure and on the coefficient of friction [69].

Tension varies along the length of a filament in spun yarn [69]. At the ends of a filament, there is no tension in the filament since there are no axial forces pulling on the filament ends. As a result of lateral forces and friction, there is a gradual buildup of the tension in the filament away from the ends until the tension reaches the level of tension in a continuous filament yarn (this value fluctuates due to the change in radial position of a migrating filament). The main losses in the load bearing contribution of a filament occur at the filament ends. Tension in the filaments also changes as the yarn’s angle of twist changes [69]. As twist increases, the lateral forces in the yarn increase, there is a faster buildup of tension in the filaments, and the regions near the filament ends that contribute little to load-bearing shorten. However, the maximum load carried by all filaments decreases due to the effects of obliquity. For a yarn to be ‘self-locking’ (no slip occurs), the filaments must be sufficiently long that the tension in the filaments reaches the tension of an equivalent continuous filament with comparable twist. Below that length, slip occurs. Therefore, strength of a spun yarn increases with longer filament length.

The strength of a yarn varies with the twist angle: yarn strength start at zero with no twist, increases to a maximum as twist is applied to the yarn, and then drops after a critical twist angle has been reached [69]. At low twists angles, there is little pressure between filaments, frictional effects are minimal, and filaments slip relative to each other, so yarn strength is low. As more twist is applied, there is a buildup of lateral pressure, resistance to slip increases, filaments begin to fracture rather than slip, and yarn strength increases. Beyond a critical twist angle, the effect of filament obliquity becomes dominant, and strength decreases. The same obliquity effect was seen in continuous filament yarns, even in the presence of migration, where strength decreased with the twist angle. The strength of spun yarn is always less than the strength of untwisted continuous filament yarn. However, at sufficiently high twist angles, the strength of both materials with the same twist angle reach about the same value once slip in spun yarn becomes a minor effect and obliquity becomes dominant. The strength of spun yarn increases with higher friction between filaments and longer filament lengths. With an optimal twist angle, high friction between filaments and long filament lengths, the mechanical behavior of spun yarn can approach the mechanical behavior of continuous filament yarn.

Hearle et al. discuss the effect of filament size in spun yarn [69]. They report that the tensile forces that cause slip are proportional to the filament cross sectional area, or \( \pi r^2 \), where \( r \) is the
filament radius. The frictional forces that cause a filament to resist friction are proportional to filament surface area, which is proportional to $2\pi r$. The ratio of forces that resist friction to forces that cause friction is on the order of $1/r$; this ratio should be large for a high performance yarn. Therefore, scaling arguments suggest that a filament is better able to overcome the tendency to slip with a smaller radius. As a result, superior yarn should be produced with finer filaments. This is a strong argument in favor of making spun yarn with CNTs.

Yarn count, or the number of filaments within a yarn cross-section, will also affect strength. For commercial textile yarn, the minimum number of filaments used varies from 20 to 100 to provide adequate load bearing capacity [69]. Scaling arguments can be applied to examine how the number of filaments in yarn can affect the yarn properties. The pressure within yarn that increases resistance to slip is highest at the center and lowest at the outer surface. It is thus advantageous to maximize the number of filaments in the middle of the yarn and minimize the number of filaments at the surface. Yarn cross-sectional area increases as $R^2$, while yarn surface area increases as $R$, where $R$ is the yarn radius. A large yarn radius, or high yarn count, keeps the ratio of cross-sectional area to surface area high, which leads to higher strength. Therefore, a larger number of filaments can lead to higher strength. Finally, packing density also affects yarn strength, with highest strength obtained with higher packing densities because more contact between filaments leads to more friction, higher pressure build-up, and a greater resistance to slip. One can apply these results to yarn made of CNTs, and conclude that barring other effects, higher strength will be observed in CNT yarn with larger cross-sectional areas and higher packing densities.

### 2.8. Ideal fiber and yarn models

Based on the theory and experimental work described in this chapter, models for ideal fibers (or continuous filament yarn) and spun yarn can be developed. The models illustrate the structure of CNTs within ideal macroscopic CNT groupings. Such groupings would be expected to have mechanical properties that closely match the mechanical properties of individual CNTs, and would be ideal materials from which to construct macroscopic CNT springs. Practical implementations of macroscopic CNT assemblies should aim to attain these types of ideal structures.

Models of an ideal fiber and an ideal yarn are shown in Figure 2-17. In fibers, the CNTs span the length of the fiber, while spun yarn contains discontinuities at the CNT ends. In both fibers and yarn, all CNTs should be straight, defect-free, and aligned with their axes along the direction of loading. To achieve the highest energy density for springs, the fibers and yarn should be made of SWCNTs and be loaded in tension. CNTs should be arranged in a perfect crystalline hexagonal lattice with 0.34 nm spacing between each CNT [44], so that the groupings have maximum packing density. Close packing of CNTs should help to increase van der Waals interactions between neighboring CNTs and maximize load transfer between CNTs. Strong inter-CNT interactions are particularly important in yarn because the CNTs are discontinuous and load must be transferred between CNTs by van der Waals forces. Research by Yakobson et al. and Qian et al. predicts that the overlaps between CNTs in yarn should be at least 10 μm to 120 μm long in order for the grouping to approach the full strength of an individual CNT [44, 47]. To
date, macroscopic groupings of CNTs in both fibers and yarn show short-range crystallinity within bundles, but they typically lack long-range crystallinity throughout the grouping.

Figure 2-17: (a) Model of an ideal CNT fiber, showing long, parallel, aligned CNTs; (b) model of an ideal spun yarn, showing discontinuities at the CNT ends within the yarn; (c) cross-section of both ideal fibers and yarn, showing CNTs arranged in an ideal crystalline lattice.
3. Carbon nanotube fibers

3.1. Introduction

A potential source of CNTs for springs is CNTs grown in forests using chemical vapor deposition. The CNTs in forests are well-aligned, densely packed, of high purity, and can be several millimeters long. Springs made of grouping of these CNTs could be used to store and release mechanical energy to power micro-scale or milli-scale systems. Before the CNTs can be incorporated as mechanical energy storage elements into real systems, a comprehensive study of the composition, structure and mechanical properties of the CNT groupings is needed. This chapter provides an overview of mechanical tests performed on CNTs grown in forests to assess the performance of the CNTs as mechanical springs. The CNTs are studied in small groupings of different sizes, with each grouping containing between hundreds of thousands of CNTs up to tens of millions of CNTs. In this work, these groupings of CNTs are called ‘fibers’. Each fiber is made up of CNTs that are parallel and aligned along the fiber axis. The length of the fibers is the same as the height of the forest in which the CNTs were grown, and each CNT spans the fiber length, with some exceptions due to defects that can cause CNT growth to terminate early. The fibers have high aspect ratios, since their length is much greater than the dimensions of their cross-sections. As such, the energy that can be stored in compression is limited by buckling, so the mechanical properties and behavior of the fibers as springs are studied in tension.

In work by Hearle et al. [69], such fibers are called ‘continuous filament yams’, yams in which each constituent filament (here, CNTs) spans the yam length. The main advantage of studying these types of fibers is that the CNTs are continuous along the fiber length. When the two ends of a fiber are gripped and the fiber is stretched in tension, in the ideal case all CNTs are gripped and loaded directly, and the strength and stiffness of the fiber should be a close match to the strength and stiffness of the constituent CNTs. Indeed, the properties of fibers can more closely match the properties of the individual CNTs than more commonly studied spun yarn which relies on overlaps between CNTs to transfer load along the yarn length. Strength and stiffness in spun yarn can both be limited by the occurrence of slip, while slip has less of an effect on the properties of the fibers described in this chapter. The primary failure mechanism for the fibers is fracture of their constituent CNTs, while spun yarn can fail by a combination of slip and fracture, which affords fibers an inherently higher strength and stiffness.

In reality, the CNTs grown in forests are imperfect; they contain defects which result in disorder, tortuosity and tangling of the CNTs. At larger scales, the packing density, defect density, tangling and alignment of CNTs throughout a forest are spatially non-uniform, both across the area of a forest and through its height, due to non-uniformities in the growth process. In turn, the fibers are also spatially non-uniform in their composition and are made of CNTs containing many defects. As such, the mechanical properties of groupings of these CNTs into fibers are expected to fall short of ideal CNT properties. Nonetheless, mechanical tests can provide valuable insights into the effects of defects and disorder on the properties of the fibers. One of the goals of this work is to understand the mechanisms that limit the mechanical performance of large CNT assemblies, in order to be able to construct higher performance CNT assemblies.
Chapter 3. Carbon nanotube fibers

This chapter presents the results of tension tests to failure and tensile cyclic loading tests performed on fibers prepared from CNT forests. The CNTs within the fibers are densified using a variety of techniques to study the effects of ordering and packing density on fiber properties. Loading and fracture mechanisms are examined using video imaging and a SEM displacement stage. Fiber strength is studied using Weibull statistics to understand size effects and the stochastic nature of fiber strength. Electrical resistance is measured across fibers during mechanical testing to gain further insight into structural changes taking place during loading, and Raman spectroscopy is performed during mechanical testing to study changes in the fibers at the atomic scale. Studies of the elasticity, energy storage and long term cyclic loading behavior of the fibers are conducted to evaluate the performance of the fibers as mechanical springs.

3.2. Carbon nanotube forests

Experiments were conducted on CNTs from two different types of forests. The first set of forests are 3 mm tall and were grown by atmospheric pressure thermal chemical vapor deposition in an ethylene/hydrogen environment at temperatures of 750-800°C, as described in [107-109]. The growth substrate was a supported catalyst layer of 1/10 nm Fe/Al2O3 deposited by electron beam evaporation on (100) Si wafers coated with 500 nm thermal SiO2. Using this same process, arrays of 1.2 mm tall pillars with 200 μm × 200 μm cross-sections were also grown using lithographically patterned catalyst film. The pillars and forests are made of MWCNTs with an average of 4-5 walls and mean outer diameters of 10 nm. The areal density of the forests is 2-2.5 \times 10^{14} \text{MWCNTs/m}^2, corresponding to a mass density of 17.6-22.1 kg/m^3. Scanning electron microscope (SEM) images of the forests and pillars are shown in Figure 3-1 and Figure 3-2. Spatial non-uniformities in the forests due to the growth process are apparent in the images. Figure 3-3 presents a schematic diagram illustrating the packing density of CNTs in a forest with a density of 2×10^{14} \text{MWCNTs/m}^2. Transmission electron microscope (TEM) images of the CNTs in the forest are shown in Figure 3-4; specimens for TEM imaging were prepared by dispersing CNTs in ethanol and placing a drop of the mixture on a TEM grid. The TEM images show that the CNTs are not straight along their length due to atomic defects. Elemental analysis of the forests using Energy Dispersive Spectrometry (EDS) revealed the composition of the forests to be 90.7% carbon, 4.2% oxygen, 2.0% aluminum, 1.8% silicon and 0.09% iron by mass. The EDS spectrum is shown in Figure 3-5.

The second set of forests are 6 mm tall CNT forests grown by modifying the growth process for the 3 mm tall forests by adding a small amount of ethanol to the ethylene/hydrogen environment during the growth process [110]. The addition of ethanol had the effect of reducing the number of walls and the outer diameter of the MWCNTs, increasing the growth rate of the CNTs, prolonging the catalyst life, and increasing the overall height of the forests. This process produced MWCNTs with 3 shells and 6 nm mean outer diameters. The areal density of the forests is 2.1×10^{14} \text{MWCNTs/m}^2, corresponding to a mass density of 7.5 kg/m^3. In both types of forests, CNTs are expected to the span the height of the forest, with some exceptions due to defects that can cause CNT growth to terminate early; the percentage of CNTs that do not span the height of the forest has not been characterized. The properties of the 3 mm tall and 6 mm tall forests are summarized in Table 3-1.
Table 3-1: Properties of 3 mm and 6 mm tall CNT forests

<table>
<thead>
<tr>
<th></th>
<th>3 mm tall CNT forests</th>
<th>6 mm tall CNT forests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer diameter</td>
<td>10 nm</td>
<td>6 nm</td>
</tr>
<tr>
<td>Number of shells</td>
<td>4-5 shells</td>
<td>3 shells</td>
</tr>
<tr>
<td>Mass density</td>
<td>17.6 - 22.1 kg/m³</td>
<td>7.5 kg/m³</td>
</tr>
<tr>
<td>Areal density</td>
<td>2 - 2.5 × 10¹⁴ CNTs/m²</td>
<td>2.1 × 10¹⁴ CNTs/m²</td>
</tr>
<tr>
<td>Forest shell area fraction</td>
<td>0.79 - 0.99% of area</td>
<td>0.336% of area</td>
</tr>
</tbody>
</table>

Figure 3-1: SEM images of two 3 mm tall forests.
Chapter 3. Carbon nanotube fibers

Figure 3-2: SEM images of arrays of 200 µm × 200 µm CNT pillars.

Figure 3-3: Schematic diagram illustrating the packing density of CNTs in a forest with a density of $2 \times 10^{14}$ CNTs/m$^2$.

Figure 3-4: TEM images of CNTs grown in forests.
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Figure 3-5: EDS spectrum of the surface of a CNT forest.

3.3. Experimental setup

3.3.1. Fiber preparation

Each fiber was created by removing a small strand of CNTs from the side of a forest, as shown schematically in Figure 3-6. The length of each fiber is the same as the height of the forest, either 3 mm long or 6 mm long. Using this technique, fibers can be prepared with a range of cross-sectional areas. The cross-sectional area of each fiber was measured using an optical microscope. The starting density of each fiber is 17.6-22.1 kg/m³ for fibers prepared from 3 mm tall forests, and 7.5 kg/m³ for fibers prepared from 6 mm tall forests. The mass of each fiber was less than 1 μg. The CNTs in the fibers are aligned along the fiber axis and span the entire fiber length, with some exceptions due to defects.

Figure 3-6: Schematic diagram showing the preparation of a fiber from a forest

3.3.2. Grips for tension tests

Grips were needed to perform mechanical tests on the fibers. Different options considered for gripping the fibers were clamping grips, capstan grips and epoxy grips. The length of the fibers of 3-6 mm made capstan grips impractical. There was a concern that clamping grips could
damage the fibers. Additionally, clamping grips come in direct contact only with the CNTs around the perimeter of a fiber, so the degree of loading of CNTs throughout the cross-section of a fiber would be unknown. The grips that were chosen for implementation were epoxy grips. Epoxy grips can be used to grip the ends of fibers that are only a few millimeters long. Fibers were mounted on thick paper frames using a non-conductive epoxy (Pacer Z-Poxy) for tensile testing (Figure 3-7a). Additional samples were prepared by mounting fibers onto frames coated with copper using a silver-based conductive epoxy (MG Chemicals 8331-14G). Thin copper wires were soldered onto the copper surface to enable resistance measurements across the fibers during tension tests (Figure 3-7b). A CNT pillar mounted on a frame using non-conductive epoxy grips is shown in Figure 3-8.

An important advantage of using epoxy grips is that the epoxy infiltrates the cross-section of the fibers, which ensures that all CNTs throughout a fiber’s cross-section are gripped directly. To examine epoxy infiltration in the fibers at the grips, the non-conductive and conductive epoxy grips were cross-sectioned using a thin, sharp blade. The blade caused the epoxy to cleave apart easily. SEM images of the cross-sections of undensified fibers, fibers densified using capillary effects, and mechanically densified fibers in conductive epoxy grips are shown in Figure 3-9 to Figure 3-11. Optical microscope images of fiber cross-sections in non-conductive grips are shown in Figure 3-12 to Figure 3-14. The pictures clearly indicate that both conductive and non-conductive epoxy infiltrate the cross-sections of the fibers. The silver particles in the epoxy remain outside of the fibers because they are too large to fit between the CNTs. The originally round or square cross-sections of the fibers became much more complex shapes as they were infiltrated by the liquid epoxy. Wetting by the epoxy occurred from the outside of the fibers towards the inside, and air pockets formed at the center of the fibers as the low density CNTs in the fibers were zipped together toward the outside of the fiber by capillary effects. Infiltration of the epoxy through the fiber cross-section ensured that all CNTs were gripped at their ends and that load was applied to CNTs across the entire cross-section of a fiber. Epoxy infiltration also ensured that no ‘pullout’ of CNTs from the grips could occur during loading.

It was important to choose an epoxy that penetrated the fiber at the grips but did not wet the fiber along its length. Many epoxies with a variety of viscosities and cure times were tested prior to choosing one that performed as desired.

A particular concern with epoxy grips was that compliance at the grips would introduce error in the strain data provided by the Nano UTM. A study of compliance in the grips was performed by imaging the fibers during tension testing; the procedure and the results are described in detail in section 3.6.3. The results showed that the forces in the fibers during tension tests were sufficiently small that no compliance in the epoxy grips could be detected in the strain data.
Figure 3-7: Schematic diagrams of fibers mounted on frames: (a) a fiber mounted on a non-conductive frame for tension testing; (b) a fiber mounted on a conductive frame using conductive epoxy to enable resistance measurements during tension tests.

Figure 3-8: Optical microscope image of a pillar densified by capillary effects mounted on a frame using non-conductive epoxy.
Figure 3-9: Cross-sections of undensified fibers in conductive epoxy grips.
Figure 3-10: Cross-sections of fibers densified using capillary effects with toluene in conductive epoxy grips.

Figure 3-11: Cross-section of a fiber densified mechanically in a conductive epoxy grip.
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Figure 3-12: Cross-sections of undensified fibers in non-conductive epoxy grips, imaged using an optical microscope.

Figure 3-13: Cross-sections of fibers densified using capillary effects with toluene in non-conductive epoxy grips, imaged using an optical microscope.

Figure 3-14: Cross-sections of fibers densified mechanically in non-conductive epoxy grips, imaged using an optical microscope.
3.3.3. Tension tests

Tension tests were conducted using a MTS Nano UTM Testing System with a 0.5 N load cell (Figure 3-15). Access to the Nano UTM was provided by the MIT Institute for Soldier Nanotechnologies. The Nano UTM provided load and strain data. The strain data was analyzed for error both due to the instrument and due to epoxy compliance in section 3.6.3; results showed very little error in the strain data due to either source. Strain gauges were not used to measure strain in the fibers since the fibers are too small and delicate.

![Figure 3-15: Fiber sample mounted in the MTS Nano UTM for tension testing.](image)

3.3.4. Scanning electron microscope displacement stage

To study structural changes taking place inside of CNT fibers during loading and failure, tension tests were conducted using a displacement stage that operates inside of a large chamber SEM (LEO VP 438). High magnification images and videos of the fibers were recorded during the tension tests. The stage was originally designed and built by Don Galler, and then adapted for testing CNT fibers. To prepare CNT fibers for testing, fibers were mounted onto copper frames using conductive epoxy (MG Chemicals 8331-14G). To apply a strain to the fibers, the frames were clamped onto a translation stage that had a linear position finely controlled by a motor. Images of the displacement stage with the SEM are shown in Figure 3-16. A load cell that was originally part of the stage was removed because of error and drift in the force readings, possibly a result of the vacuum in the chamber that caused the load cell to malfunction, particularly at the small loads (typically less than 100 mN) needed to load the fibers in tension. Therefore, strain in the fibers could be measured during loading, but there was no force data available.
3.4. Electrical properties

3.4.1. Fiber resistivity

Resistivity was calculated by measuring resistance across fibers from 6 mm forests mounted on copper frames using conductive epoxy. Since the epoxy fills the cross-section of the fiber at the grips, all CNTs throughout the cross-section of the fibers are expected to be in the conducting path. Resistance across the fibers was measured using two probe measurements. The measured resistance included the resistance of the fiber, the epoxy, the copper frame, the solder, the copper wires and the leads to the multimeter. It was assumed that the resistance due to all components except the fibers contributed a constant value $R_o$ to the measured resistance, so that the total resistance $R$ is described by

$$R = \rho \frac{L}{A} + R_o$$  \hspace{1cm} (3-1)

where $\rho$ is the fiber resistivity, $L$ is the fiber length, $A$ is the fiber cross-sectional area filled with CNT shells (neglecting the remaining area filled with air). A fiber resistivity of $4.93 \times 10^{-6} \ \Omega \ m$ at $20^\circ C$ was extracted from the fit to the measured data (Figure 3-17).
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3.5. Fiber densification

The starting density of the fibers is the density of the forests from which the fibers were removed. Fibers created from 3 mm tall forests have a density of 17.6-22.1 kg/m³, and fibers from 6 mm tall forests have a density of 7.5 kg/m³. These densities are low compared to the upper limiting densities of these materials of 927-1115 kg/m³ for fibers from 3 mm forests and 1096 kg/m³ for fibers from 6 mm tall forests, assuming tight packing of CNTs into hexagonal lattices. These densities are calculated by multiplying the density of graphite by the hexagonal packing factor, 0.91, and by a ‘fill factor’ which depends on the outer diameter and number of shells in the CNTs (0.54 for fibers from 6 mm tall forests, and 0.46-0.55 for fibers from the 3 mm tall forests) [6].

Fiber densification is of interest because CNT forests are low-density as-grown. Reducing the cross-sectional area of a fiber increases its potential for high volumetric energy density. Additionally, there are non-uniformities within fibers due to the growth process that can produce non-uniform loading throughout a fiber. Furthermore, SEM images reveal that CNTs are tortuous and tangled; since each CNT takes a unique path from one end of a fiber to the other, each CNT may be a different length, which can result in different amounts of load bearing in different CNTs. It is possible that densifying fibers can mitigate the effects of non-uniform loading among CNTs and increase the fraction of CNTs that are load-bearing by increasing the contact area between CNTs or increasing the bundle size, in order to increase inter-CNT load transfer.

Two main techniques were used to create dense groupings of CNTs from the starting forest material: densification by applying mechanical pressure to fibers, and capillary-driven densification. Fibers were mechanically densified by placing a fiber between two glass plates and sliding one plate over the other, perpendicular to the CNT orientation, so that the fiber adopted a tightly densified cylindrical shape. The densification factor, defined as the initial cross-sectional area divided by the final cross-sectional area, depended on the applied pressure and ranged between 3 and 83. Fibers were densified using capillary effects [111, 112] by placing a drop of a liquid, typically acetone or toluene, onto each fiber. As the liquid evaporated, the CNTs were
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drawn together. Densification using this technique produced variable densification between
different fibers as well as along the length of a single fiber; a conservative estimate for the
densification factor is 10, obtained by measuring the average cross-sectional areas of fibers
before and after densification. Fibers densified using this technique became sheet-like because of
the additional capillary effects between the fiber and the surface on which the fiber was placed
during the evaporation process. Additional fibers were prepared by combining mechanical and
capillary-driven densification, and by twisting fibers densified using a variety of techniques. The
changes in the structure and the geometry of the fibers as a result of mechanical densification and
densification with capillary effects can be seen in the SEM images in Figure 3-18. Both
densification techniques resulted in densities still below the upper limiting density of the
materials.

The CNTs on the surface of undensified fibers, fibers densified using capillary effects and
mechanically densified fibers were imaged with a SEM. These fibers were prepared from a 3 mm
tall forest. Images at 10,000x, 30,000x, 50,000x and 130,000x magnification are shown in Figure
3-19 to Figure 3-21. Images of the undensified fibers at low magnification show that there is
good general alignment of the CNTs along the fiber axis. At higher magnification, it is clear that
the CNTs are tortuous due to intrinsic defects, which leads to entanglement between adjacent
CNTs and imperfect packing and alignment. At the highest magnification, individual CNTs, with
a mean outer diameter of 10 nm, and small bundles of CNTs are identified. The images of fibers
densified using capillary effects show that the CNTs are assembled into a more densely packed,
highly disordered structure. At high magnifications, the direction of the fiber axis is hard to
identify from the direction of the constituent CNTs. At the highest magnification, individual and
small bundles of CNTs are identified. Densification with capillary effects seems to have
increased the amount of inter-CNT contact, but did not significantly increase the bundle size of
the CNTs. The images of fibers densified mechanically show a high packing density, and more
order than the CNTs in undensified fibers, but less disorder than in fibers densified with
capillary effects. The direction of the fiber axis can still be identified from the CNTs at high
magnifications. The CNTs in mechanically densified fibers appear to form larger bundles, and
fewer individual CNTs can be identified in the SEM images.

The diameters of about thirty clearly identifiable features were measured in each of the three
images of CNTs at 130,000x magnification; diameter distributions are shown in Figure 3-22a.
The features correspond to individual or bundles of CNTs. Normal distribution curves fit to the
feature sizes are plotted in Figure 3-22b. The mean feature sizes are 13.4 nm, 13.1 nm, and 17.0
for undensified fibers, fibers densified using capillary effects, and mechanically densified fibers
respectively, indicating that the average size of CNT bundles increases when the fibers are
densified mechanically, but not significantly when the fibers are densified using capillary effects.
The data contains a small amount of selection bias since the features selected were the ones that
were sharpest in the images, and small additional error is present in the data due to limited image
focus.

Many other densification techniques were implemented to densify fibers: densification using
a range of liquids including toluene, benzene, acetone, ethanol, hexane and isoprene;
densification with a liquid after a fiber is mounted on a frame; densification of a fiber in the
vapor of boiling acetone, before and after fibers were mounted on frames; densification after
sonication in toluene; mechanical densification by compressing fibers into flat sheets;
mechanical densification in a liquid; and mechanical densification followed by densification with
toluene. Densification with isoprene was conducted to try to polymerize the isoprene to create
cross-links between the CNTs, but preliminary tests did not show promising results; future work should pursue this idea further. Mechanical tests were performed on fibers densified using all of these techniques, but no significant changes in fiber performance were observed. Therefore, results from these tests are omitted from this document. It would be interesting to compare the mechanical properties of fibers densified mechanically into dense cylindrical shapes and densified mechanically into flat sheets; any differences between these two sets of fibers would provide insight into the effect of geometry on fiber behavior, and this is left as future work.

Twisting is one last densification technique that was attempted and that had interesting results; a further discussion of twisted fibers is presented in 3.6.11.
Figure 3-18: Structure and geometry of fibers prepared with (a) no densification; (b) densification using capillary effects; (c) densification by applying mechanical pressure.

Figure 3-19: CNTs imaged on the surface of undensified fibers at 10,000x, 30,000x, 50,000x and 130,000x magnification.
Figure 3-20: CNTs imaged on the surface of fibers densified using a solvent (toluene) at 10,000x, 30,000x, 50,000x and 130,000x magnification.
Figure 3-21: CNTs imaged on the surface of mechanically densified fibers at 10,000x, 30,000x, 50,000x and 130,000x magnification.
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3.6. Mechanical properties

3.6.1. Tension to failure

Tension tests were conducted to evaluate the stiffness, strength, and elastic properties of the fibers. Tests were performed on fibers with varying lengths, cross-sections, and densification techniques. The tension tests were performed using a MTS Nano UTM Testing System with a load cell of 0.5 N, a load resolution of 1 μN and an applied strain rate of $2 \times 10^{-3}$ s$^{-1}$. The fibers were loaded in tension until failure, and the stress-strain curves were recorded.

In the textile industry, stress is often reported in terms of N per tex, where a tex is the linear mass density of a material in units of mg/m. These are useful units for reporting stress in CNT fibers because of the fibers' variable CNT packing densities. Stress in fibers can be reported in units of N/m$^2$ using the outer area occupied by a fiber to compare the net properties of CNT fibers to the properties of other materials, but these units make it difficult to compare the properties of fibers prepared using different densification techniques. Units of tex consider the amount of material contained in a fiber independently of its outer cross-sectional area or the CNT packing density since densifying a fiber leaves its linear mass density unchanged. In this work, stress and stiffness will frequently be reported as specific stress and specific stiffness in units of N/tex since these units are useful to compare the effects of densification on the mechanical properties of fibers.

Typical specific stress vs. strain and corresponding load vs. strain curves for undensified fibers loaded in tension to failure are plotted in Figure 3-23. Fibers labeled 1 through 4 are prepared from a 3 mm tall forest, have a density of 17.6 kg/m$^3$, and gauge lengths of 1.09 mm,
1.15 mm, 1.32 mm and 1.15 mm, respectively. Their cross-sectional areas are 1.53x10^-8 m^2 (0.27 tex), 4.16x10^-8 (0.73 tex), 3.34x10^-8 (0.59 tex) and 3.04x10^-8 (0.54 tex), respectively. The curves exhibit a non-linear relationship between stress and strain. The modulus of the fibers is initially low at low strains as the CNTs begin to bear a load; the modulus increases at intermediate strains as slack is removed and CNTs across the cross-section become load bearing; finally, the modulus decreases at higher strains as CNTs in the fiber gradually begin to fracture and the fraction of load bearing CNTs across the cross-section drops. Fracture does not occur at a uniform strain across the fiber, a phenomenon clearly observed in fibers loaded to failure using the SEM displacement stage. The load from the first CNTs that fracture transfers to the remaining intact CNTs; fracture gradually propagates to the remaining CNTs and the entire fiber breaks. Fibers with cross-sectional areas between 4x10^-9 m^2 to 1.5x10^-7 m^2 typically fracture at loads less than 200 mN.

The initial low modulus and the drop in modulus near the fracture strain observed in the stress-strain curves are attributed to non-uniformities in the fibers. There are spatial non-uniformities in the packing density, defect density, tangling and alignment of CNTs throughout a forest due to the growth process, which become spatial non-uniformities throughout fibers that can lead to uneven loading. Additionally, each CNT can have a different path length from one end of the fiber to the other due to defects, leading to a different amount of slack in each CNT. Therefore, the initial modulus of the fibers is low at small strains since not all CNTs in fibers or regions of CNTs in fibers become load bearing at once. Similarly, the modulus of the fibers is low near the fracture strain since fracture occurs at different strains within different CNTs or regions of CNTs in the fibers. Partial fracture in fibers can occasionally be directly observed in stress-strain curves in the form of sudden changes in the slope. Two such curves demonstrating early partial fracture are plotted in Figure 3-24. The occurrence of partial fracture results in high fracture strains measured in the fibers; the mean fracture strain measured in undensified fibers from 3 mm tall forests is 8.6%. That is a much higher fracture strain than would be expected in an individual CNT from these fibers, given their high defect density. Instead, the fracture strain in the fibers is the final strain at which all CNTs within the fiber have fractured. Since it is clear that CNTs are not loaded uniformly across the cross-section of a fiber, the measured strength and stiffness values for the fibers are lower bounds for the strength and stiffness of the CNTs within the fibers.

Stiffness and strength are both affected by the defects in the CNTs, which can be seen in the SEM images in Figure 3-19. The stiffness of CNTs that follow a tortuous path is much lower than the stiffness of a straight CNT, since each CNT must bend as well as stretch when it is pulled in tension, and the bending modulus of CNTs decreases with increasing defect density [113]. Strength is also affected by defects, since it is at the defects that failure is most likely to occur.

By testing many fibers in tension to failure, a relationship between strength, stiffness and linear mass density was observed. Specific strength as a function of linear mass density, specific stiffness as a function of linear mass density and specific strength as a function of specific stiffness of undensified fibers prepared from a 3 mm tall forest are plotted in Figure 3-25. The same plots for undensified fibers from a 6 mm tall forest are shown in Figure 3-26. Linear mass density is the product of the cross-sectional area of a fiber and the fiber’s density, so the linear mass density and cross-sectional area of a fiber scale linearly. Despite scatter in the data, the most important conclusion comes from examining the outer envelope of the data, where the most ideal results are found. This outer envelope reveals that there is a strong relationship between the
specific strength and specific stiffness of a fiber and its linear mass density, with higher strength and stiffness values measured in smaller fibers. The strength and stiffness measurements are affected by non-uniformities within the fibers, and these effects are expected to become less pronounced in smaller fibers. Even at one particular fiber size, there is variability in the measured strength and stiffness. Spread in the strength and stiffness data is attributed to non-uniformities within a single fiber and between fibers due to the growth or densification processes, stress concentration at the epoxy grips, or uncertainty in the values of forest density, fiber cross-sectional area and fiber gauge length. The plots of specific strength vs. specific stiffness shows that strength and stiffness are strongly correlated, with a linear correlation coefficient between the two parameters of 0.53 for the fibers from the 3 mm tall forest, and 0.92 for fibers from the 6 mm tall forest. Higher strength and stiffness both increase with decreasing fiber size so the non-idealities affect both strength and stiffness in a similar manner, suggesting that the main non-idealities that cause the size effects affect the percentage of load bearing CNTs at any given time within a fiber.

Figure 3-23: (a) Specific stress vs. strain and (b) load vs. strain for typical fibers prepared from a 3 mm tall forest, loaded in tension to failure.
Figure 3-24: Specific stress vs. strain curves from two different tests on fibers from 3 mm tall forests, with sudden changes in the slope suggesting the occurrence of partial fracture in the fibers.

Figure 3-25: Specific strength vs. linear mass density, specific stiffness vs. linear mass density, and specific strength vs. specific stiffness for undensified fibers from a 3 mm tall forest.
3.6.2. Effect of densification on fiber properties

To examine the effect of densification on fiber properties, five sets of fibers were prepared. Each fiber was created by removing a small stand of CNTs from the side of a 3 mm tall forest. Fibers were prepared with varying cross-sectional areas, with areas ranging from $8.5 \times 10^{-10}$ to $2 \times 10^{-7}$ m$^2$, corresponding to a linear mass density range of 0.01 to 4 tex. The fibers have an initial density of 17.6-22.1 kg/m$^3$. The first set of fibers was not densified prior to testing. The second set of fibers was densified with capillary effects using toluene. Densification using this technique produces variable densification between different fibers as well as along the length of a single fiber; a conservative estimate for the densification factor is 10, obtained by measuring the cross-sectional areas of fibers before and after densification. Fibers densified using capillary effects became sheet-like because of the additional capillary effects between the fiber and the surface on which the fiber was placed during the evaporation process. The third set of fibers was densified mechanically. A densification factor between 3 and 83 was obtained using this
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technique, depending on the applied pressure. The fourth set of fibers was prepared using mechanical densification followed by capillary densification. The fifth set of fibers was prepared by densifying fibers mechanically, mounting them on frames using epoxy, and then applying 720° twists to the fibers by rotating one frame relative to the other.

Tension tests to failure were conducted on the five sets of fibers. Specific strength and specific stiffness are plotted as a function of fiber linear mass density in Figure 3-27 for the five sets of fibers. The plots shows that there is a strong relationship between both specific strength and linear mass density and specific stiffness and linear mass density, with higher strength and stiffness values measured in smaller fibers, regardless of the densification method. This relationship, possibly due to fiber non-uniformities or non-uniformities in the grips, which can become more pronounced in larger fibers, is observed for all densification methods. Therefore, its origin is an attribute of the undensified CNT organization or the loading technique, which is not overcome by densification.

Figure 3-28 plots specific stiffness and specific strength as a function of fiber density. Since there is a close relationship between strength, stiffness and fiber linear mass density, it is only valid to compare the effects of the densification techniques on strength and stiffness as a function of density because the distribution of fiber cross-sectional areas is similar across the five data sets, as shown in Figure 3-29. Undensified fibers and fibers densified using capillary effects can have varying linear mass densities, but they have constant densities. Mechanically densified fibers have both varying linear mass densities and densities. To study the decoupled effects of linear mass density and density on the properties of mechanically densified fibers, Figure 4-30 plots the strength and stiffness of the fibers both as a function of linear mass density and density. The plots in Figure 3-28 and Figure 3-30 indicate that capillary-based densification was the only technique that markedly increased both the strength and stiffness of the fibers. Mechanical densification marginally improved fiber strength, but had little effect on stiffness. Increasing the density of mechanically densified fibers at constant linear mass density did not improve fiber performance. Fiber strength and stiffness increased with decreasing linear mass density at constant density. Therefore, reducing the linear mass density of a fiber has a much greater effect on strength and stiffness than increasing the fiber’s density. The three sets of fibers densified mechanically had a similar performance to each other, suggesting that the twisting and capillary densification after mechanical densification did not have a significant impact.

The results indicate that densification alone does not guarantee improved fiber performance, since the best performance was observed in fibers with an intermediate level of densification. Reducing the lateral extent of the fibers by mechanical densification to create more geometrically compact fibers was expected to mitigate the effects of uneven loading in the fibers, but only a marginal increase in strength and no significant increase in stiffness were apparent in the data. Therefore, changing the geometry of a fiber into a more compact shape does not alone improve a fiber’s mechanical properties. That mechanical densification did not significantly improve fiber performance suggests that higher density and larger bundles can lead to a larger number of interfering interactions when working with imperfectly aligned CNTs, since mechanical densification can introduce additional disorder by packing the CNTs together in a haphazard manner. Capillary-based densification, which allows the CNTs to self-assemble into dense networks of disordered but highly contacting CNTs, was the most effective technique for improving fiber performance. The increased contact between adjacent CNTs may have aided load transfer throughout the fiber to reduce the effects of uneven loading. The results suggest that densifying CNT fibers is a useful technique if the densification process is conducted in an
ordered manner, such as capillary densification, and that enhanced inter-CNT interactions can indeed improve fiber performance.

The stiffness of an ideal fiber made of parallel CNTs is 448 N/tex, assuming a Young’s modulus of 1 TPa. Considering a conservative failure strain of 6%, the ideal strength is 27 N/tex. The highest recorded stiffness and strength for fibers prepared from 6 mm tall forests are 68.1 N/tex and 2 N/tex, respectively (see Figure 3-31). The highest recorded stiffness and strength for fibers prepared from 3 mm tall forests are 62.5 N/tex and 1.8 N/tex, respectively. Both of these measurements were made in fibers densified with capillary effects. The measured values are considerably lower than the ideal values, indicating that defects, disorder and potentially the loading technique significantly limit the fibers’ strength and stiffness. While densification techniques can marginally improve the strength and stiffness of fibers, more fundamental improvements in the fabrication process are needed for the properties of the macroscopic fibers to approach the ideal CNT values.

To compare the performance of fibers from 3 mm tall forests and fibers from 6 mm tall forests, the data from all tests performed on fibers (including all densification types) from these two types of forests are compiled and plotted in Figure 3-31. The results show that higher specific stiffness is measured in fibers from 6 mm tall forests. The explanation might be the smaller diameters and fewer number of shells in the CNTs from the 6 mm forests (refer to Table 3-1), or perhaps a lower defect density in the 6 mm tall forests, though the difference in defect densities between the forests has not been quantified.
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Figure 3-27: Specific strength and specific stiffness of fibers densified using different techniques as a function of fiber linear mass density.
Figure 3-28: Specific strength and specific stiffness of fibers densified using different techniques as a function of fiber density.
Figure 3-29: Distribution of the linear mass densities in the five sets of fibers densified using different techniques.

Figure 3-30: Three-dimensional plots of specific strength and specific stiffness in the five sets of fibers as a function of linear mass density and density.
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3.6.3. Analysis of tension test videos

Videos of tension tests on fibers were used to evaluate the strain data provided by the Nano UTM. Two potential sources of error in the Nano UTM strain data were instrument error and error due to compliance in the epoxy grips. Small white dots were painted onto the surface of a series of fibers and high resolution sequential images were taken of the fibers during tension tests to failure. Strain in the fibers was obtained by tracking the distance between the epoxy edges and the distance between the white dots using Vic2D imaging processing software.

Images of three fibers (undensified, densified using capillary effects and mechanically densified) and plots of strain vs. time are shown in Figure 3-32. Across 30 tests using fibers prepared from a 3 mm tall forest, there was an excellent match between the strain measured between the epoxy edges and the strain data provided by the UTM. To within the accuracy of the measurements, there was no detectable error in the strain data from the UTM due to either epoxy compliance or instrument error. The force to stretch a CNT fiber in tension to failure of less than 200 mN is sufficiently small that epoxy compliance does not significantly affect the strain measured by the Nano UTM.

While the strain between the epoxy edges matched the strain from the Nano UTM, there was not always a match between the strain measured between the white dots and the strain from the Nano UTM, as shown in the plots in Figure 3-32. Additionally, the strain measured between the epoxy edges did not always match the strain between the white dots. Deviation between these two measurements of strain could occur either near the start of a test or part way through a test. These results indicate that strain can be non-uniform along the length of a fiber. Further analysis of the strain along the length of a single fiber revealed that strain is typically highest in a fiber near one of the grips. Figure 3-33 shows the strain in three different regions of a fiber during a
tension test to failure, showing highest strain near the grips and lower strain in the middle of the fiber, between the white dots. In other tests, strain was observed to be highest near one of the grips, intermediate in the middle of the fiber, and lower near the other grip. Non-uniform strain along the length of a fiber was observed in fibers for all three densification types that have been tested. It is expected that strain is often highest near one of the grips because of stress concentrations due to the epoxy that cause CNTs to fracture. In fact, it is postulated that strain is not really higher near the grips, but simply that the CNTs begin to fracture near the grips and the fiber elongates in the region. A schematic of a CNT fiber is shown in Figure 3-34, showing the two main potential non-idealities that limit the performance of the fibers: non-uniformities throughout a fiber due to the growth process, and stress concentration caused by the grips. During tension tests, stress concentrations at the grips cause the tautest CNTs to fracture first at the grips. The fiber then elongates to redistribute the load to other CNTs. In this way, fracture in the fibers occurs gradually over a large range of strains rather than in all CNTs at once. Fracture typically occurred near the grip at the end where the highest strain was measured using video imaging, consistent with gradual fracture taking place at that end during loading. Images of gradual fracture in fibers during loading are shown in section 3.6.4. The strain measured by the UTM (or equivalently the strain between the epoxy edges) is the mean strain along the fiber, but it is not a measure of the local strain within the fiber, nor is it the strain of individual CNTs within the fiber. The strain at fracture measured by the Nano UTM is the strain at which all CNTs within a fiber have fractured, but the fracture strain of the individual CNTs is expected to be much lower. Another test shown in Figure 3-35 demonstrates how strain can vary laterally within a fiber as well as along its length, due to non-ideal grips and fiber non-uniformities.

Note that there is nothing inherently wrong with the epoxy, because the same epoxy was used to attach yarn to testing frames for tension tests as described in Chapter 4, and the yarn fractured away from the grips. Therefore, the problem here lies with the way that the epoxy interacted with the individual CNTs in the fibers.

The strength and stiffness of the fibers measured in this work are lower bounds for the actual strength and stiffness of the fibers because of the challenges of loading the CNTs across the cross-section of a fiber uniformly. These tests illustrate some of the difficulties of working with macroscopic assemblies of CNTs and highlight some of the reasons why the properties of macroscopic CNT assemblies fall short of the properties of individual CNTs. First, it is challenging to test materials with short gauge lengths and even smaller cross-sectional areas using testing equipment designed for larger materials. Second, because the features in the fibers are so small, it is difficult to study the mechanisms that lead to fracture. In this case, stress concentrations at the grips contributed to fracture, and these stress concentrations were difficult to identify, control and eliminate. Third, since the fibers contain CNTs with low packing densities, few interconnections between neighboring CNTs, and minimal load transfer between CNTs, loading all of the millions of CNTs evenly is a challenge. Fourth, there are difficulties in working with macroscopic materials that contain non-uniformities at the nanoscale and microscale because these non-uniformities lead to lower than expected performance, and the non-uniformities are difficult to identify and control. Therefore, a recommendation is that future studies of the properties of macroscopic groupings of CNTs should be done using a displacement stage connected to a load cell inside of a high resolution SEM, using much smaller groupings of CNTs. Different grips should be designed and tested until satisfactory grips are found that do not cause stress concentrations at the fibers ends.
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(a)

(b)
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Figure 3-32: Fibers on frames with white dots applied to their surface to track strain in the fibers using video imaging, for (a) an undensified fiber, (b) a fiber densified using capillary effects, and (c) a mechanically densified fiber. The picture on the left is an image of the fiber mounted on a testing frame. The plot on the right shows the strain recorded by the Nano UTM, the strain measured between the two edges of the epoxy using video imaging, and the strain measured between the two white dots using video imaging.

Figure 3-33: (a) Image of an undensified fiber labeled with different regions; (b) plot of the strain in those different regions over time.
Figure 3-34: Schematic models of (a) an ideal fiber in epoxy grips and (b) an actual fiber in epoxy grips, highlighting non-uniformities in the fiber and non-ideal gripping.

Figure 3-35: (a) Image of an undensified fiber labeled with different regions; (b) plot of the strain in those different regions over time.

3.6.4. Scanning electron microscope imaging of loading and failure

Images and videos were recorded of fibers during tension tests using a SEM displacement stage to study how the material loads and fractures. All fibers were prepared from a 3 mm tall forest and mounted onto copper frames using conductive epoxy. Successive images of an undensified fiber loaded in tension to failure in Figure 3-36 show gradual fracture in the fiber during loading. A tear in the fiber is observed near the left grip at a 7.3% strain; fracture gradually propagates through the rest of the fiber until final fracture at a strain of about 15%. Images of three other undensified fibers before and after fracture are shown in Figure 3-37. Undensified fibers often fracture near grips, and a fiber fractures by gradual tearing of the CNTs.
over a large displacement. Images of gradual fracture in a mechanically densified fiber in Figure 3-38 show that fracture occurs by gradual tearing of CNTs near the end grips, and fracture gradually propagates through the rest of the fiber with increasing strain, in a manner similar to fracture in undensified fibers. Images of several mechanically densified fibers before and after fracture are shown in Figure 3-39. In mechanically densified fibers, fracture does not always occur near the grips. In both undensified and mechanically densified fibers, fracture is disorganized and ragged, indicating that good load transfer does not take place across the fiber. Images of several fibers densified using capillary effects are shown in Figure 3-40. Fracture in fibers densified using capillary effects is more organized and less ragged than in undensified and mechanically densified fibers, suggesting that the highly contacting CNTs due to the densification process enhance load transfer and can compensate for non-uniform loading, resulting in higher strength and stiffness under ideal conditions.
Figure 3-36: Gradual fracture in an undensified fiber from a 3 mm tall forest. The strain in the fiber is indicated on each of the images. Strain increases in the images from left to right, and then from top to bottom. The scale bar shown in the first image applies to all images.

Figure 3-37: Images of three undensified fibers, before and after being loaded in tension to failure. Each row of images corresponds to a fracture test conducted on one fiber.
Figure 3-38: Gradual fracture in a mechanically densified fiber. The strain in the fiber is indicated on each of the images. Strain increases in the images from left to right, and then from top to bottom. The scale bar in the first image applies to all of the images.
Figure 3-39: Images of four fibers densified mechanically, before and after being loaded in tension to failure. Each row of images corresponds to a fracture test conducted on one fiber.
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Figure 3-40: Images of three fibers densified using capillary effects, before and after being loaded in tension to failure. Each row of images corresponds to a fracture test conducted on one fiber.

The fracture zone for spun yarn is defined as the length of the region adjacent to a broken end whose appearance differs from the rest of the yarn structure [114]. Similarly, the length of the fracture zone can also be measured in fibers. In fibers, fracture occurs only by breaking CNTs. Pullout and slip are not primary fracture mechanisms, though they may still be present in fibers if fractured CNTs continue to bear load because of interactions with neighboring CNTs that are not yet fractured. Uneven loading, poor load transfer, and low packing density are expected to lead to longer and more disorganized fracture zones since there is less interaction between CNTs. Shorter fracture zones are expected in fibers with smaller cross-sectional areas because there is less area over which uneven loading can potentially act. Geometry can play a role as well. For a given cross-sectional area, a more compact shape can mitigate uneven loading. Shorter fracture zones are also expected in fibers with either better load transfer between CNTs, or more tangling between CNTs.

The length of the fracture zones for fibers tested in tension to failure using the SEM displacement stage are plotted as a function of fiber lateral extent and fiber density in Figure 3-41. A densification factor of 10 is considered for capillary densification and a densification factor of 25 is considered for mechanical densification. The general trend is that shorter fracture
zones are measured in denser fibers and in fibers with smaller lateral extents. Short fracture zones are seen in compact, dense, mechanically densified fibers. In fibers densified using capillary effects, there is a good load transfer between CNTs but the wide lateral extent of the flat sheets can result in long fracture zones. The large cross-sectional area and low packing density of undensified fibers produced long fracture zones.

To some extent, shorter fracture zones are correlated with higher strength, since mechanically densified fibers have marginally higher strength than undensified fibers. This may be due in part to the more compact geometry of the mechanically densified fibers which can mitigate uneven loading. However, highest strength was measured in fibers densified with capillary effects, which have an intermediate density and intermediate lateral extents. This is an indication that geometry and density of fibers are not the best indicators for strength. Higher strength was measured in capillary densified fibers because of superior CNT interactions at the nanoscale, and despite disadvantageous fiber geometry. It is expected that even higher strength and stiffness could be measured in fibers densified with capillary effects into shapes more compact than flat sheets; this could be potentially be achieved by using a vapor rather than a liquid to densify the fibers [115].

![Figure 3-41: Length of the fracture zone as a function of lateral extent and fiber density for fibers densified using different techniques.](image)

### 3.6.5. Weibull statistics

The variability of the strength of the CNT fibers prepared and tested using identical techniques suggests that these properties may be stochastic. Fiber strength increased as fiber cross-sectional area decreased, a trend indicating that CNT fiber strength may be described by Weibull statistics, which assumes that a material's strength is governed by a statistical distribution of critical defects, and that the number of critical defects is proportional to the volume of the material [116, 117]. Weibull statistics have previously been used to accurately model the strength of SWCNT bundles and individual MWCNTs [116-119], so the model will be tested to see if it can apply to CNT fibers, which are arrays of MWCNTs.
To test the model for these fibers, strength data from 28 undensified fibers prepared from a 3 mm tall forest is examined. The specific strength of the fibers is plotted as a function of cross-sectional area and gauge length in Figure 3-42. The fiber data is first fit to a Weibull statistics model that neglects variations in the fiber size, with a probability of failure at or below a stress \( \sigma \) given by

\[
P(\sigma) = 1 - \exp\left[-\left(\frac{\sigma}{\alpha}\right)^{\beta}\right],
\]

and a second model that accounts for the different size of each fiber, with a probability of failure at or below a stress \( \sigma \) given by

\[
P(\sigma, V) = 1 - \exp\left[-\left(\frac{V}{V_0}\right)^{\beta}\right],
\]

where \( V \) is the fiber volume, \( V_0 \) is a reference volume, \( \beta \) is the Weibull shape parameter, and \( \alpha \) is the Weibull scale parameter. The shape parameter \( \beta \) is related to the width of the strength distribution function, while the scale parameter \( \alpha \) is the strength at which 63.2% of samples have failed. The probability of failure is calculated according to [117, 119, 120]

\[
P(\sigma_i) = \frac{i-0.5}{N},
\]

where \( i \) is the index of each sample ranked in order of increasing value of \( \sigma \) and \( N \) is the total number of samples.

To fit the fiber strength data to the first Weibull model in which size effects are neglected, equation (3-2) is rewritten as

\[
\ln(-\ln(1 - P(\sigma))) = \beta \ln\sigma - \beta \ln\alpha.
\]

A plot of \( \ln(-\ln(1 - P(\sigma))) \) as a function of \( \ln\sigma \) is used to calculate \( \beta \) from the slope and \( \alpha \) from the intercept. To account for changing fiber length and cross-sectional area, equation (3-3) is rewritten as [120]

\[
\ln(-\ln(1 - P(\sigma))) = \beta \ln\left(\frac{V}{V_0}\right)^{1/\beta} - \beta \ln\alpha
\]

\[
\ln(-\ln(1 - P(\sigma))) = \beta \ln s - \beta \ln\alpha,
\]

where \( s = \left(\frac{V}{V_0}\right)^{1/\beta} \). A least squares algorithm is implemented to solve for \( \beta \) and \( \alpha \). For data following a Weibull distribution, the average strength at a particular volume is given by [120]

\[
\bar{\sigma}(V) = \eta \left(\frac{V}{V_0}\right)^{-1/\beta} \Gamma(1 + \frac{1}{\beta}),
\]

where \( \Gamma \) is the gamma function.

A Weibull plot for the model that neglects size effects is shown in Figure 3-43a. The shape parameter \( \beta \) is 1.78, the scale parameter \( \alpha \) is 0.185 N/tex, and the correlation coefficient is 0.9326. A Weibull plot for the model that accounts for changes in the gauge length and cross-sectional area of the fibers is shown in Figure 3-43b. When size effects are taken into consideration, the shape parameter \( \beta \) is 2.84, the scale parameter \( \alpha \) is 0.1457 N/tex, and the correlation coefficient is 0.8175. In both models, the small (but greater than 1) value of \( \beta \) indicates high variability in the data. The fit of the strength data to the model that accounts for fiber cross-sectional area is not as good as a fit to the data neglecting fiber size effects, indicating that the Weibull model does not accurately describe the relationship between fiber size and failure strength. Different factors must be causing smaller fibers to exhibit higher strength. Indeed, smaller fibers also exhibit higher stiffness, so alternate factors must affect both strength and stiffness. The size effects in fiber strength and stiffness are mostly likely caused by non-
uniformities within the fibers or stress concentrations at the epoxy grips which cause only a fraction of CNTs within a fiber to be load bearing at once, effects that lower failure strength and stiffness and can become more pronounced in larger fibers. These factors are not taken into consideration in the Weibull model. When strength and stiffness are plotted as a function of cross-sectional area (or linear mass density), there is an outer envelope of strength and stiffness values where the most ideal results are found. Strength and stiffness values that fall below the outer envelope may be underperforming due to non-idealities in the fibers or the testing process. The Weibull statistics model has no way to account for these underperforming fibers, so it is not surprising that there was not a good fit to the strength data. Weibull statistics may more accurately model the strength of the fibers on the outer envelope.

Figure 3-42: Specific strength of 28 undensified fibers prepared from a 3 mm tall forest plotted as a function of cross-sectional area and gauge length.

Figure 3-43: Weibull plots for the strength of undensified CNT fibers prepared from a 3 mm tall forest, (a) neglecting size effects and (b) accounting for changes in the gauge length and cross-sectional area of the fibers, with $s = \left( \frac{V}{V_0} \right)^{1/\beta} \sigma$. 

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3.6.6. Resistance changes during tension tests to failure

Resistance was measured across fibers prepared from 6 mm tall forests during tension tests to failure to gain a further understanding of the structural changes taking place in the fibers during loading. Resistance was measured across fibers mounted on copper-coated frames using a conductive epoxy (MG Chemicals 8331-14G) with two probe measurements, using a Signametric SMU2060 Multimeter. The resistance measurements include the resistance of the wire leads, conductive epoxy, copper frame, solder, and the fiber. During a test, a change in the measured resistance is expected to be only due to changes in the fiber. Specific stress and electrical resistance vs. strain for two typical fibers during tension tests to failure are plotted in Figure 3-44. The results show that there is a gradual increase in resistance as a fiber is strained, and the resistance abruptly goes to infinity once fracture occurs. An increase in the resistance across a fiber during tension testing can occur as a result of structural changes taking place within the fiber during loading, such as induced atomic defects in the CNTs, partial fracture of the fiber, reorganization at the nanoscale, changes in the electrical pathways as CNTs straighten or change their contact with each other, or due to piezoresistance. Piezoresistance is the change in resistance of a semiconductor due to an applied stress. Since the fibers contain a random mix of chiralities, one third of the CNTs are expected to be metallic and two thirds are expected to be semiconducting, and the fibers exhibit piezoresistance.

In a given material of length \( L \), cross-sectional area \( A \) and resistivity \( \rho \), the electrical resistance across the material is

\[
R = \rho \frac{L}{A}
\]

Changes in the resistance of the material are due to changes in geometry and resistivity:

\[
\frac{\Delta R}{R} = \frac{\Delta \rho}{\rho} + \frac{\Delta L}{L} - \frac{\Delta A}{A}
\]

For a material in uniaxial tension, \( \frac{\Delta L}{L} = \varepsilon \) and \( \frac{\Delta A}{A} = -2\nu \varepsilon \), where \( \nu \) is the Poisson ratio of the material. The relative change in resistivity in a piezoresistive material loaded in uniaxial tension is given by

\[
\frac{\Delta \rho}{\rho} = \pi \sigma = \pi E \varepsilon
\]

where \( \sigma \) is the applied stress in the axial direction, \( E \) is the Young's modulus and \( \pi \) is the piezoresistive coefficient of the material. Rewriting equation (3-10),

\[
\frac{\Delta R}{R} = (\pi E + 1 + 2\nu) \varepsilon.
\]

The piezoresistive gauge factor \( GF \) is defined as the ratio of the relative change of resistance to the applied strain [121], or

\[
GF = \frac{\Delta R}{R \varepsilon}
\]

such that

\[
GF = (\pi E + 1 + 2\nu).
\]

When a strain is applied to a piezoresistive material, the expected change in resistance is

\[
\Delta R = GF \cdot R \cdot \varepsilon
\]
The gauge factor accounts for changes in geometry and resistivity due to an applied load, but it does not account for other structural changes that can take place in a fiber to affect its resistance, particularly partial fracture occurring gradually during loading. Across all fiber tests, the change in resistance from the start of a test to immediate prior to fracture was larger than the expected change in resistance due to piezoresistance alone, so structural changes must be taking place in the fiber to additionally contribute to a resistance increase.

To illustrate this observation, the expected increase in resistance due to piezoresistance can be calculated for the two tests in Figure 3-44. The mean gauge factor measured in fibers from 6 mm forests is 0.0804 with a standard deviation of 0.0415 (see section 3.6.7). The fibers from 6 mm forests have a resistivity of $4.93 \times 10^{-6}$ $\Omega$m $\pm$ $0.8 \times 10^{-6}$ $\Omega$m. In Figure 3-44a, the initial resistance across the fiber is calculated to be 29.1 $\Omega$ (this quantity is not measured directly so it is calculated from the fiber's cross-sectional area, length and resistivity). The change in resistance from the start of the test to immediately prior to fracture is 0.55 $\Omega$, and the expected change in resistance across the fiber due to piezoresistance alone is $0.15 \pm 0.8$ $\Omega$. Similarly, in Figure 3-44b, the starting resistance of the fiber is 10.2 $\Omega$, the change in resistance from the start of the test to immediately prior to fracture is 0.35 $\Omega$, and the expected change in resistance across the fibers due to piezoresistance is $0.02 \pm 0.01$ $\Omega$. Partial fracture and other structural changes in the CNTs during loading are expected to be responsible for the remaining rise in the resistance during the tests.
3.6.7. Cyclic loading and resistance changes during cyclic loading

In an actual energy-storage application, a CNT spring would undergo repeated loading and unloading cycles as energy is stored in and subsequently released from a spring. To emulate this behavior, the mechanical behavior of several sets of fibers was tested under cyclic loading. The fibers were loading sinusoidally in tension to a constant strain amplitude and with a strain rate of $3 \times 10^{-3} \text{s}^{-1}$ while measuring their stress responses. An example of specific stress plotted as a function of strain for a fiber loaded cyclically in tension to a maximum strain of 5% over five cycles is shown in Figure 3-45. The wiggle in the stress-strain curve at the maximum strain is due to error in the Nano UTM's control system as the direction of the crosshead changed from extension to compression; the wiggle is unrelated to the properties of the fibers. The stress-strain curves show nonlinearity, hysteresis and preconditioning, and an increase in the stiffness of the fibers after the first cycle. Hysteresis losses range from 3% to 30%, depending on the fiber; hysteresis is thought to be the result of energy lost as heat due to friction between CNTs during loading, though there may be other contributing factors. The recoverable energy stored in a spring corresponds to the area under the unloading curve, so to achieve a high energy density it is of interest to maintain elastic behavior and limit hysteresis. With preconditioning, the stress-strain behavior of the fibers changes significantly after the first load cycle but subsequently remain consistent, and the hysteresis loop is much larger during the first cycle than in subsequent cycles. The preconditioning is an indication of permanent structural changes taking place in the fiber during only the first load. As long as the strain of the first load is not exceeded during following cycles, little further structural damage takes place in the fiber, and the load and unloading behavior can reach a steady state.
Figure 3-45: Plot of specific stress vs. strain of a fiber during five tensile loading cycles.

The electrical resistance was measured across fibers during cyclic loading to further understand structural changes taking place in the fibers. The results showed that there is a permanent increase in the measured resistance across a fiber during the first load, followed by strain dependent, reversible resistance oscillations during the subsequent load-unload cycles. For example, Figure 3-46 plots the stress and resistance across a fiber loaded sinusoidally to a maximum strain of 5% four times. The permanent increase in resistance could be the result of induced atomic defects in the CNTs, partial fracture of the fiber, reorganization at the nanoscale, or changes in the electrical pathways as CNTs straighten or change the amount of contact with each other. The reversible resistance oscillations are attributed to piezoresistance, though there may potentially be contributions from some other factors, such as structural effects within the fibers as CNTs coming into or out of contact as the fiber stretches and contracts. The reversible resistance oscillations indicate that loading may be elastic once preconditioning has occurred. In the test shown in Figure 3-46, the resistance across the fiber permanently increases by 0.12 Ω from the start to the end of the test, with reversible resistance oscillations with an amplitude of 0.06 Ω due to an applied strain of 5%. Both the mechanical and resistance measurements indicate permanent modification of the structure of the fiber during the first cycle; specific stress peaks at 0.036 N/tex during the first loading cycle, and then stays more or less constant at 0.032 N/tex afterwards.

Partial fracture is the most likely explanation for the preconditioning seen in the mechanical and electrical responses of cyclically loaded fibers. By examining the internal structural of the fibers (Figure 3-19), one can see that while there is general alignment of the CNTs along the fiber axis, the CNTs show significant tortuosity, presumably in response to atomic defects, leading in turn to entanglement between adjacent CNTs and imperfect packing and alignment. As a result, each CNT in the fiber contains a variable amount of slack, and different CNTs will become taut at different applied strains. Not only is there variable amount of slack between neighboring CNTs, but there is also a varying amount of slack between different regions within a fiber due to growth non-uniformities in the forest. As such, a strain applied to a fiber below the
ultimate failure strain may cause a small fraction of the CNTs in the fiber to fracture, leading to a jump in resistance during the first load of a cyclic loading test. Since subsequent load cycles do not increase the strain above the maximum strain of the first load, they do not cause significant amounts of additional CNT fracture and thus demonstrate consistent, repeatable behavior. Applying a strain likely straightens some of the CNTs within a fiber, so that the first load removes the slack in a portion of the CNTs. In subsequent cycles, an increase in stiffness is observed because more CNTs become taut at the same time and contribute to bearing the load.

Figure 3-46: (a) Stress plotted as a function of strain during four cyclic loading cycles and (b) stress and electrical resistance plotted as a function of time for the same test.

Figure 3-47 shows the stress-strain curves resulting from five cyclic loading tests on a fiber, where each test has four cycles; the maximum applied strain in each test is increased step-wise from 5% to 13% by increments of 2% until fracture. Non-linearity, hysteresis, preconditioning,
and an increase in stiffness after the first load in each test are again observed. On the first load of each test beyond the first one, the fiber initially follows the loading path of the previous test. Once the fiber reaches the maximum applied strain of the previous test, the stiffness starts to decrease. The corresponding electrical resistance and stress across the fiber as a function of time for the tests are plotted in Figure 3-47. Electrical resistance across the fiber is permanently increased after the first load cycle in each test, indicating that permanent changes take place in the fiber as a result of increasing the maximum applied strain beyond its previous limit.

Figure 3-47: (a) Specific stress plotted as a function of strain during five sequential cyclic loading tests, each with a progressively higher strain amplitude; (b) electric resistance and specific stress as a function of time during the same five tests.
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The reversible oscillations in the resistance across the fibers after preconditioning can be used to calculate the piezoresistive gauge factor of the fibers. This is an approximation of the gauge factor since there may be other factors (beyond the geometry and resistivity effects) that contribute to reversible resistance changes during cyclic loading, such as CNTs coming into or out of contact as the fiber stretches and contracts. The gauge factor is defined as the ratio of the relative change of resistance to the applied strain (see section 3.6.6), or

\[ GF = \frac{\Delta R}{R \Delta \varepsilon}. \]

The resistance across the fibers is not known since this quantity is not measured directly, but it can be calculated from the fiber's cross-sectional area, length and resistivity. Considering a fiber resistivity of \(4.93 \times 10^{-6} \Omega m\), the mean piezoresistive gauge factor of the fibers is 0.0804, with a standard deviation of 0.0415.

This is a relatively low piezoresistive gauge factor, considering that gauge factors as high as 600-1000 have been measured in individual CNTs [122-124]. However, gauges factors can be both positive and negative and CVD-grown forests contain a random mix of chiralities, so it is not surprising that the net piezoresistive gauge factor of the fibers is low.

### 3.6.8. Long-term cyclic loading and resistance measurements

It is useful to examine the behavior of the fibers tested in tension over a large number repeated of loads cycles, to simulate loading conditions that would be expected of a spring in a practical application. Figure 3-48 plots the specific stress, percentage of maximum peak load and electrical resistance across a fiber loaded sinusoidally 77 times in tension to a fixed strain amplitude of 2% at a strain rate of \(3 \times 10^3\) s\(^{-1}\). This particular fiber reversibly stores energy with a volumetric energy density of about 21 kJ/m\(^3\). There is an initial jump in the resistance across the fiber and an initial drop in the specific stress, associated with preconditioning. Subsequently, stress levels begin to stabilize and the resistance increases only slightly during the cycles, which indicates that there is potential for longer-term, reversible behavior in energy-storing fibers as springs. Cyclic load tests over a much larger number of cycles will be necessary to demonstrate the fibers' potential long-term stability for actual energy-storage applications.
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3.6.9. Energy and energy density

The performance of the CNT fibers as springs is evaluated by measuring the energy stored in the fibers. The work done on a fiber to stretch it in tension is equal to the area under the loading portion of a cyclic loading curve, while the energy released by the fiber is the area under the unloading portion of a cyclic loading curve, which accounts for losses due to hysteresis. The useful stored energy in a fiber is the area under the unloading curve. Three experiments were conducted to study energy and energy density in the fibers. The first experiment examined the
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The relationship between stored energy, volumetric energy density, gravimetric energy density, and fiber linear mass density, using fibers prepared from a 6 mm tall forest. The second experiment compared the energy storage capabilities of fibers that were undensified and densified using capillary effects, using fibers prepared from a 3 mm tall forest. The third experiment compared the energy storage capabilities of fibers that were undensified, densified using capillary effects, and densified mechanically with fibers prepared from another 3 mm tall forest. Within each of the three experiments, all fibers were prepared from the same forest.

In the first experiment, 22 fibers with linear mass densities ranging from 0.07 to 0.8 tex (corresponding to cross-sectional areas of 8.8x10^-9 to 1.0x10^-7 m^2) were prepared from a 6 mm tall forest. The fibers were densified using capillary effects by placing a drop of toluene on each fiber and allowing the toluene to evaporate. The fibers were loaded to a strain of 1% for 5 cycles; the cyclically applied strain was incrementally increased by 0.5%, remaining for 5 cycles at each strain level, until the fiber fractured. The stored energy and volumetric and gravimetric energy density for each fiber was calculated by numerically integrating the area under the unloading portion of the stress-strain curve of the fifth cycle at the maximum applied strain before fracture. Integrating the fifth cycle to obtain the energy in the fibers provides only an estimate for the energy and energy density of the fibers because the load carried by a fiber loaded cyclically in tension continues to decrease beyond the fifth cycle. Load and strain for the tests were obtained from the Nano UTM. Strain output by the Nano UTM was evaluated by placing small white dots on the surface of fibers and tracking the position of the white dots during a test using video imaging and image processing. A comparison of the strain data from the video imaging and the strain data output by the Nano UTM showed that there was an excellent match between the two sets of strain data, so the strain output by the Nano UTM contains little instrument error and little error due to epoxy compliance. An example of a stress-strain curve of a fiber tested in this experiment is shown in Figure 3-49. A densification factor of 10 was assumed for each fiber, to obtain conservative calculations of volumetric energy density. The stored energy, gravimetric energy density and volumetric energy density of the fibers are plotted as a function of linear mass density in Figure 3-50. As expected, higher stored energy was measured in larger fibers, though higher energy densities were measured in smaller fibers, consistent with higher strength and higher stiffness values measured in smaller fibers. The maximum energy density measured in this set of fibers is 518 kJ/m^3 or 6.9 kJ/kg. Across all linear mass density values, the mean gravimetric energy density is 1.9 kJ/kg with a standard deviation of 1.6 kJ/kg, and the mean volumetric energy density is 143 kJ/m^3 with a standard deviation of 118 kJ/m^3.

To determine whether loading fibers cyclically degrades their strength, the strength of the fibers loaded cyclically in this experiment were compared to the strength of a set of identically prepared fibers from the same forest that were loaded in tension to failure. The strength values are plotted for comparison in Figure 3-51, showing that cyclically loading fibers does not significantly degrade their strength.
Figure 3-49: Specific stress vs. strain for a fiber with a linear mass density of 0.0663 tex prepared from a 6 mm tall forest, densified using toluene and loaded cyclically five times to a maximum strain of 3.7%. The wiggle in the loading curve is due to an improperly functioning control system in the testing instrument and is not related to the properties of the material. An estimate of the energy output by the fiber is calculated by integrating the area under the fifth unloading curve. This fiber stores 0.55 $\mu$J of energy with a density of 518 kJ/m$^3$ or 6.9 kJ/kg.
Figure 3-50: Energy, gravimetric energy density and volumetric energy density of fibers prepared from a 6 mm tall forest and densified using capillary effects, plotted as function of linear mass density.
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Figure 3-51: Comparison of the strength of fibers loaded cyclically with the strength of identically prepared fibers loaded in tension to failure.

A second experiment was conducted to study the effect of densification on energy storage. Fibers were prepared from a 3 mm tall forest: a first set of 16 fibers were left undensified, and a second set of 12 fibers were densified using capillary effects using toluene as the solvent. The fibers were prepared with a range of linear mass densities, ranging from 0.09 to 1.7 tex (corresponding to cross-sectional areas of $5.0 \times 10^{-9}$ to $9.4 \times 10^{-8}$ m$^2$). Both sets contained fibers with a similar distribution of linear mass densities. To measure the energy stored in each fiber, the fibers were tested using the same procedure described for the first experiment. A densification factor of 10 was assumed for fibers densified using capillary effects, to obtain conservative calculations of volumetric energy density. The stored energy, gravimetric energy density and volumetric energy density of the fibers are plotted as a function of linear mass density in Figure 3-52. As observed in the first experiment, higher energy is measured in larger fibers and higher energy densities are measured in smaller fibers, for both densification techniques. As expected, higher volumetric energy density is obtained in fibers densified using capillary effects simply because they have a higher packing density of CNTs. The effect of densification is evaluated by comparing the stored energy and gravimetric energy density of the two sets of fibers, since both of these quantities are independent of the packing density of the CNTs in the fibers. No significant difference in the stored energy or gravimetric energy density between the two sets of fibers was detected, so densification did not improve the performance of the fibers as springs.
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- Undensified
- Capillary effects

Linear mass density (tex)

Energy (\(\mu\))

Volumetric energy density (KJ/m^3)

Linear mass density (tex)

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A third experiment was performed to increase the volumetric energy density of the fibers by densifying a subset of the fibers mechanically. Three sets of fibers were prepared from a 3 mm tall forest (a different forest than used in the second experiment): 27 undensified fibers, 28 fibers densified using capillary effects with toluene, and 28 fibers densified mechanically. The fibers were prepared with a range of linear mass densities, with a similar distribution of linear mass densities for each set. To measure the energy stored in each fiber, the fibers were tested using the same procedure described for the first experiment. Three typical specific stress vs. strain curves from fibers (undensified, densified with capillary effects, mechanically densified) loaded cyclically in tension are shown in Figure 3-53. Such cyclic loading curves were used to calculate the energy and energy density of each fiber. A densification factor of 10 was assumed for fibers densified using capillary effects, to obtain conservative calculations of volumetric energy density. A densification factor between 4 and 86 was obtained using mechanical densification, depending on the applied pressure. Therefore, undensified fibers and fibers densified using capillary effects had constant densities while the densities of the mechanically densified fibers were variable. The energy measured in the fibers is plotted as a function of linear mass density and density in Figure 3-54. The fiber's volumetric energy densities are plotted in Figure 3-55 and the fiber's gravimetric energy densities are plotted in Figure 3-56, both as a function of linear mass density and density. Finally, volumetric energy density is plotted as a function of gravimetric energy density in Figure 3-57. Across all densification techniques, higher energy is measured in larger fibers while higher energy density is measured in smaller fibers. Due to their high densification, mechanically densified fibers have the highest volumetric energy density. The effect of densification is evaluated by comparing the fibers' gravimetric energy density. Capillary and mechanical densification produced fibers with consistently higher gravimetric energy density as a result of their higher strength. The highest energy density measured in these fibers is 2.9 kJ/kg or 677 kJ/m$^3$. For undensified fibers and across all linear mass density values,
the mean gravimetric energy density is 0.34 kJ/kg with a standard deviation of 0.26 kJ/kg, and the mean volumetric energy density is 5.9 kJ/m$^3$ with a standard deviation of 4.6 kJ/m$^3$. For fibers densified with capillary effects and across all linear mass density values, the mean gravimetric energy density is 0.45 kJ/kg with a standard deviation of 0.29 kJ/kg, and the mean volumetric energy density is 79 kJ/m$^3$ with a standard deviation of 50 kJ/m$^3$. For mechanically densified fibers and across all linear mass density values, the mean gravimetric energy density is 0.56 kJ/kg with a standard deviation of 0.54 kJ/kg, and the mean volumetric energy density is 215 kJ/m$^3$ with a standard deviation of 195 kJ/m$^3$. 

![Graph (a)](image)

![Graph (b)](image)
Figure 3-53: Typical specific stress vs. strain curves used to calculate energy and energy density in fibers, showing cyclic loading curves for (a) an undensified fiber, (b) a fiber densified using capillary effects, and (c) a fiber densified mechanically.

Figure 3-54: Energy stored in the fibers as a function of fiber linear mass density and density.
Figure 3-55: Volumetric energy density plotted as a function of fiber linear mass density and density.
Figure 3-56: Gravimetric energy density plotted as a function of fiber linear mass density and density.
Figure 3-57: Volumetric energy density plotted as a function of gravimetric energy density.
Figure 3-58: (a) Volumetric and (b) gravimetric energy density plotted as a function of linear mass density for fibers densified using capillary effects, prepared using three different forests; (c) distribution of fiber gauge lengths from the three forests.

The data from the three experiments is used to examine how growth conditions in forests can affect the properties of fibers. Fibers in the three experiments were taken from three different forests, a 6 mm tall forest in the first experiment, and two 3 mm tall forests in the second and third experiments. The volumetric and gravimetric energy density of fibers all densified using capillary effects with toluene from the three experiments are compared in Figure 3-58. The fibers from the 6 mm tall forest had consistently higher gravimetric and volumetric energy densities,
suggesting that the growth conditions to produce 6 mm tall forests are better than the growth conditions to grow 3 mm tall forests for fibers for springs. There was no significant difference in the energy densities of fibers from the two 3 mm tall forests. All of the fibers were prepared and tested using identical techniques, so any differences between the data are mainly due to differences in the forests. The fiber gauge lengths in the three sets of data are plotted in Figure 3-58c, showing that the 6 mm tall forests had marginally longer gauge lengths. Across all fiber experiments, there was little correlation between gauge length and energy density of fibers, so the longer gauge lengths of the fibers from the 6 mm tall forests are unlikely to explain their better performance. Instead, higher energy density measured in fibers from the 6 mm tall forest is more likely to be related to smaller CNT diameters and fewer shells, or perhaps lower CNT defect density. Recall that the CNTs from 6 mm tall forests have 6 nm mean outer diameters and about 3 shells, while CNTs from 3 mm tall forests have 10 nm mean outer diameters and 4-5 shells. MWCNTs with fewer shells and smaller diameters are predicted to have better mechanical performance because they can reach high packing densities and have fewer inner shells that potentially do not contribute to load bearing.

In conclusion, the highest recoverable energy density measured in the fibers to date is 518 kJ/m$^3$ or 6.9 kJ/kg in fibers from 6 mm forests, and 677 kJ/m$^3$ or 2.9 kJ/kg in fibers from 3 mm forests. In general, higher energy density is measured in smaller fibers. Densifying fibers mechanically can increase their volumetric energy density by a factor as high as 80, but increases in gravimetric energy density as a result of fiber densification were relatively small. The energy density measured in fibers is compared to the energy density of conventional energy storage technologies and ideal CNT fibers in Figure 6-2. The recorded energy density in the CNT fibers is more than an order of magnitude higher than the gravimetric energy density of steel springs, and more than half the volumetric energy density of steel springs (the relatively low density of the CNTs within the fibers limits their volumetric energy density). The recorded energy density of fibers remains three orders of magnitude lower than the theoretically predicted maximum energy density for CNTs because of fiber non-idealities.

### 3.6.10. Raman spectroscopy during tension testing

Raman spectroscopy was performed on fibers during tension tests to study changes in the atomic structure of the CNTs during loading. Raman spectra were measured in fibers tested in tension to failure and tested cyclically in tension. A displacement stage (Figure 3-59) was designed and built for the experiment. Tests were conducted on fibers that were undensified, densified using capillary effects, and densified mechanically to assess the effects of densification on the Raman spectra of the fibers during loading. Fibers with gauge lengths between 1-1.5 mm were mounted on frames using epoxy (Figure 3-60). A micropositioner with 1 μm displacement resolution was used to extend the fibers and the force in the fibers was measured using a 0.3 N force sensor (Strain Measurement Devices, ABB3277). The displacement stage is shown with the Raman microscope in Figure 3-61. Raman spectra were recorded using a Horiba Jobin-Yvon LabRAM Raman Microscope with a 633 nm HeNe laser.

Raman spectroscopy can be used to monitor strain in CNTs because stretching the carbon-carbon bonds weakens the bonds, lowers their vibration frequency, and produces downshifts in the D, G, and G’ Raman peak positions [125, 126]. The magnitude of the downshifts of the D, G
and $G'$ peak frequencies vary with chirality [126]; since the fibers are made up of tightly packed MWCNTs with a random mix of chiralities, and the Raman signal is measured with a spot size of about 1 μm, the Raman spectra measured in the fibers are the result of signals averaged over many CNTs and chiralities. A typical spectrum measured in a CNT fiber is shown in Figure 3-62. The dominant features are a D band at 1320 cm$^{-1}$, a G band at 1570 cm$^{-1}$, and a $G'$ band at 2630 cm$^{-1}$. The G band is associated with vibrations of the carbon atoms tangential to the surface of the CNT, either along the CNT axis ($G_+$) or in the circumferential direction ($G$). In MWCNTs, the G band is wide and asymmetric due to the summed effects of diameter and chirality distribution [127]. The D band is due to a one-photon second-order Raman scattering process, while the $G'$ band is due to a two-photon second-order Raman scattering process [127]. The D band is observed only in the presence of disorder, defects or impurities in a CNT, particularly the presence of amorphous carbon [125, 128], while the $G'$ band does not require disorder to be observed since it is a two phonon process [125]. Defects in CNTs can include hetero-atoms, vacancies, heptagon–pentagon pairs, kinks, or impurities [128]. The ratio of the intensities of the G band peak to the D band peak can be used to assess the defect density in the CNTs [129].

![Figure 3-59: A displacement stage with a 0.3 N force sensor for stretching fibers while performing Raman spectroscopy.](image)
Figure 3-60: Fibers on frames prepared for Raman spectroscopy: (a) an undensified fiber; (b) a fiber densified using capillary effects; (c) a mechanically densified fiber.
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Figure 3-61: The displacement stage and the Raman spectroscopy system.

![Figure 3-61: The displacement stage and the Raman spectroscopy system.](image)

Figure 3-62: Typical Raman spectrum of a CNT fiber.

![Figure 3-62: Typical Raman spectrum of a CNT fiber.](image)

The Raman data was analyzed by performing baseline correction and then fitting Lorentzian functions to the bands. A single Lorentzian function was fit to the D and G' bands, while a sum of three Lorentzian functions was fit to the more complex, asymmetric G band. The peak amplitudes and frequencies of the bands were extracted from the curve fitting. Each Lorentzian function has the form

\[ y = \frac{I}{1 + \left(\frac{x - x_0}{y}\right)^2}, \]  

(3-17)

where \( I \) is the amplitude of the peak, \( x_0 \) is the center frequency and \( y \) is the half-width at half-maximum.

To measure the Raman spectra of fibers during tension to tests to failure, each fiber was extended in small increments of about 5-10 μm. After each displacement increment, a spectrum was recorded at three specific positions along the fiber. Strain in the fiber was measured by measuring the distance separating the edges of the two sides of the frame after each displacement.
increment using the optical microscope. The process of incrementing the displacement and then measuring the spectrum at three locations was repeated until the fiber fractured, and a final spectrum was recorded at each of the three positions after fracture. The direction of polarization of the laser was perpendicular to the axis of the fiber.

The results from 9 fibers tested in tension to failure showed that there was a decrease in the G/D and G'/D peak intensity ratios as the fibers were strained. On average, the G/D ratio decreased by 0.0041 per % strain (standard deviation of 0.0060 per % strain), while the G'/D ratio decreased by 0.0038 per % strain (standard deviation of 0.0060 per % strain) during loading, prior to fracture. From the start of a test to immediately before fracture, on average the G/D and G'/D ratios decreased by 0.061 and 0.057, respectively. The decrease in these ratios is an indication of defects accumulating in the fibers during loading. After fracture, the G/D and G'/D ratios typically did not return to the original values at the start of the test, so at least a portion of the defects induced in the fibers during tension to failure tests were permanent. The high standard deviation in the intensity ratios is due to significant variation in the spectra with position along the surface of the fiber and through its depth, which reflects spatial variations in the fiber’s composition and structure. The tests attempted to take spectra at three identical positions during loading. However, these three positions were difficult to identify exactly after each fiber extension. Deviating from the correct chosen position on the fiber by only a few microns changed the frequencies of the resonant peaks and peak intensity ratios, thereby introducing error and uncertainty in the results and making it more challenging to extract the effect of strain on the spectra.

Shifts in the resonance peaks were measured to study the strain in the CNTs. On average across all tests, the D band peak shifted by 0.016 cm\(^{-1}\) per % strain (standard deviation of 0.18 cm\(^{-1}\) per % strain), the G band peak shifted by 0.005 cm\(^{-1}\) per % strain (standard deviation of 0.26 cm\(^{-1}\) per % strain), and the G' band peak shifted by -0.034 cm\(^{-1}\) per % strain (standard deviation of 0.31 cm\(^{-1}\) per % strain). The standard deviation in the data is much larger than the mean, reflecting a large degree of scatter in the data. Downshifts in the band peak frequencies were expected due to the lowered vibrational frequency of the carbon atoms from the applied strain, however the considerable scatter in the band peak data made trends difficult to detect. The band peak frequencies were expected to return to their starting frequencies once fracture occurs and the strain in the material was released, but noise in the data made it difficult to detect whether or not this actually occurred. There were two main sources of noise in the data. First, the spectra varied substantially with position along the surface of the fiber and through its depth. Although this may reflect spatial variations of strain throughout the fiber, it more likely simply reflects spatial variations in the fiber’s composition and structure. The difficulties of taking measurements at exactly the same three positions within a fiber over the course of a test introduced error into the band peak frequency data. Second, there was an upward drift in the frequencies reported by the instrument of up to 4 cm\(^{-1}\) from the start to the end of each tension test, measured by taking a spectrum of cyclohexane before and after each tension test. The drift in the instrument produced considerable error in the data and masked shifts in the resonance peaks due to strain in the fibers since the amplitude of the shifts in the peaks over the course of a test was of the same magnitude as the amplitude of the drift in the instrument. To try to compensate for error in the instrument, the band peak data can be adjusted using a linear correction for the drift in the instrument over the course of each test. Using this correction, the mean shift in the D band peak is -0.18 cm\(^{-1}\) per % strain (standard deviation of 0.29 cm\(^{-1}\) per % strain), the mean shift in the G band peak is -0.19 cm\(^{-1}\) per % strain (standard deviation of 0.39...
cm\(^{-1}\) per \% strain), and the mean shift in the \(G'\) band peak is -0.23 cm\(^{-1}\) per \% strain (standard deviation of 0.42 cm\(^{-1}\) per \% strain). While these values may be more accurate representations of the actual peak downshifts in the strained fibers, it is difficult to draw conclusions from this data because it is likely that the drift in the instrument was not perfectly linear.

Previous Raman spectroscopy studies of strained CNTs have measured much larger peak downshifts than were measured in this work. Downshifts of as much as 37.3 cm\(^{-1}\) per \% strain and 23.6 cm\(^{-1}\) per \% strain have previously been measured in individual SWCNTs \([5, 126]\). One possible explanation for the much smaller downshifts measured in this work is that the CNTs in the fibers are actually tortuous; when CNTs in the fibers are strained, there is a good possibility that the CNTs bend at kinks where defects are located, so that less stretching of the graphitic lattice in the CNTs occurs. Since there would be less strain in the graphitic carbon bonds, smaller than expected downshifts in the peak positions would be measured. A second possible explanation is that the direction of polarization of the laser was perpendicular to the axis of the fibers, so lower than expected shifts could have been measured.

The results showed that there was no measureable difference in the spectra of fibers densified using different techniques, both before load testing as well as during tension tests to failure. If there were any distinctions in the spectra of fibers densified using the different techniques, these distinctions were smaller than variations due to composition and structure between fibers and within a single fiber. There was no significant difference in the \(G/D\) peak intensity ratios of the three types of densified fibers at no strain, indicating that densification did not introduce new defects into the fibers. This is a particularly important result for mechanically densified fibers, because it means that the pressure applied to the fibers during densification did not measurably damage the CNTs.

The results from a tension test to failure on a mechanically densified fiber are shown in Figure 3-63. Figure 3-63a shows the fiber's load-strain curve during the test. Spectra were taken at each marker on the curve. Figure 3-63b shows the legend for the next five plots: each of the three colors represents a unique location in the fiber. The peak frequencies of the \(D\) band, \(G\) band, and \(G'\) band are plotted as a function of strain in Figure 3-63c-d. The instrument upshifted by 2.1 cm\(^{-1}\) from the start to the end of this particular test, about the same amplitude as the shifts seen in the \(D\) and \(G\) band peaks. It is expected that the upshifts seen here in the \(D\) and \(G\) band peaks are due to instrument error. The downshift in the \(G'\) band is more significant since a net downshift in the \(G'\) band peak is seen despite the 2.1 cm\(^{-1}\) upshift in the instrument. The \(G/D\) and \(G'/D\) peak intensity ratios, plotted in Figure 3-63e-g, decrease linearly with strain; it is apparent from these two plots that the spectra can vary significantly according to the position in the fiber, since the data points fall on three distinct lines. Finally, Figure 3-63h shows the change in spectra at ‘Position 1’ in the fiber at different strains. The spectra are normalized to the intensity of the \(G\) band. From the plot, it is apparent that the intensity of the \(D\) band increases relative to the intensity of the \(G\) band as the fiber becomes strained.
Chapter 3. Carbon nanotube fibers

(a)

(b)

(c)

(d)

(e)
Next, the Raman spectra of fibers were measured during tensile cyclic loading. Cyclic loading tests were performed only on mechanically densified fibers. To run these tests, a spectrum was taken at three specific locations on a fiber with no applied strain. Using the micropositioner, a strain was alternately applied to and then removed from the fiber over multiple cycles, each time taking spectra at the same three locations. At each step, strain was
recorded by measuring the distance separating the edges of the two sides of the frame using the optical microscope.

The test results showed that there was a net drop in both the G/D and G'/D peak intensity ratios each time the yarn was loaded, followed by partial recovery once the load was removed. Over the course of several cycles, the G/D and G'/D peak intensity ratios in the unstrained fiber gradually dropped, indicating that cyclically loading the fibers is only a partially elastic process since permanent defects accumulate in the CNTs, an important result. Averaging over all tests, the ratio of the G/D intensities dropped by 0.047 per cycle, and the ratio of the G'/D intensities dropped by 0.013 per cycle. As seen with the tension tests to failure, the ratios of the peak intensities were affected by spectra that varied with position in the fiber, which introduced noise and scatter into the data. Detecting shifts in the resonance peaks during cyclic loading was more difficult because of both spatial variations of the spectra in the fibers and drift in the instrument of as much as 4 cm\(^{-1}\) from the start to the end of a cyclic loading test. Nonetheless, the most apparent trend was that the D, G and G' band peak frequencies dropped each time a load was applied to the yarn, and recovered once the load was removed. Any net change in the band peak frequencies from the start to the end of the test are attributed to instrument drift.

The results from a cyclic loading test on a mechanically densified fiber are shown in Figure 3-64. Figure 3-64a shows the force applied to the fiber during the cycles. Figure 3-63b shows the legend for the next five plots; each of the three colors represents a unique location in the fiber, filled markers represent loading, and unfilled markers represent no loading. The peak frequencies of the D band, G band, and G' band are plotted as a function of strain in Figure 3-63c-d. Oscillations in the band peak frequencies can be seen as the fiber is loaded and unloaded. Any net changes in the frequencies over the course of the test are attributed to an upshift in the instrument of 2.1 cm\(^{-1}\) from the start to the end of this test. The G/D and G'/D peak intensity ratios, plotted in Figure 3-63f-g, decrease once a load is applied, and partially recover once the load is removed, with a net decrease in the G/D and G'/D ratios of from the start to the end of the test of 0.015 and 0.014 respectively, indicative of permanent defects induced in the fiber. Finally, Figure 3-63h shows the change in spectra at 'Position 1' at cycle 1, cycle 4 and cycle 8. The spectra are normalized to the intensity of the G band. From the plot, it is apparent that the intensity of the D band increases relative to the G band over the course of the testing cycles.
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Position 1 - Unload
Position 1 - Load
Position 2 - Unload
Position 2 - Load
Position 3 - Unload
Position 3 - Load

(a)

1 mm scale

(b)

1328
1327
1326
1325,

(c)

E 1326
12
C

W
1325,

(d)

2 3 4 5 6 7 8
Cycle

(e)

2 3 4 5 6 7 8
Cycle

(f)

2 3 4 5 6 7 8
Cycle

(g)

2 3 4 5 6 7 8
Cycle
3.6.11. Effect of twisting on fiber properties

Twists were applied to fibers in order to try to improve their properties. In a fiber containing twist, the CNTs in the fiber follow a helical path from one end of the fiber to the other. Once a tensile load is applied to a fiber, a radial pressure is generated within the fiber's cross-section as the CNTs attempt to straighten. The radial pressure is expected to more uniformly distribute a load throughout a fiber's cross-section, increase the fraction of load-bearing CNTs in the fiber, and mitigate effects due to uneven loading from forest non-uniformities. Twisting a fiber also inherently lowers its stiffness and strength because the CNTs are being loaded at an angle to the fiber axis. Strength and stiffness will both decrease by a factor of $\cos^2 \alpha$, where $\alpha$ is the angle between the CNTs on the outer surface of the fiber and the fiber axis (see section 2.7.1). A net increase in strength and stiffness will be observed in twisted fibers if the effect of more uniform load sharing among CNTs is greater than the effect of obliquity.

Two experiments were conducted to study the effects of twisting. In the first experiment, undensified fibers were prepared from a 3 mm tall forest and mounted on frames. Before testing, the fibers were twisted by rotating one frame relative to the other. Sets of fibers were prepared with no twist, one twist (360° rotation), two twists (720° rotation), and three twists (1080° rotation). SEM images of an undensified fiber with two twists loaded in tension to failure are shown in Figure 3-65, showing fracture at one of the grips. The specific strength and specific stiffness of the sets of fibers are plotted as a function of linear mass density in Figure 3-66.
results show that more twist leads to consistently lower strength and stiffness, with a more pronounced decrease in the stiffness values. The relationship between strength, stiffness and fiber size remains present in twisted fibers, with higher strength and stiffness measured in fibers with smaller linear mass densities. The decrease in stiffness must be due to the effects of obliquity. The twists became localized at the center of the fibers as the fibers were stretched because of the short gauge length of the fibers and the low initial packing density of the CNTs. There was added strain at the edges of the grips, as shown schematically in Figure 3-67, and fracture consistently initiated at the edge of one of the grips. The reduction of strength with twist angle must be due to both the effects of obliquity and the added strain at the grip edges.

A similar experiment was conducted with fibers densified using capillary effects with acetone as the solvent. Fibers were prepared from a 3 mm tall forest, densified using acetone, and mounted on frames. Before testing, the fibers were twisted by rotating one frame relative to the other. Sets of fibers were prepared with no twist, a half twist (180°), one twist (360° rotation), two twists (720° rotation), and three twists (1080° rotation). SEM images of a fiber densified with capillary effects and two twists are shown during loading and fracture in Figure 3-68; fracture initiated at one of the grip edges. The specific strength and specific stiffness of the sets of fibers are plotted as a function of linear mass density in Figure 3-69. Again, the results show that more twist leads to consistently lower stiffness because of the effects of obliquity. It is unclear whether twisting promotes more uniform load distribution because obliquity and higher strain at the grip edges reduce strength. In fibers densified using capillary effects, there is the added complication that the fibers densify as flat sheets; twisting adds a considerable amount of strain near the grip edges, and this is where fracture initiates.

The experiments on twisting have shown that twisting fibers reduces their strength and stiffness. The effects of obliquity and added strain near the grip edges made it difficult to determine whether there was any enhancement of load distribution throughout the CNTs in the fibers. It is possible that twisting could be more effective in dense fibers with round cross sections, in which there would be less additional strain near the grip edges. To test the effects of twisting on load distribution without increasing the strain at the grips, it would be best to twist the fibers and then mount them on frames.
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(a)  
(b)  
(c)  
(d)  
(e)  
(f)
Figure 3-65: SEM images of an undensified fiber with two twists (720° rotation) stretched in tension to failure. Strain increases from (a) through (g), with the exception of image (d) which is a higher magnification view of the twisted portion of the fiber in (c). Image (h) is a higher magnification view of the fracture zone in (g).
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Figure 3-66: Specific strength and specific stiffness as a function of linear mass density of undensified fibers with no twist, one twist (360° rotation), two twists (720° rotation), and three twists (1080° rotation).

Twisting improves load distribution

Higher strain leads to fracture near grip edges

Figure 3-67: Schematic diagram of the effect of twisting in fibers: the twists localize in the center of a fiber, resulting in higher strain at the grips.
Figure 3-68: Set of images showing loading and fracture of a fiber densified using capillary effects with two twists (720° rotation) stretched in tension to failure. Strain increases in the images from (a) through (d).
Figure 3-69: Specific strength and specific stiffness as a function of linear mass density of fibers densified with capillary effects using acetone, containing no twist, a half twist (180° rotation), one twist (360° rotation), two twists (720° rotation), and three twists (1080° rotation).

### 3.6.12. High magnification imaging during tension tests

Examining the CNTs in forests with a SEM reveals that the CNTs are tortuous and contain many kinks, due to atomic defects. The imperfect structure of the CNTs is apparent in the images in Figure 3-19. When a grouping of these CNTs is stretched in tension, it is expected that the CNTs must unbend as they are stretched. An interesting study would be to image the CNTs in a fiber inside of a SEM as strain is applied to the fiber. Such an undertaking would answer the
following questions: how much do the CNTs bend when they are stretched in tension? Does bending occur mainly at the kinks where the defects are concentrated? How does bending affect the overall stiffness in tension of such a CNT? Are deformations uniform among neighboring CNTs? Does fracture in a CNT occur before or after the CNT becomes taut? Does fracture in a CNT initiate at a location containing defects? A displacement stage inside of a high resolution SEM is needed to perform such an experiment and answer these questions. The displacement stage described in section 3.3.4 provides focused images of the surface of the CNTs fibers only up to about 4000x magnification, too low a magnification to be able to distinguish individual CNTs. Nevertheless, images of the surface of the fibers were recorded at the highest magnification possible to study changes in the microstructure of the fibers as the fibers were stretched in tension.

In one test, an undensified fiber was stretched in tension in small increments. Images were acquired at ten strain increments, starting at no strain in the fiber up until fracture. At each step, images of the surface of the fiber were taken at one particular location near the left grip, at both 2500x and 4000x magnification. Selected images of the fiber and the fiber surface are shown at four different levels of strain in Figure 3-70. Ripples can be seen on the surface of the fiber, which form as a result of the growth process. The CNTs presumably contain periodic defects that cause them to bend, thereby producing a three-dimensional ripple pattern. The wavelengths of the two-dimensional projections of the ripples were measured at random locations across the ten images at 2500x and 4000x magnification. The mean wavelengths are plotted as a function of strain in Figure 3-71, showing considerable scatter in the data. To try and compensate for this scatter, which may be due to the random selection of ripples to measure across the images, three specific ripples (Figure 3-72) were chosen that were easily identifiable and in focus in all of the images at each strain level. The wavelengths of the two-dimensional projections of the ripples were measured at different strains (Figure 3-73). Despite scatter still present in the data, now due to limited focus in the images, the data suggests that there is a small increase in the ripple wavelengths as the fiber is stretched, followed by a partial decrease in the wavelengths after fracture occurs. After fracture, the wavelengths do not return to their original measured lengths due to some initial slack present in the fiber, which is apparent in the images. What the results conclusively indicate is that the ripples seen on the surface of the fiber do not completely disappear as the fiber is strained up to fracture, so the CNTs never straighten out completely. It is possible that fracture occurs due to high localized stresses concentrated near the grips (near the right grip in this case), and that most of the CNTs are not fully strained along their length by the time fracture occurs. Indeed, the actual length of each CNT is much longer than the length of the fiber due to the tortuous path of each CNT. Even at a failure strain of 13.4% for this fiber, the CNTs may still contain substantial slack, so that only marginal measured changes in the wavelengths of the ripples on the surface of the fiber would be measured by the time the fiber fractured due to stress concentrations at the right grip.

Several similar tests were conducted on other fibers to further study structural changes in the fibers during loading, but the quality of the high magnification images was not sufficiently satisfactory to make reliable measurements. There is considerable scope for further investigation on this topic, but a better experimental setup is needed, specifically a higher resolution SEM equipped with a displacement stage. To study changes in the CNTs during loading, it would be particularly useful to work with individual or very small groupings of CNTs, since the large fibers studied in this work become unwieldy to work with when studying CNTs at high magnifications.
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Figure 3-70: Selected images of a fiber and its surface during a displacement experiment at different levels of strain. At each level of strain, an image of the fiber is shown on the left, and an image of the surface of the fiber near the left grip is shown on the right.

Figure 3-71: Mean measured ripple wavelength on the fiber surface as a function of fiber strain, (a) measured at 2500x magnification and (b) measured at 4000x magnification. The error bars show the standard deviation of the measurements.
Figure 3-72: Three locations on the surface of the fiber at which ripple wavelengths were measured, labeled A, B and C.

Figure 3-73: Measured wavelengths of the ripples as a function of strain at (a) location A, (b) location B, and (c) location C.
3.7. Conclusions

Carbon nanotubes grown as forests using a thermal chemical vapor deposition process have been investigated as a material for springs. Macroscopic groupings of continuous CNTs in fibers have demonstrated maximum reversible energy storage of 670 kJ/m\(^3\) or 6.9 kJ/kg, more than ten times the gravimetric energy density of steel springs, and half the volumetric energy density of steel springs. Higher volumetric energy density could be achieved with greater densification of the CNTs in the fibers, which is currently limited by CNT tangling and disorder. The highest recorded stiffness and strength of the fibers are 68 N/tex and 2 N/tex, respectively. The ideal stiffness and strength of CNTs are 448 N/tex and 27 N/tex (considering a conservative 6% elastic strain limit), respectively. The measured stiffness and strength of the fibers fall short of ideal CNT properties because of non-idealities in the testing process and non-idealities in the material. Specifically, the structure of the CNTs in the fibers deviates significantly from the ideal model of perfectly aligned, defect-free, crystalline CNT bundles. The energy density and specific strength and specific stiffness of CNT fibers are plotted in Figure 6-1 and Figure 6-2 to compare the properties of CNT fibers to the properties of CNT yarn and other common engineering materials.

SEM and TEM imaging, tension tests, video imaging, Raman spectroscopy, and resistance measurements during tension tests have provided valuable insights into the structure of the fibers and the mechanisms governing their mechanical behavior. While elastic loading is optimal for reversible energy storage, many of these tests have indicated that there are mechanisms taking place within the fibers that cause loading of the CNTs to deviate from purely elastic behavior. It has been shown that CNTs bear load non-uniformly within a fiber so that the measured strength, stiffness and energy storage capabilities of the fibers are lower bounds. Densification using capillary effects was shown to be an effective way to consolidate CNTs and create high performance fibers since the CNTs self-assemble into dense, interacting networks that promote load transfer; mechanical densification, which is done in a more disorderly manner, proved to be less effective. Raman spectroscopy revealed that loading fibers cyclically to emulate conditions expected of a spring in real applications results in the gradual accumulation of permanent defects in the CNTs.

Many of the conducted experiments have highlighted challenges of working with macroscopic groupings of CNTs. These include difficulties of loading all of the millions of CNTs in fibers uniformly at once, particularly because the CNTs are tangled and disordered, have different lengths because of their tortuous paths, and few interconnections between CNTs result in minimal inter-CNT load transfer. Measured strength, stiffness and energy density increase with decreasing fiber size because non-uniformities in the fibers and non-idealities in the grips become more pronounced in larger CNT groupings. The dependence of strength, stiffness and energy density on fiber size limits the usefulness of reporting the mean values of these properties since the mean values largely reflect the span of fiber sizes tested rather than the potential of this material, which is better represented in smaller fibers in which the effects of non-idealities are less pronounced. Grips can lead to stress concentrations, so it is particularly important to design grips that grip all CNTs throughout a cross-section and load them uniformly.

Further work is needed to improve the properties of CNTs from forests as a material for springs. More research is needed to study the forest growth process in order to produce aligned arrays of CNTs with much lower defect densities, less tortuosity, better alignment, and higher packing densities. Greater crystallinity of the CNTs within the fibers would increase load transfer
and improve the elasticity of the springs. Growing forests made of SWCNTs rather than MWCNTs is an important step towards producing fibers with better performance as springs because it can be difficult to transfer load to the inner shells of MWCNTs, and these shells therefore do not contribute to storing energy. SWCNTs have smaller diameters and can be packed more densely to achieve higher energy density. It is possible that coatings on the CNTs or functionalization could be used to improve inter-CNT load transfer, as long as they don’t degrade the CNT properties. Progress in many of these areas could significantly improve the elastic properties of the fibers and increase their energy storage capacity as springs, toward their eventual realization as elements of microscale power systems.
4. Carbon nanotube yarn

4.1. Introduction

The second type of carbon nanotube material studied is carbon nanotube yarn. Samples of yarn for study have been provided by Nanocomp Technologies Inc. The yarn is made of individual CNTs spun together into a dense network. The yarn is composed of only CNTs, without a matrix material. The fibers (or continuous filament yarn) discussed in Chapter 3 contain CNTs that span the length of each fiber, while spun yarn is instead made of CNTs that are shorter than the total length of the yarn. In yarn, the constituent CNTs are tightly woven together to create a continuous, load-bearing material. The spinning process can be used to control the diameter of the fabricated yarn, and can produce yarn of any desired length, from millimeters to kilometers. The scalability of the process makes yarn a promising material for springs since the size of the spring, which controls energy storage capacity, can be tailored for different applications. For high performance springs, it is necessary for yarn to closely match the elasticity and properties of the constituent CNTs. Scaling arguments and spun yarn models suggest that CNTs are an ideal material for yarn: higher strength spun yarn is achieved as filament diameter decreases, as the number of filaments increase, and as packing density increases (refer to section 2.7.2). Models of spun yarn further suggest that spun yarn made of CNTs can be expected to closely match the strength of the constituent CNTs if the yarn contains an optimal twist angle to maximize radial pressure while minimizing effects of obliquity, high friction between CNTs, long CNT lengths, a high degree of migration, and high packing density.

Mechanical tests were conducted to characterize the properties of the yarn and to study its performance as a potential material for energy storing springs. These mechanical tests include tension tests to failure, cyclic loading tests, creep and stress relaxation tests, simultaneous stress and resistance measurements, video imaging, SEM imaging during tension testing, and Raman spectroscopy during tension testing. The tests were used to measure the elasticity of the yarn, to relate the structure of the yarn to its mechanical properties, to study structural changes and defect formation within the yarn as a result of loading, to measure its energy density, and evaluate its potential as a material for reversible energy storage.

4.2. Synthesis and morphology

The yarn (Figure 4-1) is made of CNTs that are synthesized using a chemical vapor deposition process and spun into yarn from the vapor phase. The CNTs are reported to be 1 nm diameter single-walled CNTs (SWCNTs) and about 1 mm long, though neither the diameter nor the length of the CNTs have been confirmed. Variations in the growth process, including temperature, gas composition and catalyst, and variations in the spinning process, including the twisting technique and solvent densification, can produce yarn with different cross-sectional shapes, areas, densities and properties. The particular yarn that has been studied in this thesis has a round cross-sectional area with an average outer diameter of 47 μm, a linear mass density of 2 mg/m, and a density of 1152.8 kg/m³.
Assuming that the yarn is composed of 1 nm diameter SWCNTs with a shell density of 2230 kg/m$^3$, and considering a shell thickness of 0.34 nm, the linear mass density of each of SWCNT is $2.382 \times 10^{-9}$ mg/m. Assuming alignment of the CNTs along the axis of the yarn, approximately 840 million CNTs pass through the yarn’s cross-section.

SEM pictures of the yarn in Figure 4-2 show that the yarn has a relatively uniform diameter along its length. Wave-like ripples on the surface of the yarn show evidence of densification using a solvent, and the twist applied to the yarn during spinning is visible in the structure at low magnification. At the highest magnification, dense networks of disordered but highly contacting CNT bundles are visible. Alignment of the bundles is not necessarily along the direction of the yarn axis.

Figure 4-1: CNT yarn wrapped around a spool.
4.3. Experimental setup

4.3.1. Tension tests

Tension tests were conducted using an Instron 8848 MicroTester with a 10 N load cell in the MIT NanoMechanical Technology Lab. To grip the yarn during testing, short yarn samples were mounted onto thick paper frames using epoxy (Pacer Z-Poxy) (Figure 4-3a). Additional samples were prepared by mounting yarn samples onto frames coated with copper using a silver-based conductive epoxy (MG Chemicals 8331-14G) (Figure 4-3b). Thin copper wires were epoxied onto the copper surface to enable four-point probe resistance measurements during tension tests using a Signametrics SMU2060 multimeter.

To measure the displacement and strain in the yarn during a tension test, small white paint dots were applied to the surface of the yarn. Sequential, high resolution images were taken of the yarn during loading using a Spot Idea camera. Displacement data was obtained by analyzing the
images using Vic-2D image processing software to track the displacement of the dots during a test. This technique provided accurate displacement data for the yarn, and eliminated the need to consider the effects of epoxy compliance or inaccuracies in the Instron’s displacement data. Strain gauges can typically not be used for material of such small size. The testing setup, showing the Instron, the imaging equipment and a yarn sample mounted for testing in the Instron grips, is shown in Figure 4-4. The setup for measuring the resistance across yarn samples during testing is shown in Figure 4-5.

![Figure 4-3: Schematic diagram of yarn samples mounted on frames for tension testing.](image)

Figure 4-3: Schematic diagram of yarn samples mounted on frames for tension testing.

![Figure 4-4: (a) Testing setup showing the Instron, the imaging equipment, and a yarn sample; (b) a yarn sample mounted on a frame in the Instron grips; the small white dots on the surface of the yarn are used to track yarn displacement.](image)

Figure 4-4: (a) Testing setup showing the Instron, the imaging equipment, and a yarn sample; (b) a yarn sample mounted on a frame in the Instron grips; the small white dots on the surface of the yarn are used to track yarn displacement.
4.3.2. Grips for tension tests

Grips were needed to perform mechanical tests on the yarn. Different options for gripping the yarn considered were clamping grips, capstan grips and epoxy grips. There were challenges to working with each of these three types of grips. With clamping grips, there were concerns about the material slipping between the grips since the diameter of the yarn (~50 μm) is so small and the possibility that the clamps could add stress concentrations near the edges. Capstan grips require wrapping a material around the grips several times; the material wrapped around the grips carries an exponentially decreasing load and so it can extend during a tension test, creating compliance at the grips. Epoxy grips can easily be used to test small yarn samples, but the epoxy at the grips can be compliant. Epoxy grips were selected because they were straightforward to implement, could easily be used to test samples with small gauge lengths, and epoxy compliance, though measured to be small, does not affect the displacement and strain measured in the yarn using video imaging. A particular advantage of epoxy grips is that the epoxy can infiltrate the inside of the yarn. With capstan grips or clamping grips, only the perimeter of the yarn is directly gripped, and load transfer within the yarn is needed to transfer the load from the perimeter to the cross-sectional area. If epoxy infiltrates the yarn at the grips, then the grips load the entire yarn cross-section, making it the most effective of the three gripping techniques.

To examine epoxy infiltration in the yarn, the epoxy grips were cross-sectioned using a sharp blade. The blade caused the epoxy to cleave apart easily, and the cross-section shows that the yarn is cut cleanly across its cross-section with no fraying. The yarn is typically difficult to cut with a blade and otherwise fractures in a frayed manner, so the clean cleaving of the yarn in the grips suggests that the epoxy fully infiltrated the yarn’s cross-section. Within the epoxy, the typically round cross-section of the yarn takes on a more skewed shape. The silver particles in the epoxy do not infiltrate the yarn since the particles are too large. SEM images of yarn in conductive epoxy grips are shown in Figure 4-6, and optical microscope images of yarn in non-
conductive grips are shown in Figure 4-7. Both sets of images indicate that epoxy has infiltrated the yarn cross-section, to enable loading across the entire cross-section.

Figure 4-6: Cross-sections of yarn in conductive epoxy grips: (a) cross-section showing the yarn in epoxy on the copper frame; (b) and (c) show the yarn in the epoxy surrounded by silver particles that do not infiltrate the yarn; (d) close-up of the yarn from the image in (c).
4.3.3. Scanning electron microscope displacement stage

To image the loading and fracture of the yarn, tension tests were conducted using a displacement stage that operates inside of a large chamber SEM (LEO VP 438). High resolution images and videos of the yarn were recorded during tension tests. The stage was originally designed and built by Don Galler, and then adapted for testing CNT fibers and yarn. To prepare the yarn for testing, yarn samples were mounted onto copper frames using conductive epoxy (MG Chemicals 8331-14G). To apply a strain to the yarn, the frames were clamped onto a translation stage that had a linear position finely controlled by a motor. Images of the displacement stage with the SEM are shown in Figure 3-16. A load cell that was originally part of the stage was removed because of error and drift in the force readings, possibly a result of the vacuum in the chamber that caused the load cell to malfunction. Therefore, strain in the yarn was known during loading, but there was no force data available.

4.4. Electrical properties

4.4.1. Yarn resistivity

The resistivity of the CNT yarn was measured using four-point probe resistance measurements with a SMU2060 multimeter. Resistance measurements were taken across different yarn lengths and at different yarn locations to account for variations of yarn properties. Measured resistance is plotted as a function of length divided by area in Figure 4-8 (considering a constant mean yarn diameter of 47 μm). A linear fit to the data was used to calculate a mean resistivity of 3.35 x10^-6 Ω m.
4.5. Mechanical properties

4.5.1. Tension to failure

Stress-strain curves of several yarn samples tested in tension to failure are shown in Figure 4-9. The 6 yarn samples whose stress-strain curves are plotted in Figure 4-9 all have a gauge length of 5 mm ± 0.09 mm. The curves show that the yarn loads non-linearly, with a high initial stiffness and a gradual decrease in stiffness up to the failure strain. The curves also display a distribution of curve shapes, and strength, stiffness and failure strain values vary among samples that are nearly the same length, indicating a degree of variability in the properties of the yarn.

To test the properties of the yarn at a given length, 34 yarn samples with average gauge length of 4.8 mm (standard deviation of 0.25 mm) were prepared and tested in tension to failure at an extension rate of 0.004 mm/s. Each piece of yarn was originally 1.5 cm long before being attached to a testing frame, and the order in which the yarn samples were cut from the yarn spool was tracked in order to study how the properties of the yarn varied with spatial position. Strength, stiffness and failure strain are plotted as a function of gauge length, and specific strength is plotted as a function of specific stiffness in Figure 4-10. Based on these samples, at a mean gauge length of 4.8 mm, the yarn has an average strength of 0.86 N/tex or 1.0 GPa, with a standard deviation of 0.093 N/tex or 0.11 GPa. The average yarn stiffness is 44.7 N/tex or 51.5 GPa, with a standard deviation of 8.4 N/tex or 9.7 GPa. The yarn has an average failure strain of 0.034, with a standard deviation of 0.005. The plot of specific strength as a function of specific stiffness shows a correlation between the strength and stiffness of the yarn samples, with a correlation coefficient of 0.62. In ideal yarn, strength should be governed by the weakest point in the yarn caused by defects, while stiffness is determined by the average modulus throughout the yarn cross-section and yarn length and should be less affected by defects [69], so a correlation between the two properties is unexpected. A correlation between the two properties suggests that the yarn is not ideal and some mechanism must affect both the yarn’s stiffness and the load at which it fails. One hypothesis is that the mechanism is slip. If more slip occurs during loading at low strains, then measured stiffness is lower and failure will likely occur at a lower strength.
Correspondingly, if less slip occurs during loading at low strains, then higher stiffness will be measured and the yarn is more likely to reach a higher strength before failure. Alternatively, the correlation between strength and stiffness in the yarn may be due to variations in the yarn diameter over the entire gauge length or a portion of the gauge length of each sample, since the analysis assumes a fixed diameter of 47 μm.

The strength, stiffness and failure strain of the samples are plotted as a function of the order in which each sample was cut from the yarn spool in Figure 4-11 to study how properties vary spatially along the yarn length. The results show that while the data contains considerable scatter, some spatial structural continuity must be present in the yarn as it is spun since the strength, stiffness and failure strain of a yarn sample are sometimes close to the mean of the properties of its two neighbors. The period of the correlation appears to be no more than 5 samples, which corresponds to a yarn length of 7.5 cm. Strength shows the most spatial continuity, while failure strain appears to be most random.

Figure 4-9: Stress-strain curves of yarn samples tested in tension to failure. The samples have a gauge length of 5 mm.
Figure 4-10: Strength, stiffness and failure strain plotted as a function of gauge length and specific strength plotted as a function of specific stiffness for yarn samples with an average gauge length of 4.8 mm.
The next step was to determine whether there was a relationship between the mechanical properties of a yarn sample and its gauge length. Fifty three yarn samples were prepared with gauge lengths ranging from 0.98 mm to 44.2 mm. The samples were tested in tension to failure at an extension rate of 0.004 mm/s. Strength, stiffness and failure strain are plotted as a function of gauge length, and specific strength is plotted as a function of specific stiffness in Figure 4-12. Failure strain and strength appear to decrease with gauge length, although to establish a more definite relation a greater number of data points, particularly at larger gauge lengths, would be needed. This is an expected result since strength and failure strain are determined by the weakest point in the yarn, and longer samples have a higher probability of containing weak locations. The correlation coefficient between specific strength and specific stiffness is 0.08, indicating a weak relation between the two properties. It is not known why the correlation coefficient here is much lower than the value seen previously for samples with mean gauge lengths of 4.8 mm. Many more samples were tested at a mean length of 4.8 mm than at other lengths, and there was greater variability at that single gauge length than at smaller or larger gauge lengths. This suggests that a similar variability would be observed for samples both longer than and shorter than 4.8 mm, though more samples would be needed for confirmation.

In this data set, the yarn has an average strength of 0.84 N/tex or 0.97 GPa, an average stiffness of 48.2 N/tex or 55.5 GPa, and an average failure strain of 0.031.
recorded strength of the yarn is 1.0 N/tex or 1.15 GPa, and the maximum recorded stiffness of the yarn is 97.4 N/tex or 112 GPa.

Videos and images of the yarn during loading in tension and failure were obtained using the SEM displacement stage. The images in Figure 4-13 show a yarn sample prior to testing and after fracture has occurred. Video recordings of yarn tension tests show that fracture occurs very suddenly and frames showing intermediate or partial fracture could not be obtained. The fracture zone is defined as the length of yarn immediately adjacent to the failed end whose appearance differs from the remaining yarn [114]. The fracture zone of the yarn is short, typically no more than 20-30 μm long, which is small relative to the diameter of the yarn of about 50 μm and the length of the constituent CNTs of about 1 mm. Failure in yarn could be the result of pullout due to slip between CNTs, fracture of the CNT covalent bonds, or a combination of both. Fracture dominated by slip is associated with weak inter-CNT interactions and low radial pressure, while higher strength and stiffness are expected if fracture occurs by breaking the covalent bonds. Given that the short length of the fracture zone is much smaller than the average CNT length of 1 mm, failure of the yarn must be dominated by fracture of the constituent CNTs.

Figure 4-12: Strength, stiffness and failure strain as a function of gauge length, and specific strength as a function of specific stiffness for a range of gauge lengths.
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Figure 4-13: Images of yarn tested in tension to failure using the SEM displacement stage showing the yarn before testing and after fracture, along with higher magnification images of the fractured ends.
4.5.2. Strain distributions in yarn during tension tests to failure

Strain measurement using video imaging can be used to measure strain in different regions of a yarn sample. During loading to failure, strain can vary within the yarn because of structure non-uniformities or varying slip along the yarn length. Figure 4-14 shows results from a test in which three dots were applied to the surface of a sample of yarn. The strain between the upper two white dots was higher than the strain between the lower two white dots, while the strain between the outer two white dots was a weighted mean of the strain in the two sub-sections. When one part of the yarn had a higher strain than other regions, fracture occurred in that region in most cases. For example, in the yarn sample shown in Figure 4-14, fracture occurred between dots 1 and 2 where strain was higher. Similarly, in the test shown in Figure 4-15, highest strain was measured between dots 3 and 4, and this is where fracture occurred. Nonetheless, some tests showed nearly uniform strain across the yarn. The yarn sample shown in Figure 4-16 had only small variations in the strain between the top and bottom pairs of white dots. In cases where uniform strain was measured, it is more difficult to predict where fracture would occur.

Figure 4-14: (a) Strain as a function of time during a tension test to failure, measured in different regions of the yarn; (b) image of the yarn before the test, indicating the different yarn regions; (c) image of the yarn after fracture. Fracture occurred in the yarn in the region with the highest strain.
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Figure 4-15: Strain as a function of time during a tension test to failure, measured in different regions of the yarn; (b) image of the yarn before the test, indicating the different yarn regions; (c) image of the yarn after fracture. Fracture occurred in the yarn in the region with the highest strain.

Figure 4-16: (a) Strain as a function of time during a tension test to failure, measured in different regions of the yarn; (b) image of the yarn before the test, indicating the different yarn regions; (c) image of the yarn after fracture. In this case, strain was nearly uniform in the yarn, so the location of fracture was difficult to predict.

4.5.3. Analysis of yarn strength using Weibull statistics

The variability of the yarn's strength data at one gauge length as well as at different gauge lengths suggests that yarn failure is stochastic. Weibull statistics assume that a material's...
strength is governed by a statistical distribution of pre-existing critical defects in the material, based on a weakest-link model, and that the number of critical defects is proportional to the volume of the material [116, 117]. Such a model could explain why shorter yarn samples have higher strength. Certainly, non-homogeneity in the composition of the yarn apparent in SEM images at both the microscale and the nanoscale suggests that critical flaws could be randomly distributed throughout the yarn, which would lead to variations in the yarn properties. Weibull statistics have previously successfully been used to explain the stochastic distribution of fracture strengths of individual CNTs [116-119], but yarn failure is the result of a more complex combination of the fracture of many CNTs as well as interfacial slip between many CNTs. Indeed, flaws in yarn that can cause failure can be the result of defects in the individual CNTs, or flaws in the yarn’s organization, related to packing density, bundling, twisting, microbuckling or migration [130]. Nonetheless, previous work on cotton-polyester yarn has shown that a classical Weibull weakest-link model can accurately model the relationship between yarn strength and gauge length as long as the gauge length remains greater than the length of the constituent filaments [114]. In this section, Weibull statistics are studied to determine whether the models can be used to predict the strength of CNT yarn.

To test the model for yarn, strength data from 34 tests on yarn with average gauge length of 4.8 mm (standard deviation of 0.25 mm) is first examined. The specific strength of these yarn samples is plotted as a function of gauge length in Figure 4-10. Next, strength data from 53 tests on yarn with gauge lengths ranging from 0.976 mm to 44.2 mm is examined to study whether the Weibull model can account for strength variations as a function of gauge length. The specific strength of these yarn samples is plotted as a function of gauge length in Figure 4-12. Note that the data set contains many more measurements at a mean gauge length of 4.8 mm than at smaller and longer gauge lengths; this is a limitation of the data set that could affect the results. The yarn strength data is first fit to a Weibull statistics model that neglects variations in the gauge length, with a probability of failure at or below a stress \( \sigma \) given by

\[
P(\sigma) = 1 - \exp \left[ -\left( \frac{\sigma}{\alpha} \right)^{\beta} \right].
\]

(4-1)

and a second model that accounts for different gauge lengths of yarn samples, with a probability of failure at or below a stress \( \sigma \) given by

\[
P(\sigma, L) = 1 - \exp \left[ -\left( \frac{\sigma}{\alpha} \right)^{\beta} \right].
\]

(4-2)

where \( L \) is the yarn length, \( L_0 \) is a reference length, \( \beta \) is the Weibull shape parameter, and \( \alpha \) is the Weibull scale parameter. The shape parameter \( \beta \) is related to the width of the strength distribution function, while the scale parameter \( \alpha \) is the strength at which 63.2% of samples have failed. The probability of failure is calculated according to [117, 119, 120]

\[
P(\sigma_i) = \frac{i-0.5}{N},
\]

(4-3)

where \( i \) is the index of each sample ranked in order of increasing value of \( \sigma \) and \( N \) is the total number of samples.

To fit the yarn strength data to the first Weibull model in which length effects are neglected, equation (4-1) is rewritten as

\[
\ln(-\ln(1 - P(\sigma))) = \beta \ln \sigma - \beta \ln \alpha.
\]

(4-4)

Plotting \( \ln(-\ln(1 - P(\sigma))) \) as a function of \( \ln \sigma \) is used to calculate \( \beta \) from the slope and \( \alpha \) from the intercept. To account for changing gauge lengths, equation (4-2) is rewritten as [120]
\[ \ln(-\ln(1 - P(\sigma))) = \beta \ln \left( \frac{L}{L_0} \right)^{1/\beta} \sigma - \beta \ln \alpha. \]  \hspace{1cm} (4-5) \\
\[ \ln(-\ln(1 - P(\sigma))) = \beta \ln s - \beta \ln \alpha, \]  \hspace{1cm} (4-6)

where \( s = \left( \frac{L}{L_0} \right)^{1/\beta} \sigma \). A least squares algorithm is implemented to solve for \( \beta \) and \( \alpha \). For data following a Weibull distribution, the average strength at a particular length \( L \) is given by [120]

\[ \bar{\sigma}(L) = \alpha \left( \frac{L}{L_0} \right)^{-1/\beta} \Gamma(1 + \frac{1}{\beta}). \]  \hspace{1cm} (4-7)

where \( \Gamma \) is the gamma function.

Considering only the yarn data with a mean gauge length of 4.8 mm, a Weibull plot for the model that neglects changes in the gauge length is shown in Figure 4-17a. The shape parameter \( \beta \) is 9.8760, the scale parameter \( \alpha \) is 0.9022 N/tex, and the correlation coefficient is 0.9566. Accounting for changes in gauge length in the model, the shape parameter \( \beta \) is 9.9905, the scale parameter \( \alpha \) is 0.9011 N/tex, and the correlation coefficient is 0.9567; the Weibull plot is shown in Figure 4-17b. With the small range of gauge lengths considered, accounting for the changing gauge length in the model only slightly improves the performance of the model. The high correlation coefficient in both cases indicates a good fit of the Weibull model to the data.

Considering the entire data set of 53 yarn samples with lengths ranging from 0.976 mm to 44.2 mm, a Weibull plot for the model that accounts for changes in the gauge length is shown in Figure 4-18. The shape parameter \( \beta \) is 12.13, the scale parameter \( \alpha \) is 0.8808 N/tex, and the correlation coefficient is 0.8465. The lower correlation coefficient once strength data at a wide range of gauge lengths is considered suggests that the yarn does not strictly follow the weakest-link theory.

The results indicate that Weibull statistics can be accurately used to model the stochastic nature of the failure strength of yarn at one gauge length, but it is less successful at modeling the dependence of strength on gauge length. There are a few possible explanations why that is the case. First, there may not be sufficient data at short and long lengths to accurately depict variation of strength with gauge length, since more variability was measured at a mean length of 4.8 mm, where more than half of the data was taken, than at longer and shorter gauge lengths. Second, there is a similar level of variability in the yarn stiffness data as there is in the strength data. Flaws modeled in Weibull statistics would affect the variability of strength but not stiffness data, so there may be additional phenomena taking place during loading, such as the effects of slip, that affect both the strength and stiffness data that are not accounted for in the Weibull model. Third, yarn failure is a complex process that may not depend primarily on individual critical flaws. Slip and the resulting yarn elongation observed during tension tests weaken the yarn and occur throughout the length of the yarn, not only at localized regions. Additionally, the fracture of a single CNT can be accommodated in the yarn through a buildup of lateral pressure due to the yarn’s twist angle, so that a single critical flaw in a CNT does not ultimately result in yarn failure [69]. It is postulated that yarn failure occurs due to a combination of slip and fracture of many CNTs in one region of the yarn, which creates an instability and ultimately leads to failure, a sufficiently complex process that is not completely described by the two-parameter Weibull model.

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Figure 4-17: Weibull plots for the strength of CNT yarn samples with a mean length of 4.8 mm, (a) neglecting changes in the gauge length and (b) accounting for changes in the gauge length, with \( s = \left( \frac{L}{L_0} \right)^{1/\beta} \sigma \).

Figure 4-18: Weibull plot for the strength of CNT yarn with a gauge length range of 0.98 mm to 44.2 mm, accounting for changes in the gauge length, with \( s = \left( \frac{L}{L_0} \right)^{1/\beta} \sigma \).

4.5.4. Resistance changes during tension tests to failure

Resistance was measured across the yarn during tension tests to failure to gain a further understanding of structural changes taking place in the yarn during loading. Resistance across the yarn was measured using a four-point probe measurement. The resistance measurement includes the resistance of the wire leads, the conductive epoxy and the yarn. During a test, a change in the measured resistance is expected to be only due to changes in the yarn. The yarn samples tested
were on average 4.6 mm long and were loaded in tension at an extension rate of 0.004 mm/s. The results showed a gradual increase in the resistance as the yarn was strained, and the resistance abruptly rose to infinity once fracture occurred. Specific stress and resistance during a typical test are plotted in Figure 4-19. In this test, the starting resistance across the wires, yarn and epoxy was 28.5 Ω, which increased to 45.1 Ω immediately before fracture. The increase of 16.6 Ω is the result of structural and resistivity changes in the yarn.

In a given material of length $L$, cross-sectional $A$ and resistivity $\rho$, the electrical resistance across the material is

$$ R = \rho \frac{L}{A}. \quad (4-8) $$

Changes in the resistance of the material are due to changes in geometry and resistivity:

$$ \frac{\Delta R}{R} = \frac{\Delta \rho}{\rho} + \frac{\Delta L}{L} - \frac{\Delta A}{A}. \quad (4-9) $$

For a material in uniaxial tension, $\frac{\Delta L}{L} = \varepsilon$ and $\frac{\Delta A}{A} = -2\nu \varepsilon$ where $\nu$ is the Poisson ratio of the material.

Piezoresistance is the change in resistance of a semiconductor due to an applied stress. Since the CNT yarn contains a mix of chiralities and includes some semiconductors, it exhibits piezoresistivity. The relative change in resistivity in a material loaded in uniaxial tension is given by

$$ \frac{\Delta \rho}{\rho} = \pi \sigma = \pi E \varepsilon \quad (4-10) $$

where $\sigma$ is the applied stress in the axial direction, $E$ is the Young’s modulus and $\pi$ is the piezoresistive coefficient of the material. Rewriting equation (4-9),

$$ \frac{\Delta R}{R} = (\pi E + 1 + 2\nu)\varepsilon \quad (4-11) $$

The piezoresistive gauge factor $GF$ is defined as the ratio of the relative change of resistance to the applied strain [121], or

$$ GF = \frac{\Delta R}{R \varepsilon} \quad (4-12) $$

such that

$$ GF = (\pi E + 1 + 2\nu). \quad (4-13) $$

When a strain is applied to a piezoresistive material, the expected change in resistance is

$$ \Delta R = GF \cdot R \cdot \varepsilon \quad (4-14) $$

The gauge factor accounts for both changes in dimensions and changes in resistivity due to an applied load, but it does not account for other structural changes that could be taking place in the yarn to affect resistance: changes in CNT network interactions, slip between CNTs, and atomic defect generation in the CNTs. For the test shown in Figure 4-19, the starting measured resistance was 28.5 Ω, of which 9.5 Ω is attributed to the resistance across the yarn considering a yarn resistivity of $\rho = 3.35 \times 10^{-6} \, \Omega \cdot m$, a gauge length of 4.9 mm and a yarn diameter of 47 μm. The expected increase in resistance in the yarn from 0 strain up to the failure strain of 0.034 is 2.1 Ω considering a gauge factor of 6.4 (see section 4.5.7). Since the actual change in resistance is 16.6 Ω, additional structural changes must be contributing to the increase in resistance.
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4.5.5. Cyclic loading

Mechanical springs are expected to store and release energy repeatedly. Elasticity is an important characteristic of a spring to ensure that the spring’s performance does not degrade over time. To test the behavior of the yarn as a mechanical spring, yarn samples were loaded cyclically in tension.

A stress-strain curve from a cyclic loading test is shown in Figure 4-20a. The yarn had an initial length of 5.39 mm long and was loaded five times to strains between 0 to 2.23% at a rate of 0.05 cycles per second. Nonlinearity, hysteresis, and stress softening are all observed in the stress-strain curves. Stress softening, or preconditioning, is a change in the loading behavior following the first load. The loading behavior changes significantly as a result of the first load cycle, but subsequently remains mostly consistent, which indicates that permanent changes have taken place in the fiber as a result of increasing the maximum applied strain for the first time. Hysteresis may be the result of heat dissipation due to friction between CNTs or energy lost due to translation of defects within the CNTs. The peak amplitude of the specific stress during the test is plotted in Figure 4-20b, showing a decrease in the peak amplitude during the cycles. The length of the yarn is plotted in Figure 4-20c at the start of the test and at the end of each load cycle once the load in the yarn returns to zero, showing elongation of the yarn over the course of the test. Images of the yarn at the start of the test and at the end of each load cycle are shown in Figure 4-20d; elongation of the yarn is apparent in the images. The biggest increase in yarn length occurs during the first load cycle, with continual, gradual increases over subsequent cycles. The elongation is most likely attributed to slip between CNTs as the yarn is loaded. Since displacement control is being used to administer the test, the actual strain being applied to the yarn during a test decreases as the yarn elongates, and so it is expected that the load carried by the yarn would decrease. While elongation will contribute to a drop in stress, other factors such as defect generation or changes in the network interactions between CNTs may play a role as well. Figure 4-20e plots the measured specific stress and strain in the yarn as a function of time.

Figure 4-19: Specific stress and resistance during a tension test to failure while measuring the resistance across the yarn.
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The yarn carries no load during a portion of each cycle because it becomes slack as a result of the elongation. Strain is calculated to be the change in displacement between two points in the yarn divided by the distance between those two points at the start of the test. This calculation becomes inaccurate as the yarn permanently elongates over the course of a test, and the actual strain in the yarn will be lower. An accurate measure of strain was difficult to determine since the yarn can continuously elongate over the course of a test. The error in the strain data is apparent in Figure 4-20e since strain should be zero whenever load is zero.

To account for this error, strain is re-calculated to be the change in displacement between two points in the yarn divided by the distance between those two points at the start of each cycle. The length of the yarn at the start of each cycle is measured using video images. Note that this method provides a lower bound for the length of the yarn because the images provide only a two-dimensional projection of the yarn. This method does not account for elongation taking place during that cycle, but it does account for elongation from all previous cycles. Strain during the first cycle will contain the most error since that is when the most elongation occurs, but calculated strain in subsequent cycles should more closely match the actual strain. An updated stress-strain curve and a plot of specific stress and strain as a function of time using strain data that accounts for yarn elongation are presented in Figure 4-21. Now, the strain is closer to zero when the load is zero.
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![Graph showing specific stress at peak vs cycle number](image)

![Graph showing yarn length at end of cycle vs cycle number](image)

![Images of test samples at different cycles](image)
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Figure 4-20: (a) Stress vs. strain curve of yarn loaded cyclically in tension; the load cycles are numbered in order from 1 to 5; (b) specific stress at the peak load during each cycle; (c) yarn length at the start of the test and at the end of each cycle showing permanent yarn elongation; (d) images of the yarn at the start of the test and at the end of each cycle, showing yarn elongation; (e) specific stress and strain plotted as a function of time for the same test. Plots in (a) and (e) use a calculation of strain that does not account for yarn elongation.
Figure 4-21: (a) Stress vs. strain curve and (b) specific stress and strain as a function of time, using strain data that accounts for yarn elongation. The load cycles are numbered in order from 1 to 5 in (a).

4.5.6. Strain distributions in yarn during cyclic loading

Tension tests to failure showed that strain is not necessarily uniform in different regions of load-bearing yarn, and a similar result was observed when the yarn was loaded cyclically. Strain as a function of time for a representative test is plotted in Figure 4-22, accounting for yarn elongation in the strain calculation. It can be seen that higher strain was measured between the upper two dots than between the lower two dots. Strain between the outer two dots is the weighted mean strain of the strain between the upper and lower pairs of dots.
4.5.7. Resistance changes during cyclic loading

Resistance was measured across yarn samples during cyclic loading. Stress and resistance measured during a representative test are plotted in Figure 4-23. Resistance rises during the load portion of the first cycle, and then oscillates in a relatively stable manner during the following cycles. The initial jump in the resistance is associated with the preconditioning seen in the stress data. The resistance increase is attributed to a combination of permanent structural changes taking place in the yarn on the first load cycle that change the yarn’s conductivity (slip, changes in network interactions, defect generation), as well as to piezoresistance as strain is applied to the yarn. Based on the resistance and cyclic loading curves, the most significant structural changes take place in the yarn during the first load cycle. After the first load cycle, the relatively stable oscillations in the resistance are attributed mainly to piezoresistance (which includes changes in both geometry and resistivity), and that suggests that loading is predominantly elastic and reversible from the second to the fifth cycle. Note that other factors may contribute to the oscillations of the resistance in the yarn during cyclic loading in addition to piezoresistance; for instance, CNTs coming into or out of contact with each other as the fiber stretches and contracts would affect the resistance reversibly, so that the calculations for the piezoresistive gauge factor outlined below are approximate.

The resistance measurement plotted in Figure 4-23 includes the resistance of the conductive epoxy, lead wires and the yarn. However, any changes in the measured resistance are expected to be only the result of changes in the yarn. As seen in section 4.5.4, the piezoresistive gauge factor is defined as

\[
GF = \frac{\Delta R/R}{\varepsilon},
\]

(4-15)

where \( \varepsilon \) is the applied strain, \( R \) is the starting resistance of the material and \( \Delta R \) is the change in resistance due to the applied strain. For the yarn, cyclic loading tests are used to calculate the
gauge factor. The starting resistance across the yarn is estimated using the yarn’s resistivity, length and cross-section area, since this value is not measured directly. The change in resistance due to the applied strain $\Delta R$ is taken to be the mean amplitude of the stable resistance oscillations. The calculated piezoresistive gauge factor of the yarn is 6.4 with a standard deviation of 2.4.

The specific stress and resistance measured in a yarn sample during a cyclic loading test in which the applied displacement in the yarn was incremented after each set of five cycles are shown in Figure 4-24. At the end of the test, the yarn fractures and the measured resistance becomes infinite. The resistance across the yarn permanently increases after the first load cycle in each set, indicating that permanent changes take place in the yarn as a result of increasing the maximum applied strain for the first time. Following the first load of each set, the resistance oscillates in a relatively stable manner, suggesting the yarn can behave elastically after preconditioning has occurred, at any level of applied strain below the fracture strain.

Figure 4-23: Specific stress and resistance as a function of time during 5 loading cycles.
4.5.8. Long-term cyclic loading and resistance measurements

Yarn samples were loaded cyclically over many load cycles to measure their performance under conditions similar to those expected of a real application. The resistance across the yarn was simultaneously measured during the tests to gain additional insight into structural changes taking place in the yarn over the long-term. The results from a 4.65 mm long yarn sample cycled 200 times in tension are shown in Figure 4-25, and the results from a second 4.18 mm long yarn sample cycled 300 times are shown in Figure 4-26. In both tests, a sinusoidal strain with an amplitude of 2% was applied to the yarn at a rate of 0.05 cycles per second. The first plot in both figures shows the specific stress and resistance across the yarn during the first 20 cycles of the test, while the second plot shows the percentage of the maximum peak load reached in the yarn at each cycle and the resistance changes over the entire test.

The results show an initial increase in the resistance during the first load cycle, associated with structural changes taking place during preconditioning. After the first cycle, the resistance oscillates as load is applied and removed from the yarn. Beyond the first few cycles, the resistance across the yarn increases as it oscillates. Substantial increases in the resistance occur during the first 100 cycles, followed by more gradual increases from 100 cycles until the end of the tests. The changes in the resistance of the yarn during the tests are attributed to changes in the structure of the yarn. Examining the evolution of the peak load in the yarn, one can see that there is a rapid drop in the peak load of the yarn during the first 50 cycles, followed by a more gradual decrease from 50 cycles to the end of the tests. In both tests, there is no sign of stabilization occurring in the peak load. The observations are analogous to fatigue, though the mechanism for fatigue in yarn is likely not dislocations and nucleation of cracks as seen in a continuous material. The most likely explanation for the drop in the peak load is the gradual elongation of the yarn as a result of slip. As was seen previously in tests in which yarn was loaded cyclically five times in section 4.5.5, the most elongation occurs during the first cycle but continues
gradually over following cycles. Elongation may decrease the number of interconnections between CNTs, thereby increasing the yarn’s electrical resistance; loading may also promote nucleation or growth of defects or change the network interactions between CNTs, all of which may contribute to increasing the yarn’s resistance.

These tests indicate that loading of the yarn during 200 or 300 cycles is far from elastic, as structural damage accumulates in the material over time. Before implementing CNT yarn in a real device as a spring, the gradual drop in the load carried by the yarn as it is cyclically loaded must be addressed. The yarn could be preconditioned before being incorporated into a device, which would account for the change in elongation and loading behavior during the first few loading cycles. However, preconditioning will not account for the gradual change in behavior over subsequent cycles. The evolution of the mechanical behavior of the yarn as it is cyclically loaded must be accounted for by improving the organization of the CNTs within the yarn. SEM images of the yarn show considerable disorder at the nanoscale. Structural improvements within the yarn could include longer CNTs and longer CNT overlaps to increase inter-CNT load transfer; recall that overlap lengths of 10-120 μm have been suggested as minimum lengths required for bundles made of discontinuous CNTs to overcome the effects of slip (see section 2.1.3) [44, 47]. Yarn elasticity could potentially be improved with increased bundle size, longer range crystallinity, lower defect density, better alignment of CNTs along the yarn axis, increased packing density, and shorter CNT migration periods. These improvements should decrease the effects of slip and increase the elasticity of the yarn, which would make the yarn a more attractive material for implementation as an energy storage element in real devices.
Figure 4-25: Specific stress and resistance during 200 load cycles: (a) specific stress and resistance during the first 20 cycles; (b) evolution of the peak load and the resistance over the full 200 cycles.
4.5.9. Creep and stress relaxation

Given the evolution of the structure of the yarn over repeated load cycles, tests were conducted to evaluate whether the mechanical behavior of the yarn has a time-dependent component. Creep or stress relaxation exhibited by the yarn has important implications for its applicability as a mechanical spring. For a spring to be an effective energy storage element, it should load and store energy elastically. Yarn as an energy storage element in a practical device would be expected to carry a constant load over a long period of time at a given extension; any substantial degradation of the structure of a spring material while it is storing energy in a strained configuration would diminish the value of that material as a spring for energy storage.

Creep tests and stress relaxation tests were conducted on the yarn. Yarn samples were mounted on frames using epoxy. Strain and displacement in the yarn during the tests were measured by tracking small white dots painted onto the surface of the yarn. Since epoxy is a polymer that can exhibit viscoelastic behavior in series with the yarn, careful attention was paid to measure only stress relaxation and creep in the yarn.

To study creep, a 1 N load (corresponding to a specific stress of 0.5 N/tex or stress of 576 MPa) was applied to yarn samples over a period of five minutes. On average, the strain in the yarn increased by about 0.1% over a period of 5 minutes, and did not show signs of stabilization during this relatively short time period. Strain plotted as a function of time during a creep test is shown in Figure 4-27. Slip between CNTs is the most likely mechanism for creep in the yarn.

To study stress relaxation, a constant strain between 1.7-2% (depending on the sample) was applied to yarn samples during tests lasting 5 minutes or 60 minutes. Load in the yarn was
measured over the course of the test. The strain in the yarn was measured by tracking the distance between the white dots to verify that the strain in the yarn remained constant over the course of the test. This was done to ensure that there was no creep in the epoxy and that any measured changes in load were a result only of structural changes in the yarn. Across all stress relaxation tests, the measured strain in the yarn remained constant, to within measurement accuracy, indicating that there was no measureable creep in the epoxy. Figure 4-28 plots specific stress as a function of time for a test run for 5 minutes, and Figure 4-29 plots specific stress as a function of time for a test run for 60 minutes. In all tests, there was a rapid drop in the stress during the first few seconds of the test, followed by a slower, gradual drop in the stress over the remainder of the test. On average, the stress in the yarn dropped by 22% from the start to the end of a test over 5 minutes, and the stress dropped on average by 27% over 60 minutes. The majority of the stress relaxation occurred at the start of the test, though little stabilization could be observed in the stress data even after 60 minutes. As with creep, the primary mechanism responsible for stress relaxation is probably slip, which causes the yarn to permanently elongate so that the load carried in the yarn decreases over time.

These tests have shown that there is a time-dependent component in the mechanical behavior of the yarn, and that the yarn’s behavior deviates significantly from desired elastic behavior. Yarn that exhibits stress relaxation is impractical as a spring for long-term energy storage. Further improvements in the structural makeup of the yarn are still needed for the yarn to be implemented in real devices.

Figure 4-27: (a) A yarn sample mounted on a frame with epoxy for viscoelastic testing, showing the white dots used to measure strain in the yarn; (b) strain as a function of time during a creep test.
Figure 4-28: (a) Specific stress as a function of time during a stress relaxation test lasting 5 minutes; (b) plot of strain as a function of time for the same test showing that the strain in the yarn remains constant during the test.

Figure 4-29: (a) Specific stress as a function of time during a stress relaxation test lasting 60 minutes; (b) plot of strain as a function of time for the same test showing that the strain in the yarn remains constant during the test.

4.5.10. Energy and energy density

The reversible energy stored in the yarn was calculated by integrating the area under the unloading curves of yarn samples loaded cyclically. Yarn samples were cyclically loaded at a rate of 0.05 cycles per second to a maximum strain just below the failure strain of the yarn (which is variable for each sample). Each yarn sample was cyclically loaded five times, and the
energy stored in the yarn was calculated by integrating the area under the unloading curve of the fifth cycle. Using the fifth cycle to obtain the energy in the yarn provides only an estimate for the energy and energy density of the yarn because the load carried by the yarn loaded cyclically in tension continues to decrease beyond the fifth cycle, with little stabilization after several hundred cycles. Strain in the yarn was obtained by tracking white dots painted on the surface of the yarn, while load data was obtained from the Instron. Thirty samples were tested, with a range of gauge lengths from 1.9 mm up to 45.9 mm. An example of a cyclic loading curve used to calculate energy and energy density is shown in Figure 4-20.

Figure 4-30 plots the energy, energy per unit length, and volumetric and gravimetric energy density measured in yarn samples of different gauge lengths. While the properties of each yarn sample can vary to produce different measurements of energy and energy density, much of the scatter in the energy measurements is due to the difficulty of measuring the maximum energy density of each sample. The yarn was loaded cyclically to a strain just below its failure strain, and if the yarn did not fracture, further tests were performed, gradually increasing the applied strain with each test. Loading the yarn to an optimally high value of strain without causing fracture was challenging. Many tested samples had a mean length of 5 mm, and a smaller number of samples had a range of lengths below and greater than 5 mm. As expected, stored energy scaled linearly with gauge length. While a small dependence of energy density on length can be seen in the plots, suggesting that energy density decreases with yarn length, more variability was measured at the single length of 5 mm than at other lengths. It is expected that similar variability would be seen at lengths smaller and greater than 5 mm if a larger number of samples had been tested. From the data, a definitive relationship between energy density and length is difficult to establish.

Based on yarn samples with a mean length of 5 mm, the yarn had an average energy per unit length of 8.4 mJ/m (standard deviation of 2.0 mJ/m), an average gravimetric energy density of 4.2 kJ/kg (standard deviation of 1.0 kJ/kg), and an average volumetric energy density of $4.9 \times 10^3$ kJ/m$^3$ (standard deviation of $1.2 \times 10^3$ kJ/m$^3$). The highest measured energy density in the yarn is 7723.5 kJ/m$^3$ or 6.7 kJ/kg.
4.5.11. Raman spectroscopy during tension testing

Raman spectroscopy was performed on yarn during tension tests to study changes in the atomic structure of the CNTs during loading. Raman spectra were measured in yarn tested in tension to failure and tested cyclically in tension. A displacement stage was designed and built for the experiment. The stage is the same one described in section 3.6.10, though the 0.3 N force sensor used to measure the force in fibers was replaced with a 2 N force sensor (Strain Measurement Devices, S100), as shown in Figure 4-31. A micropositioner with 1 μm displacement resolution was used to extend the yarn. Yarn samples with gauge lengths between 2.9-3.5 mm were mounted on frames using epoxy (Figure 4-32). The displacement stage is shown with the Raman microscope in Figure 4-33. Raman spectra were recorded using a Horiba Jobin-Yvon LabRAM Raman Microscope with a 633 nm HeNe laser.

As described in section 3.6.10, Raman spectroscopy can be used to monitor strain in CNTs because stretching the carbon-carbon bonds weakens the bonds, lowers their vibration frequency, and produces downshifts in the D, G, and G’ Raman peak positions [125, 126]. Since the Raman signal is measured with a spot size of about 1 μm, the Raman spectra measured in the yarn are the result of signals averaged over many CNTs. A typical spectrum measured in the yarn is shown in Figure 4-34. The dominant features are a D band near 1330 cm⁻¹, a G band near 1585 cm⁻¹, and a G’ band near 2640 cm⁻¹. The G band is associated with vibrations of the carbon atoms tangential to the surface of the CNT, either along the CNT axis (G+) or in the circumferential direction (G.). In MWCNTs, the G band is wide and asymmetric due to the summed effects of diameter and chirality distributions [127]. The D band is due to a one-photon second-order Raman scattering process, while the G’ band is due to a two-photon second-order Raman scattering process [127]. The D band is observed only in the presence of disorder, defects or impurities in a CNT, particularly the presence of amorphous carbon [125, 128], while the G’
band does not require disorder to be observed since it is a two phonon process [125]. Defects in 
CNTs can include hetero-atoms, vacancies, heptagon–pentagon pairs, kinks, or impurities [128]. The ratio of the intensities of the G band peak to the D band peak can be used to assess the defect 
density in the CNTs [129].

Figure 4-31: A displacement stage with a 2 N load cell for simultaneously performing tension 
testing and Raman spectroscopy on CNT yarn.

Figure 4-32: Yarn mounted on a frame for testing.
The Raman data was analyzed by performing baseline correction and then fitting Lorentzian functions to the peaks. A sum of two Lorentzian functions was fit to the D, G and G' peaks since a single Lorentzian function did not fit the shape of the peaks satisfactorily. The frequencies and amplitudes of the bands were extracted from the curve fitting. Each Lorentzian function has the form
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\[ y = \frac{I}{1 + \left(\frac{x - x_0}{\gamma}\right)^2} \]  \hspace{1cm} (4-16)

where \( I \) is the amplitude of the peak, \( x_0 \) is the center frequency and \( \gamma \) is the half-width at half-maximum.

To measure the Raman spectra of the yarn during tension to tests to failure, each yarn sample was extended in small increments of about 10 \( \mu \text{m} \). After each displacement increment, a spectrum was recorded at three specific positions along the yarn. Strain in the yarn was measured by measuring the distance separating the edges of the two frames after each displacement increment using the optical microscope. The process of incrementing the displacement and then measuring the spectrum at three locations was repeated until the yarn fractured, and a final spectrum was recorded at each of the three positions after fracture. The direction of polarization of the laser was perpendicular to the axis of the yarn.

The results showed that there was a linear decrease in the \( G/D \) and \( G'/D \) peak intensity ratios as the yarn was strained. The \( G/D \) ratio decreased by 0.036 per \% strain (standard deviation of 0.037 per \% strain), while the \( G'/D \) ratio decreased by 0.0094 per \% strain (standard deviation of 0.011 per \% strain) during loading, prior to fracture. From the start of a test to immediately before fracture, on average the \( G/D \) and \( G'/D \) ratios decreased by 0.18 and 0.050, respectively. The decrease in these ratios is an indication of defects accumulating in the yarn during loading. After fracture, the \( G/D \) and \( G'/D \) ratios typically did not return to the original value at the start of the test, so at least a portion of the defects induced in the yarn during tension to failure tests were permanent. Some scatter in the data is present due to variations in the spectra with position in the yarn, which reflects spatial variations in the yarn’s composition and structure. The tests attempted to take spectra at three identical positions during loading. Deviating from the correct chosen position on the yarn by only a few microns changed the frequencies of the resonant peaks and the peak intensity ratios, thereby introducing error and uncertainty in the intensity ratios.

Shifts in the resonance peaks were measured to study the strain in the CNTs. On average across all tests, the \( D \) band peak shifted by 0.12 cm\(^{-1}\) per \% strain (standard deviation of 0.16 cm\(^{-1}\) per \% strain), the \( G \) band peak shifted by 0.13 cm\(^{-1}\) per \% strain (standard deviation of 0.21 cm\(^{-1}\) per \% strain), and the \( G' \) band peak shifted by -0.44 cm\(^{-1}\) per \% strain (standard deviation of 0.58 cm\(^{-1}\) per \% strain). Downshifts in the band peak frequencies were expected due to the lowered vibrational frequency of the carbon atoms from the applied strain, however the considerable noise in band peak data made trends difficult to detect. The band peak frequencies were expected to return to their starting frequencies after fracture and once the strain in the yarn was released, but noise in the data made it difficult to detect whether or not this actually occurred. There were two main sources of noise in the data. First, the spectra varied substantially with position along the length of the yarn and through its depth due to spatial variations in the yarn’s composition and structure. The difficulties of taking measurement at exactly the same three positions within the yarn over the course of a test introduced error into the band peak frequency data. Second, there was an upward drift in the frequencies reported by instrument of up to 3.1 cm\(^{-1}\) from the start to the end of each tension test, measured by taking a spectrum of cyclohexane before and after each tension test. The drift in the instrument produced considerable error in the data and masked shifts in the resonance peaks due to strain in the fibers since the amplitude of the shifts in the peaks over the course of a test was of the same magnitude as the amplitude of the drift in the instrument. To try to compensate for error in the instrument, the band peak data can be adjusted using a linear correction for the drift in the instrument over the
course of each test. Using this correction, the mean shift in the D band peak was $-0.065 \text{ cm}^{-1}$ per % strain (standard deviation of $0.080 \text{ cm}^{-1}$ per % strain), the mean shift in the G band peak was $-0.057 \text{ cm}^{-1}$ per % strain (standard deviation of $0.16 \text{ cm}^{-1}$ per % strain), and the mean shift in the G' band peak was $-0.62 \text{ cm}^{-1}$ per % strain (standard deviation of $0.49 \text{ cm}^{-1}$ per % strain). While these values may be more accurate representations of the actual peak downshifts in the strained yarn, it is difficult to draw conclusions from this data because it is likely that the drift in the instrument was not perfectly linear. Lower than expected shifts in the band peak frequencies could have been measured because the direction of polarization of the laser was perpendicular to the axis of the yarn.

The results from a tension test to failure on a yarn sample are shown in Figure 4-35. Figure 4-35a shows the stress-strain curve for the yarn during the test. Spectra were taken at each marker on the curve. Note that the failure strength is below the average of 0.84 N/tex, and the failure strain is greater than the average of 0.031; the lower strength and higher failure strain reflect creep taking place in the yarn over the course of a test. A complete test could take as long as 3 hours to run. During this time, the yarn had the opportunity to elongate due to creep, which contributed to high failure strain and weakened the yarn, resulting in a lower than expected failure strength. Figure 4-35b shows the legend for the next five plots: each of the three colors represents a unique location in the fiber. The peak frequencies of the D band, G band, and G' band are plotted as a function of strain in Figure 4-35c-d. The instrument upshifted by 1 cm$^{-1}$ from the start to the end of this particular test, about the same amplitude as the shifts seen in the D and G band peaks, therefore the upshifts seen in the D and G band peaks are attributed to instrument error. The downshift in the G' band is more significant since a net downshift in the G' band peak is seen despite the 1 cm$^{-1}$ upshift in the instrument. The G/D and G'/D peak intensity ratios, plotted in Figure 4-35f-g, decrease approximately linearly with strain; it is apparent from these two plots that the spectra can vary according to the position in the fiber, since the data points fall on three distinct lines. Finally, Figure 4-35h shows the change in spectra at ‘Position 1’ in the fiber as the yarn becomes strained. The spectra are normalized to the intensity of the G band. From the plot, it is apparent that the intensity of the D band increases relative to the G band as the yarn is strained.
Chapter 4. Carbon nanotube yarn

Next, the Raman spectra of the yarn were measured during tensile cyclic loading. To run these tests, a spectrum was taken at three specific locations in a yarn sample with no applied strain. Using the micropositioner, the yarn was alternately loaded to 1 N (0.5 N/tex), and then unloaded back to 0 N over multiple cycles, each time taking spectra at the same three locations. At each step, strain was recorded by measuring the distance separating the edges of the two frames using the optical microscope.

The test results showed that there was typically a drop in both the G/D and G'/D peak intensity ratios each time the yarn was loaded, followed by partial recovery once the load was removed. Over the course of several cycles, the G/D and G'/D peak intensity ratios in the yarn at zero load gradually dropped, indicating that cyclically loading yarn is only a partially elastic process since permanent defects accumulate in the CNTs. Averaging over all tests, the ratio of the G/D intensities dropped by 0.070 (standard deviation of 0.044) per cycle, and the ratio of the G'/D intensities dropped by 0.023 per cycle (standard deviation of 0.014). Drops in these ratios were consistent across all tests. As with the tension tests to failure, the ratios of the peak intensities were affected by spectra that varied with position in the yarn, which introduced noise into the data. Detecting shifts in the resonance peaks during cyclic loading was more difficult because of both spatial variations of the spectra in the fibers and drift in the instrument by as much as 1.1 cm\(^{-1}\) from the start to the end of a test. Nonetheless, the most apparent trend was that
the D, G and G' band peak frequencies often dropped each time a load was applied to the yarn, and recovered once the load was removed, with some scatter overlaid upon this trend. Any net change in the band peak frequencies from the start to the end of the test is mainly attributed to instrument error.

The results from a cyclic loading test on a yarn sample are shown in Figure 4-36. Figure 4-36a shows the specific stress in the yarn during the cycles. Figure 4-36b shows the legend for the next five plots: each of the three colors represents a unique location in the yarn, filled markers represent loading, and unfilled markers represent no loading. The peak frequencies of the D band, G band, and G' band are plotted as a function of strain in Figure 4-36c-d. Oscillations in the band peak frequencies can be seen as the yarn is loaded and unloaded. There are no net significant changes in the peak frequencies from the start to the end of the test, as expected (since there was no net instrument shift during this particular test). The G/D and G'/D peak intensity ratios, plotted in Figure 4-36f-g, decrease once a load is applied, and partially recover once the load is removed, with a net decrease in the G/D and G'/D ratios from the start to the end of the test of 0.125 and 0.329 respectively, indicative of permanent defects induced in the fiber. Finally, Figure 4-36h shows the change in spectra at ‘Position 1’ at cycle 1, cycle 3 and cycle 5. The spectra are normalized to the intensity of the G band. From the plot, it is apparent that the intensity of the D band increases relative to the G band over the course of the testing cycles.

Raman spectroscopy during tension tests to failure and cyclic loading on yarn complements the results of mechanical testing because Raman spectroscopy can provide insight into changes taking place at the atomic scale within the yarn. Both mechanical tests and Raman spectroscopy have revealed that loading yarn cyclically as a spring produces irreversible structural changes in the yarn: mechanical tests have revealed that the yarn elongates, and Raman spectroscopy has shown that permanent defects gradually accumulate. These results indicate that as yet the yarn is an imperfect material for springs since its loading is not fully elastic. Improvements in the structure of the yarn are still needed for the yarn to be a useful as a spring for practical implementation in real devices.
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**Position 1 - Unload**
**Position 1 - Load**
**Position 2 - Unload**
**Position 2 - Load**
**Position 3 - Unload**
**Position 3 - Load**

![Image](image.jpg)

(b)

(c)

(d)

(e)

Cycle

D band frequency (cm⁻¹)

G band frequency (cm⁻¹)
Figure 4-36: Results from a cyclic loading test on yarn: (a) specific stress in the yarn during the cycles; (b) legend explaining colors and markers for plots c-g: red, blue and black represent a unique location in the yarn, filled markers represent loading, and unfilled markers represent no loading; (c) D band peak frequency as a function of cycles; (d) G band peak frequency as a function of cycles; (e) G’ band peak frequency as a function of cycles; (f) ratio of the intensities of the G band to the D band; (g) ratio of the intensities of the G’ band to the D band; (h) overlay of the spectra normalized to the G band intensity at cycles 1, 3, and 5.
4.6. Conclusions

Tension tests to failure and cyclic loading tests were conducted to measure the properties and energy storage capabilities of CNT yarn. The mean strength of the yarn is 0.84 N/tex or 0.97 GPa, and the mean stiffness of the yarn is 48.2 N/tex or 55.5 GPa. The maximum recorded strength of the yarn is 1 N/tex or 1.15 GPa and the maximum stiffness of the yarn is 97.4 N/tex or 112 GPa. The yarn reversibly stores energy with a mean energy per unit length of 8.4 mJ/m and with a mean energy density of $4.9 \times 10^3$ kJ/m$^3$ or 4.2 kJ/kg. The maximum measured energy density in the yarn is $7.7 \times 10^3$ kJ/m$^3$ or 6.7 kJ/kg. The energy density and specific strength and specific stiffness of the yarn are plotted in Figure 6-1 and Figure 6-2 to compare the properties of yarn to the properties of CNT fibers and other common engineering materials.

SEM imaging of the yarn revealed that the yarn is made of dense networks of disordered but highly contacting CNT bundles, with imperfect alignment of the bundles along the yarn axis. Variation in the structure and composition of the yarn produced variability in the measured strength and stiffness of the yarn along its length. Cyclic loading curves showed hysteresis and preconditioning, so yarn behavior is far from the ideal elastic behavior expected of a spring. Strain was non-uniform along the length of the yarn, both during tension tests to failure and during cyclic loading tests, because of either structure non-uniformities or varying slip along the yarn length. A correlation between the strength and stiffness of yarn samples suggests that slip between CNTs affects both of these properties and plays an important role in the behavior of the yarn. As a result of slip, the yarn permanently elongated when it was stretched cyclically in tension. Slip resulted in stress relaxation, creep, and a gradual drop in the load bearing capability of the yarn when it was loaded cyclically in tension, akin to fatigue. Nonetheless, the short fracture zone in the yarn indicated that yarn failure occurred primarily as a result of fracture, rather than slip, though slip may play a role in weakening the yarn. To simulate conditions of a real spring, the yarn was loaded cyclically several hundred times in tension. During these tests, there was little stabilization in the drop in the load carried by the yarn or in the increase in the resistance across the yarn. Therefore, preconditioning the yarn before incorporating it as an energy storage element in a device would not account for the gradual deterioration of the yarn’s structure during long-term loading. Raman spectroscopy performed during tension to failure and cyclic loading tests complemented the results from the mechanical testing. The Raman spectra of the yarn revealed that atomic defects gradually accumulate in the yarn during cyclic loading, indicating that yarn behavior deviates substantially from elastic behavior as it is cyclically loaded in tension.

In its current form, the CNT yarn is not yet ready for implementation as a material for high performance springs. Improvements are still needed in the yarn’s composition and structure, which could include longer CNTs and longer CNT overlaps, increased bundle size, lower defect density, better alignment of CNTs along the yarn axis, increased packing density, more long range crystallinity, and shorter CNT migration periods. Potentially, cross-links between CNTs within the yarn could further improve load transfer; cross-links could be introduced through irradiation, functionalization of the CNTs, or through various CNT coatings. The objective of these improvements is to decrease the effects of slip, increase the elasticity of the yarn, increase the energy storage density of the yarn, and make the yarn more viable as a spring material for energy storage applications.
5. Devices powered by carbon nanotube springs

5.1. Introduction

As the properties of carbon nanotubes assemblies improve, the frontier for research into CNT springs moves to systems engineering and applications. This chapter presents practical demonstrations of devices powered by the energy stored in CNT springs. These devices have been built to study the system architecture needed to store energy in a spring and efficiently couple the spring to an external load, and to develop a set of guidelines that can be used to design more complex systems. Several of the designs discussed in this chapter remarkably combine CNTs, a material discovered only 20 years ago, with centuries-old power regulation technologies for springs developed by the watch-making industry. The practical implementations of CNT springs discussed in this chapter illustrate the potential of this new energy storage medium: CNT springs have the ability to drive both mechanical and electrical loads, can store small or large amounts of energy by scaling the size of the spring, and can output energy at range of power levels which can be tuned for different applications.

To date, the best CNT springs are those made of individual CNTs. An ideal system powered by a CNT spring with an energy density near the theoretical limit would have to be fabricated at the nanoscale with an individual or a small bundle of CNTs as the spring. Indeed, near-ideal strength and stiffness have been measured in individual and small bundles of CNTs, but the amount of energy that they can store is small since the energy stored in a spring scales with the cube of its linear dimension. The expectation is that there would be specialized applications for CNT springs at the nanoscale and at the microscale in MEMS devices, but there would be many more applications for CNT springs at the macroscale, particularly for applications that operate at high temperatures, high pressures, or require a combination of high energy density and high power density. While the properties of macroscopic assemblies of CNTs still fall short of ideal CNT properties, their properties have continued to improve over time. As a result, this work focuses on using macroscopic CNT assemblies to drive macroscopic loads.

The two materials studied in this thesis, fibers and yarn, are both candidates for springs to drive practical systems. The small size and good alignment of CNTs grown in forests make this material a suitable candidate for springs to drive nano and micro-scaled system. For larger scale systems, CNT yarn is more appropriate as a spring material. The yarn has consistent, well-characterized properties. The amount of energy stored in a spring made of yarn is flexible and can be adjusted by changing the size of the spring, since stored energy in a spring made of yarn scales with length and with the number of strands of yarn plied together across the cross-section. The devices described in this chapter use CNT yarn as the spring material. The yarn has been provided by Nanocomp Technologies Inc. The yarn has a diameter of 50 μm, a linear density of 2 mg/m, a mass density of 1152.8 kg/m³, and its properties and energy storage capabilities have been studied in Chapter 4. In section 5.7.2, a second, thicker type of yarn has been used; this yarn is flat and wide, has a width of 1 mm, a linear mass density of 9.55 mg/m and a mean ultimate strength of 970 MPa.

The first section in this chapter examines design considerations involved with using springs as power supplies, including issues of power output, friction and system architectures. The following sections describe in detail the design, operation and performance of a range of different CNT-powered devices: slingshots, escapements, mechanical watches, a kinetic energy
Chapter 5. Devices powered by carbon nanotube springs

harvester, a piezoelectric generator, and an electromagnetic generator. Particular emphasis is placed on examining the energy density, power density, and energy conversion efficiency of each of the devices.

5.2. Design considerations

5.2.1. System architecture

To store energy in a spring, the spring must first be deformed elastically. The spring must be latched in its deformed configuration in order to hold the stored energy in the system until use. To release the energy from the spring, the latch is removed and the energy stored in the spring is transmitted to the desired load as the spring returns to its undeformed shape. For springs to be useful energy sources, they require a supporting architecture. Mechanisms are needed to input energy to the spring, hold the spring in its deformed configuration, and transmit the energy to a load. When a spring is storing energy in its deformed configuration, a support structure is needed to support the load by providing a reaction force. When that reaction force is removed, energy is typically released from a spring in a single, rapid burst. However, the operation of many devices requires that they receive low power over a long period of time. To control power from a spring, power-regulation mechanisms are required. The details of the mechanisms implemented are application-specific and must be tailored to each spring and device design.

Both the spring and its supporting architecture must be taken into account when evaluating the net energy density of the energy storage system. Any mechanisms that couple to the spring should be kept lightweight and compact to maintain the volumetric and gravimetric energy density advantage of CNT springs. A good general guideline is to keep the percentage of weight of CNTs in the overall energy storage system as high as possible to keep the overall energy density high. Energy losses within the supporting architecture (for instance, in the power regulation mechanism) should be kept to a minimum to maximize the energy that can be transmitted to a load.

5.2.2. Friction

The energy storage system, comprising the spring and its supporting architecture, should be compact to maintain high energy density. When working with CNT yarn as a spring, compactness is a challenge because the yarn loads in tension. Bending, torsion and compression are impractical deformation modes for the long, thin CNT yarn. In comparison, springs made of metal can load in bending and can take on compact shapes such as the spiral shape of a torsional spring.

Yarn can be made more compact by wrapping it around a structure and then loading it in tension, but the effects of friction must be carefully considered once there is an interaction between the yarn and a surface. The experimentally measured static coefficients of friction between the yarn and bronze, parylene and teflon are listed in Table 5-1. Lubrication applied to a surface in contact with yarn typically made the yarn gummy and did not lower friction.

When a material in tension is wrapped around a surface, the capstan effect becomes relevant. When a typical rope is stretched in tension, the tension is uniform along the length of the rope.
Chapter 5. Devices powered by carbon nanotube springs

When tension is applied to a rope wrapped around a shaft, the capstan effect decreases the tension in the rope along its length. If a tension $T_o$ is applied to a rope and the rope is wrapped around a shaft, as shown in Figure 5-1, the tension in the rope decreases exponentially with the wrapping angle, according to

$$T(\theta) = T_0 e^{-\mu \theta}$$  \hspace{1cm} (5-1)

where $\mu$ is the coefficient of friction between the rope and the shaft, and $\theta$ is the wrapping angle.

The capstan effect would make it difficult to uniformly load a spring made of yarn wrapped around a surface because the load carried by the yarn would decrease exponentially with the wrapping angle. Because of the relatively high coefficient of friction between the yarn and other materials, stretching a spring in tension while it is wrapped around a surface is an ineffective way to load a spring.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Coefficient of friction</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT yarn Bronze</td>
<td>0.43</td>
</tr>
<tr>
<td>CNT yarn Parylene</td>
<td>0.68</td>
</tr>
<tr>
<td>CNT yarn Teflon</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Figure 5-1: Diagram illustrating the capstan effect.

5.2.3. Controlling the rate of energy release from a spring

On its own, a spring stores potential energy when an external force is applied to it, but the energy is released in a rapid burst once the force is removed. The operation of many devices requires that they receive a smaller amount of power over a longer period of time. One way to control the rate of energy release from a mechanical spring is with an escapement mechanism, a carefully designed set of gears that has been used in mechanical clocks and watches for centuries. In an escapement mechanism, energy is stored in a spring, and that spring applies a torque to a gear called an escape wheel. Without any additional mechanisms, the escape wheel would accelerate and release all of the energy from the spring rapidly. A second component called a pallet is employed to control the rotation of the escape wheel. The pallet is connected to a pivot and is driven to oscillate by a torsional spring called a balance spring. Each oscillation of the pallet allows the toothe escape wheel to rotate by a small increment. The escape wheel transfers energy to the balance spring on each increment of rotation, so that the amplitude of the balance spring oscillations remains large over time despite damping losses. The period of the balance spring oscillations regulates the net angular velocity of the escape wheel, and thus the rate at which the spring releases its energy. Using such a mechanism, the energy stored in a spring is released in small increments over time. Several escapement mechanisms have been
adapted to control the rate of energy release from a CNT spring, and these mechanisms are described in detail in later sections.

5.3. **Carbon nanotube slingshot**

CNT slingshots were built to demonstrate rapid energy release from CNT springs. The slingshots convert mechanical strain energy into kinetic energy of a projectile. The material used for the elastic portion of the slingshot is CNT yarn. To operate the slingshot, a projectile was placed against the yarn, pulled back using a microprobe tip to stretch the yarn, and then released. The motion of the projectile after release was tracked using a high speed camera to calculate its kinetic energy. The energy input to the yarn and the kinetic energy of the projectile were compared to determine the efficiency of the energy transfer. Several tests and their results are described in detail in the following sections.

5.3.1. **Setup**

The setup for the projectile tests is shown in Figure 5-2. The slingshot consists of a short (5-10 mm) length of CNT yarn strung between two posts on a Teflon surface. A high speed camera (Fastec InLine camera) is mounted on a microscope above the slingshot. The high speed camera was used to record images of the slingshot at 250, 500 and 1000 frames per second. A force sensor (Strain Measurement Devices, S100 Thin Film Load Cell) was used to characterize the force-displacement curve of the yarn in order to determine the work done on the yarn by the microprobe tip.

![Figure 5-2: Setup for the yarn slingshot experiment.](image_url)
5.3.2. Nut projectile recorded at 500 frames per second

In a first experiment, the projectile was a small nut with a mass of 175 mg, a width of 4.7 mm, a height of 2.35 mm, and a moment of inertia about its center axis of $6.25 \times 10^{-10}$ kg m$^2$. The slingshot was a 41.1 mm piece of yarn attached between two posts on a Teflon surface. The nut was placed against the yarn, pulled back against the yarn using a microprobe tip, and then released. Images of the nut recorded at 500 frames per second before release and during 40 ms following its release are shown in Figure 5-3. The nut lifted off the Teflon surface once it lost contact with the yarn so friction was not a major source of energy loss, and the nut rotated as it translated. The plots in Figure 5-4 show the linear displacement, linear velocity, angular displacement and angular velocity of the nut as a function of time. Linear and angular displacement were measured using the high speed camera images and contain some uncertainty due to a small amount of image blur. Linear and angular velocity were calculated by numerically differentiating the displacement data. The kinetic energy of the nut over time is plotted in Figure 5-5. Most of the kinetic energy in the nut was energy due to translation, rather than rotation. The maximum kinetic energy of the nut in this test was $3 \times 10^{-5}$ J.
Figure 5-3: Images taken at an interval of 2 ms showing the trajectory of a nut after being propelled forward by a CNT yarn slingshot. The images are in sequence from left to right, and then from top to bottom.

Figure 5-4: Linear displacement, angular displacement, linear velocity and angular velocity of the nut as a function of time after its release from the slingshot.
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Figure 5-5: Kinetic energy of the nut as a function of time after its release.

The force-displacement curve was not characterized prior to running this test, so an accurate measure of the work done on the yarn prior to releasing the projectile is unavailable. However, a rough estimate of the work done on the yarn can be obtained using video images knowing that the length of the yarn at the start of the test was 41.1 mm, and the strain applied to the yarn was about 1%. Integrating a typical stress-strain curve of cyclically loaded yarn, an estimate for the energy in the yarn is $1.64 \times 10^{-4}$, so a rough estimate for the efficiency of the energy transfer is 18%.

### 5.3.3. Screw projectile recorded at 250 frames per second

The second type of projectile tested was a small screw with a flat and wide head, a short body for latching onto the yarn, and a low center of mass. The screw has a diameter of 2.4 mm and a mass of 11.7 mg. A piece of yarn 12.4 mm long was attached between the two posts. The screw was placed against the yarn, pulled back against the yarn using a microprobe tip, as shown in Figure 5-6, and then released. Images of the screw were recorded at 250 frames per second with an exposure time of 2 ms. The screw typically lifted off the Teflon surface once it lost contact with the yarn. The screw rotated as it translated, and it collided once with the surface at about 50 ms after its release. The plots in Figure 5-7 show the linear displacement and velocity in the x and y directions as a function of time. Linear displacement was measured using the high speed images, and contains some uncertainty due to image blur. Velocity was calculated by numerically differentiating the displacement data. The kinetic energy of the screw as a function of time is plotted in Figure 5-8. The angular velocity of the screw was neglected in the calculation of kinetic energy because the rotation was difficult to measure from the images, and the rotational energy was expected to be much smaller than the translational energy. The maximum measured kinetic energy of the screw was $6 \times 10^{-7}$ J.

The force-displacement curve was not characterized prior to running this test, so an accurate measure of the work done on the yarn prior to the release of the projectile is unavailable. However, a rough estimate of the work done on the yarn can be obtained using video images knowing that the length of the yarn at the start of the test was 12.4 mm, and the strain applied to
the yarn was about 1.2%. Integrating a typical stress-strain curve of cyclically loaded yarn, an estimate for the energy in the yarn is \(4.8 \times 10^{-5}\) J, so a rough estimate for the efficiency of the energy transfer is 1%.

The elongation of the yarn as a result of the test can be clearly seen in the images from the high speed camera. The yarn was taut at the start of the test, and the yarn is visibly longer after the slingshot was released. This was the first slingshot test performed on this particular piece of yarn, so the yarn had not been preconditioned. Consequently, it is expected that a significant amount of the work done on the yarn by the microprobe tip was lost due to hysteresis in the yarn. In general, it is better to precondition the yarn prior to use because that reduces hysteresis and improves efficiency.

The slingshot experiment with the nut described in section 5.3.2 had a higher efficiency of about 18%. In the experiment with the nut, the yarn had been preconditioned because it had been used for many slingshot runs prior to the test that is presented in the data. Lack of preconditioning in the yarn in the experiment with the screw is expected to partly account for the lower efficiency of about 1%.

Figure 5-6: (a) Yarn and projectile before running the test; (b) yarn, projectile and microprobe tip at maximum yarn strain in the frame prior to releasing the projectile.
Figure 5-7: Images taken at an interval of 4 ms showing the displacement of the screw as a function of time. The images are in sequence from left to right, and then from top to bottom.
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Figure 5-8: Linear displacement and velocity of the screw in the x and y directions as a function of time after its release from the slingshot.

Figure 5-9: Kinetic energy of the screw as a function of time after its release.

5.3.4. Screw projectile recorded at 500 frames per second

The previous two experiments showed that strain energy in yarn can be effectively transferred to kinetic energy of a projectile, but only rough estimates of the efficiencies of the energy transfers were available. In a third experiment, the force-displacement characteristics of the yarn were measured to more accurately determine the work done on the yarn and the overall efficiency of the energy transfer. Images of the projectile were recorded at 500 frames per second.

In this experiment, yarn with an initial length of 7.49 mm was strung between two posts (Figure 5-10a). The projectile was the same small screw that was used in the second experiment. Several practice runs with a projectile were done to precondition the yarn, and the yarn visibly
lengthened (Figure 5-10b). The length of the yarn prior to the start of the experiment was 7.65 mm. Three projectile runs were conducted, and each run is described in detail below; for convenience, the three runs are labeled ‘run 1’, ‘run2’ and ‘run3’.

![Figure 5-10: (a) The yarn attached to the posts prior to running any projectile tests. Between the posts, the yarn has a length of 7.49 mm. (b) The same yarn after several projectile tests, showing elongation. The yarn now has a length of 7.65 mm.](image)

The images in Figure 5-11 show the projectile pulled against the yarn in the frame immediately prior to the projectile’s release for each of the three runs. The yarn was extended to nearly the same displacement for each run to ensure that any structural changes induced in the yarn between runs were minor. Images showing the trajectories of the screw after its release are shown in Figure 5-12 for run 1, Figure 5-13 for run 2, and Figure 5-14 for run 3. Each image was taken at an interval of 2 ms. The linear displacement, linear velocity, and kinetic energy of the projectile as a function of time are plotted in Figure 5-15 for run 1, Figure 5-16 for run 2, and Figure 5-17 for run 3. Rotational energy was neglected in the calculation of kinetic energy since the screw’s angle of rotation in three dimensions was difficult to obtain from the images, and kinetic energy due to rotation is expected to be much smaller than the kinetic energy due to translation. The maximum kinetic energy of the projectile was 3.983 pJ for run 1, 1.275 pJ for run 2, and 5.098 pJ for run 3.

The force displacement curve of the yarn was characterized after the three runs. Characterization was done after the runs rather than before because yarn cyclic loading behavior is repeatable as long as a previously applied maximum strain is not exceeded. During characterization, the displacement of the yarn could exceed the maximum displacement applied during the three runs because the yarn was no longer needed. To measure the force-displacement curve of the yarn, a force sensor was attached to the yarn using a high stiffness thread. The force sensor was used to extend the yarn slowly while recording the yarn’s displacement using a video camera. The images from the video were used to obtain yarn displacement as a function of time, and force as a function of time was obtained from the force sensor. By matching up the force and displacement data according to time, the data was used to construct a force-displacement curve for the yarn, plotted in Figure 5-18. The second order polynomial fit to the force-displacement
data was \( F = 3.21x^2 - 12.06x + 11.22 \), which is valid for \( 2.06 \text{ mm} < x < 2.33 \text{ mm} \), where \( x \) is the distance between the tip of the extended yarn and inner edge of the slingshot posts (Figure 5-18). To calculate the work done on the yarn by the microprobe tip, the force-displacement curve was integrated up to the maximum applied displacement in the yarn for each run, measured from the images in Figure 5-11. For each of the three runs, the yarn was extended up to a maximum displacement of \( x = 2.17 \text{ mm} \), so the work done on the yarn is calculated to be 9.05 \( \mu \text{J} \).

The efficiency of the energy transfer from the work done by the microprobe tip on the yarn to the output kinetic energy of the projectile was 44.0\%, 14.1\%, 56.3\% for run1, run2 and run3 respectively. From the trajectory images, it can be seen that the most efficient run, run 3, introduced the least amount of rotation in the projectile. The manner of contact between the microprobe tip, the screw and the yarn during the launch can affect the efficiency of the energy transfer.

For the most efficient run, run 3, a lower bound for energy released by the yarn is 5.1 \( \mu \text{J} \) (since there were losses between the energy released by the yarn and the energy transferred to the projectile). An upper bound for the time that it took for the yarn to contract is 2 ms. The contraction of the yarn took place between two successive frames, which means that contraction actually occurred in less than 2 ms. Using these measurements, lower bounds of the power output and power density of the yarn are 2.6 mW and 196 MW/m\(^3\) or 170 kW/kg, respectively. Lower bounds of output energy density from the spring are 393 kJ/m\(^3\) and 341 J/kg.

Figure 5-11: Images showing the position of the projectile in the frame before its release for the three runs, for (a) run 1, (b) run 2, and (c) run 3.

Figure 5-12: Images taken at an interval of 2 ms showing the trajectory of the projectile for run 1. The images are in sequence from left to right, and then from top to bottom.
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Figure 5-13: Images taken at an interval of 2 ms showing the trajectory of the projectile for run 2. The images are in sequence from left to right, and then from top to bottom.

Figure 5-14: Images taken at an interval of 2 ms showing the trajectory of the projectile for run 3. The images are in sequence from left to right, and then from top to bottom.
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Figure 5-15: Position, velocity and kinetic energy of the projectile as a function of time after its release for run 1.

Figure 5-16: Position, velocity and kinetic energy of the projectile as a function of time after its release for run 2.

Figure 5-17: Position, velocity and kinetic energy of the projectile as a function of time after its release for run 3.
5.3.5. Sources of energy losses

Energy was transferred from a microprobe tip to the yarn to a projectile with at most 55% efficiency, and in most cases, lower efficiency. Less than one hundred percent efficiency is attributed to hysteresis in the yarn due to internal friction between CNTs, friction between the probe tip and the projectile during release, imperfect contact between the yarn and the projectile during the entire period of yarn contraction, and friction between the projectile and the surface. A disadvantage of using yarn for the elastic material in a slingshot is that the yarn permanently elongates each time that it is strained, which changes the loading characteristics of the yarn after each run and makes the properties of the slingshot difficult to characterize. To maximize the energy density and power density of the slingshot, the yarn should be strained nearly to its limit, but it is difficult to find that limit without breaking the yarn, particularly since that limit changes as the yarn elongates. Each run using the slingshot gradually weakens the yarn as it elongates, so these slingshots have a finite lifetime.

5.4. Power regulation using an escapement

To demonstrate that it is possible to control the rate at which energy is released from a CNT spring, an escapement mechanism coupled to a CNT spring has been built. The device is shown in Figure 5-19. The escapement mechanism consists of a balance spring, a pallet and an escape wheel. The spring is made of two strands of yarn plied together. One end of the plied yarn is attached to and wrapped around a driving gear, while the other end of the yarn is attached to a winding gear on a ratchet. From the winding gear to the driving gear, the spring is 12.2 cm long. Turning the ratchet gear by one increment stretches the yarn in tension to a strain of 0.33%, which applies a torque to the driving gear and drives the motion of the escapement for 8 seconds.
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The strain induced in the yarn as a result of turning the ratchet gear was measured by applying small white paint dots to the surface of the yarn, and recording high resolution sequential images of the yarn as the ratchet was turned. Images of the dots on the yarn before and after turning the ratchet gear by one increment are shown in Figure 5-20. The change in the position of the dots provided an accurate measure of strain.

When CNT yarn is stretched, it can provide a relatively large force but its extension is small. The diameter of the driving gear is 13 mm. A strain of 0.33% in yarn 12.2 cm long corresponds to an extension of 0.4 mm in the yarn, and a rotation of 1.76 degrees of the driving gear as the yarn contracts. The escape wheel rotates by half of the angular spacing between two of its teeth with each balance spring oscillation. Since the period of the balance spring oscillations depends mainly on its spring constant, to increase the time that it takes for the spring to contract it is necessary to increase the angular rotation of the escape wheel for a given yarn extension using a series of transmission gears. Both the gear ratio and the period of the oscillations of the balance spring determine the rate at which the spring contracts and the power output from the spring. A range of gear ratios were tested to maximize the angular rotation of the escape wheel while maintaining sufficient torque on the escape wheel to drive the oscillations of the balance spring. The chosen gear ratio from the driving gear to the escape wheel was 7:496. With this design, a 0.33% strain in the spring rotates the driving wheel by 1.76 degree and the escape wheel by 125 degrees, while the torque in the escape wheel is 1.4% of the torque in the driving gear. Using the escapement, the small strain in the stretched yarn is gradually released over a period of 8 seconds.

To run the escapement, a minimum force of 0.3 N must be applied to the driving gear, which corresponds to a force of 0.15 N in each of 2 strands. Each time the escapement runs, the gears stop rotating once the tension in the spring reaches this minimum value, so the tension in the spring does not return to zero. The next time the spring is stretched to drive the escapement, there is already an initial tension present in the spring. By integrating stress-strain curves of the yarn loaded cyclically in tension from a starting load of 0.15 N up an incremental strain of 0.33%, it is estimated that the work done on the yarn to stretch it in tension by 0.33% is 268.4 μJ. Once work is done to stretch the yarn, there are energy losses due to hysteresis in the yarn, losses in the form of energy required to drive the transmission gears and the escapement, and there are losses due to friction in the bearings.
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5.5. Carbon nanotube powered mechanical watches

Mechanical watches are an example of a common device that is powered by a mechanical spring. In a watch, energy is stored in a mainspring, a narrow strip of steel that is wrapped into a spiral around a pin called a barrel arbor and fit into a cylindrical gear called a barrel. Winding up a watch increases the curvature of the steel, storing energy in bending. A strained mainspring applies a torque to the barrel, and that torque is transmitted via a series of gears to an escapement mechanism that regulates the energy release rate from the mainspring. The escapement mechanism is made of an escape wheel, a pallet and a balance spring. The torque from the barrel is transmitted to the escape wheel. The pallet is on a pivot and is driven to oscillate by the balance spring. Each oscillation of the pallet allows the toothed escape wheel to rotate by a small increment, which also transfers energy from the escape wheel to the balance spring to compensate for damping. The balance spring and pallet have been carefully designed so that their oscillation frequency remains nearly constant even with variation in the driving torque, to
ensure that a watch keeps accurate time as the mainspring unwinds. The components that make up a modern mechanical watch are shown in Figure 5-21. Studying mechanical watch design is a useful endeavor since watches are cleverly engineered, low-power, highly efficient mechanisms whose power source is a mechanical spring. Several technologies from mechanical watches can be adapted for CNT springs, particularly the low friction gearing and the escapement mechanism that provides a high degree of control over the output power from the spring.

Several mechanical watches have been redesigned to be driven by CNT spring rather than by a mainspring. The designs demonstrate not only how CNT springs can be used to power a watch, but also how CNT springs coupled with watch technology can be used to drive any type of mechanical load with a high degree of control over output power. When adapting a typical watch for a CNT spring, the main difference is the deformation mode of the spring. Mainsprings are compact springs that store energy in bending and can be housed in a small cylindrical casing. Yarn stores energy best in tension. As a result, a mainspring cannot be directly replaced with a CNT spring without additional coupling mechanisms. The following sections present three designs of mechanical watches powered by CNT springs, along with advantages and drawbacks of each design.

![Standard components of a mechanical watch.](image)

**Figure 5-21:** Standard components of a mechanical watch.

### 5.5.1. First design

The first CNT-driven mechanical watch was a compact design in which the barrel and mainspring were removed from a watch and replaced with a thin spool made of bronze that fit around the barrel arbor (Figure 5-22). CNT yarn 2 cm long was wrapped around the spool. One end of the yarn was tied through a hole in the spool, while the other end was tied to a fixed post in the watch casing. The spool and barrel arbor were replaced into the barrel’s original location in the watch. The watch is wound by turning the watch crown. Winding the watch rotates the spool, which applies a strain to the yarn, which in turn applies a torque to the watch gears, and
drives the operation of the watch. Operation of the watch lasted for 5 seconds, and winding beyond a narrow limit would break the yarn.

The main difficulty with the design was the friction between the yarn and the spool. The yarn was wrapped around the spool and then stretched in tension, which prevented the entire length of the yarn from being strained due to the capstan effect. The load carried by the yarn decreased exponentially along its length, so the majority of the load was carried by a short segment of yarn near one end. To compensate for the friction between the yarn and the bronze spool, the bronze spool was coated with a thin layer of parylene. The coefficient of friction between the bronze spool and CNT yarn was measured to be 0.43, and the coefficient between the bronze spool coated with parylene and the CNT yarn was 0.68. Coating the spool with parylene was supposed to reduce the friction, but it had the opposite effect. The bronze gear was then replaced by a gear made of Teflon. The coefficient of friction between the Teflon spool and the CNT yarn was measured to be 0.12, a good improvement. However, the Teflon was too soft and the ‘D’ shaped fit between the Teflon spool and the barrel arbor rounded out after a few test runs in the watch. A potentially more useful material to use for the spool would have been Delrin, a low friction material that is harder than Teflon. Even with a spool made of a lower friction material, there were two main problems with the design that hindered the performance of the watch: the small size of the spool limited how much yarn could be wrapped around its surface and the thus the amount of energy that could be used to run the watch, and the friction between the yarn and the surface of the spool made it difficult to apply a strain along the entire length of the yarn. These issues were addressed in the next two watch designs.

![Mechanical watch with a CNT spring](image)

**Figure 5-22:** Mechanical watch with a CNT spring: (a) a watch with its barrel and mainspring removed, and replaced with a spool around which CNT yarn is wrapped; (b) design of the spool that fit around the barrel arbor.

### 5.5.2. Second design

The second watch design shown in Figure 5-23 addressed the problems with friction in the first watch design by eliminating the contact between the stretched yarn and a surface. The watch piece was removed from the casing of a watch and the mainspring was removed. Two sheets of clear acrylic were screwed together across 3 mm tall spacers. A 2.5 cm diameter hole was cut in one of the sheets of acrylic, and the watch piece was pinned over the hole with the watch hands through the hole. Three teflon pulleys spanning the 3 mm space between the acrylic sheets were
built, and a driving gear constructed using the barrel from another watch was added so that a torque on the driving gear applied a torque to the barrel gear in the watch. The spring was made of four strands of yarn plied together. One end of the plied yarn was attached to and wrapped around the driving gear. The plied yarn was wrapped around the three pulleys, and the other end of the yarn was attached to a winding gear on a ratchet. From the winding gear to the driving gear, each strand of yarn was 41.25 cm long. Rotating the ratchet gear extended the yarn; the tension in the strained yarn applied a torque to the driving gear, which applied a torque to the barrel, and began operation of the watch.

Each incremental turn of the ratchet applied a strain of 0.0732% to the yarn. This strain was measured by applying small white paint dots to the surface of the yarn and tracking the displacement of the dots while turning the ratchet gear using high resolution sequential imaging and image processing.

Turning the ratchet by three increments created a strain of 0.22% in the yarn and ran the watch for 15 minutes and 15 seconds. The driving gear requires a minimum force of 0.1 N to run the watch, which corresponds to a force of 0.025 N in each of 4 strands. This is the tension that remains in the spring after running the watch, and the initial tension in the spring the next time the watch is run. Work done on the yarn is calculated by integrating a typical stress-strain curve from a starting load of 0.025 N up an increment of 0.22%, which yields an estimate for the energy input to a single strand of yarn of 259.2 μJ. The energy required to stretch 4-ply yarn to a 0.22% strain is estimated to be 1.0 mJ.

The performance of the CNT spring in this device can be compared to the performance of a mainspring. A standard steel mainspring with a mass of 405 mg runs a typical watch for 41 hours, so the mainspring provides 364 seconds of watch operation per milligram of spring. In the CNT-driven watch, the watch operates for 915 seconds using a spring with a mass of 3.3 mg, so the CNT spring provides 277 seconds of operation per milligram of spring. So far, the mainspring is more effective at running the watch.

The three pulleys were included in the design in order to use longer yarn while keeping the design more compact. The pulleys were intended to rotate as the yarn stretched around them to reduce the effects of friction, but instead the yarn slipped over the pulleys. As a result, the pulleys acted as posts rather than pulleys and limited transmission of load throughout the yarn due to the capstan effect. There was less tension in the last segment of yarn wrapped around the driving gear than in the first segment of yarn attached to the winding gear, so the friction in the pulleys reduced the torque driving the watch. Improved pulleys were implemented in the third design.
5.5.3. Third design

The third watch design (Figure 5-24) was similar to the second design but had improved pulleys. The two new pulleys were Teflon posts on ball bearings, designed to rotate with very low friction. Stretching the yarn by rotating the winding gear caused the pulleys to rotate, so that the load was more evenly shared between the three segments of yarn separated by each pulley. In this design, the spring was made of 6-ply yarn. The number of strands in the yarn was increased in the third design to increase the torque on the driving gear.

With the yarn wrapped around the two pulleys, the yarn length from the driving gear to the winding gear was 68.9 cm, and the longest recorded watch operation time was 7 minutes and 35 seconds. The mass of the spring is 8.3 mg, so the watch operates for 55 seconds per milligram of spring. Winding the yarn further to obtain longer operation caused the yarn to fracture, which always occurred between the winding gear and the first pulley. Despite the pulley rotations, the
yarn was tauter between the winding gear and the first pulley than between the two pulleys, and between the second pulley and the driving gear.

To test whether the pulleys limited the transmission of load along the yarn, the yarn was drawn directly from the winding gear to the driving gear, as shown in Figure 5-24b, so that the spring had a shorter length of 23.5 cm. With this new spring configuration, the longest recorded watch operation time was 23 minutes and 21 seconds. Turning the ratchet by three increments created a strain of 0.32% in the yarn. The driving gear requires a minimum force of 0.1 N to run the watch, which corresponds to a force of 0.0167 N in each of 6 strands. This is the tension that remains in the spring after running the watch, and the initial tension in the spring the next time the watch is run. Work done on the yarn to stretch it by 0.32% was calculated by integrating a typical stress-strain curve from a starting load of 0.0167 N up an increment of 0.32%, which yielded an estimate for the energy input to a single strand of yarn of 113.3 µJ. The work done to stretch the 6-ply yarn by 0.32% is estimated to be 679.6 µJ. The spring has a mass of 2.8 mg, so the watch operated for 497 seconds per milligram of CNT yarn. Considering a yarn density of 1153 kg/m³, the operation time of the watch per unit volume of spring was $5.7 \times 10^{11}$ seconds per m³. For comparison, a standard watch driven by a steel mainspring runs for 364 seconds per milligram of spring, or $2.8 \times 10^{12}$ seconds per m³ (considering a density of 7800 kg/m³ for steel). The CNT spring improved the watch operation time per unit mass of the spring by 40% compared to a steel mainspring, though it fell short of the operation time per unit volume of a mainspring by 80%.

The third watch design showed that yarn is more effective as a spring without pulleys than with pulleys. All contact between CNT yarn and a surface should be avoided because friction limits transmission of load along the yarn length. Compactness is an important challenge of working with CNT yarn for energy storage because yarn must stretch in tension. Pulleys were originally incorporated into the designs to enable the use of a longer spring while keeping the design compact. The advantage of a longer spring is more extension and greater energy storage. This work has shown that it is more effective to use a short, thick spring than a long, thin spring. In both cases, energy storage will be the same, but the short, thick spring is more compact. With a short, thick spring, the displacement of the stretched spring is smaller but the applied force is higher. If the end load requires a bigger displacement than that provided by the extension of the spring, then the ratio of force to displacement can simply be adjusted using gears or some similar mechanism. These guidelines were taken into consideration in all subsequent designs.
5.6. Kinetic energy harvester

The design of a kinetic energy harvester that stores energy in a CNT spring is shown in Figure 5-25. Two mechanical watches were removed from their watch casings and taken apart. The first watch was a self-winding watch with an inertial proofmass. The escapement, mainspring, barrel, gear train and watch hands were removed from the first watch, leaving only the proofmass, its low-friction bearing and a few winding gears. The mainspring was removed from the second watch. Both watches were fixed between two acrylic sheets, with holes cut out in the acrylic for the proofmass and the watch face. A winding spool made of bronze attached to a barrel arbor (Figure 5-26) was placed into the original location of the barrel in the first watch.
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A driving gear was connected to the barrel of the second watch. The spring was made of 4-ply CNT yarn. One end of the yarn was attached to the winding spool inside of the first watch, and the other end of the yarn was connected to and wrapped around the driving gear. Rotating the inertial proofmass winds the yarn around the winding spool and stretches the yarn in tension. The stretched yarn applies a torque to the driving gear which drives the operation of the second watch.

The strain induced in the yarn by rotating the proofmass was measured by applying white paints dots to the surface of the yarn, and measuring the strain in the yarn during winding by tracking the motion of the dots using video imaging and image processing. Each revolution of the proofmass applied a strain of 0.033% to the yarn. One and a half revolutions of the proofmass applied a strain of 0.05% to the yarn and ran the watch for 4 minutes and 45 seconds.

Rotating the proofmass continually extends the yarn, and excessive rotations will break the yarn. No mechanism to prevent over-winding has been implemented to date, but such a mechanism should be implemented in future designs. If the proofmass was rotated at an appropriate rate to keep a constant tension in the yarn, then the spring could run the watch for an indefinite period of time. This design shows how CNT yarn can be used as an energy storage element for energy harvesters, particularly for applications in which the input energy source and the output load are in the mechanical domain.
Figure 5-25: Kinetic energy harvester: (a) top view of the full device; (b) top view of left side showing the rotating inertial proofmass; (c) top view of the right side; (d) bottom view of the left side showing the winding spool; (e) bottom view of the right side showing the watch face.

Figure 5-26: Yarn winding spool around a barrel arbor: (a) model and (b) actual spool.

5.7.  Carbon nanotube-powered electric batteries

The previous designs have demonstrated the use of CNT springs to power mechanical devices. It is also of interest to study how energy can be stored in a mechanical spring and output as electricity. The design and performance of two CNT-powered electric batteries are described in the following sections. The first battery uses piezoelectric cantilevers to convert the mechanical energy in the spring into electricity, and the second device uses an electromagnetic generator as the transducer.

5.7.1. CNT-driven electric battery using a piezoelectric generator

The first prototype of a CNT-powered battery uses a piezoelectric cantilever beam to convert mechanical energy stored in a CNT spring into electricity. An escapement mechanism regulates the rate at which energy is released from a CNT spring, so that one winding of the spring generates electricity over a controlled period of time. The device is shown in Figure 5-27. The
spring is made of 12-ply CNT yarn. One end of the plied yarn is attached to a winding gear connected to a ratchet, and the other end is attached to a driving gear. The length of the yarn between the two gears is 21.1 cm. The CNT yarn is stretched in tension using the winding gear. A series of transmission gears convert the high torque and small angular displacement of the driving gear into a smaller torque and larger angular displacement on the escape wheel to increase the time taken for the spring to contract. The gear ratio from the driving gear (gear 1) to the escape wheel (gear 4) is 1:531, so that the escape wheel rotates 531 times faster than the driving gear but with 0.19% of the torque. The teeth of gear 3 periodically collide with the end of a piezoelectric cantilever and cause it to oscillate. Energy is input to the system by stretching the yarn using the winding gear, and energy is output from the system as electricity from the piezoelectric cantilever beam. The input and output energy are compared to determine the overall efficiency of the energy transfer. Two cantilevers have been tested: a 25.4 mm long, 0.51 mm thick bending bimorph made of PZT (Piezo Systems, T220-A4-203X) and a flexible, 12 mm long polymer cantilever beam coated with PVDF (Measurement Specialties, MiniSense 100NM). PZT is too stiff to be driven by the escapement gears directly, so a thin polymer tip 6 mm long is used to extend the PZT beam. The gears drive the polymer tip, which in turn bends the PZT beam.

The output voltage from the piezoelectric cantilever beam was measured across a resistor. To maximize power, the resistor was chosen to be $1/(\omega C)$, where $\omega$ is the resonant frequency of the beam and $C$ is the capacitance of the piezoelectric beam. The resonant frequency of the PZT cantilever was measured to be 330 Hz and its capacitance is 7.4 nF. The resonant frequency of the PVDF cantilever was measured to be 325 Hz and its capacitance is 245 pF. The calculated resistor values to optimize power were 65.2 kΩ for the PZT beam and 1.998 kΩ for the PVDF beam. The actual values of the resistors used were 64.7 kΩ for the PZT beam and 1.993 MΩ for the PVDF beam. The voltage output was measured using a data acquisition card (National Instruments, PCI 2661) using a 5 kHz sampling rate. Power across the resistor was calculated as

$$P = \frac{V^2}{R}.$$

To run the device, the winding gear was turned by one ratchet increment to extend the yarn. One ratchet increment applied a strain of 0.12% to the yarn. This was calculated by applying small white dots to the 12-ply yarn and using a camera and image processing to track the change in position of the dots as the yarn was strained (Figure 5-30). The driving gear requires a minimum force of 0.9 N to run the escapement, which corresponds to a force of 0.075 N in each of 12 strands. This is the tension that remains in the spring after running the device, and the initial tension in the spring the next time the device is run. Work done on the yarn is calculated by integrating a typical stress-strain curve from a starting load of 0.075 N up an increment of 0.12%, which yields an estimate for the work done on a single strand of yarn of 3.386×10^{-5} J. Assuming that all 12 strands of yarn in the spring carry a uniform load (perfect plying), then the total energy input to the yarn in one ratchet gear rotation is 0.406 mJ.

With a rotation of one ratchet gear increment, the system typically runs between 30 to 40 seconds. Voltage and power as a function of time using the PZT beam are plotted in Figure 5-28. Voltage and power as a function of time using the PVDF beam are plotted in Figure 5-29. The power spectral density of the voltage output from the PZT beam shows a resonance frequency peak at 330 Hz, while power spectral density of the voltage output from the PVDF beam shows a resonance frequency peak at 325 Hz. The output energy from the system was calculated by integrating the power output from each of the cantilever beams during the period of operation.
Chapter 5. Devices powered by carbon nanotube springs

Using the PZT cantilever, the energy output was $4.15 \times 10^{-8}$ J, corresponding to an output energy density of $8.2 \times 10^{-3}$ J/kg or 9.4 J/m$^3$. Considering a run time of 35 seconds, the mean power output is $1.2 \times 10^{-9}$ W, corresponding to a mean power density of $2.3 \times 10^{-4}$ W/kg or 0.3 W/m$^3$. Using the PVDF cantilever, the energy output was $3.36 \times 10^{-12}$ J, corresponding to an output energy density of $6.6 \times 10^{-7}$ J/kg or $7.6 \times 10^{-4}$ J/m$^3$. Considering a run time of 25 seconds, the mean power output is $1.3 \times 10^{-13}$ W, corresponding to a mean power density of $2.7 \times 10^{-8}$ W/kg or $3.1 \times 10^{-5}$ W/m$^3$. The calculations of output energy density and output power density consider the output energy from the device (accounting for losses from the energy stored in the spring to the output electrical energy), but consider only the mass and volume of the spring, neglecting the mass and volume of the rest of the device. In a real battery, the mass and volume of the spring and any supporting architecture would need to be considered. However, only the mass and volume of the spring are considered for now because the device is not yet optimized.

The efficiency of the energy transfer from the mechanical domain to the electrical domain was 0.01% using the PZT cantilever, and $8.3 \times 10^{-7}$% using the PVDF cantilever.

An examination of the system revealed a number of areas where losses occurred. Hysteresis can reduce the energy that is output from the yarn by as much as 30%. An analysis of the gears showed that the total energy over the course of a run needed to accelerate the gears each time the pallet rotated was $5.6 \times 10^{-6}$ J. The energy needed for the balance spring to oscillate was $3.0 \times 10^{-6}$ J. There is friction in the balance spring’s bearing, friction in the gears’ bearings and friction between gears. It was apparent that load was not carried evenly among all strands in the plied yarn. The piezoelectric cantilever beams extracted only a small fraction of the energy in the escapement, since the escapement had to bend the cantilever beam without impeding its own operation. Finally, piezoelectric conversion from mechanical to electric energy is less than 100% efficient. The sum of these losses is substantial, but it is expected that the greatest source of loss is friction in the escapement mechanism.

There are a number of ways to improve the efficiency of this piezoelectric CNT battery, particularly by reducing the friction in the gears and improving the coupling between the mechanical system and the piezoelectric cantilevers. Elimination of sources of energy losses and further device optimization are needed to improve the performance of the battery. This device has shown that the inclusion of a power regulation mechanism in a spring-based battery comes at the cost of reducing the system’s energy transfer efficiency.
Figure 5-27: CNT-driven electric battery using a piezoelectric generator: (a) whole system; (b) close-up view of the gears with the PZT cantilever beam; (c) close-up view of the gears with the PVDF cantilever beam.
Chapter 5. Devices powered by carbon nanotube springs

(a) 

Voltage (V) 

Time (s) 

0 5 10 15 20 25 30 35 40

(b) 

Voltage (V) 

Time (s) 

14 15 16 17 18 19 20 21
Figure 5-28: Electrical output from the CNT-driven electric battery using a PZT cantilever: (a) output voltage during the entire time of operation; (b) output voltage during a subset of the time of operation; (c) output voltage during a smaller subset of the time of operation, showing the voltage oscillations after one collision; (d) power spectral density of the PZT cantilever's voltage output showing a resonance frequency peak at 330 Hz; (e) output power from PZT cantilever during the entire time of operation.
Chapter 5. Devices powered by carbon nanotube springs

(a)

(b)
Figure 5-29: Electrical output from the CNT-driven electric battery using a PVDF cantilever: (a) output voltage during the entire time of operation; (b) output voltage during a subset of the time of operation; (c) output voltage during a smaller subset of the time of operation, showing the voltage oscillations after one collision; (d) power spectral density of the PVDF cantilever’s output voltage showing a resonance frequency peak at 325 Hz; (e) output power from PVDF cantilever during the entire time of operation.
5. Devices powered by carbon nanotube springs

Figure 5-30: Images of dots on the yarn (a) before loading and (b) immediately after turning the ratchet gear by one increment, showing an applied strain of 0.12%.

5.7.2. CNT-driven electric battery using an electromagnetic generator

The first electric battery was effective at regulating the power output from a spring, but its efficiency was low. A second electric battery was built for higher efficiency. To minimize losses, the second battery does not regulate power and energy is released from the spring rapidly. An electromagnetic generator was used to convert the mechanical energy to electricity. Electromagnetic generators operate best when they are driven at high velocities, so such a device is well suited to convert the energy released rapidly from a spring. Several design guidelines drawn from work on other CNT-driven devices were used to guide the design of this device: (i) maximize energy storage and compactness using a thick spring rather than a long spring; (ii) minimize friction by removing contact between load-bearing regions of a spring and surfaces; (iii) convert the force in a spring to a torque using a couple rather than a force to reduce friction in the gears; (iv) the yarn plying technique is important to obtain even loading in all strands.

The electric battery that was built is shown in Figure 5-31. The battery stores energy in two springs made of yarn. The yarn in this battery is a different, thicker yarn than what was used in all of the previous devices. The thick yarn can support a load of up to 4 N, four times greater than the load carried by the yarn previously used, so it was chosen as the spring material in order to drive the electromagnetic generator with a greater torque. The yarn is flat and wide, with a width of about 1 mm, a linear mass density of 9.55 mg/m and a mean ultimate strength of 970 MPa. SEM pictures of the yarn are shown in Figure 5-32. Each of the two springs is made of 6 strands of yarn, plied together using a braiding technique to tightly hold the stands together. One end of each of the two springs was wound around a spool attached to a driving gear, while the other end was attached to a winding spool on a ratchet. The gear ratio from the driving gear to the generator shaft is 39:1.

Energy is input to the springs by stretching them in tension, which can be done by winding the winding spool, winding the driving gear or by applying a voltage to the generator to run it in reverse as a motor. Once the springs are stretched, the driving gear is latched in place and the energy is stored. To release the energy, the latch is removed. The forces in the springs apply a torque to the gears, which rotate until the forces in the springs can no longer drive the generator. The voltage output by the generator is measured across a load resistor to calculate the power.
output. The power over time is integrated to measure the output energy and the efficiency of the system’s mechanical to electrical energy conversion.

The two springs have lengths of 16.3 cm and 15.0 cm, measured from the winding spool to the driving spool. To drive the generator, the yarn is loaded from a strain of 0 to a strain of 1.2% in the first spring and 1.3% in the second spring. Strain was measured by applying white dots to the surface of the spring and measuring the displacement of the dots from zero extension to maximum extension, as shown in Figure 5-33. The energy input to the system or equivalently the work done on the springs is 0.0146 J, calculated by integrating the yarn’s stress-strain curve from zero strain to maximum strain.

A typical example of voltage output from the generator is plotted as a function of time in Figure 5-34a. The energy is released from the springs over a period of about 100 ms. A typical plot of power as a function of time is shown in Figure 5-34b. Figure 5-35 shows how the output electrical energy changes with different output resistance values. The maximum electrical energy measured was 3.4 mJ with an output resistance of 18 Ω. Using a 18 Ω resistance, the maximum output power from the generator was 0.15 W and the mean output power during the discharge time was 0.042 W, corresponding to a mean output power density of 4.7 MW/m³ or 2.5×10³ W/kg. Energy was released from the spring and converted to electricity at a density of 885 J/kg or 1.77×10⁶ J/m³. The output energy density and output power density calculations consider only the mass and volume of the spring, neglecting the mass and volume of the rest of the system. In a real battery, the mass and volume of the entire system would need to be considered, but for now only the mass and volume of the springs are considered because the entire system is not yet optimized. The maximum efficiency of the energy transfer from the work done on the yarn to the electrical output was 23%.
Figure 5-31: CNT-driven electric battery using an electromagnetic generator, (a) showing a top view and (b) showing a side view.
Chapter 5. Devices powered by carbon nanotube springs

Figure 5-32: Pictures of the thick CNT yarn used in the CNT-driven battery with an electromagnetic generator, showing the yarn on a spool and SEM images of the yarn.

Figure 5-33: White dots painted on the surface of the yarn to calculate the strain in the yarn, (a) before extension and (b) after applying a strain of 1.2%.
Figure 5-34: (a) Voltage and (b) power output measured across a 18 Ω resistor.
5. Devices powered by carbon nanotube springs

5.8. **Summary of device performance and conclusions**

The six devices described in this chapter, namely slingshots, a CNT-driven escapement, mechanical watches, a kinetic energy harvester, and two electric batteries, demonstrate that CNT yarn can function as an effective mechanical spring to drive real systems. The performance characteristics of the devices are summarized in Table 5-2. Note that the output energy density and output power density reported for the devices are calculated using the output energy transmitted to the load (accounting for losses in transmitting the energy from the spring to the load), but considering only the mass and volume of the spring (and not accounting for the mass and volume of the additional system architecture). For the escapement and the mechanical watch, the energy input to the spring is known, but the energy output from the devices is not known. Therefore, the output power of these two systems is listed only as an upper bound estimate, since there will be losses as the energy from the spring is transmitted to drive the final load.

The systems that have been described in this chapter are initial demonstrations of ways to store energy in a spring and transmit that energy to a load. The devices provide design guidelines for a next generation of improved devices. These devices are not yet optimized for maximum efficiency or overall energy density and power density, nor do they demonstrate the limits of energy storage that can be achieved with CNT springs.

By changing the size of the spring and the mechanisms to which the spring is coupled, the energy stored and the power output from the spring can be adjusted by several orders of magnitude. The output power was varied from 490 nW, using a small spring and metering the energy output from the spring with an escapement mechanism, up to 42 mW with a large spring that released its energy rapidly. Mechanisms to control the rate of energy release can increase the discharge time of a spring and lower the output power and power density, but they do so at the expense of reducing the efficiency of the overall energy transfer from the spring. The devices have demonstrated that it is possible to use mechanical energy storage in springs to drive both electrical and mechanical systems. The highest recorded efficiencies were 56% for the slingshots that output energy in the mechanical domain, and 23% for the CNT electromagnetic generator that outputs energy as electricity. These efficiencies are lower bounds for what can eventually be
achieved in a next generation of devices with improved designs. The devices that have been built to date demonstrate the considerable potential and versatility of CNT springs as an energy storage medium.

Across the devices, the highest measured output power density was 190 MW/m$^3$ or 170 kW/kg; these values were measured in the slingshots, which had the fastest rate of energy release from the springs. The highest measured energy density output was 1770 kJ/m$^3$ or 885 J/kg, measured in the CNT electromagnetic generator. The energy density that could be output by the devices that were built was limited by two main factors: energy losses during the energy transfer from the spring to the desired load, and the energy density limit of the yarn. The average energy density in the yarn measured using cyclic loading tests was 4900 kJ/m$^3$ or 4.2 kJ/kg. The energy density of the yarn was measured by loading the yarn cyclically just below its failure strain, therefore 4900 kJ/m$^3$ and 4.2 kJ/kg limits are the mean upper bounds for the energy density of the yarn. In the devices, it was difficult to know the strain at which the yarn would fail, and it was also difficult to know the exact applied strain in the yarn at a given time. Consequently, to run the devices, strain was applied to the yarn conservatively to avoid breaking the spring, so the energy stored in the yarn was below the yarn’s limit. Before energy transfer losses, the stored energy density in the best performing slingshot’s yarn was 602 J/kg, or 14% of the mean energy density upper bound of the yarn; the energy density in the slingshot’s yarn was low because the strain applied to the yarn to launch the slingshot was far below the yarn’s fracture strain. The energy density of the current devices can be improved in two ways. First, larger strains can be applied to the yarn to get closer to the energy density limit of the yarn. Second, energy losses in the devices, such as energy losses due to friction, can be further reduced. These same techniques will also increase the power density of the devices. An additional way to obtain a higher measure of power density would be to get a more accurate estimate of the time that it takes for stretched yarn to contract, since the contraction time was shorter than the time between successive video image frames in the slingshot experiment.

Nonetheless, substantial increases in output energy density and output power density will require replacing the current spring material with a spring material with a higher energy density limit. A Ragone plot in Figure 6-3 compares the energy density and power density of the slingshots and the CNT-driven electromagnetic generator to the energy density and power density of ideal CNT springs and other conventional energy storage technologies. The energy density limit of the yarn is shown as a dashed line on the plot. Using the current yarn material for springs, the energy densities of devices that are powered by these springs cannot reach energy densities above the dashed line. Further discussion of the Ragone plot can be found in Chapter 6.
Chapter 5. Devices powered by carbon nanotube springs

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6. Summary of experimental results

This chapter provides an overview of the mechanical properties and energy storage capabilities of yarn and fibers, using the results from Chapter 3 to Chapter 5. The specific strength and specific stiffness of fibers and yarn are compared to the mechanical properties of common engineering materials. The gravimetric and volumetric energy density of fibers and yarn are compared to the energy density of conventional energy storage technologies. Finally, the energy density and power density of the devices discussed in Chapter 5 are compared to the energy density and power density of conventional storage technologies on a Ragone plot.

6.1. Comparison of theoretical and experimental results

6.1.1. Strength and stiffness

The maximum specific strength and specific stiffness measured in CNT fibers and CNT spun yarn are plotted in Figure 6-1, along with the properties of some common engineering materials. The maximum recorded specific strength of the fibers is 2 N/tex and their maximum recorded specific stiffness is 68.1 N/tex. For CNT yarn, the maximum recorded specific strength is 1 N/tex and the maximum recorded specific stiffness is 97.4 N/tex. The ideal specific stiffness and specific strength of individual CNTs is 448 N/tex and 27 N/tex (assuming a conservative 6% elastic strain limit), respectively. It is not surprising that the properties of the fibers and yarn fall short of the properties predicted of CNTs because of the non-idealities in their structure. To date, the fibers and yarn surpass the specific stiffness and specific strength of many engineering materials, including many metals, but fall short of the mechanical properties of some high performance materials like carbon fiber and Kevlar.
6.1.2. Energy density

The gravimetric and volumetric energy density measured in CNT fibers and CNT spun yarn are plotted in Figure 6-2, along with the energy density of conventional energy storage technologies and the predicted energy density upper bounds of ideal CNTs. The energy density predicted for ideal CNT springs is $7.7 \times 10^6$ kJ/m$^3$ or $5 \times 10^3$ kJ/kg. The highest demonstrated reversible energy storage is 7720 kJ/m$^3$ or 6.7 kJ/kg for CNT yarn, and 677 kJ/m$^3$ or 6.9 kJ/kg for CNT fibers.

To date, fibers and yarn fall short of the energy density predictions for ideal CNTs by about three orders of magnitude. Significant improvements in the structure of these two materials are needed before springs made of macroscopic groupings of CNTs are ready for practical implementation in real devices. The current springs made of CNT yarn store energy with seven times higher volumetric energy density and nearly fifty times higher gravimetric energy density than mechanical springs made of steel. CNT fibers store energy with about the same gravimetric energy density as CNT yarn, but their volumetric energy density is more than ten times lower. Higher volumetric energy density in fibers could be achieved with greater densification of the CNTs in the fibers, which is currently limited by CNT tangling and disorder. Both the current yarn and fibers have energy densities below the estimated energy density upper bound for mechanical springs made of isoprene (natural rubber) or carbon fiber, for instance. To date, the best mechanical springs should be made of these alternate materials rather than CNTs. However, springs made of CNTs remain the ultimate goal.
Chapter 6. Summary of experimental results

Figure 6-2: Comparison of gravimetric and volumetric energy density of different energy storage technologies. HMCF refers to high modulus carbon fiber, HSCF refers to high strength carbon fiber, Li-ion refers to a lithium-ion battery, Ni-MH refers to a nickel-metal hydride battery, and Ni-Cd refers to a nickel-cadmium battery. The values for CNT fibers and CNT yarn are the highest measured energy densities for these materials. Note that the energy density of fuel considered in this plot is the energy density of the fuel alone, without considering the reduction of energy density due to equipment needed to convert the fuel into a usable form. Similarly, the energy density of ideal CNT springs is the energy density of the spring alone, without considering the mass and volume of any supplemental architecture needed to operate the springs.

6.1.3. Energy density and power density

The energy density and power density that were output by the CNT-driven electromagnetic generator and the CNT slingshot are plotted on a Ragone plot in Figure 6-3, along with the energy density and power density of some conventional energy storage technologies. The slingshot has a highest output energy density of 341 J/kg and a highest output power density of 170 kW/kg. The CNT-driven electromagnetic generator has an output energy density of 885 J/kg and an output power density of 2.5 kW/kg. Note that the energy density and power density reported for the slingshot and electromagnetic generator are calculated using the output energy transmitted from the spring to a load (accounting for losses), but considering only the mass of the spring (and not accounting for the mass of additional architecture). The goal is to eventually be able to build CNT energy storage springs with a combination of high energy density and high power density, as shown on the plot. To date, the slingshot and the CNT electromagnetic generator demonstrate encouraging power density values, although considerable improvements are still needed to increase their energy density. First, the devices need to more effectively make
use of the spring material. To date, the output energy densities of the devices fall short of the energy density limit of the yarn because the strain applied to the springs in the devices was below the yarn’s strain limit, and because of losses in transferring energy from the spring to the final load. Second, the energy density limit of the spring material eventually needs to increase, to eventually reach the limit of ideal CNT springs. The current mean gravimetric energy density in the CNT yarn is $4.2 \text{ kJ/kg}$ or $4.9 \times 10^3 \text{ kJ/m}^3$, which limits the energy density of the springs in the devices. Improvements of the spring material that can result in higher output energy densities in the devices will also result in increased output power densities.

![Ragone plot showing the energy density and power density of ideal CNT springs and different conventional energy storage technologies. The energy density and power density of CNT spring-driven devices designed in Chapter 5 are included for comparison. The plot is adapted from [17].](image-url)
7. Conclusions and future work

The present work has shown that springs composed of highly ordered bundles of parallel carbon nanotubes form the basis for a new class of promising energy storage devices. CNT springs have the potential to achieve energy densities and self-discharge rates comparable to electrochemical batteries, and like supercapacitors, and these springs have the potential to be discharged and recharged rapidly, repeatedly and safely even at extreme temperatures.

Experiments have been conducted to study the mechanical properties of CNTs assembled into fibers and yarn and examine the performance of these materials as mechanical springs. The highest recorded strength and stiffness of the fibers are 2 N/tex and 68 N/tex, respectively, and the fibers have maximum demonstrated reversible energy storage of 670 kJ/m$^3$ or 6.9 kJ/kg. The spun yarn has a maximum specific strength of 1 N/tex, a maximum specific stiffness of 97 N/tex, a highest recorded energy density of 7720 kJ/m$^3$ or 6.7 kJ/kg, and a maximum demonstrated power density of 190 MW/m$^3$ or 170 kW/kg. Ideal CNTs are predicted to have a specific stiffness of 448 N/tex, a specific strength of 27 N/tex (considering a conservative 6% elastic strain limit), and an energy density of 7.7×10$^6$ kJ/m$^3$ or 5×10$^3$ kJ/kg. A comparison of the specific strength, specific stiffness and energy density of ideal CNTs and practical CNT spring demonstrations reveals that practical implementations of macroscopic CNT springs fall short of the upper bound predictions. While elastic loading is optimal for reversible energy storage, many of the tests conducted have indicated that there are mechanisms taking place within the fibers and yarn that cause loading of these materials to deviate from purely elastic behavior. Creep, stress relaxation, partial fracture, and gradual atomic defect accumulation within these materials have been observed, and this behavior limits the applicability of these materials as springs. Much of the work has highlighted challenges of working with macroscopic groupings of millions of CNTs: maintaining order, alignment, crystallinity, high packing density, good load transfer, and uniform loading throughout all of the CNTs. These are particularly tough challenges because the small scale of the CNTs makes them difficult to manipulate and study. Furthermore, the small scale of the CNTs makes it difficult to fully study and understand all of the mechanisms taking place within the CNT assemblies during loading and failure. It is much easier to make a model of an ideal CNT spring material than it is to build one in practice.

Studies of fibers made of millimeter-long, continuous CNTs have revealed that defects causing tortuosity in individual CNTs, non-uniformities among CNTs throughout a fiber, and stress concentrations at the testing grips all restrict the ability to evenly load all CNTs throughout a fiber and limit the mechanical performance of the fibers. Higher strength, stiffness and energy density were measured in smaller fibers because non-idealities become more pronounced in larger CNT groupings. Densification using capillary effects was shown to be an effective way to consolidate CNTs and create high performance fibers since the CNTs self-assemble into dense, interacting networks that promote load transfer; mechanical densification, which is done in a more disorderly manner, proved to be less effective.

The mechanical characterization of spun yarn has shown that CNTs can effectively be spun into a dense, load-bearing material. One of the advantages of yarn as a spring material is that the spinning process can produce yarn with varying diameter and length, from millimeters to kilometers; the scalability of the yarn allows that the size of the spring, which controls energy storage capacity, to be tailored for different applications. Load transfer at CNT overlaps is as yet imperfect, with significant elongation of the yarn observed during mechanical testing due to slip.
Chapter 7. Conclusions and future work

Improvements are still needed in the yarn's composition and structure, which could include longer CNTs and longer CNT overlaps, increased bundle size, lower defect density, better alignment of CNTs along the yarn axis, increased packing density, more crystallinity, and shorter CNT migration periods. These improvements should decrease the effects of slip, increase the elasticity of the yarn, increase the energy storage density of the yarn, and make the yarn more viable as a spring material.

In their current forms, macroscopic assemblies of CNTs into the fibers and yarn studied in this work are not yet ready for implementation as springs in practical energy storage applications; more work is first needed to improve their structure and composition. Nonetheless, CNTs were first documented only twenty years ago, and a tremendous amount of research has been conducted since then. Judging by the considerable progress in the fabrication techniques and the properties of macroscopic CNT assemblies reported in the literature from year to year, there is every reason to believe that the properties of macroscopic CNT assemblies will continue to improve. As higher performance macroscopic CNT materials are developed, energy storage in CNT mechanical springs will become more realizable. While the energy densities of current implementations of CNT springs fall three orders of magnitude short of predictions, and the morphologies of current macroscopic CNT assemblies are far from the ideal fiber or yarn structure, the remarkable potential for high energy density and high power density in CNT springs should continue to motivate research in this area.

As the properties of CNT assemblies improve, the frontier for research moves to systems engineering and applications. Practical demonstrations of devices powered by the energy stored in CNT springs have successfully demonstrated that CNT springs can effectively store energy and transmit that energy to power small-scale systems. CNT springs have the ability to drive both mechanical and electrical loads, can store small or large amounts of energy by scaling the size of the spring, and can output energy at a wide range of power levels that can be tuned for different applications. The highest recorded efficiencies of the storage systems were 56% for energy output in the mechanical domain, and 23% for energy output as electricity. These efficiencies are lower bounds for what can eventually be achieved in a next generation of devices with improved designs that focus on maintaining high efficiency, minimizing losses, and maximizing the energy density of the spring. Eventual storage systems should be able to provide a high degree of control over output power. The eventual goal is to build energy storage systems using CNT springs that provide energy densities and power densities matching the upper bounds predicted for ideal CNTs.
References


