RICE UNIVERSITY

Macroscopic Neat Single-Wall Carbon Nanotube Fibers

by

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ABSTRACT

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Measured and predicted properties of individual single wall carbon nanotubes (SWNT) suggest that bulk SWNT materials will exhibit a variety of exceptional properties. Due to the anisotropic nature of SWNTs, fibers are a logical candidate for these objects. The first ever macroscopic fibers, consisting entirely of SWNTs, were successfully produced and characterized. Nanotubes were dissolved at high concentrations (6 – 10 wt%) in 102% sulfuric acid. The SWNT / sulfuric acid system exhibited unique one-dimensional liquid crystalline phase behavior and interesting rheological characteristics. Fibers were extruded using a wet-jet solution-spinning approach into diethyl ether without extensional drawing. Structural analysis showed them to be the highest aligned neat SWNT material produced to-date, with a revealing substructure of coagulated liquid crystalline domains. Additional characterization showed useful electrical and thermal properties and promising mechanical properties. Finally, the Spinning Bob Mixer (SBM), a custom laboratory mixer / extruder, was designed and
successfully tested. Various features of the apparatus were demonstrated and shown to be valuable experimental tools for understanding the production of neat SWNT fibers. This research has begun the exploration of an interesting and new field of nanotube science by providing a foundation of understanding and enabling future experiments.
Acknowledgements

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Many others deserve recognition for their role in this thesis’ research. The daily hard work of creating these fibers would not have been possible without the help of Hua Fan and Joey Sulpizio. The elaborate machining demands of creating the Spinning Bob Mixer were accomplished only through the experience and skill of the Research Support Shop and its hard workers: Dwight Dear, Jack Gless, Jr., and Eliberto Batres. Yuhuang Wang and Myung Jong Kim provided critical information through the development and use of their special UV/Ozone microtoming technique. Prof. Jack Fischer and his team (Juraj Vavro, Wei Zhou, Csaba Guthy, and Reto Haggenmueller) at the University of Pennsylvania provided invaluable fiber characterization. Nichols Parra-Vasquez assisted in the rheological experiments.

In addition to direct assistance in this research, others deserve recognition. One of the most important is Dr. Deron Walters. He was my first mentor at Rice University and showed me what it means to be an experimental scientist. I still find myself approaching problems the way Deron showed me. Thank you. Erik Haroz provided the less glamorous, but no less important, task of reading my entire thesis and providing editing comments. I would not be nearly as proud of this thesis without him.

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1. Introduction

Over the last decade of nanoscale science and technology, a Holy Grail of sorts has always been a macroscopic object that possesses all of the remarkable properties of individual single-wall carbon nanotubes (SWNTs). Since the discovery of multi-wall carbon nanotubes (MWNTs) by Iijima in 1991 [1], and the subsequent discovery of single-wall carbon nanotubes in 1993 [2, 3], researchers have marveled at the impressive properties of these macromolecules. Individual SWNTs may be the strongest, most electrically conductive, thermally robust molecular entities in the world. They are stronger than high performance steel [4 – 6], with a ballistic electrical conductance better than copper [7], and a thermal conductivity equivalent to diamond [8]. To truly realize the full potential of carbon nanotubes, it is essential that routes towards macroscopic neat materials consisting entirely of single-wall carbon nanotubes be developed. However, developing these super nano-materials is a difficult endeavor that will require a solid foundation of neat SWNT materials research to build upon.

Of all the types of high performance materials, fibers are an obvious choice for SWNTs. Due to their anisotropic geometry and associated anisotropic properties, SWNTs lend themselves to being made into macroscopic fibers. Conventional fibers of rod-like macromolecules are spun from a concentrated liquid crystalline phase using controlled extrusion methods. The subsequent fibers exhibit a high degree of alignment and crystallinity, resulting in impressive anisotropic fiber properties [18]. Over the last 4 years, composite SWNT fibers have been produced with notable success. The nanotubes have been found to improve the mechanical, electrical, and thermal properties of a variety
of polymer systems [9 – 12]. However, these improvements have been marginal compared to the potential of neat SWNT materials.

Neat SWNT materials research has faced several challenges that have limited its proliferation in the nanotube community. Only a handful of researchers have produced macroscopic objects consisting of only SWNTs. Strands of nanotube bundles have been produced by two different processes but lack the crystallinity and abundance for further development [13, 14]. Neat films of SWNTs show promising properties. Such films have been produced by controlled aggregation from an acid solvent [15] as well as magnetically assisted filtration [16]. The development of neat SWNT materials is made difficult by the high cost of SWNTs. Commercialization of the HiPco process [17] by Carbon Nanotechnologies Inc. hopes to change this.

Producing macroscopic neat SWNT fibers is also a challenging endeavor. Creating such a fiber requires two key stages. First, single-wall carbon nanotubes must be dispersed as individuals at high concentrations to form a liquid crystalline phase. Then, that sample must be extruded in a controlled manner utilizing a suitably robust apparatus using a viable spinning technique. Fibers comprised of rod-like polymers are solution spun from concentrations of 5 – 45 wt% [18]. However, dispersing SWNTs in solution is difficult because of strong attractive van der Waal forces, which make the nanotubes readily aggregate. Organic solvents, such as dimethyl formamide or dichlorobenzene, are typically limited to concentrations less than 0.5 wt% [19]. Higher concentrations have been attained utilizing aqueous surfactants [12] and polymer wrapping [20], but using these suspending agents introduces the added complication of having to remove them during or after fiber production. This thesis’ solution is to use conventional rigid rod
polymer engineering as a template to guide both the sample preparation and fiber spinning.

Rigid rod fibers are spun from high concentrations of polymer in super acids (e.g. polyphosphoric acid, 100% sulfuric acid). The acid protonates the rod-like molecules, providing a strong electrostatic repulsive force, which solvates the individual molecules and keeps them separate and distinct. This research demonstrates that SWNTs are also dispersed in super acids at high concentrations. SWNTs readily dissolve in 102% sulfuric acid and form a distinct liquid crystalline phase.

SWNTs in 100% sulfuric acid exhibit a unique one-dimensional liquid crystalline phase. The SWNT / sulfuric acid system displays the three traditional regimes observed in solutions and dispersions of rod-like molecules: isotropic, biphasic, and single phase liquid crystal. At low concentrations, the SWNTs form an isotropic phase of solvated individual SWNTs. As the concentration of nanotubes increases, the system transitions to a biphasic state. Optical microscopy reveals a biphasic phase that consists of an isotropic phase of individual SWNTs and an ordered liquid crystalline phase. The SWNTs in the liquid crystalline phase are highly aligned and mobile, and were found to organize themselves into one-dimensional domains, called SWNT Spaghetti. This phase appears to be unique to SWNTs. At higher concentrations, the system transitions to a single liquid crystalline phase. Here, all nanotubes exist in aligned domains and the system exhibits strong birefringence, as observed under polarized optical microscopy. In addition, the sample possesses rheological properties common to liquid crystals – high viscosities that follow a power law behavior and exhibit strong shear thinning. It is from this single phase that the first ever macroscopic neat SWNT fibers were produced.
Macroscopic neat SWNT fibers were spun from 102% sulfuric acid using a wet-jet solution-spinning approach. Concentrated samples of 6 – 10 wt% purified HiPco SWNTs were mixed in 102% sulfuric acid using a conventional mixer. Samples were mixed in anhydrous environments for multiple days and then loaded into a stainless steel syringe. Neat fibers were then successfully extruded into diethyl ether without any extensional drawing and collected by hand.

The resulting neat SWNT fibers showed remarkable structure and interesting characteristics. Scanning electron microscopy revealed the fibers to be highly aligned, dense structures. Additional structural analysis by polarized Raman ratios and x-ray diffraction (XRD) showed that the fibers are the most aligned neat SWNT material produced to-date. Polarized Raman ratios were observed as high as $28 \pm 3$ and XRD full-width half-maximum mosaic angles as low as $\chi = 31^\circ$ [21]. A special microtoming technique provided access to the cross-section of the fibers [22]. The resulting bisected fibers revealed information on their coagulated structures and void fraction. In addition, surface images and cross-sectional images suggest that the neat fibers possess a substructure of SWNT Spaghetti domains, providing a fascinating link back to the starting liquid crystalline phase. A variety of mixing, extrusion, and coagulation conditions were explored and the resulting fibers were characterized and compared.

Additional characterization provided information on the mechanical, electrical, and thermal properties of the neat SWNT fibers. Strength testing showed the fibers to be relatively weak, but promising, considering the lack of applied tension. The fibers possessed a tensile strength of $\tau = 1 – 5$ MPa and an elastic modulus of $Y = 50 – 1000$ MPa. The fibers were found to be p-doped with residual acid in their as-spun (i.e. green)
state, which was removed upon annealing. Electrical resistivities of green fibers were found to be $\rho \approx 0.5\ \text{m}\Omega\cdot\text{cm}$, which increased by a factor of ten after annealing. In addition, thermal conductivities of $\kappa \approx 20\ \text{W/K}\cdot\text{m}$ were measured for the fibers [21]. These fibers are a promising first generation of neat SWNT fibers.

To facilitate future neat SWNT fiber research, the Spinning Bob Mixer (SBM) was designed. The SBM combines a mixer and extruder into a single integrated laboratory apparatus. The machine can mix higher concentrations in a corrosion-resistant sealed environment, while monitoring the sample’s mixing evolution. The sample can then be seamlessly extruded from the same apparatus in a controlled fashion. The SBM has modular mixing and extrusion components capable of handling high pressures (1500 psi) and high temperatures (150°C). A central bob engineered into the SBM enables experiments involving shear-assisted spinning and shear-improved alignment. The various features of the SBM were successfully tested. The experiments demonstrate the abilities of the apparatus, as well as providing additional preliminary research into the field of neat SWNT fibers.

Like most aspects of SWNT research, neat SWNT fibers are a complicated field of science. It is a field which merges the domain of fiber engineering with the nanoscience of SWNTs, and in the process brings the challenges of both. However, it is at the intersection of traditional sciences that the future of technology will be born. A basic foundation of understanding that incorporates the principles and backgrounds of all constituent sciences will be necessary for such progress to be made. This thesis begins the journey of neat SWNT fibers research. The first generation of macroscopic neat
SWNT fibers has been created and the tools needed for future research designed and demonstrated.
2. Background

Macroscopic neat single-wall carbon nanotube (SWNT) fibers involve two distinct fields of science – SWNT research and fiber processing. SWNTs have been unique since their discovery. They have produced a field of research that bridges and involves many different types of science, and yet remains distinct due to SWNTs’ unusual behavior and properties. Fiber processing, on the other hand, is solidly in the realm of chemical engineering and brings with it a detailed history and canon of knowledge. To understand and appreciate a truly pure SWNT fiber, one must first explore the backgrounds of SWNTs, fiber engineering, and the macroscopic SWNT materials that provide the prologue to this research.

2.1. Carbon Nanotube Background

Carbon nanotubes were first discovered by Sumio Iijima of NEC Corporation in 1991 [1]. When voltage was applied between two carbon electrodes contained within an argon environment, carbon needles were observed on the negative electrode and examined by transmission electron microscopy. They appeared to be microtubules of graphitic carbon, most containing multiple shells, like concentric hollow cylinders. These objects became known as carbon nanotubes.
2.1.1. Nanotube Synthesis

The first nanotubes produced and studied were predominantly multi-wall nanotubes (MWNTs). MWNTs were discovered by accident in the surrounding soot of a carbon arc apparatus. Such apparatuses, which work by applying a high voltage between two carbon electrodes, have been used to produced carbon whiskers since the 1950s and more recently to produce the nanotube’s predecessor, C₆₀ [23]. A year later, two independent research groups found that by adding small amounts of transition metals, namely cobalt, nickel, or iron, growth would favor single-wall carbon nanotubes (SWNTs) [2, 3]. The arc-discharge method of nanotube production results in nanotubes with few structural defects, and is still widely used in the field of nanotube production today. Its only disadvantage is a small batch yield (~100 mg / day) [24].

Three additional methods for SWNT synthesis exist, each with their own advantages and disadvantages. Chemical vapor deposition (CVD) is the most common method because it is easy and cost-effective. Metal catalyst particles on a substrate are exposed to hydrocarbon gas at high temperatures, resulting in a clean substrate of SWNTs. The yield of CVD synthesis is typically low (~30 mg/day) [112], although recent developments have enabled batch yields as high as ~1 g / day [113, 114].

The third method for producing SWNTs is called pulsed laser vaporization (PLV) [25]. A rotating target of pressed graphite containing small amounts of cobalt and nickel powder is subjected to nanosecond laser pulses on the order of 2.5W of power. The incident laser creates a plume of plasma, wherein the metal particles catalyze SWNT growth. The entire process occurs in a sealed atmosphere of flowing argon. The product
is then carried downstream and collected. The PLV process can produce an order of magnitude more nanotubes than current arc-discharge methods (~1 g / day) [26].

Material used throughout this research was produced by the latest process for SWNT production – HiPco. The high pressure carbon monoxide (HiPco) method of production has revolutionized SWNT research because of its large yields (>10g/day) of high-purity nanotubes [17]. Single-wall carbon nanotubes are grown using a gas-phase chemical vapor deposition process. SWNTs grow in high-pressure (30–50 atm), high-temperature (900–1100 °C) flowing CO on catalytic clusters of iron. The clusters are formed in situ: Fe is added to the gas flow in the form of Fe(CO)$_5$. Upon heating, the Fe(CO)$_5$ decomposes and the iron atoms condense into clusters. These clusters serve as catalytic particles upon which SWNTs nucleate and grow (in the gas phase) via CO disproportionation. The HiPco process is by far the most viable, scalable method for SWNT mass production. The availability of large quantities of high purity HiPco SWNTs made possible research on neat SWNT fibers.

2.1.2. General Properties of Carbon Nanotubes

A carbon nanotube can best be thought of as a sheet of graphite, which has been rolled into a narrow, long cylinder and then capped at each end by a hemisphere. Another appropriate visualization is that of a spherical fullerene that has been cleaved in half and then elongated, with a graphite sheet of carbon atoms filling the gap between the two distanced halves. Either way, the end result is a nanotube, approximately 100 – 1000 nm in length and 1 nm in diameter.
Like graphite, nanotubes are comprised of interconnected six-member rings, or hexagons, of carbon atoms. These hexagons of carbon span the entire surface of a nanotube and are the source of many of the peculiar properties of nanotubes. The spatial orientation of the hexagon with respect to the nanotube’s axis is not unique, resulting in three chirality classifications of nanotubes – armchair, zigzag, and chiral. Armchair and zigzag nanotubes are named after the pattern of bonds exposed on their open ends. All other nanotubes are classified as chiral. Figure 2.1 depicts the three types of nanotubes.

(a)

(b)

(c)

Figure 2.1: The three types of nanotubes are shown with their cross-sections exposed – (a) armchair, (b) zigzag, and (c) chiral. Nanotubes were named after the general shape of their cross-section. Note the varying orientation of the hexagons with respect to the nanotube axis [27].

Single-wall carbon nanotubes are defined by two unit vectors that define the hexagonal plane of a graphene sheet [27]. Integer values of these two unit vectors (Fig. 2.2) define a given SWNT, providing a naming index \((n, m)\). A SWNT can be visually
constructed by rolling a graphene sheet and overlaying the origin and the endpoint of the chiral vector. The chiral vector then defines the circumference of the nanotube, with the translation vector defining the unit cell. The type of nanotube, semiconducting vs. metallic, can also be determined from a SWNT's index. Through analysis of SWNT electronic properties with respect to symmetry, it is found that a given \((n, m)\) nanotube is metallic if \(n - m = 3q\), where \(q\) is an integer [27]. To avoid double-counting SWNT types, indexing is restricted to a 30° arc on the graphene sheet. In most syntheses, a distribution of diameters, types, and lengths is produced.

![Graphene sheet diagram](image)

**Figure 2.2:** A graphene sheet is shown depicting the chiral, \(C_n\), and translation, \(T\), vectors of a SWNT. The vectors for a (6,2) semiconducting nanotube are shown as an example.

In addition to their unique molecular composition, SWNTs aggregate themselves into ordered structures. The smooth tubular surface of SWNTs has a significant van der Waals binding energy of \(-500\) eV / \(\mu\)m of tube-tube contact [25, 28]. Because of this, nanotubes prefer to surround themselves with other nanotubes in an aligned fashion. Such aggregates are called *bundles* and/or *ropes*, names that have become more or less interchangeable (Fig. 2.3). SWNT research initially focused on characterization and
applications involving SWNT ropes due to their more manageable size (~1 \( \mu \text{m} \) in diameter and 10 – 50 \( \mu \text{m} \) in length). However, as the field matures experiments that focus on individual SWNTs are becoming more common.

![Figure 2.3: A transmission electron micrograph of a bundle of SWNTs head-on [29].](image)

A second common aggregated collection of SWNTs is buckypaper. Buckypaper is made by filtering a suspension of SWNTs onto an appropriate membrane. The result is a mat of randomly oriented large SWNT bundles that extend throughout each other in a tangled macroscopic material (Fig. 2.4). Measurement of bulk properties of SWNTs is often restricted to buckypaper because of its availability. However, due to the anisotropic properties of individual SWNTs, the interesting neat SWNT materials will require macroscopic objects of aligned SWNTs.
The same reason that SWNTs easily form *ropes* and *bundles* causes difficulties when attempting to suspend nanotubes in a liquid medium. Stable suspensions are critical to most nanotube research, with suspensions of individual SWNTs as the ultimate goal. The strong van der Waals attractive force between SWNTs has plagued chemists since their discovery, and has led to many different methods for suspending SWNTs. Many different approaches have been developed that produce suspensions of SWNT bundles, including aqueous surfactants [30, 31], chemical derivatization [32, 33], and polymer-wrapping [20]. While several groups have reported successful routes that produce individual-enriched suspensions, only recent work involving centrifuged suspensions of aqueous surfactant-coated SWNTs has produced dispersions of individual SWNTs [34]. However, none of these methods produce dispersions of individual SWNTs at high concentrations (< 0.5 wt%).

The novelty of carbon nanotubes extends well beyond an appreciation of their physical uniformity and uniqueness. Over the last decade, research has provided theoretical and experimental insight into many of these properties, showing nanotubes to
be truly impressive entities, exhibiting electrical conductivity better than copper, thermal conductivity better than diamond, and mechanical properties better than steel.

Theoretical work predicted that nanotubes could be metallic or semi-conducting, depending on their chirality [35, 36]. Experimental work involving scanning tunneling microscopy and spectroscopy has already confirmed these electronic properties [37, 38]. The different types of SWNTs allow for a variety of nanotube-based electronic devices. Conductivity measurements have shown that individual metallic single-wall nanotubes display ballistic conductance along their length with a room temperature resistivity of $\sim1 \mu\Omega\cdot\text{cm}^2$ [7]. Ropes of SWNTs have been shown to possess electrical resistivities along their axes of $0.03 - 0.1 \, \text{m}\Omega\cdot\text{cm}$ [25], while buckypapers of randomly aggregated SWNTs exhibit electrical resistivities of $10 \, \text{m}\Omega\cdot\text{cm}$ and $0.5 \, \text{m}\Omega\cdot\text{cm}$ when acid-doped [26]. In comparison, copper has a room temperature resistivity of $\rho = 1.7 \, \mu\Omega\cdot\text{cm}$ [110]. An effective field-effect transistor has also been successfully engineered and demonstrated [39] using individual SWNTs. The high conductivity is the result of an unmodified $sp^2$ bond structure running the length of the nanotube. The conductivity is reduced as more scattering sites are introduced, either through chemical or physical means [40]. In addition, the electronic properties of carbon nanotubes are inevitably linked to their strength characteristics; resistance measurements of strained nanotubes have shown a relationship between electrical conductivity and plastic deformation [41]. Finally, the unique electronic properties of SWNTs result in interesting and useful resonant Raman enhancement.

Raman spectroscopy is a useful and established tool for probing molecular structures. Incident laser photons scatter off a sample, and in doing so, impart some of
their energy to molecular vibrational modes via phonon energy. Each kind of vibrational mode has a characteristic energy associated with it; therefore, based on the shift in photon energy the molecular structure of a sample can be investigated.

In the case of SWNTs, there exists a resonance enhancement due to strong electron-phonon coupling. When the excitation frequency is close to a frequency of high optical absorption the resulting Raman signal is significantly enhanced. This enhancement is due to the one-dimensional van Hove singularities of the electronic density of states [42]. One of the useful experimental results of this strong coupling is that the geometry of a SWNT determines much of the Raman spectrum.

Within a SWNT Raman spectrum, there exist several distinct bands that originate from different aspects of the nanotube (Fig. 2.5). They are valuable experimental indicators of the type, size, and orientation of SWNTs. The first band encountered in the spectrum is a series of peaks around $100 - 300 \text{ cm}^{-1}$ shift. These are the Radial Breathing Modes (RBM) of the SWNTs being probed. These peaks originate from an out-of-plane radial vibration of the nanotube and are directly dependent on SWNT diameter [42, 43]. The D-band (i.e. disorder peak), and its second order $G'$-band, are highly dispersive bands associated with inherent disorder in the electronic states of the SWNT. Any situation where a nanotube will have an increase in electron-phonon scattering will result in an increase of the D-band intensity [42]. Increases in the disorder peak intensity have been experimentally attributed to SWNT defects [44] and chemical side-wall functionalization [32, 45]. The third band of interest is the most relevant to this thesis' research.
Figure 2.5: A Raman spectrum for a SWNT bundle. The various Raman peaks are shown: (RBM) Radial Breathing Modes, (D) D-band disorder peak, (G) G-band. The inset shows the two G-band peaks associated with axial (G' peak) and radial (G' peak) in-plane molecular vibrational modes.

The G-band in a SWNT Raman spectrum is the result of in-plane vibrational modes. The band appears as two peaks: the $G'$ peak associated with in-plane axial carbon atom vibrations and the $G'$ peak associated with in-plane circumferential vibrations. Because of the high, anisotropic polarizability of SWNTs [46], the $G'$ peak is strongly dependent on the relative orientation between the excitation source polarization vector and the nanotube axis. The result is that the peak is much stronger when the incident polarized laser light is parallel to the nanotube's axis, versus when it is perpendicular. This relationship has been shown theoretically [46], as well as experimentally [47].

Polarized Raman spectroscopy has been used to probe the orientation of SWNTs, both as individuals and in macroscopic objects. On individuals and small
bundles, these investigations have provided information on the fundamental nature of SWNT polarizability and resonance effects [42]. For macroscopic samples, polarized Raman spectroscopy provides a valuable tool for examining the orientation of individual SWNTs within the bulk [16, 47, 48]. The ratio of the maximum \(G^+\) peak intensity to the minimum intensity provides a direct experimental measurement of the overall degree of alignment present within a given sample. In addition, comparisons can be made between samples probed with the same excitation laser wavelength.

The second interesting property of SWNTs is their thermal conductivity. For the same reasons that transport of electrons is efficient along the length of a nanotube, phonon transport is also efficient. The theoretical thermal conductivity of SWNTs has been reported to be similar to that of in-plane graphite or diamond (~1000 W/K·m) [8]. Experimental work has shown ropes and mats of aggregated SWNTs to only have a thermal conductivity on the order of \(\kappa \approx 35\) W/K·m [49]. However, measurements on an individual MWNT, have shown a room temperature thermal conductivity of \(\kappa > 3000\) W/K·m, whereas a buckypaper formed from the same MWNTs produced a conductivity of only \(\kappa \approx 20\) W/K·m [50]. These values exceed those of in-plane graphite or diamond (both 2000 W/K·m) [50] and suggest even higher properties for individual SWNTs. Unfortunately, experimental difficulties have so far prevented the measurement of the thermal properties of an individual SWNT.

The third type of SWNT property that has received tremendous attention is mechanical. Because of their uniform structure and strong carbon bonds, nanotubes have been expected to have high strength from their discovery. Early on, nanotubes were found to be very flexible and durable macromolecules. Iijima et al. presented TEM
images of MWNTs captured in bent positions along with proof that such bending was reversible and elastic [51]. Further theoretical simulations showed that high degrees of repeated bending and torsion would not damage single-wall nanotubes [52]. Theoretical research has reported a strain-to-failure for individual SWNTs of 5 – 30% [53]. In addition, simulations report a Young’s modulus for an individual SWNT to be close to that of in-plane graphite (1 TPa) [54, 55]. These results have been confirmed experimentally. By observing free-standing, individual SWNTs under a transmission electron microscope (TEM) in a controlled temperature environment, Krishnan et al. obtained a Young’s modulus for individual SWNTs, $Y_{\text{avg}} = 1.25^{+0.45}_{-0.35}$ TPa [4]. Other mechanical properties have been measured on ropes of SWNTs due to difficulties in handling and manipulating individual nanotubes. Using an atomic force microscope to strain SWNT ropes, values of their strain-to-failure (~5%) and tensile strength (~47 GPa) have been measured by multiple research groups [5, 6]. These values are recognized as lower bounds on the properties of individual nanotubes, but are appropriate when discussing potential neat SWNT fibers.

2.2. Fiber Background

Fibers have been produced for over a hundred years and have infused themselves into every aspect of modern life. They are used in areas as diverse as aerospace, textiles, civil engineering, and law enforcement. A fiber can be defined as any material that possesses a length at least 100 times greater than its diameter and a high degree of flexibility. Because of these anisotropic requirements, polymers or other large anisotropic
molecules are necessary for successful fiber production (also called fiber spinning). The production of any fiber can be described by four steps:

1. Preparation of the fiber-forming polymer,
2. Preparation of the liquid sample (i.e. dope),
3. Extrusion of the fiber,
4. Post-processing treatments.

It is important to recognize that fiber-making is a complicated technology. All four of these steps affect the resulting fiber and are not independent of each other.

There are many different types of fiber systems. The polymer can be rigid or flexible. Rigid rod polymers and some semi-flexible polymers assemble in an aligned liquid crystalline phase, while other flexible polymers receive their alignment solely from the extrusion process. Because of the rigid anisotropic nature of SWNTs, fibers formed from rigid rod polymers are the most appropriate analogy. In addition, the fiber-forming dope can be a melt or a solution. Melt spinning involves melting a polymer sample, pressure-driven extrusion, and coagulation through cooling into a solid. Single-wall carbon nanotubes decompose prior to melting (around 750° C in air and 2000° C in an inert environment). Because of this, melt spinning is not an option; solution spinning is the only viable approach. Therefore, an examination of the four steps in the context of solution spinning of rigid rod liquid crystals provides an appropriate template for SWNT fiber creation.
2.2.1. Fiber-Forming Polymer

The first step in the production of a fiber is the creation or modification of a suitable molecular constituent. The formation of a liquid crystalline phase (see Sec. 2.2.2.) is highly desirable. In general, polymer molecules that are capable of forming such a phase are rigid or semi-rigid molecules that consist of a rigid back-bone structure connected to flexible side-chains [56]. For synthetic (i.e. manufactured) fibers, two principal mechanisms can be utilized for the synthesis of suitable polymers – condensation and addition polymerization [18]. Condensation polymerization involves a series of reactions of functional groups to form the larger polymer. Addition polymers are formed by the addition of monomers to the main chain without chemically modifying the monomers. Organic (i.e. natural) fibers are produced through chemically modifying naturally occurring polymers to improve their spinnability and remove impurities [57]. Both organic and synthetic polymers can form liquid crystal samples, depending on their molecular properties.

2.2.2. Liquid Crystalline Polymers

In general, a polymer is not useful for fiber production if it cannot be spun in an aligned fashion. Two principal types of rigid rod polymer samples exist in fiber spinning: melts and solutions. Both involve systems where the individual molecules are highly aligned prior to extrusion as a fiber and it is this intrinsic alignment that provides the necessary anisotropic properties found in rigid rod polymer fibers. The key to useful
fibers is the combination of molecular properties and the ability of those molecules to form a phase of matter between a traditional solid and liquid – the liquid crystal.

Liquid crystals are systems that possess some long-range molecular orientational order, while lacking the full three-dimensional positional order of a solid (i.e. they maintain the fluidity of a liquid). Orientational order means that the molecules tend to point in the same direction as each other, along a common axis called the director. A lack of full positional order means that the centers of mass of the molecules do not lie on a three-dimensional lattice. Molecules that form liquid crystals are usually oblate (disk-like) or prolate (cigar-like) in shape while possessing some rigidity. Three basic kinds of liquid crystal systems exist – nematic, smectic, cholesteric. Nematic liquid crystals possess orientational order about a director, but do not possess any long range positional order. The molecules are aligned in the same direction, but do not organize in planes. Smectic liquid crystals possess the same degree of orientational order as nematic systems, but also possess one-dimensional positional order. Finally, cholesteric liquid crystals are a kind of nematic which has been twisted periodically about an axis normal to the director. The director effectively rotates as it translates long this perpendicular direction. This twisted structure arises from the chiral nature of the constituent molecules themselves. In addition to the ordering of a liquid crystal, the phase behavior of a given system can vary between polymer systems.
Figure 2.6: A drawing showing the differences between nematic, cholesteric, and smectic liquid crystals. Nematic systems have orientational order, cholesteric have twisting orientational order, and smectic systems have both orientational and positional order [58].

Two types of liquid crystalline polymers exist – thermotropic and lyotropic. Fibers made from thermotropic liquid crystals are melt spun, while lyotropic crystals form fibers through solution spinning. Thermotropic liquid crystals are one-component materials; the temperature range in which the liquid crystal exists is bounded from below by a transition to a solid and bounded from above by a transition to an isotropic liquid. In the intermediate liquid crystalline phase, the polymer molecules possess sufficient kinetic energy to move around, but are still spatially constrained to assemble in ordered domains with the molecules roughly parallel to one another within a given domain. Melt spinning can be performed on thermotropic liquid crystalline polymers which are solid at room temperature and liquid crystalline at reasonable higher temperatures.
Lyotropic liquid crystalline polymer systems, those which require a solvent, obtain their ordering in a different way. In those systems, a model consisting of solvated rigid rods can be used to explain and predict the phase behavior and rheological regimes of stiff polymer molecules in solution. When rods are dissolved in a solvent, the phase of the system depends on the concentration of the species present. As the concentration increases, the system will transition through four distinct regimes (Fig. 2.7).

**Figure 2.7: A pictorial representation of the four different phase regimes of a liquid crystalline system of rigid rods [59].**

In the dilute regime, the concentration is low and the rods do not interfere with each other; they are free to translate and rotate. No positional or orientational order exists in the system and the entities contribute little to the overall viscosity of the solution. As the concentration increases, the rods first begin to hinder each other’s rotation (semidilute) and then translation (isotropic concentrated). Order still does not exist between the rods, but their motion is hindered and therefore the viscosity starts to increase rapidly. In addition, alignment of the entities due to an induced shear field can reduce the overall viscosity. The rods are less hindered by each other when partially aligned.
At high concentrations, the molecules are forced to organize into aligned domains due to spatial constraints. Due to their anisotropic geometry, the rods will align parallel to each other to minimize their interactions and increase packing density. In most systems there exists a range of concentrations where an isotropic phase and a liquid crystalline phase coexist. Some of the rods exist in aligned domains, while a volume fraction of the system still consists of non-aligned entities. Exchange between the isotropic and aligned regions exists but the system as a whole is entropically stable. In this regime, reorientation of the rods due to elongational or shear flow involves large groupings of rods. The system exhibits substantial shear-thinning, i.e. the viscosity decreases as a function of applied shear.

The final phase transition is from a biphasic system to a single liquid crystalline phase. The viscosity of the system increases substantially with increasing volume fraction of the aligned phase (Fig. 2.8). Prior this transition, the anisotropic phase becomes the dominant one and the viscosity starts decreasing as a function of increasing concentration. The system becomes a single liquid crystalline phase and the viscosity continues to decrease until the ideal close-packing of the aligned phase is reached. Concentration increases beyond that point can increase the viscosity dramatically while maintaining a single phase [56]. Such rheological phase behavior is an important tool to develop a viable fiber spinning approach.
Figure 2.8: A plot of viscosity vs. polymer concentration for PPTA in sulfuric acid [18].

Polymeric liquid crystalline systems are also known to possess a handful of distinct qualities. Understanding these properties can aid in identifying and handling a liquid crystal sample. The first distinct characteristic of traditional polymer liquid crystals is the viscosity behavior as a function of applied shear rate. In general, liquid crystalline systems follow a three-region viscosity vs. shear rate curve (Fig. 2.9). The curve consists of an initial region of high shear-thinning at low shear rates. The second region is a Newtonian plateau, followed by a third region described by a power law.

Figure 2.9: A three-region model of typical liquid crystalline polymer viscosity vs. shear rate. Region I is absent in some polymer systems [56].
Region I shear-thinning has not been observed for all liquid crystalline polymer systems, but is the most distinguishing liquid crystalline feature in a viscosity vs. shear rate curve. The behavior of liquid crystalline polymers in this region is still not fully understood. It is believed that in highly viscous nematic systems, stresses associated with defects become effectively trapped; minor amounts of shear allow the liquid to reorient around them [56]. The plateau in Region II originates from a simple inability for the shear to influence the orientation of the liquid crystal’s molecules, similar to the viscosity behavior of isotropic solutions. Region III is where the shear rate is sufficient to influence the molecules. The rigid rod polymer molecules exist in aligned domains, but possess some distributional deviation from the domain’s overall alignment direction. This closely packed system is very viscous at low shear rates, but as the applied shear increases, the liquid crystalline domains shift their orientation and the molecules within also become more aligned, such that the internal friction between domains and between molecules is reduced. The result is that, in Region III, the viscosity decreases as a function of shear rate (Fig. 2.10) and is described by a power law:

\[ \eta = m\dot{\gamma}^{n-1} \]  \hspace{1cm} (2.1)

where \( \eta \) is the viscosity, \( \dot{\gamma} \) is the applied shear rate, and \( m \) and \( n \) are constants.
Another common characteristic of liquid crystals is birefringence. When examined under a polarized optical microscope, incident polarized white light is transmitted at different efficiencies through the liquid crystal sample based on the angular orientation between the polarization vector and a given domain’s director. Incident light that is parallel to a domain’s alignment is more easily absorbed due to polarization of the constituent molecules and therefore a lower intensity is transmitted. Liquid crystal samples appear as light and dark regions, with the shape and size of these regions dependent on the polymer involved and slide preparation. The regions observed are different liquid crystalline domains that possess varying orientations within the sample. By rotating an analyzing polarizer in between the sample and the viewing objective, the domains are seen to light off and on. The presence of birefringence is a common first indicator of a liquid crystalline system.
In addition to unusual rheological and phenomenological characteristics, the phase diagram for a given polymeric liquid crystal often provides valuable information for fiber spinning. Figure 2.12 depicts a typical phase diagram for rigid rod polymers and shows the various phase regions. While transitions to the liquid crystalline state are governed by concentration changes for lyotropic systems, temperature still plays a role. At low concentrations, the individual molecular entities gain kinetic energy with increased temperature, which hinders orientational alignment into liquid crystalline domains. At the other end of the concentration regime, high concentrations are in fact aided by increased temperature because the kinetic energy allows domains to reorganize more readily to incorporate isotropic molecules and heal defects. In addition, almost all liquid crystal systems possess a biphasic chimney, over a certain temperature range, which separates the isotropic phase from the single phase liquid crystal. By understanding the phase diagram of a given system, one can better plan the spinning of fibers from single-phase, well-aligned liquid crystalline samples.
Figure 2.12: A typical phase diagram for rigid rods showing temperature vs. volume concentration of polymer. The isotropic phase (I) is separated from the single phase liquid crystal (LC) by a biphasic region (I + LC), which includes a narrow biphasic chimney above some critical temperature [58].

2.2.3. Fiber Spinning

Because of the nature of SWNTs, melt spinning is not an option. Only solution spinning provides a viable route to industrial quantities of neat SWNT fibers. Solution spinning is a more complicated process due to the removal of solvent and the recovery and handling of the resulting fiber [18]. There are two basic methods for spinning lyotropic liquid crystalline polymers into fibers. Both methods involve pressure-driven extrusion of the dope through small orifices into a coagulation region. Orifice sizes can vary, but are typically 50 – 250 μm in diameter for both methods [18]. The methods are defined by the way in which the solvent is removed and the fiber coagulated.

Dry-spinning, the first solution spinning method, involves coagulation of the fiber by solvent evaporation. The fiber is spun into a heated chamber, wherein the solvent evaporates. This method of coagulation is slower than melt-spinning and consequently, the achievable spinning speeds of the fiber line are considerably less than in melt-
spinning processes. Dry-spinning dopes are typically 15 – 45 wt% polymer solids. Example fibers produced by dry-spinning include secondary cellulose acetate, cellulose triacetate, acrylic (e.g. Orlon™), Spandex™-type polyurethane elastomeric fibers (e.g. Lycra™), polyvinyl chloride (PVC), and chlorinated PVC [18].

The second method of solution-spinning is called wet-spinning. In this approach, the emerging fiber filaments are coagulated in a precipitation bath. The solvent leaves the fiber by diffusing into the bath, solidifying the extruding fiber. Because of the coagulation process, wet-spinning involves slower extrusion speeds and less polymeric solids in the dope (5-30 wt%) than dry-spinning. In addition, some modern high performance aromatic polyamide fibers utilize a modified wet-spinning method.

![Diagram of fiber spinning processes](image)

**Figure 2.13:** Examples of the three main types of fiber spinning – (a) melt spinning, (b) dry solution spinning, and (c) wet solution spinning [62].
Aramid fibers, like poly(p-phenylene terephthalamide) (PPTA) and poly(p-phenylene benzobisoxazole) (PBO), have adopted a modified wet-spinning process that has been found to greatly improve those fibers' properties. These fibers are spun from solution into a coagulant bath with a short air gap between the spinneret and the coagulant surface. This process allows for the use of a low temperature coagulant bath without freezing the spinning solution. The dope can be maintained at a higher temperature, thus allowing a higher concentration to be spun at reasonable pressures. Dry-jet wet-spinning produces PPTA fibers possessing twice the modulus and half the strain-to-failure as wet-jet wet-spun PPTA fibers [18].

![Diagram](image)

Figure 2.14: A cartoon depicting the dry-jet wet-spinning technique used to produce aramid fibers, like PPTA [18].

Coagulation of a fiber in wet-spinning is a complicated and critical stage in the formation of a usable fiber. During its residence time in the coagulation bath, the fiber solidifies due to a number of complicated factors. These factors include solvents used, polymer involved, coagulant bath temperature, flow rates, and orifice diameter. The coagulant is chosen to be miscible with the dope's solvent while being a poor solvent for, and having a low diffusion rate into, the fiber. This allows the solvent to easily leave the
fiber, while solidifying the remaining constituents. Coagulation is a mass transfer phenomenon wherein the solvent from the dope diffuses into the coagulant bath. A skin of solidified fiber forms during extrusion around a core of uncoagulated proto-fiber. The skin increases radially during exposure, providing structural stability to the proto-fiber and allowing tension to be applied to the fiber line.

![Diagram](image)

*Figure 2.15: A drawing depicting the skin-core effect during coagulation [57].*

The final shape of a fiber’s cross-section is dependent on both the diffusion of the solvent outward from the fiber and by the diffusion of the coagulant inward. The solvent should have high miscibility with the coagulant and moderate diffusivity out of the fiber [57]. Depending on the flux of solvent out ($j_s$) and of coagulant in ($j_c$), three situations can occur (Fig. 2.16).

1. If the inward flux of coagulant is greater than the outward flux of solvent, then the fiber swells and results in a circular cross-section.

2. If the inward flux is less than the outward flux, and the fiber skin is soft and deformable, then the fiber shrinks uniformly and results in a circular cross-section.
3. If the inward flux is less than the outward flux, but the preliminary skin is rigid, then the fiber will resist radial deformation and will instead collapse into a flattened fiber. Often, the fiber collapses into a thick "U" shaped cross section, called "dog-boned".

Spinning conditions where the diffusivities of the coagulant and solvent are matched will result in no change in size during coagulation and will provide a circular cross section. In the absence of tension during spinning, this last situation is experimentally difficult to obtain. Non-uniform coagulation can be prevented by careful selection of coagulant and, to a lesser extent, by the application of tension during spinning [57].

\[
\begin{align*}
\text{Proto-Fiber} & \quad \text{Soft Skin} & \quad \text{Rigid Skin} \\
\text{\( \dot{j}_s > \dot{j}_c \) & \quad \text{(a)} & \quad \text{(b) \quad \dot{j}_s < \dot{j}_c \)} & \quad \text{(c) \quad \dot{j}_s > \dot{j}_c} \\
\end{align*}
\]

\( j_s \) - Flux of Solvent out of the fiber
\( j_c \) - Flux of the Coagulant into the fiber

Figure 2.16: A depiction of the different possible coagulation situations. (a) \( \dot{j}_s/\dot{j}_c > 1 \) with a soft skin, (b) \( \dot{j}_s/\dot{j}_c < 1 \), and (c) \( \dot{j}_s/\dot{j}_c > 1 \) with a rigid fiber skin.

Regardless of the extrusion method used to produce a fiber, solidification of the fiber and the "freezing" of its internally aligned structure in a uniform manner are greatly assisted by the application of tension during extrusion. Without drawing a fiber (i.e.
tension), solidification occurs through evaporation/elution of the solvent, leaving an aligned crystalline structure behind. The internal alignment of the fiber is limited by the molecular alignment in the liquid crystalline dope, which will have a significant solvent volume that is left void. Drawing promotes fiber densification while the solvent leaves, improving fiber properties in the process. Once a fiber is produced, the remaining step is post-processing.

2.2.4. Fiber Post-Processing

The final stage of fiber formation is post-processing treatment of the fiber. Even after the appropriate application of optimal spinning, coagulation, and drawing conditions, a fiber can be further improved. Liquid crystal polymer systems are viscoelastic liquids; they act as solids over short times and liquids over long times. Such liquids can store stresses in the polymer configurations of the concentrated phase. During extrusion, the polymer liquid crystal undergoes tremendous shear and extensional strain. Drawing during coagulation alleviates most of this stored stress, but often the fiber still possesses internal stresses that will relax over time. Post-processing treatments often involve heating the fiber under tension. The stored stresses in the fiber relax more quickly while the fiber maintains its uniformity and high degree of alignment. In industrial operations, such post-processing is an integral part of the fiber spinning process.
2.2.5. Conventional Fibers

Fiber engineering is a large and lucrative industry that produces hundreds of
different kinds of fibers on a daily basis. High performance fibers are produced for one or
more of three kinds of applications: mechanical, electrical, or thermal. All three of these
areas are important; fibers that possess poor mechanical properties, but excellent
electrical properties are still valuable. Current fiber engineering has been focusing
increasingly more and more on multifunctional fibers, fibers that possess two or more
useful properties. Implementation of such fibers reduces costs and space, and improves
versatility. To understand the role in which single-wall carbon nanotubes (SWNTs) have
played in composite fiber research, a general treatment of high-performance fibers in
each of these application areas is useful.

Fibers have been prized for their mechanical properties since their creation. High
strength, low weight fibers have been produced for almost 100 years [18]. Inherent
molecular strength combined with a highly crystalline structure leads to the remarkable
mechanical properties of polymer fibers. Because almost all fibers have at least moderate
strength, applications often balance cost against maximum mechanical properties needed.
Fibers can be sorted into four different categories, based on their mechanical properties
[63]. Table 2.1 lists the categories and includes examples of each class. Tenacity is
defined as the mass stress, or force per unit linear density, and is a common mechanical
property measured in the fiber industry. It has units of gram·foot per denier and converts
to stress as [18]:

\[(\text{Tenacity})(\text{g·ft/d}) \times (\text{density})(\text{g/cm}^3) \times (8.83 \times 10^5) = \text{Stress (Pa)}.\]  (2.2)
The various fiber acronyms listed are as follows: stainless steel (SS), polypropylene (PP), poly(ethylene terephthalate) (PET), poly(acrylonitrile) (PAN), poly(p-phenylene terephthalamide) (PPTA), poly(p-phenylene benzobisthiazole) (PBZT), and poly(p-phenylene benzobisoxazole) (PBO).

Table 2.1: Mechanical Properties of Conventional Fibers [18]

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Tenacity [gfd⁻¹]</th>
<th>Tensile Strength [GPa]</th>
<th>Elongation to break</th>
<th>Elastic Modulus [gfd⁻¹]</th>
<th>Density [g / cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>3 - 5</td>
<td>0.14 - 0.18</td>
<td>35%</td>
<td>30 - 60</td>
<td>1.31</td>
</tr>
<tr>
<td>- Wool</td>
<td>1.2 - 1.6</td>
<td>0.14 - 0.18</td>
<td>29 - 43%</td>
<td>2.3 - 34.4</td>
<td>1.31</td>
</tr>
<tr>
<td>- SS Metal Fiber</td>
<td>1.4 - 2.0</td>
<td>1 - 1.4</td>
<td>&lt; 1%</td>
<td>280</td>
<td>8.0</td>
</tr>
<tr>
<td>- Acrylic</td>
<td>2.0 - 3.3</td>
<td>0.20 - 0.34</td>
<td>20 - 50%</td>
<td>67 - 78</td>
<td>1.16</td>
</tr>
<tr>
<td>Above Average</td>
<td>7 - 8</td>
<td>0.36 - 0.73</td>
<td>16 - 65%</td>
<td>25 - 100</td>
<td>1.14</td>
</tr>
<tr>
<td>- Nylon 6</td>
<td>3.6 - 7.2</td>
<td>0.31 - 0.71</td>
<td>15 - 35%</td>
<td>22 - 33</td>
<td>1.14</td>
</tr>
<tr>
<td>- PP</td>
<td>3.9 - 8.9</td>
<td>0.87 - 0.94</td>
<td>18 - 25%</td>
<td>53 - 85</td>
<td>1.14</td>
</tr>
<tr>
<td>Superior</td>
<td>8 - 20</td>
<td>0.95 - 1.35</td>
<td>31 - 47%</td>
<td>1400 - 3300</td>
<td>1.31</td>
</tr>
<tr>
<td>Outstanding</td>
<td>15 - 50</td>
<td>1.8 - 7.1</td>
<td>0.5 - 2.4%</td>
<td>460 - 1300</td>
<td>1.45</td>
</tr>
<tr>
<td>- PAN-based Carbon</td>
<td>11 - 44</td>
<td>2.2 - 2.8</td>
<td>1.2 - 3.7%</td>
<td>2300</td>
<td>1.58</td>
</tr>
<tr>
<td>- Kevlar™ (PPTA)</td>
<td>29</td>
<td>4.1</td>
<td></td>
<td>2600</td>
<td>1.58</td>
</tr>
<tr>
<td>- PBZT</td>
<td>41</td>
<td>5.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

While fibers with impressive mechanical properties are readily available, electrical conductivity is a more elusive property. Because of their extensive covalently bonded molecular structure, polymer fibers are inherently good electrical insulators [18]. To obtain useful electrical properties, two approaches are commonly used. The first is to include electrically conductive fillers or additives, which percolate the fiber’s structure and provide viable conductive pathways. Examples of this approach include polypropylene fibers loaded with vapor-grown carbon fibers (VGCFs) [65] and nylon fibers loaded with carbon, metal, or metal oxide [18]. The second method is to chemically modify the starting polymer to disrupt its bond structure or to encourage the fiber to take on water from the atmosphere, effectively doping the fiber. Examples of
chemical doping include nylon polymer chains with polyether or polyacrylamide units [18] and polyaniline emeraldine base (PAn-EB) doped with HCl [66]. Both methods of improving the electrical properties of a fiber often cause the mechanical properties to suffer, unless the additive is also inherently strong (e.g. VCGF). Nylon with a 10 – 20 wt% electroconductive filler possesses a resistivity of 100 Ω·cm with a ~30% lower tenacity [18], while PAn-EB fibers suffer a 64% loss in tenacity after doping with HCl, but exhibit a resistivity of 6.25 mΩ·cm [66]. In addition, both methods require more complicated processing, such as additional reaction chemistry, increased polymer blending, or more elaborate spinning methods. Electrically active fibers are used in a variety of applications, with different applications requiring different degrees of resistivity. The approximate resistivities required for the more common applications are: static dissipation, 10^{12} Ω·cm; electrostatic paint, 10^6 Ω·cm; and radio frequency interference shielding, 10 Ω·cm [67]. Table 2.2 lists example fibers commonly used in such applications (references included with individual entries).

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Electrical Resistivity (Ω · cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile / vinyl acetate (86/11) doped with Cu⁺ [18]</td>
<td>33</td>
</tr>
<tr>
<td>Nylon 6 w/ 10 – 20 wt% electroconductive filler [18]</td>
<td>100</td>
</tr>
<tr>
<td>Poly(acrylonitrile) / PPTA (30/70) [66]</td>
<td>10</td>
</tr>
<tr>
<td>Polypyrrole / PPTA [68]</td>
<td>1.5</td>
</tr>
<tr>
<td>Polypropylene w/ 15 vol% VGCF [67]</td>
<td>1</td>
</tr>
<tr>
<td>Nylon w/ 15 vol% VGCF [67]</td>
<td>1</td>
</tr>
<tr>
<td>Polyaniline emeraldine base doped with HCl [66]</td>
<td>6 x 10^{-3}</td>
</tr>
<tr>
<td>Poly(acrylonitrile)-based Carbon [18]</td>
<td>1 x 10^{-3}</td>
</tr>
<tr>
<td>Mesophasis pitch-based Carbon [18]</td>
<td>1.8 x 10^{-4}</td>
</tr>
</tbody>
</table>

The third type of application for fibers is thermal. For many of the same reasons that most polymeric fibers have poor electrical transport, thermal conductivity is also low. However, while chemical modifications and electroconductive fillers can relatively
easily improve the electrical properties of a fiber, the thermal properties are often more
difficult to improve. By far, the most useful fibers for thermal applications are carbon
fibers, such as mesophase pitch-base, PAN-based, or polymer fibers loaded with VGCFs.
This fact bodes well for SWNT-based composites and neat SWNT materials. Table 2.3
lists various fibers and other materials for comparison.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity (W / K·m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air [69]</td>
<td>0.024</td>
</tr>
<tr>
<td>Polypropylene [18]</td>
<td>0.144</td>
</tr>
<tr>
<td>Teflon™ [70]</td>
<td>0.259</td>
</tr>
<tr>
<td>Polyimide [69]</td>
<td>0.33</td>
</tr>
<tr>
<td>Alumina [69]</td>
<td>22</td>
</tr>
<tr>
<td>VGCF loaded Epoxy Composite [71]</td>
<td>695</td>
</tr>
<tr>
<td>Carbon fiber [69]</td>
<td>800</td>
</tr>
</tbody>
</table>

2.3. Macroscopic SWNT Materials

Individual single-wall carbon nanotubes (SWNTs) excel in all three primary areas
where conventional fibers are used. Not surprisingly, nanotubes were put into polymer
composites soon after their discovery, first with MWNTs and then later with SWNTs. A
complete treatment of all SWNT composites would be exhausting and not entirely
relevant. Yet, a discussion of the state of research at this time in the fields of composite
SWNT fibers and macroscopic neat SWNT objects will provide an appropriate context
for understanding the importance and scope of this thesis’ research.
2.3.1. Composite SWNT Fibers

The field of composite SWNT fibers is underdeveloped given the obvious potential of SWNTs. The first years of composite SWNT materials research has seemed to focus almost exclusively on epoxies and thermoplastics, leaving fiber development to the more abundant and cost-effective MWNTs. The past four years have seen a notable increase in this field and will undoubtedly expand further over the next four years. However, there have been a couple of significant challenges to the development of SWNT composites in general.

Composite SWNT fibers suffer from two main problems that have limited their development – dispersion and load transfer. Both are also common problems when non-SWNT additives are included in a polymer matrix, but are aggravated in the case of SWNTs. The first challenge is the homogenous dispersion of the secondary component throughout the primary component [72, 73]. Whether it is silica fibers, nanoclusters, or SWNTs, improvements will be limited if the secondary component cannot provide its properties evenly to the bulk phase. Because of the predilection for SWNTs to aggregate into bundles and their relatively large surface contact energies, standard mixing approaches are often insufficient to break apart the large bundles and disperse the SWNTs evenly throughout the bulk. MWNT composites also suffer from this problem, but to a lesser extent.

The second challenge in SWNT composites is load transfer [74, 75]. In electrical and thermal applications, this is not important, but in mechanical applications it is critical. While SWNTs have a strong van der Waals attractive force between each other, they are smooth hydrophobic molecular entities that do not covalently bond to the
polymer matrix. Transferring load to the SWNTs is essential to take advantage of their mechanical properties. Efforts to chemically functionalize the sides or ends of SWNTs have been somewhat successful [76, 77], but load transfer still remains an important problem.

Despite these challenges, many groups have been successful in producing and characterizing SWNT composite fibers. These fibers have focused equally on all three primary properties – mechanical, electrical, and thermal. SWNTs have been incorporated into a variety of polymer fibers with varying levels of success. Composite SWNT fibers have been made from petroleum pitch, PMMA, polycarbonate, polypropylene, PBO, and PVA.

Some of the first work involving SWNT composite fibers was performed by Andrews et al. in 1999 involving pitch [9]. Pitch was used because of its potential carbon affinity to SWNTs and the range of properties available to pitch fibers. SWNTs, provided by Carbolex Inc., were purified and mixed with isotropic petroleum pitch in quinoline. The dispersion underwent sonication, followed by solvent removal before being melt spun as fibers. The fibers were drawn during extrusion, followed by two-stage heat treatment in air and nitrogen. Dispersions were made from 1, 5, 8, and 10 wt% SWNT loading, but during spinning the 8 and 10 wt% dopes produced weak fibers that could not be collected. However, the resulting 1 and 5 wt% SWNT fibers exhibited an improvement in both mechanical and electrical properties. Table 2.4 lists the fibers' properties and shows a ~90% increase in tensile strength, ~150% increase in elastic modulus, and a ~70% decrease in electrical resistivity. SWNTs were shown to be an important composite material for pitch fibers.
Table 2.4: Properties of SWNT / Pitch Fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength [MPa]</th>
<th>Elastic Modulus [GPa]</th>
<th>Electrical Resistivity [mΩ·cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pitch</td>
<td>480</td>
<td>33</td>
<td>8.4</td>
</tr>
<tr>
<td>Pitch / 1 wt% SWNTs</td>
<td>620</td>
<td>41</td>
<td>2.5</td>
</tr>
<tr>
<td>Pitch / 5 wt% SWNTs</td>
<td>850</td>
<td>77</td>
<td>2.2</td>
</tr>
</tbody>
</table>

A different composite fiber system, which also saw promising improvements from SWNT loading, came from Haggenmueller et al.'s work involving SWNT / poly(methyl methacrylate) (PMMA) fibers [10]. Raw and purified pulsed laser vaporization (PLV) SWNTs from Tubes@Rice were dispersed with PMMA in dimethyl formamide (DMF). The DMF was then evaporated away, leaving pellets of PMMA / SWNTs which were melt spun into fibers. Loadings up to 8 wt% SWNT in PMMA were examined, but 10 wt% SWNTs / PMMA was too viscous for the melt spinning apparatus used. A variety of spin-draw ratios were explored. At a draw ratio of $\lambda = 4$, electrical conductivity of the composite fibers was found to increase as the loading increased from 1.3 and 6.6 wt% SWNTs loading – from $\sigma = 0.118$ to 11.5 S/m in the axial fiber direction and $\sigma = 0.078$ to 7.0 S/m radially. In addition, the elastic modulus at $\lambda = 70$ was measured at $Y = 3.1, 3.3, 5.0, 6.0$ GPa for 0, 1, 5, and 8 wt% SWNT loading, respectively. SWNTs improved the mechanical and electrical properties of the fibers and it was found that draw ratios as little as $\lambda = 4$ further improved both of these properties as well. As the SWNT loading increased, the maximum sustainable draw ratio was found to decrease. Modulus was found to have a moderate dependence on the draw ratio, while the yield stress had a more dramatic dependence, doubling in the 5 wt% SWNT / PMMA fibers when going from $\lambda = 40$ to 300. The improvement in properties as a function of draw ratio was further evident in the narrow mosaic angle of fiber examined via x-ray diffraction (XRD), $\phi = 4^\circ$. Although the SWNT / PMMA composite fibers exhibit notable improvements in both
mechanical and electrical properties, the increases did not follow the rule of mixtures for composites.

A third composite fiber system, SWNTs & MWNTs in polycarbonate fibers, was explored by Sennett et al. [73]. MWNTs were produced via CVD and HiPco SWNTs were obtained from Carbon Nanotechnologies Inc. The work does not report any characterization of resulting fibers and instead focuses on dispersability of the nanotubes within the polycarbonate matrix. Nanotubes were mixed with polycarbonate in a twin-screw microcompounder and then melt spun as fibers. MWNT fibers were produced, but SWNT fibers could not be collected because of consistent fiber breakage. However, a couple of observations are still relevant. SWNTs were found to be more difficult to disperse in polycarbonate than MWNTs, requiring almost an order of magnitude increase in mixing time to produce homogenous blends. Also, orientation was found to increase in MWNT / polycarbonate fibers with increasing draw ratios. Further work in producing and characterization SWNT / polycarbonate fibers will certainly be forthcoming.

Next, Bhattacharyya et al. have provided initial work into developing SWNT polypropylene (PP) composite fibers [78]. Soft-baked purified HiPco SWNTs (see App A.) were mixed with polypropylene at a loading of 1 wt% and then filtered for impurities, resulting in a final composite of 0.8 wt% SWNTs. Optical microscopy of the blends were performed to study phase behavior and crystallization of the composite system. The SWNTs were dispersed in the polymer as ropes and found to act as nucleating agents for PP crystallization. Composite fibers were produced via melt spinning with a draw ratio of $\lambda = 4.5$. XRD and polarized Raman spectroscopy showed the fibers to be highly aligned, with the SWNTs more highly aligned than the PP. The SWNTs possessed a
Herman’s orientation factor of ~0.93, with an orientation factor of ~0.86 for the PP. This difference is explained by the flexible chain of the PP having more inherent disorder than the more rigid SWNTs. Polarized Raman measurements showed a ratio ~20:1 for the G' peak intensity with the fiber parallel and perpendicular to the excitation polarization.

Unfortunately, mechanical characterization of the composite fibers yielded no difference between the pure PP fiber and the 0.8 wt% SWNT / PP fiber ($\tau = 0.4$ GPa, $Y = 4$ GPa, elongation to break = 30%).

The future of SWNT / PP composite fibers is still promising, however. Kumar et al.’s work involving vapor-grown carbon fiber (VGCF) / PP fibers have produced good results [65]. VGCFs from Pyrograf Products Inc. were mixed with PP (5 wt% loading) in a twin-screw extruder and then melt-spun. The resulting fibers showed an improvement in both tensile and compressive mechanical properties. Table 2.5 lists these properties. The elongation to break actually decreased upon adding VGCFs, indicating that the nanofibers provided stiffness to the PP fibers. Because of the inherent similarities between VGCFs and SWNTs, it is reasonable to expect SWNT / PP fibers to see similar improvement in properties with improved mixing and spinning techniques. Like Haggenmueller et al.’s SWNT / PMMA fibers, these VGCF / PP fibers did not follow the rule of mixtures with respect to property improvements.

Table 2.5: Mechanical Properties of VGCF / PP Fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (GPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Compressive Strength (GPa)</th>
<th>Strain-to-failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>490 ± 60</td>
<td>4.6 ± 0.7</td>
<td>25 ± 1</td>
<td>23 ± 5</td>
</tr>
<tr>
<td>PP / 5 wt% VGCF</td>
<td>570 ± 70</td>
<td>7.1 ± 0.9</td>
<td>48 ± 10</td>
<td>16 ± 2</td>
</tr>
</tbody>
</table>
One of the more interesting conventional SWNT / polymer composite fibers developed was Kumar et al.'s SWNT / poly(p-phenylene benzobisoxazole) (PBO) fibers [11]. PBO fibers are some of the strongest fibers commercially produced [18]. The addition of SWNTs actually served to increase their mechanical properties. Soft-baked purified HiPco SWNTs (see App. A) were dispersed with PBO in poly(phosphoric) acid at 5 and 10 wt% loadings. The solution showed no SWNT aggregates and good birefringence. The liquid crystalline dope was dry-jet wet-spun into water with a 10 cm air gap and draw ratios as high as $\lambda = 10$. XRD analysis of the PBO fibers showed that the presence of SWNTs did not disrupt the alignment of PBO. Table 2.6 lists the SWNT / PBO fibers and their mechanical properties. Mechanical properties for both 5 and 10 wt% SWNT fibers showed improvements, thus making outstanding fibers even better.

Table 2.6: Mechanical Properties of SWNT / PBO Fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Modulus (GPa)</th>
<th>Strain to Failure (%)</th>
<th>Tensile Strength (GPa)</th>
<th>Compressive Strength (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBO</td>
<td>138 ± 20</td>
<td>2.0 ± 0.2</td>
<td>2.6 ± 0.3</td>
<td>0.35 ± 0.6</td>
</tr>
<tr>
<td>PBO / 5 wt% SWNTs</td>
<td>156 ± 20</td>
<td>2.3 ± 0.3</td>
<td>3.2 ± 0.3</td>
<td>0.4 ± 0.6</td>
</tr>
<tr>
<td>PBO / 10 wt% SWNTs</td>
<td>167 ± 15</td>
<td>2.8 ± 0.3</td>
<td>4.2 ± 0.5</td>
<td>0.50 ± 0.6</td>
</tr>
</tbody>
</table>

The most impressive composite fiber to-date is a SWNT / polyvinyl alcohol (PVA) fiber first developed by Vigolo et al. [12]. Raw SWNTs, produced by the carbon-arc method, were dispersed via sonication in an aqueous solution of sodium dodecyl sulfate (SDS). Optical microscopy was used to examine the dispersability of the SWNTs as a function of nanotube concentration and surfactant concentration. The optimal suspension for this spinning technique was found to be 0.35 wt% SWNTs in 1.0 wt% aq. SDS. A gel-spinning technique was used to make the SWNT / PVA fibers. The suspension was extruded into a co-flowing stream of 5 wt% PVA (MW 7000), resulting
in a gel-like ribbon of aggregated SWNTs and PVA. The proto-fibers were then washed and dried. The SWNT / PVA fibers possessed a density of 1.3 – 1.5 g/cm³ and showed a core of aligned SWNTs and PVA surrounded by a shell of carbon impurities. The fibers could be tied into a knot without damage and exhibited interesting mechanical properties: tensile strength, $\tau \approx 150$ MPa; elastic modulus, $Y \approx 9 – 15$ GPa; and strain-to-failure of 3%. In addition, the first generation of SWNT / PVA fibers possessed an electrical resistivity of $\rho \approx 0.1$ $\Omega\cdot$cm.

Figure 2.17: Scanning electron micrographs of Vigolo et al.’s SWNT / PVA fibers at various magnifications. (A) Medium magnification image showing the fiber’s alignment (black arrow is main axis of fiber) and surface contaminants (scale bar = 667 nm). (B) An overview of the fiber (scale bar = 25 $\mu$m). (C) Cross section of a fiber showing a core of SWNTs and PVA with a surrounding skin of carbon impurities (scale bar = 16.7 $\mu$m). (D) High Magnification of the central SWNT / PVA region (scale bar = 1 $\mu$m) [12].
Further improvements of the process have been developed. Vigolo et al. used a post-processing for the fibers that involved rewetting and drying under tension [79]. This treatment was shown to improve the internal SWNT alignment and mechanical properties. XRD analysis of the raw and stretched SWNT / PVA fibers show in increase in alignment with the full-width half-maximum (FWHM) mosaic angle decreasing from $75 - 80^\circ$ to $50^\circ$. In addition, the elastic modulus of stretched fibers increased to $Y = 40$ GPa, with a doubling of tensile strength ($\tau \approx 300$ MPa).

Recent improvements in the SWNT / PVA fiber engineering process have been performed by Dalton et al. [80]. These fibers used a lithium dodecyl sulfate aqueous surfactant and HiPco SWNTs obtained from Carbon Nanotechnologies Inc. The aqueous suspension was injecting into the center of a flowing cylindrical pipe of PVA coagulant. The SWNT stream collapsed into a gel-like proto-fiber which was wound onto a mandrel for further processing. The gel fibers were then taken through a series of acetone and water baths, where solvent removal and tensioning occurred. The resulting SWNT / PVA fibers contained less contaminants that Vigolo et al.’s original fibers, but still only possessed 60 wt% SWNTs. However, the mechanical properties of the predominantly SWNT fibers were impressive: tensile strength of $\tau = 1.8$ GPa and elastic modulus of $Y = 80$ GPa. Because of the high volume concentration of SWNTs, these fibers have also been shown to be supercapacitors with impressive electroactuation [81].

While the field of composite SWNT fibers has seen notable progress over the last 4 years, their final potential will be ultimately restricted by two significant facts. The first is that all composite materials must address dispersability and load transfer issues. Any material object that consists of multiple components is more difficult to homogenize than
a single component system. Localized defects and distribution of the supplementary component's properties are dependent on homogeneous mixing. Secondly, because of the smooth inert molecular structure of SWNTs, effective transfer of mechanical loads is difficult. This means that, while marginal improvements in properties is reasonable, truly accessing the fully properties of individual SWNTs is very unlikely. For such properties to be witnessed, the more arduous task of developing neat SWNT materials is essential.

2.3.2 Neat SWNT Materials

Neat SWNT materials will eventually be the ultimate realization of the impressive properties of nanotubes at the macroscopic scale. As has been touted by many researchers, nanotubes are perhaps the strongest, most electrically conductive, and most thermally robust material in the world. Therefore, no composite which incorporates a lesser material will match the properties of its neat counterpart, for the lesser material will only serve to dilute its performance. However, the creation of such neat materials is a difficult endeavor, and one that is only recently being tackled by the nanotube research community. The difficulties stem primarily from two places – availability and nanoscale manipulation. Prior to the invention of the HiPco process for making SWNTs, a viable large-scale route to mass production had not yet been realized. While individual prototype objects can be created, the adoption of SWNTs into the cutting edge of industrial technology requires nanotubes to be readily available and cheap, something that companies like Carbon Nanotechnologies Inc. are facilitating. The second challenge facing neat SWNT materials is simply ignorance in how to handle, modify, and manipulate individual SWNTs and SWNT bundles to obtain useful neat objects. The field
is still relatively new and the unique molecular nature of SWNTs is slowly but surely being digested and investigated. Because of these challenges, only four research groups have successfully produced something that could be classified as macroscopic neat SWNT material.

The only readily available macroscopic neat SWNT material is the buckypaper (see Sec. 2.1.2). Filtering a suspension of SWNTs onto a membrane, washing the membrane, and then drying it results in a tangled mat of randomly oriented large SWNT bundles with 70 – 90% void volume [82]. Most macroscopic neat materials’ properties use the buckypaper as a standard for comparison. Mechanical, electrical, and thermal characterization of various buckypapers have been performed by a number of research groups. Buckypapers usually possess an elastic modulus of $Y \approx 1 \text{ GPa}$ and a strain-to-failure of $\sim 1\%$ [81]. Transport through a buckypaper is reasonably good because of the inherently high conductivity of individual SWNTs: electrical resistivity of $\rho \approx 0.01 \Omega \cdot \text{cm}$ [26, 83] and thermal conductivity of $\kappa \approx 35 \text{ W/K} \cdot \text{m}$ [49]. All of these properties set useful benchmarks for neat SWNT materials.

The first kind of neat SWNT material is a SWNT strand. Two groups have produced short strands consisting of only nanotubes. Zhu et al. directly synthesized strands of SWNTs in the gas-phase by pyrolysis of n-hexane using a vertical floating technique [13]. The strands were $\sim 20 \text{ cm}$ in length and $0.3 \text{ mm}$ in diameter. The SWNT strands possessed 5 wt% of metal catalyst particles and did not possess continuous nanotubes along their entire length, but instead were a preferentially aligned aggregation of large SWNT bundles possessing a volume fraction of 48%. Mechanical testing of the SWNT strands showed an elastic modulus of $Y = 49 – 77 \text{ GPa}$ with a tensile strength of $\tau$
\approx 800 \text{ MPa}. Electrical measurements of the SWNT strands revealed a resistivity of \( \rho = 0.5 - 0.7 \text{ m\Omega\cdot cm} \) over a temperature range of 90 – 300 K. While these properties are impressive, because of the size and nature of the SWNT strand, they are more analogous to naturally aggregating SWNT bundles. Their potential for macroscopic applications is limited by their availability and size.

![Image: Scanning electron micrographs showing (A) Zhu et al.'s SWNT strand. (B) High resolution SEM of pieces pulled off from the main strand show a loose network of large bundles. (C) TEM images indicate the individual bundles are crystalline [13].](image)

A similar SWNT filament has been created by Gommans et al. [47]. A carbon fiber was lowered into a suspension of SWNTs in dimethyl formamide and a voltage applied. As the carbon fiber was translated out of the suspension, a cloud of aggregated SWNT bundles were drawn out as a neat filament. The resulting filaments were 1 – 5 cm in length and 2 – 10 \( \mu \text{m} \) in diameter. The objects were used to explore the anisotropic Raman properties of SWNTs and displayed a Raman ratio of \(~5:1\). These filaments suffer from the same problems as Zhu et al.'s SWNT strands – availability and size. Neither are the macroscopic fibers necessary for industrial applications.
Figure 2.19: (A) Gommans et al.'s SWNT filaments are drawn out of a SWNT/DMF suspension by a carbon fiber electrode. (B) SEM micrograph of the resulting filament [47].

The first macroscopic neat SWNT material that was created in an organized and controlled manner was the magnetic assembly produced by Walters et al. [84]. Aqueous suspensions of purified PLV SWNTs, obtained from Tubes@Rice, were filtered in a controlled manner on a membrane within a high strength magnetic field (26 Tesla). Because of the anisotropic magnetic susceptibility of SWNTs [85], they preferentially aligned themselves parallel to the applied magnetic field during filtration. This work was improved and expanded upon by Casavant et al. utilizing a more controlled flocculation during filtration and a more reasonable magnet field (7 T) [16]. The resulting aligned assemblies were 10 μm thick and possessed void volumes of 30%. XRD analysis showed the SWNTs to be highly aligned, with a FWHM mosaic angle of 25 - 35° [82] and a polarized Raman ratio of 3 - 4 [86]. Characterization of the magnetic assemblies' properties resulted in an electrical resistivity of $\rho = 0.085 \, \text{m}\Omega\cdot\text{cm}$ for the 26 T sample, which upon vacuum annealing increased to $\rho = 0.55 \, \text{m}\Omega\cdot\text{cm}$. The 7 T assembly exhibited a vacuum annealed resistivity of $\rho = 0.41 \, \text{m}\Omega\cdot\text{cm}$ [86]. Thermal conductivity for the assemblies were $\kappa = 10 \, \text{W/K} \cdot \text{m}$ and $\kappa = 60 \, \text{W/K} \cdot \text{m}$ for the 7 and 26T samples, respectively [86]. The magnetic assemblies proved to be the first neat SWNT
macroscopic material which exhibited a high degree of alignment with useful anisotropic properties.

Figure 2.20: SEM image of Walters et al.'s SWNT magnetic assembly (scale bar, 500 μm). The assembly has been peeled from the membrane substrate and neatly cleaves along the direction of the magnetic field [84].

The last neat macroscopic SWNT object to be developed, prior to this thesis’ research, came from Sreekumar et al.'s work involving SWNT films [15]. This work originated from much of the same observations and experiments involving SWNTs in super acids that are focused on in this thesis. Purified soft-baked HiPco SWNTs (see App. A) were dissolved in oleum (20 wt% excess SO₃) at 0.25 wt%. The SWNTs readily dispersed as individuals and small bundles due to extensive protonation of the nanotubes’ sidewalls (see Sec. 3.2). The solution was poured into a Petri dish and, over the course of a couple days, allowed to slowly aggregate from exposure to ambient moisture. The film was washed with acetone and water and then dried in moderate temperatures. The ambient moisture disrupted the protonation and facilitated a controlled aggregation into a dense, buckypaper (see Sec. 2.1.2). The resulting films possessed a density of 0.9 g/cm³ and several interesting properties. Films exhibited an in-plane electrical conductivity of
$1.3 \times 10^5$ S/m for as-prepared films and $\rho = 9.0 \times 10^4$ S/m for heat-treated films. Out-of-plane conductivities were one order lower. Raman analysis confirmed that the as-prepared SWNT films were p-doped with residual acid, as seen by an up-shift of the $G^+$ peak from a contraction of C–C bonds. Protonation of SWNTs has been shown to produce such shifts [87]. In addition polarized Raman analysis showed the films to be isotropic, with no macroscopic bulk alignment. Finally, mechanical properties of the neat SWNT films were promising, with an elastic modulus of 8 GPa, tensile strength of 30 MPa, and elongation to break of 0.5%.

The introduction of SWNTs into materials development has already proven itself a valuable and interesting field. SWNT composite fibers have been produced which shown markable improvements in all three key areas – mechanical, electrical, and thermal. SWNTs can turn a normally electrically insulating polymeric fiber into a reasonably good conductor, increase the thermal transport notably, and make the strongest fibers in the world a little more impressive. Neat SWNT materials are beginning to attract the attention they deserve, both from a scientific and an industrial perspective.

The development of macroscopic neat SWNT fibers is an important task that will require considerable effort, but one that will be well worth the returns.

**Table 2.7: Summary of Macroscopic SWNT Material Properties**

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<tbody>
<tr>
<td>SWNT / PVA Fiber</td>
<td>--</td>
<td>50°</td>
<td>1800</td>
<td>80</td>
<td>$&lt; 0.1$</td>
<td>--</td>
</tr>
<tr>
<td>SWNT Buckypaper</td>
<td>70 – 90</td>
<td>--</td>
<td>$&lt; 10$</td>
<td>1</td>
<td>0.01</td>
<td>35</td>
</tr>
<tr>
<td>SWNT Strand</td>
<td>48</td>
<td>--</td>
<td>800</td>
<td>49 – 77</td>
<td>$6 \times 10^4$</td>
<td>--</td>
</tr>
<tr>
<td>SWNT Magnetic Assembly</td>
<td>30</td>
<td>25 – 35°</td>
<td>--</td>
<td>--</td>
<td>$8.5 \times 10^{-5}$</td>
<td>10 – 60</td>
</tr>
<tr>
<td>SWNT Films</td>
<td>--</td>
<td>--</td>
<td>30</td>
<td>8</td>
<td>$7.7 \times 10^4$</td>
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3. Thesis Research

This thesis research involved the creation of the first ever macroscopic neat single-wall carbon nanotube (SWNT) fiber. SWNTs were found to form a lyotropic nematic liquid crystal in super acids, specifically 102% sulfuric acid. This liquid crystalline phase displayed unique one-dimensional characteristics. Optical microscopy and rheological measurements were used to confirm the existence of the liquid crystal. The highly-aligned single phase was then extruded into fibers using a conventional wet-spinning approach. Two different forms of purified SWNTs were used to create fibers and were found to produce different morphologies under the same extrusion conditions. A variety of basic extrusion conditions were explored. The resulting fibers’ mechanical, electrical, thermal, and structural properties provide insight into the phase behavior and extrusion process. Finally, a custom-made mixer/extruder was designed, built, and tested successfully. This apparatus will allow a more robust exploration of the extrusion of macroscopic neat SWNT fibers in the future.

3.1. Sample Preparation

Sample preparation for this research involved two stages: purifying SWNTs and mixing them in 102% sulfuric acid. The purification involved soft-baking at moderate temperatures, followed by a hydrochloric acid treatment. The purified SWNTs were then mixed via two methods. The first involved a magnetic bar stirrer and the second utilized a helical blade mixer.
3.1.1. Single-Wall Nanotube Purification

SWNTs produced via the Smalley Group's High Pressure Carbon Monoxide (HiPco) reactor were used exclusively throughout this research. Raw SWNT material from the HiPco reactor has a notable amount of metal catalyst particles, amorphous carbon, and giant fullerenes within it (> 30 wt%) [88]. Figure 3.1 provides thermogravimetric analysis (TGA) of raw and purified SWNTs. The raw material initially gains weight as all available metal oxidizes and then both samples lose mass as carbon oxidizes away. The raw material has over five times the metal content of purified material. These impurities are detrimental to the fiber spinning process, acting as mechanical, electrical, and thermal defects as well as disrupting liquid crystalline formation and structural alignment of the fiber. This is an unavoidable side-effect of the HiPco process, but something that can be removed through chemical processing of the SWNT material. This research utilized two methods for purifying the raw SWNT material.

![Thermogravimetric Analysis in Air of HiPco SWNTs](image)

**Figure 3.1:** Graph displaying the weight loss of typical raw and purified HiPco SWNTs during TGA in air. The final impurity concentrations are included. Metal atom percentages calculated assuming ash is Fe$_2$O$_3$.
SWNTs for this research were processed using a soft-bake purification process first developed by Chiang, et al. [88]. The primary impurity in raw HiPco SWNT is metal catalyst particles left over from the growth process, most of which are adsorbed to the ends or sides of SWNTs. Many of these particles are overcoated with a graphitic layer, making them inaccessible to chemical dissolution. The purification protocol involves several steps. First, the material was baked at high temperature in a wet-air environment to oxidize the carbon overcoating of the metal particles along with any amorphous carbon. After baking, the material was removed from the oven and stirred in HCl to dissolve the now exposed metal particles. Finally, the slurry was neutralized with water, exchanged with methanol, and air dried.

In an effort to improve the porosity and dissolution of purified SWNTs, a second purification process was adopted for some of the research in this thesis. Instead of neutralizing in water and drying from methanol, hexanes was added to the HCl slurry and shaken. The nanotubes were found to readily migrate into the hexane layer. Once neutralized through repeated dilution with water, the nanotube material was allowed to dry from the hexanes slurry. The entire process is still not fully understood, but it is believed that when the solution is shaken, small droplets containing loose networks of SWNT travel into the hexane layer and maintaining their porous structure even after drying. Both purification protocols are described in full detail in Appendix A.
3.1.2. SWNT / 102% Sulfuric Acid Samples

For microscopy and rheological experiments, samples were prepared via two methods. In both methods, materials and SWNTs were fastidiously dried by heating at 80 – 100 °C under vacuum for 3+ hrs. In addition, 102% sulfuric acid (2 wt% excess SO₃) was used in most of this research to further protect against the ingress of water. Low concentration samples (< 1 wt%) were mixed in a sealed Erlenmeyer flask at room temperature for 24+ hrs using a magnetic stir bar. The solutions would rapidly disperse into a clear homogenous brown liquid and remain stable for long periods of time (at least months).

More concentrated samples were too viscous for magnetic stirring and required mechanical mixing. These samples were mixed in a Daca Double Helix Mixer (Daca Instruments) that consisted of two concentric screws, one stationary and the other rotating. The mixing screws were inside a glass cylindrical vessel with ports at the top for gas access and sampling. The mixer was modified to maintain a completely anhydrous environment. The samples were mixed at ~100 °C for ~72 hrs with a constant positive pressure of dry argon gas. Concentrations above 6 wt% were difficult to dissolve during early stages of mixing and would hinder rotation of the mixer blades. For higher concentrations, this complication could be bypassed through hand mixing with a mortar and pestle in a purged dry glove box and then loading the “pre-mixed” paste into the Daca Mixer. The well-mixed final samples were found to be viscous homogeneous pastes with minor degrees of extensibility. Both soft-baked and hexane-extracted SWNT / 102% sulfuric acid samples were prepared in the same fashion. Qualitatively, the hexane-
extracted SWNTs appeared to dissolve into the sulfuric acid more easily than the soft-baked material.

Figure 3.2: A picture of the Daca Double Helix Mixer in use. The mixer shaft is connected to a motor through a sealed adapter. A positive pressure of argon is provided through a side port and a hot plate with thermometer or thermocouple (not shown) is used to control the mixing temperature. The unmodified mixer is shown in the inset to illustrate the interweaving mixing blades.

3.1.3. SWNT Alewives

Early on in this research it was discovered that unusually ordered aggregates would form if a SWNT / 102% sulfuric acid sample was exposed to minor amounts of water (Fig 3.3). These tactoid aggregates were named *SWNT Alewives* because of their similarity in appearance to a school of fish. Sample mixing and slide preparation for optical microscopy were found to be susceptible to alewife formation if precautions were not adopted. Moisture from the normal atmosphere was sufficient to stimulate the
formation of these aggregates. This thesis does not focus on SWNT alewifes, but provides a general description of the phenomenon in the context of something to avoid when spinning neat SWNT fibers. A detailed analysis of SWNT alewifes has been performed by Ramesh et al. [89].

Figure 3.3: A scanning electron microscopy image of SWNT alewifes. The sample was prepared by exposing a 0.25 wt% mixture to moisture, quenching in diethyl ether, and carefully collecting on an SEM stub.

3.2. SWNT Liquid Crystalline Phase Behavior

The first step in the creation of any fiber is the dissolution of the molecular constituents at significant concentrations. One of the main challenges in single-wall nanotube (SWNT) research since the beginning has been finding routes to dissolve, or at least disperse, SWNTs (see Sec. 2.1.2). This research uses super acids to extensively protonate individual SWNTs. The nanotubes exfoliate from aggregated bundles and separate due to electrostatic repulsion [90]. Protonation via super acids is also the primary way that traditional lyotropic rigid rod polymers are dissolved [18]. Several super acids were initially explored as possible mediums for spinning neat SWNT fibers and did display liquid crystalline behavior – oleum (fuming sulfuric acid with 20% excess SO₃), trifluoromethane sulfonic acid, 102% sulfuric acid (concentrated sulfuric acid with an
appropriate amount of oleum added to remove residual water). Methane sulfonic acid and polyphosphoric acid were also tried, but were found to not be good solvents for SWNTs. Preliminary experiments were performed on SWNTs in oleum because of oleum’s high acidity [91]. However, research shifted to 102% sulfuric acid because of concerns that the SWNTs may be irreversibly chemically oxidized during prolonged exposure to oleum. The research in Section 3.2 was performed in parallel with the development of neat SWNT fibers and is partially the work of others [90, 92]. The microscopy and rheology work provide critical opening chapters to this thesis’ research.

3.2.1. Polarized Optical Microscopy

Polarized optical microscopy was used to characterize the various phases of SWNTs in 102% sulfuric acid. Such examinations can provide information on the phase of a system at a given concentration, the degree of dissolution, and the existence of any birefringent structures. All investigations were performed using a Zeiss Axioplan 2 microscope equipped with an oil immersion objective (63X, 1.4 NA). A rotating stage was mounted between the polarizer and analyzer. Samples were prepared in an anhydrous glove box by placing a small drop of liquid sample on a dried microscope slide, placing a cover slide, and sealing the edges with aluminum tape. Performing optical microscopy experiments without using a completely anhydrous environment resulted in tactoid-shaped SWNT aggregates, called SWNT Alewives (see Section 3.1.3).

The SWNT / 102% sulfuric acid system was found to possess three main phases. The exact concentrations at which the system transitions between the various phases has not been determined, but concentrations at which the phases are observed are provided.
At low concentrations (~0.01 wt%), SWNTs were found to completely dissolve in the acid leaving a clear brown liquid with no notable aggregates or domains. The nanotubes were not concentrated enough to be sterically influenced into any long-range order and are free to move as individuals.

At moderate concentrations (< 0.25 wt%), the system became biphasic. A small portion of the nanotubes were still in the isotropic phase, while the majority of the nanotubes formed a uniform one-dimensional liquid crystalline phase (Fig. 3.4). These domains, called SWNT Spaghetti, formed a unique phase. Under transmission optical microscopy, the SWNT Spaghetti appeared to be uniform in diameter and endless. No ends could be found into the system; when a specific spaghetti strand appeared to disappear it would in fact travel into or out of the plane of focus and could be followed. The only plausible explanation for this uniform, endless phase is a one-dimensional liquid crystal, wherein the individual SWNTs are free to translate axially, but are loosely bound to the phase radially. A common first-order prediction for the transition to a biphasic system for mono-dispersed rigid rods is given by:

\[
\phi_1^* \approx \frac{8}{L/D} \left(1 - \frac{2}{L/D}\right),
\]  

(3.1)

where \(\phi_1^*\) is the volume concentration at the transition and \(L/D\) is the aspect ratio of the rod-like molecules [58]. Using the aspect ratio of \(L/D = 470 \pm 30\), as determined from rheological experiments performed on dilute solutions (see below) and Equation 3.1, this transition should occur at \(\phi_1^* = 1.7\) vol\%, or \(c_I = 1.5\) wt\% (see App. B). The fact that a biphasic system was observed at 0.25 wt\%, indicates that this approximation involving non-interacting rods is not an appropriate model. Given the unusual one-dimensional
geometry of SWNT Spaghetti this is not surprising. A more detailed theoretical treatment is necessary, but will not be discussed here. However, the existence of these mobile strands of aligned SWNTs will become critical during structural analysis of neat SWNT fibers (see Sec. 3.3.2).

Figure 3.4: An optical microscopy image of the SWNT Spaghetti. The sample is biphasic with a dilute isotropic phase and concentrated liquid crystalline domains. The spaghetti strands are actually endless, moving in and out of the plane of focus.

At high concentrations (~2 wt%), the system became a single liquid crystalline phase. All of the nanotubes existed within aligned domains. The transition to a single liquid crystalline phase at volume concentration, $\phi^*_2$, is predicted to first-order by the following equation [58]: 
\[ \phi_2^* \approx \frac{12}{L/D}. \]  

(3.2)

Again, using the aspect ratio of \( L/D = 470 \pm 30 \), one gets a transition concentration to single phase liquid crystal of \( \phi_2^* = 2.6 \text{ vol\%} \), or \( c_1 = 2.3 \text{ wt\%} \) (see App. B). This theoretical transition concentration is more reasonable than that calculated for the transition from isotropic to biphasic. The fact that the single liquid crystal phase did not exhibit unusual characteristics, while the biphasic system did, probably explains the difference in agreement.

The opacity of the sample made substructure within the single phase difficult to distinguish by transmission optical microscopy. However, polarized optical microscopy revealed the phase to be highly birefringent. Because of the aligned SWNTs, the incident polarized light will have a specific angular relationship with a given domain. Walters et al. showed experimentally that the intensity of polarized light transmitted through arrays of aligned SWNTs has a sinusoidal dependence on the angle between the alignment director and the polarization vector [84]. As the analyzer is rotated through 0 – 90°, the intensity of light transmitted through a given domain goes from dark to bright (Fig. 3.5). The birefringence of SWNTs in 102% sulfuric acid shows that the samples were comprised entirely of domains of aligned rod-like species, and are indicative of a single phase liquid crystal. It is from this highly aligned, single phase that fibers were spun.
3.2.2. Rheology

In addition to optical microscopy, rheology can be used to probe the phase behavior of a liquid crystalline system. Prior to this research, very little rheological research had been performed on SWNT systems, and none had been performed on SWNTs in super acids, like 102% sulfuric acid. Rheology experiments provided three items important to this thesis research: viscosity as a function of shear rate, the effect of concentration on viscosity, and the aspect ratio of SWNTs in solution.
Rheological testing was carried out at 25°C using an ARES FRT (Force Rebalance Transducer) and a RDA III strain controlled rheometers (Rheometric Scientific). Hastelloy and stainless steel testing fixtures were used because of their corrosion resistance. In general, a large couette (bob to cup diameter ratio of $\kappa = 0.97$) was used for the lower viscosity samples and a small parallel plate or cone and plate (diameter = 25mm) geometry for the higher viscosity samples. However, a number of solutions were tested in both configurations to ensure that the data was not an artifact of the fixture type. An anhydrous environment was achieved by enclosing the fixtures in a desiccant chamber, with continuously flowing dry argon or nitrogen (Fig. 3.6). Samples were loaded from a syringe through a side port in the chamber. For many samples, a layer of perfluorinated oil, Flourinert® (3M), was placed on top of the SWNT sample to further prevent the possibility of any moisture ingress.

![Figure 3.6: (A) The Ares FRT rheometer connected to a tank of Argon. (B) A desiccant chamber, purged with argon, maintained an anhydrous environment during testing.](image)

The first rheological characteristic of note was that SWNTs in 102% sulfuric acid were viscous. At concentrations where fiber spinning would occur (i.e. 4+ wt%), the low shear rate ($\dot{\gamma} = 0.0001 \text{ sec}^{-1}$) viscosity was on the order of 5 MPa·s (Fig 3.8). Such high
viscosities are not unexpected given the large aspect ratio of SWNTs [56]. Other rigid rod
ylotropic liquid crystalline systems possess similar zero-shear viscosities [56]. However,
this fact suggests that significant pressures may be required for extrusion of concentrated
SWNT / super acid samples during fiber production.

Like all liquid crystalline systems, SWNTs in 102% sulfuric acid exhibited strong
shear-thinning. As described in Section 2.2.2, at moderate to high shear rates, the
viscosity of traditional polymeric liquid crystalline systems follows a decreasing power
law function. Rheology experiments using a small parallel plate geometry were
performed on various sample concentrations. The viscosity of the SWNTs samples was
found to follow the same decreasing power law with an index of $n = 0.2$ (Fig. 3.7).

![Figure 3.7: A log-log plot of viscosity vs. shear rate for 4 wt% SWNTs in 102% sulfuric acid. The system possess a power law index of 0.2.](image)

A broader examination of the viscosity behavior as a function of shear rate over
the entire concentration range provides insight into the phase behavior of SWNTs in
102% sulfuric acid. In the absence of shear, liquid crystalline polymers are composed of domains with varying directors. Moreover, within each domain, the molecules are roughly aligned along a common director, but there is a small angular distribution about that axis. As applied shear increases, the system’s degree of internal alignment increases. First, domains tumble. Then, the angular distribution of molecules about their domain directors decreases. Finally, the domains align in the direction of shear. The increases in internal alignment result in a reduction of the viscosity of the system. The rheology of SWNTs in 102% sulfuric acid is similar to liquid crystalline polymers; therefore, it is believed that the system follows the same molecular alignment behavior as polymers when subjected to shear. At dilute concentrations, the system behaved Newtonian with a viscosity close to that of sulfuric acid. At moderate to high concentrations, the viscosity was high and decreased with shear rate (Fig 3.8). During fiber spinning, high shear rates are common. The low-shear viscosity may be extremely high for SWNTs in 102% sulfuric acid, but the viscosity during spinning will likely involve realistic extrusion pressures.
Figure 3.8: A log-log plot of viscosity vs. shear rate for a range of concentrations of SWNTs in 102% sulfuric acid.

The viscosity of concentrated SWNT / 102% sulfuric acid samples provides a guide for appropriate fiber spinning conditions. As discussed in Section 2.2.2, the viscosity as a function of concentration in a polymer liquid crystal goes through a maximum and then a minimum during the transition from biphasic to a single phase liquid crystal. Rheological experiments performed on concentrated samples are shown in Figure 3.9. Steady rate sweeps over a range of shear rates were performed, and the viscosities at a shear rate of \( \dot{\gamma} = 0.1 \text{ sec}^{-1} \) used to construct the viscosity vs. concentration plot. The viscosity of the system was found to increase and then decrease as it transitioned to a single-phase. Once an ideally spaced single phase was achieved, the viscosity increased again, dramatically. Fiber spinning is traditionally performed at concentrations a little higher than the concentration minimum, which suggest an ideal spinning concentration around 5 – 10 vol\%, or 4 – 8 wt\%.
Figure 3.9: A plot of viscosity vs. volume concentration of SWNTs. Data collected at a shear rate of 0.1 s\(^{-1}\). The dashed line is not a fit, but included to aid interpretation.

The third piece of information obtained from rheology was the aspect ratio of the SWNTs in the sulfuric acid. The viscosity of a sample is governed by the anisotropic size of the solvated molecules involved. The relationship between the aspect ratio, \(L/d\), has been researched extensively for the dilute regime. The theory for Brownian rods should be applicable to dilute SWNTs in 102% sulfuric acid. The Batchelor correction [93] to the Kirkwood-Auer equation for mono-dispersed rods [56] is given by:

\[
\frac{\eta - \eta_S}{\eta_S \phi} = \frac{(L/R)^3}{45 \ln(L/R)} \left[ \left( 1 + \frac{0.64}{\ln(L/R)} \right) \left( 1 - \frac{1.15}{\ln(L/R)} \right) + \frac{1.659}{\ln(L/R)} \right],
\]

(3.3)

where \(\frac{\eta - \eta_S}{\eta_S \phi}\) is the reduced viscosity of the system and includes the measured viscosity, \(\eta\), the solvent viscosity, \(\eta_S\), and the volume concentration of the sample, \(\phi\). In addition, the equation includes the length of the rod, \(L\), and the rod’s radius, \(R\). Equation 3.3 is a only function of the aspect ratio, \(L/D\), with \(D = 2R\). By plotting the reduced viscosity vs.
shear rate for dilute samples the aspect ratio can be obtained from the intercept (Fig. 3.10). The resulting aspect ratio for SWNTs in 102% sulfuric acid is $L/d = 470 \pm 30$. This aspect ratio represents a mass average. Due to polydispersity, individual SWNTs could be much longer or shorter. This information is valuable from both a basic understanding of the SWNT / 102% sulfuric acid liquid system, as well as a potentially useful tool for examining the effects of mixing, chemical oxidation, and purification techniques in future research.

![Graph showing reduced viscosity vs. shear rate for different concentrations](image)

Figure 3.10: A plot of the reduced viscosity, $(\eta - \eta_0)/(\eta_0\phi)$, v. shear rate in the dilute regime. The data follows the theory of dilute Brownian rods. The intercept can be used to determine the aspect ratio of the SWNTs in 102% sulfuric acid.

The phase behavior and rheology provided a valuable foundation for spinning macroscopic neat SWNT fibers. Without an exploration into the liquid crystalline behavior and rheological properties of SWNTs in 102% sulfuric acid, a complete picture of neat SWNT fiber spinning would not be possible. The phase behavior showed the system to follow the classical rigid rod polymer liquid crystalline model, which included
an isotropic, biphasic, and liquid crystalline state. The microscopy revealed a fascinating and unique one-dimensional liquid crystal domain, which proved to be the building block of neat fibers (see Sec. 3.3.2). Rheology also provided important insights into the nature of this system. The nanotube / acid dispersions were found to follow traditional liquid crystalline viscosity behavior, which included a high viscosity at low shear rates and notable shear-thinning. The knowledge provided by these two research avenues provided a solid foundation for the experimental creation of the first ever neat SWNT fiber.

3.3. Daca SWNT Fibers

Once single-wall carbon nanotubes (SWNTs) were dissolved at high concentrations in a liquid crystalline phase, macroscopic neat fibers consisting of only SWNTs were extruded using a conventional wet-spinning approach. This thesis presents the first experimental exploration of neat SWNT spinning by providing a broad treatment of the various spinning variables traditionally involved in fiber spinning. These include coagulation solvent, extrusion needle orifice diameter, and needle length. Characterization of the resulting fibers was performed using scanning electron microscopy (SEM), polarized Raman spectroscopy, and mechanical testing. Collaborative research provided x-ray diffraction (XRD) information, electrical resistivity, and thermal conductivity measurements for the neat SWNT fibers.
3.3.1. Syringe Extrusion

The first extrusion set-up for spinning neat SWNT fibers involved controlled extrusion from a syringe into a coagulant bath. Fiber extrusion from SWNTs in 102% sulfuric acid had not been attempted before this research; the behavior and complications of the experiments were unknown. As such, a straightforward method of testing the solution spinning of these fibers was adopted. Solution spinning of neat SWNT fibers was found to produce the best results when extruded into diethyl ether. This solvent is an effective coagulant for these fibers because it is miscible with sulfuric acid and evaporates rapidly in air upon removal of the fiber from the bath. During coagulation, the SWNTs did not have time to reorient and the fiber quickly collapsed into a dense structure. Other coagulants were briefly explored (see Table 3.3), but the coagulation and collection method described here was optimized for spinning into diethyl ether.

In fiber spinning, the extensibility of a polymer sample increases with increasing polymer concentration. Extensibility arises from an “entangled” resistance to extensional flow due to interactions between the solvated molecules within the liquid crystal [56, 95]. The spacing between the individual molecules directly affects the extensibility of the liquid crystal sample, and since the spacing within a liquid crystal decreases with increasing concentration, the extensibility also will increase. It is extensibility that allows the crystallinity of a system to be maintained under stress (e.g. tensioning). Therefore, higher concentration can support higher stresses and the liquid crystal maintains its structural integrity. Because of this, the majority of initial fiber spinning research was performed at the practical concentration limit of the Daca Double Helix Mixer – 6 wt% (see Sec. 3.1.2).
The experiments used a remote high pressure syringe pump to control the extrusion process. A Harvard Apparatus Remote 44 Syringe Pump was used with a maximum linear force of 175 lbs. A stainless steel syringe was selected because of its moderate maximum volume (8 mL), its corrosion resistance (316SS), and its reasonably small cross-sectional area (0.11 in$^3$), which translated to a high maximum applied pressure (1590 psi). In addition, the syringe possessed a Swagelok™ tubing adapter, which allowed for extrusion needle modularity.

The syringe pump was mounted vertically on a stable frame above a coagulant bath (Fig. 3.12). The bath’s height was adjustable so that the extrusion needle could be placed below the liquid surface or slightly above it. This configuration enabled dry-jet wet-spinning or wet-jet wet-spinning extrusion with the same coagulant. In addition, different extrusion needle lengths could be used with only minor adjustments.

The coagulant bath used was a 1 L graduated cylinder. Other vessels were tried as well, but the graduated cylinder had several advantages. The vessel had sufficient volume to prevent significant changes in the temperature of the bath due to chemical reactions or heats of mixing. The exposed surface area of the cylinder was large enough to work inside, but not so large that evaporation of ether or condensation of ambient moisture was a problem. Finally, the graduated cylinder was deep enough to allow long lengths of fiber to be extruded without significant bending or coiling.

As discussed in Section 2.2.3, fiber collection and coagulation are two important parts of fiber spinning. They involve many of their own variables and approaches and are, in fact, often the entire focus of other theses’ research. This work focused on the creation and characterization of the first neat SWNT fibers and was unable to involve a detailed
exploration of these aspects of fiber spinning. Neat SWNT fiber samples were extruded and collected in the following manner.

Once the SWNTs in 102% sulfuric acid were completely mixed, the gas ports to the Daca Mixer were closed and the mixer was disconnected from the motor without exposing the sample to any ambient moisture. The mixer was transferred into a glove bag which had been purged thoroughly with dry inert gas. Also inside were the other clean and dried materials for transferring the sample out of the mixer into the SS syringe. The SWNT / acid paste coated the blades and sat as a large plug of mixed material at the bottom of the mixer. Typically, 10 – 15 mL of sample would be mixed at a time and would yield 4 – 8 mL of paste. The majority of sample loss was due to material coating the length of the interior glass mixer and the mixing blades.

Parallel research involving the Daca Double Helix Mixer and SWNT / 102% sulfuric acid has shown that there can be small concentration gradients in the mixer, which become magnified over prolonged mixing (i.e. 10 – 30 days) [94]. In addition, there was concern that the upper region of the mixer did not exhibit much shear during operation. As such, material was collected preferentially at the bottom of the mixer and along the bottom half of the mixer blades. The SWNT / 102% sulfuric acid samples appeared as a thick homogenous paste with minor degrees of extensibility. The paste was smooth and had no chunks or irregularities. It would flow easily under pressure, but would retain its shape under the absence of shear. The extensibility of samples was tested qualitatively by lightly pressing a metal spatula on the material and then quickly pulling away normal to the surface. The pastes would form small spikes from the motion and hold the shape (Fig. 3.11). Well mixed samples at 6 and 10 wt% SWNT in 102% sulfuric
acid would typically have spikes 1 – 10 mm high. However, this minor degree of extensibility was insufficient to support tensioning during spinning.

![SWNT Paste Diagram](image)

**Figure 3.11:** A cartoon depicting the qualitative method used for testing the extensibility of a SWNT / 102% sulfuric acid paste. The small spikes were 1 – 10 mm in height.

SWNT paste was collected from the Daca Mixer and transferred into the rear bore of a stainless steel syringe. Once all the desired material was inside the syringe, the plunger was carefully inserted and the free volume expelled by infusing the plunger. Lubrication of the syringe and plunger beforehand often made loading easier and avoided unwanted expulsion of SWNT paste. The syringe end would be wrapped tightly with paraffin tape and removed from the glove bag.

Before securing in the vertically mounted syringe pump, a needle would be quickly attached to the end of syringe. The syringe used had a 1/16” Swagelok™ fitting at its end which allowed for 1/16” OD lengths of pre-cut 316 stainless steel tubing with a precision-drilled hole (Upchurch Scientific). These needles are available in lengths as short as 2” with orifice diameters as small as 125 μm. For needle lengths shorter than 2”, tubing pieces were cut and the ID bore cleared by hand with a precision drill bit. Although these short tubes have a perpendicularly cut end, the term needle will be used to describe them in this thesis.
With the syringe secured to the syringe pump, the coagulant bath was filled and positioned below the needle. For experiments involving diethyl ether, only freshly opened dry bottles of ether were used. The bath was raised such that the end of the needle was submerged ~1 cm below the liquid surface. The concentrations and coagulant baths attempted were found to not support an air gap. The fiber would weaken in the air gap and could not be collected. This effect was likely due to the fiber absorbing moisture from the environment and aggregating into SWNT Alewives, which resulted in a loss of extensibility and a localized reduction of viscosity. The proto-fiber would break within the air gap, making collection difficult. Since air gaps are often used in rigid rod polymer spinning to provide additional extension and alignment (see Sec. 2.2.3), revisiting an air gap in a dry inert atmosphere would be an interesting experiment for future research.

![Diagram of syringe extrusion process](image)

**Figure 3.12**: A drawing depicting the syringe extrusion process. The drawing is not to scale, but shows the extrusion and collection method.
Finally, fiber extrusion would commence. The SWNT / 102% sulfuric acid samples were found to possess a notable yield stress at the beginning of extrusion. At the beginning, the syringe pump would be set to infuse at a moderate speed (e.g. 0.01 mL/min). No material would be seen coming out and pressure would build up inside the syringe. Then once the pressure was high enough to overcome the nanotube paste’s yield stress, fiber would quickly extrude out. The speed would be adjusted to a comfortable extrusion rate that would allow for easy collection (~0.5 cm/sec). Typical extrusion rates that produced continuous, efficient fiber collection were around $v_{ex} = 0.005 - 0.02$ mL/min.

Neat SWNT fibers were collected by hand. Tweezers or a thin short length of rod (e.g. thick copper wire, short wooden stick) were used to grab the fiber, which would then be brought out of the coagulant onto a glass roller. To allow for sufficient time in the coagulant bath, the needle extrusion was allowed to continue for several seconds before turning the roller. This resulted in a long length of fiber hanging in the coagulant bath in a “U” shape. Some samples were collected by tweezers instead of collecting on a roller. In that case, a 10 – 30 cm length of fiber was allowed to extrude and the proto-fiber was cut off at the needle orifice by grasping with tweezers.

During extrusion, the proto-fiber could be seen to shrink inside the diethyl ether coagulant bath as sulfuric acid left the fiber. The acid could be visibly seen leaving the fiber through wavy changes in the index of refraction of the solvent near the fiber line. The flux of coagulant into the fiber was less than the flux of sulfuric acid out. Upon removal from ether, the neat SWNT fibers quickly shrunk in both diameter and length as
the ether evaporated. Fiber samples that were left in the ether bath for long periods of time (>1 min) were more difficult to collect. They did not possess the same structural integrity of other neat fibers. The fibers also appeared to swell slightly. These qualitative observations suggest that there is an optimal residence time in the ether coagulant such that fiber removed too quickly still retains some sulfuric acid and will loose its structure over the next 12 – 24 hrs, while fibers left in the coagulant for too long also lose some strength.

Figure 3.13: A picture of a spool of neat SWNT fiber spun from 6 wt% SWNTs in 102% sulfuric acid.

It is important to note that, while these experiments were successful in producing neat SWNT fibers, the starting dope did not exhibit sufficient extensibility to support tension during extrusion with the given apparatus. The impressive properties of rod-like polymer fibers are often achieved only after drawing during spinning (see Sec. 2.2.3). Nevertheless, these neat SWNT fibers yield interesting properties.
3.3.2. Scanning Electron Microscopy

The primary tool used to characterize the morphological and structural properties of neat SWNT fibers was SEM. This microscopy technique provided a qualitative measure of the degree of alignment along the surface of a fiber as well as its overall shape. The resolution of SEM was high enough to see small bundles of SWNTs as well as any substructure within the fiber. Fibers produced from soft-baked purified SWNTs and hexane-extracted SWNTs were both examined under SEM. Samples were mounted on a standard aluminum stub using conductive tape and observed in a JSM-6500F SEM (JEOL) without using a conducting coating.

The first kind of neat SWNT fiber analyzed was extruded from soft-baked SWNTs. In general, the fibers were very highly aligned. Even when viewed at low magnifications (<1000x), the SWNTs possessed a visible alignment parallel to the fiber axis (Fig. 3.14A). At higher magnifications, a structure consisting of large SWNT ropes 200 – 600 nm in diameter exists (Fig. 3.14B – D). The ropes on the surface of the fiber can be seen to be moderately packed together with some interpenetration between ropes. The neat SWNT fiber appeared to be made up of these large ropes. At very high magnifications (>50,000x), a finer substructure of smaller ropes can be seen (Fig. 3.14D). These “primary” ropes are approximately 10 – 30 nm in diameter and make up the larger ropes, suggesting a structural hierarchy to neat SWNT fiber.

In addition to the substructure, the surface morphology of the neat soft-baked SWNT fibers is interesting. It is relatively smooth and clean, without notable contaminants from either the solution or the spinning process. The starting material did contain ~1 at% metal impurities left over from the HiPco process (see Sec. 3.1.1). These
metal particles are not easily found on the fiber’s surface, even at high magnifications. Although, the surfaces of the soft-baked SWNT fibers are smooth and aligned, they are not uniform. There are surface variations and an overall asymmetric shape to the fiber that is indicative of uneven coagulation. The collapsed, uneven surface is consistent with the observation in Section 3.3.1 that the proto-fiber shrunk upon entering the coagulation bath. The soft-baked SWNT / 102% sulfuric acid dope formed a rigid, dense skin during coagulation, and since the outward flux of sulfuric acid was greater than the inward flux of ether, radially uniform coagulation was not possible. The rigid skin resisted the coagulation and collapsed the fiber (see Sec. 2.2.3).

![Figure 3.14: Scanning electron micrographs depicting a 6 wt% soft-baked neat SWNT fiber spun into ether. The four images show the same fiber region at increasing magnification. A finer substructure is revealed at high magnifications.](image)
The second type of neat SWNT fiber produced utilized a newer method of nanotube purification. The soft-baked purification process produced hard, fused chunks of SWNT that required pulverizing before mixing. The SWNTs processed with the hexane-extraction purification scheme (see App. A) were instead a loose powder that did not require grinding. The material appeared to maintain the loose, fluffy nature of raw HiPco SWNTs, while being discrete and dense enough to be easily handled. The first fibers made with these purified nanotubes were spun from 6 wt% hexane-extracted SWNTs in 102% sulfuric acid. The dopant was mixed at 100°C for 3 days, as per the standard mixing procedure (see Sec. 3.1.2). The fibers were extruded using the previously described wet-spinning syringe method into a dry diethyl ether column.

The resulting neat SWNT fibers were similar to the soft-baked SWNT fibers with a couple of notable differences. Both fibers possessed a qualitatively high degree of SWNT alignment that was observable at low to high magnifications. The hexane-extracted fibers also appeared to be made of large ropes 200 – 600 nm in diameter. Finally, the surface of both fibers appeared clean, devoid of notable contaminants. However, the hexane-extracted fibers possessed a high degree of uniformity in surface morphology and SWNT rope size. Where the soft-baked fibers had irregularities in surface roughness on the ~10 μm scale, the hexane-extracted fibers were uniform. They did not have odd dips and hills along their surface. In general, these fibers appeared to have coagulated in a uniform fashion. A softer, more permeable skin was formed during coagulation which allowed the proto-fiber to shrink evenly. Secondly, the large ropes that are the building blocks of these fibers were more uniform in the hexane fibers and appear
to interpenetrate each other more often. Overall, the fibers were like the soft-baked neat SWNT fibers, only better.

![Figure 3.15: Scanning electron micrographs of a 6 wt% hexane-extracted SWNT fiber at various magnifications. The images show a highly aligned clean fiber consisting of large SWNT ropes.](image)

In addition to 6 wt% hexane-extracted neat SWNT fibers, fibers were also produced from a pre-mixed 10 wt% sample. Because of the highly viscous nature of this higher concentration, the sample was “pre-mixed” by hand and injected into the Daca Double Helix Mixer. The dopant was then mixed at 100°C for 3 days, as per the standard mixing procedure (see Sec. 3.1.2). The fibers were extruded using the wet-spinning syringe method into a dry diethyl ether column. The resulting 10 wt% hexane-extracted
SWNT fibers were nearly identical to their 6 wt% counterparts. They had a uniform surface free of contaminants, exhibited high degrees of alignment, and possessed a substructure of large ropes (Fig. 3.16C) and smaller primary ropes (Fig. 3.16D).

Figure 3.16: Scanning electron micrographs of a 10 wt% hexane-extracted neat SWNT fiber. The fiber appears to have a uniform surface free of contaminants (A). At higher magnifications the fiber is shown to consist of large (B, C) and primary (D) SWNT ropes.

Surface SEM analysis of fiber samples provided useful information, but could not provide information on the interior structure and composition of fiber samples. SWNT fibers that were simply broken in half did not provide useful information about the interior structure. The end of the broken fiber consisted of uneven SWNT bundles sticking out into the air like a frayed rope (Fig. 3.17A). To gain access to the interior, a
procedure was developed by Wang et al. that combined traditional microtoming with chemical polishing [22]. Fiber samples were embedded in sucrose and microtomed with a diamond blade. The sucrose was then dissolved away with water. At this stage, the end of the cut fiber consisted of uneven SWNT bundles combed over the cross-sectional surface, obscuring the interior structure. To obtain a representative cross-section of the fiber, the cut fiber sample was mounted into a custom high vacuum chamber and subjected to a highly reactive UV/Ozone treatment. UV/Ozone is known to etch SWNTs [96]. The resulting sample was a bisected neat SWNT fiber with a normal cross-sectional plane (Fig 3.17B). Once a fiber sample was microtomed and etched with UV/Ozone, the cross-sectional shape was revealed and the internal structure of the neat SWNT fiber was exposed for further investigation.

![Scanning electron micrographs depicting a 6 wt% hexane-extracted neat SWNT fiber after (A) simple breaking and after (B) the UV/Ozone microtome technique. The 6 wt% hexane fiber was found to have a roughly uniform, circular cross-section measuring 36 ± 3 μm in diameter.](image)

As previously mentioned, there were difference observed between the surface morphologies of the soft-baked SWNT fibers and the hexane-extracted SWNT fibers. These differences were even more evident when observing the cross-sections of the two
fiber types. The soft-baked SWNT fibers exhibited uneven, collapsed cross-sections which were the result of a mismatch in coagulation. As discussed in Section 2.2.3, coagulation of a fiber is a complicated process controlled by the diffusion of solvent out of the fiber and of coagulant into the fiber. Figure 3.18 shows three soft-baked fibers extruded under similar conditions, but from three different experiments. Fibers A and C show a clear skin-core formation during coagulation. The diffusion of sulfuric acid from the fiber into the bath was much more rapid than diffusion of ether into the fiber. A dense, rigid skin formed that collapsed from deformation stresses during coagulation. Fiber B appears to have formed a slightly less rigid skin, which allowed a more controlled reduction in size during coagulation. Moderate voids were revealed within all three soft-baked SWNT fibers. The voids were not homogenously distributed throughout the internal structure.
The hexane-extracted neat SWNT fibers possessed much better cross-sections. Fig 3.17B and Fig 3.18D show cross-sections of 6 and 10 wt% hexane-extracted neat SWNT fibers. Both display a near-ideal circular cross-section with very few voids. The voids that do exist are small and homogenously distributed throughout the fiber volume. A softer, more flexible skin clearly developed in these fibers, which allowed the fiber to shrink evenly during coagulation. The cross-sectional analysis of both types of fibers is consistent with the surface SEM images.
The void fraction for these SWNT fibers is a useful measure of the efficacy of coagulation. It can be calculated given extrusion variables and the measured diameter of a given fiber sample. With the volume concentration known for a given sample (see App. B), the void fraction can be determined using the geometry of the extrusion needle and the measured fiber diameter. The fiber is extruded from a needle with an orifice diameter, $d_0$, which theoretically expels all solvent during coagulation, resulting in a fiber of diameter $d_{th}$. In the absence of drawing, the theoretical fiber diameter is defined by

$$\frac{\text{vol}^\%}{100} \times \frac{d_0^2}{\pi} = \frac{d_{th}^2}{\pi} \Rightarrow \frac{\text{vol}^\%}{100} \times d_0^2 = d_{th}^2. \quad (3.4)$$

In reality, some void spaces will form during coagulation resulting in a larger experimental diameter, $d_{exp}$. The percentage of the fiber's internal volume occupied by voids, $\text{Void}^\%$, is defined by

$$\frac{d_{exp}^2}{\pi} - \frac{d_{th}^2}{\pi} \times \frac{4}{4} = \text{Void}^\% \Rightarrow \frac{d_{exp}^2 - d_{th}^2}{d_{exp}^2} \times 100 = \text{Void}^\%. \quad (3.5)$$

To determine the void fraction for a given fiber sample, Equation 3.4 is substituted into Equation 3.5:

$$\frac{d_{exp}^2 - \left(\frac{\text{vol}^\%}{100} \times d_0^2\right)}{d_{exp}^2} \times 100 = \text{Void}^\%. \quad (3.6)$$

Using the above analysis, the void fractions for a 6 wt% soft-baked neat SWNT fiber (Fig. 3.18B), 6 wt% hexane-extracted SWNT fiber (Fig. 3.17B), and a 10 wt% hexane-extracted SWNT fiber (Fig. 3.18D) can be calculated. An error of ± 0.5 wt% was assigned to the weight concentration based on minor concentration gradients observed in Daca mixing studies [94]. All three fiber samples were extruded from a needle orifice of
\(d_0 = 125 \text{ } \mu\text{m}\). The density of 102\% sulfuric acid is 1.88 \text{ g/cm}^3. For HiPco material, the density of packed SWNTs is approximately 1.32 \text{ g/cm}^3 (see App. B). Admittedly, the neat SWNT fibers consist of a wide distribution of nanotube lengths and diameters, but this density is a good approximation. Using these values, and the measured fiber diameters, the void fractions for the three fibers samples was calculated and is shown in Table 3.1.

Table 3.1: Void Fractions for Neat SWNT Fibers

<table>
<thead>
<tr>
<th>Fiber Sample</th>
<th>Packed Volume Concentration (vol%)</th>
<th>Needle ID ((d_0))</th>
<th>Theoretical Fiber Diameter ((d_\text{th}))</th>
<th>Measured Fiber Diameter ((d_{\text{exp}}))</th>
<th>Void Fraction (Void%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 wt% Soft-Baked</td>
<td>8.3 ± 0.7 %</td>
<td>125 (\mu\text{m})</td>
<td>36 ± 2 (\mu\text{m})</td>
<td>54 ± 7 (\mu\text{m})</td>
<td>56 ± 22 %</td>
</tr>
<tr>
<td>6 wt% Hexane</td>
<td>8.3 ± 0.7 %</td>
<td>125 (\mu\text{m})</td>
<td>36 ± 2 (\mu\text{m})</td>
<td>36 ± 3 (\mu\text{m})</td>
<td>0 ± 15 %</td>
</tr>
<tr>
<td>10 wt% Hexane</td>
<td>13.7 ± 0.6 %</td>
<td>125 (\mu\text{m})</td>
<td>46 ± 1 (\mu\text{m})</td>
<td>50 ± 2 (\mu\text{m})</td>
<td>15 ± 15 %</td>
</tr>
</tbody>
</table>

The void fraction for the hexane-extracted fibers is notably smaller than that of the soft-baked SWNT fiber. Obviously a fiber cannot possess less than zero void volume, but the calculations are based on an approximation of the close-packed SWNT density within the fiber. Since all three fibers were mixed and extruded under the same conditions, these results would indicate that the hexane-extracted material can more easily expel its solvent during the coagulation process. Given the material’s loose powdery form prior to mixing, as compared to the hard form of soft-baked SWNTs, it is no surprise that the acid would more fully dissolve the hexane-extracted material, and therefore form a softer, more flexible skin during coagulation. Also worth noting is that the cross-sectional images of the other soft-baked fibers do show denser fibers. However, they possess an undesirable non-uniform shape. It is possible that the three cross-sections, collapsed soft-baked, void-filled soft bake, and uniform hexane-extracted fibers,
represent the end products of three levels of mixing efficiency. The fibers in Figures 3.18A & C were produced from the same kind of sample as the fiber shown in Fig. 3.18B. This suggests that other factors may effect the fiber coagulation. Regardless, these experiments have shown the hexane-extracted SWNT fibers to have better coagulation than ones made from soft-baked purified SWNTs, and that the coagulation process is indeed a complicated one worthy of further research.

In addition to a morphological analysis, the SEM images revealed a substructure of the neat SWNT fibers. As discussed previously, the surface of neat SWNT fibers appeared to consist of two levels of structure: larger 200 – 600 nm bundles and smaller 10 – 30 nm primary ropes. Both of these nanotube structures can be seen within the cross-sections of the neat SWNT fibers. The first level of structure, the larger SWNT bundles, provided a fascinating link to the SWNT / 102% sulfuric acid liquid crystalline phase. Prior to extrusion and coagulation, the SWNTs in 102% sulfuric acid existed in a single liquid crystalline phase, as described in Section 3.2.1. The system consisted of many SWNT Spaghetti domains that aligned during shear flow. These SWNT Spaghetti appear to constitute the structure of the neat fibers.

From optical microscopy, SWNT Spaghetti was measured to be at most 600 nm in diameter. The large SWNT bundles that make up the structure of the neat SWNTs were measured to be of similar size, both in soft-baked neat fibers (Fig 3.14) and in hexane-extracted neat fibers (Fig. 3.15 & 3.16). The spaghetti domains appear to have coagulated as distinct entities, packed together and interconnected to give the fiber its structural support and strength. The bundles on the outer surface of hexane-extracted fibers provide a clearer picture of this transition. In fact, the shape of unformed alewives (see Sec. 3.1.3)
can be seen in the coagulated spaghetti strands, suggesting the tactoid aggregates form out of de-stabilized SWNT Spaghetti.

A close examination of the cross-section of the hexane-extracted fibers reveals further evidence of SWNT Spaghetti’s presence (Fig. 3.19). At high magnifications, the cross-sections of the individual SWNT bundles can be imaged. They are approximately 200 – 600 nm across (Fig. 3.19C), the same size as the surface bundles and the SWNT Spaghetti liquid crystalline domains. In these uniformly coagulated fibers, the spaghetti substructure extends throughout the fiber. This suggests that, given the homogenous nature of the fibers, the inherent structure of neat fibers was SWNT Spaghetti and that it was not a surface artifact of coagulation.

![Image](image_url)

**Figure 3.19:** Scanning electron micrographs depicting a 10 wt% hexane-extracted SWNT fiber prepared with the microtome/UV-Ozone technique. Higher magnifications (B, C) reveal large SWNT bundles similar to the surface bundles that are that same size as SWNT Spaghetti liquid crystal domains. Very high magnification (D) reveals primary ropes.
In addition to the large SWNT bundles, a smaller substructure of primary ropes is also evident in the cross-sectional images. Just like the large SWNT bundles, both the soft-baked and the hexane-extracted neat SWNT fibers exhibited this finer structure. The origin of these primary ropes is more of a mystery than the larger bundles. If such ropes did exist in the liquid phase, they could not have been observed by optical microscopy due to the limits of visible light. Dispersion of the SWNTs onto a substrate suitable for imaging by other methods (e.g. atomic force microscopy, scanning electron microscopy) has not been successfully performed due to complications involving handling the super acid solvent. Because of the use of substrate dispersion methods, even if a sample could be created, doubts would surround any such observed structures. In situ probes will be necessary to start exploring their origin and have not been performed to date. However, these primary ropes may not exist in the solution phase at all. Traditional rod-like polymer fibers also exhibit similar sized fibrils. Similar elemental microfibrils are commonly observed in many rod-like polymer fibers, and are believed to be formed during the coagulation of a liquid crystalline sample during the extrusion process [97]. Their origin, however, has not been definitively proven and is still one of the unanswered questions in fiber engineering.

The quality of fibers from an extrusion experiment is dependent on many variables. On a couple of occasions, fibers produced revealed that the system had been compromised to some degree. There are many opportunities for the process to be compromised, resulting in less-than-ideal fibers. Due to moisture sensitivity, errant ingress of minute amounts of water during handling is usually to blame. A detailed study
of the effects of moisture exposure was not performed. A better understanding of the mixing and extrusion processes will be needed before such efforts will be efficiently executed. However, examining the fibers that result from compromised systems provides insights into what should be avoided. Three different kinds of compromised fibers were observed in the research.

The most commonly encountered compromised fiber was one which was of marginally lesser quality than a standard fiber. The fiber still maintains a degree of alignment and homogenous morphology, but is notably rougher and uneven in its appearance (Fig. 3.20A & B). Higher magnification SEM images show a rougher bundle structure (Fig. 3.20C) that contains larger SWNT bundles than normal fibers (Fig. 3.20D). The smaller primary rope substructure is still present and is of the same size as normal fibers. Why a neat fiber turned out to have such a rough, uneven surface is not well understood. Most likely, it was the result of mixing complications – slightly less than 102% sulfuric acid or a higher than normal metal content in the starting purified material.
Figure 3.20: Scanning electron micrographs depicting a marginally poor 6 wt% soft-baked neat SWNT fiber. The images show a generally stable fiber with a rough surface which contains larger SWNT bundles.

While some fibers are of only marginally lesser quality, some experiments were completely compromised and resulted in very poor fibers. This is inevitably the result of a miscalculation in acid strength (98% vs. 102% sulfuric acid) or significant exposure to moisture during mixing. The resulting fiber is extremely rough with little structural continuity (Fig. 3.21A). At moderate SEM magnifications (Fig. 3.21B), SWNT bundles cannot be resolved and appear as rough bumpy aggregates along the fiber's surface. The presence of SWNTs can be confirmed only at high magnification (Fig. 3.21C). The bundles at high magnification were observed to have non-uniform sizes and little to no
alignment. In addition, voids are much more prevalent along the fiber's surface. When microtomed (no UV/Ozone treatment), SWNT bundles do not extend from the end of the fiber, but instead the fiber is rough and brittle, breaking off at discrete aggregates (Fig. 3.22D). These fibers were rare since compromising events were usually identified prior to extrusion and the experiment discarded.

![Figure 3.21: Scanning electron micrographs depicting a poor 10 wt% soft-baked neat SWNT fiber. The fiber surface is very rough and uneven. At high magnifications, the SWNT bundles appear tangled, unaligned, and of varying size. When cut, the fiber breaks in a brittle fashion with no extending SWNT bundles.](image)

The third class of sub-normal fibers was fibers extruded into coagulants other than diethyl ether. During the initial stages of neat SWNT fiber research, it was determined
that fibers spun into diethyl ether produced the best fibers. Qualitatively, the fibers were
easier to extrude and possessed higher structural stability. Quantitatively, the ether fibers
possessed a higher polarized Raman ratio (see Sec. 3.3.3), a clear indication of alignment.
However, an examination of fibers extruded into alternative baths is still useful, even
prior to designing and implementing a coagulation / take-up system.

One such example is a 10 wt% hexane-extracted SWNT fiber extruded into water
and then transferred to a second bath of diethyl ether. The fiber was allowed to remain in
the water bath for less than ten seconds before being transferred. The second bath was
used in lieu of evaporative annealing steps that would be needed to remove water within
the fiber. The ether exchanged with the water and then evaporated upon removal from the
bath, similar to what occurs under normal extrusion directly into an ether bath. The
resulting fiber shows many of the same good qualities of its ether counterpart, including a
high polarized Raman ratio (see Sec. 3.3.3), but possessed a couple of key differences.

Under SEM, at low and medium levels of magnification, there exists a sporadic
coverage of unaligned large SWNT bundles over the dominant highly aligned structure.
These bundles appear to have started forming SWNT Alewives (see Sec. 3.1.3), but their
formation was halted before fully separating from the bulk fiber. A longer dwell time in
the water bath would probably have resulted in a more pronounced pre-alewife presence.
Large SWNT bundles that retained their place in the larger structure did not escape the
adverse effects of the water. At high magnification (Fig. 3.22D) the large ropes that make
up the overall fiber structure are not as uniform in diameter as observed in hexane-
extracted fibers spun directly into ether. The ropes neck down at places while merging
and spanning the length of the fiber. Since the overall fiber retains the same diameter as
its ether spun counterpart (≈ 50 μm), the internal structure is not expected to be different. The water coagulation destabilized some of the surface SWNT bundles and performed minor degrees of coagulation, while the ether bath probably completed the majority of the internal solidification.

![Figure 3.22](image)

Figure 3.22: Scanning electron micrographs of a 10 wt% hexane-extracted neat SWNT fiber extruded into water and then transferred into diethyl ether. At low to medium magnifications (B, C), pre-formed SWNT alevives are present on the fiber surface, while at high magnification (D) the SWNT bundles have pronounced variations in their diameter.

SEM has allowed a detailed qualitative analysis of neat SWNT fibers. Examinations of the sides of fibers provided information on the homogeneity and bulk alignment of SWNTs within the fibers, while high magnification analyses allowed a
better understanding of their structure. Cross-sectional images of fiber samples, produced by the microtome / UV-Ozone method [22], allowed for a unique view of the internal structure of the fibers. The structure of the fibers was linked to the one dimensional SWNT Spaghetti liquid crystalline phase of SWNTs in 102% sulfuric acid, providing a fascinating look into the extrusion process. In addition, a smaller substructure of 10 – 30 nm primary SWNT ropes was observed that mimics microfibrils observed in traditional rigid rod polymer fibers.

The revelation that the neat SWNT fibers are effectively a coagulated collection of SWNT Spaghetti is of critical importance to the improvement of neat SWNT fiber properties. The fibers currently appear to consist of long spaghetti strands that, at some locations, merge into each other in a seamless fashion, while at other locations, are linked together through surface van der Waals contacts. All of the important properties of the fibers (mechanical, electrical, thermal) will be seriously limited by the number of surface contacts within the fiber. They will act as local strain defects in the case of mechanical properties, and points of high transport resistance for electrical and thermal conductance. Therefore, perhaps the most important future direction of neat SWNT fiber research will be the growth and continuity of SWNT Spaghetti. A neat SWNT fiber that consists of a single endless spaghetti domain of SWNTs will be an impressive material.

### 3.3.3. Raman Analysis

One of the techniques used to quantitatively probe the alignment of neat SWNT fibers was polarized Raman spectroscopy. As discussed in Section 2.1.2, SWNTs possess unique Raman characteristics due to their anisotropic geometry and resonance
enhancement. The intensities of many of these Raman bands are dependent on the orientation between the nanotube and the excitation laser’s polarization vector. This anisotropic Raman response is a valuable tool for probing the surface alignment of SWNTs in macroscopic objects.

Raman spectra were collected with a Renishaw Microraman System 1000 employing a 780 nm wavelength diode laser. An average $G^+$ Raman peak intensity (at $\sim 1590$ cm$^{-1}$ shift) was recorded for parallel and perpendicular orientations. The ratio of the average parallel vs. perpendicular intensities was used to gauge the relative degree of fiber alignment. To capture a neat SWNT fiber’s Raman spectrum, a short fiber length (1 – 2 cm) was attached to a microscope slide using double-sided tape. Because of the fiber curvature, the sample was lightly rolled with a clean glass pipette to flatten the fiber surface. Parallel vs. perpendicular Raman spectra were obtained for multiple locations along a given fiber sample. Multiple fiber pieces from a given batch of extrusion conditions were probed to prevent anomalous results.

![Graph showing a typical neat SWNT fiber's spectrum oriented parallel and perpendicular to the excitation laser's polarization vector.](image)

Figure 3.23: A graph showing a typical neat SWNT fiber’s spectrum oriented parallel and perpendicular to the excitation laser’s polarization vector.
Polarized Raman ratios were collected for both soft-baked neat SWNT fibers and hexane-extracted neat SWNT fibers from a variety of extrusion conditions. This analysis was used to explore the effect individual variables had on fiber alignment. Unless otherwise specified, fibers were extruded from 6 wt% soft-baked SWNTs in 102% sulfuric acid. Different needle lengths, needle diameters, and coagulants were used during extrusion.

One of the motivations for these experiments was to explore the effects of needle length and orifice diameter on the degree of alignment within a fiber sample. Shear flow can induce alignment of liquid crystalline domains and their constituent rod-like molecules. However, studying the effect of shear on the size and alignment of the liquid crystal domains within the dopant has been complicated by the need for an anhydrous environment and the black, opaque nature of optical microscopy samples prepared from concentrated SWNT mixtures. Instead, studying the effect of shear on the fibers themselves was attempted. Different needles were used to extrude a variety of samples. All were extruded into diethyl ether from the same starting mixture. Table 3.2 lists the polarized Raman ratios of the various fibers produced. Figures 3.24 – 3.26 present portions of the data to better visualize the effects of the variables individually while other conditions remained constant.
Table 3.2: 6 wt% Soft-baked Fiber Raman Results

<table>
<thead>
<tr>
<th>Orifice Diameter</th>
<th>Needle Length</th>
<th>Coagulant</th>
<th>Polarized Raman Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 μm</td>
<td>1”</td>
<td>Diethyl Ether</td>
<td>15 ± 4</td>
</tr>
<tr>
<td>500 μm</td>
<td>2”</td>
<td>Diethyl Ether</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>500 μm</td>
<td>3”</td>
<td>Diethyl Ether</td>
<td>11 ± 5</td>
</tr>
<tr>
<td>500 μm</td>
<td>4”</td>
<td>Diethyl Ether</td>
<td>11 ± 5</td>
</tr>
<tr>
<td>250 μm</td>
<td>2”</td>
<td>Diethyl Ether</td>
<td>14 ± 2</td>
</tr>
<tr>
<td>125 μm</td>
<td>2”</td>
<td>Diethyl Ether</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>125 μm</td>
<td>4”</td>
<td>Diethyl Ether</td>
<td>21 ± 3</td>
</tr>
</tbody>
</table>

The first variable explored was the needle orifice diameter. As the liquid crystal material flows through a needle, alignment due to shear occurs. Like other polymer liquid crystals, SWNTs in 102% sulfuric acid behave as a power law fluid (see Sec. 3.3.2). For a power law fluid flowing through a pipe (i.e. needle), the velocity profile is that of a blunted parabola, becoming more plug-like with decreasing power index, n. The shear rate is greatest near the walls of the pipe and is given by [95]:

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \left[ \frac{3}{4} + \frac{1}{4n} \right],$$

(3.7)

where Q is the volume flow rate during extrusion, R is the pipe radius, and n is the power law index (n = 0.2 for SWNTs in 102% sulfuric acid, see Sec. 3.2.2). This function is a useful approximation for understanding the effect shear has on fiber alignment. As the diameter of the needle is reduced, the SWNT dope should experience greater shear alignment, and therefore greater alignment of SWNT individuals and bundles within the resultant fiber. Figure 3.24 shows that for fibers made from 6 wt% SWNTs in 102% sulfuric acid, the surface alignment decreased with increasing orifice diameter. More data will be required to clearly determine the relationship between the two variables, but this plot does suggest the Raman ratio has a non-linear decreasing dependence on the needle orifice diameter, akin to Equation 3.7.
Figure 3.24: A plot of polarized Raman ratio vs. needle size for various 6 wt% soft-baked SWNT fibers extruded from 2" long needles. A smaller needle diameter results in increased fiber alignment.

The second variable explored was needle length. If the orientation time of the SWNTs in solution is much less than the time spent by the fluid traversing the needle, then changing the needle length from 1 – 4" should not have much effect. Conversely, if the time needed for the nanotubes to reach an equilibrium shear is comparable to the dwell time in the needle, the lengths used should show an effect. Neat SWNT fibers were extruded at varying needle lengths and the polarized Raman ratio investigated. The orifice diameter was kept constant, $d_0 = 500$ μm, as was the starting material, 6 wt% soft-baked SWNT in 102% sulfuric acid. The results do not show needle length to have a clear effect on alignment (Fig. 3.25). The uncertainty precludes any conclusion beyond a constant relationship between the Raman ratio and the needle length; however a slight inverse relationship may exist.
Figure 3.25: A plot showing the polarized Raman ratio vs. needle length for various 6 wt% soft-baked SWNT fibers extruded from a 500 μm needle diameter. The effect of needle length is unclear.

These results suggest that the shear flow alignment at this orifice diameter is not significantly different in 1 – 4" long needles. The closest rheological characteristic to describe this situation is the healing time for the spontaneous disappearance of defects in a nematic liquid crystal. Davis et al. estimate the healing time for a 500 μm thick sample of SWNTs in 102% sulfuric acid to be on the order of a year [92]. Their estimate uses a viscosity of $\eta = 400 - 500 \text{ Pa}\cdot\text{s}$. From Equation 3.7, the shear rate at the wall of the extrusion needle is approximately $\dot{\gamma}_w \approx 12 \text{ sec}^{-1}$, which results in a viscosity of $\eta \approx 100 \text{ Pa}\cdot\text{s}$ for a 6 wt% sample (Fig. 3.8). Given that the time spent by the sample in the needle is on the order of ten seconds, the alignment of the SWNT liquid crystalline sample is not expected to change. In all likelihood, the majority of the fiber’s alignment comes, not from shear flow in the needle, but from extensional flow when transitioning from the larger syringe bore to the smaller needle orifice. Either explanation is consistent with both the lack of needle length influence and the notable effect of needle orifice size (Fig. 3.24) on fiber alignment. Future improvements in this experiment should include the use of smaller orifice diameters, or increased gradations in needle lengths. The first change
will increase the shear flow within needles; the second will reduce the proportionality of the uncertainties relative to needle lengths.

In polymer fiber engineering, the length to diameter ratio has been found to be a useful variable to characterized extrusion processes [57]. Both length and diameter influence the degree of shear flow experienced by the liquid crystal prior to extrusion. In addition, both variables effect the pressure required to spin a fiber, a common limiting factor in industrial operations [18]. The L/D of the extrusion needle allows a comparison between fibers extruded under different orifice diameters and needle lengths; only the starting sample concentration needs to be fixed.

Fibers were extruded from a variety of needle lengths and orifices. All fibers were extruded from 6 wt% soft-baked SWNTs in 102% sulfuric acid in diethyl ether (Table 3.2). Typical L/D ratios for polymer fiber spinning range from $L/D = 1 - 5$ [61]. Due to the fiber spinning method used to produce these fibers (see Sec. 3.3.1), long needle lengths were required. Figure 3.26 shows the Raman ratio as a function of $L/D$ for the various fibers. A clear relationship is not obvious, although the polarized Raman ratio may follow an increasing non-linear function with respect to $L/D$ with an asymptote around 20:1. The fact that this analysis involves two potentially influential variables makes it difficult to interpret. Future analyses are better left exploring the variables independently to establish a better basic understanding of the origins of neat SWNT fiber alignment.
Figure 3.26: A plot showing the polarized Raman ratio vs. L/D ratio for various 6 wt% soft-baked SWNT fibers. No clear relationship is evident.

The second aspect of neat SWNT fiber spinning explored via polarized Raman spectroscopy was the effect of various coagulant solvents on alignment. Diethyl ether was one of the first coagulants used because of its known solvation of sulfonated $C_{60}$ molecules [98]. Sulfuric acid diffused into the ether efficiently with little inward ether diffusion. Ether within the fiber quickly evaporated upon the fiber’s removal from the bath, eliminating the need for extensive post-processing steps (see Sec. 3.3.1). It was effective at solidifying fibers, but a coordinated comparison of difference coagulants is important. Dilute aqueous sulfuric acid was used because of its use in Kevlar$^{TM}$ (PPTA) fiber spinning [99]. Ethylene glycol diethyl ether is effectively a long-chain version of diethyl ether, and was chosen in an effort to slow down the coagulant mechanisms associated with diethyl ether. Many other common organic solvents (e.g. acetone, methanol) were tried, but did not produce recoverable fibers with any degree of structural integrity.

Table 3.3 shows a clear difference in the degree alignment from the various coagulants. There was some concern that diethyl ether might be extracting the acid
solvent too quickly, disrupting the fiber alignment in the process. However, the slower coagulants are shown to have a lower degree of alignment. These results are consistent with experiments by Ramesh et al. involving SWNT alewife formation, which showed that slow exposure to moisture was necessary for alewife formation [89]. The slower coagulants resulted in more disruption in the fiber's surface alignment, while the diethyl ether quickly locked in the fiber's alignment. SEM analysis of fibers produced from alternate, slower solvents agree with this interpretation (Fig. 3.22).

Table 3.3: Raman Results for Various Coagulation Baths

<table>
<thead>
<tr>
<th>Orifice Diameter</th>
<th>Needle Length</th>
<th>Coagulant</th>
<th>Polarized Raman Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>125 μm</td>
<td>2”</td>
<td>Diethyl Ether</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>125 μm</td>
<td>2”</td>
<td>10% H₂SO₄ in Water, then Diethyl Ether</td>
<td>14 ± 3</td>
</tr>
<tr>
<td>125 μm</td>
<td>2”</td>
<td>10% H₂SO₄ in Water</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>125 μm</td>
<td>2”</td>
<td>Ethylene Glycol Diethyl Ether</td>
<td>5 ± 2</td>
</tr>
</tbody>
</table>

Polarized Raman spectroscopy was also performed on fibers produced from hexane-extracted SWNTs. SEM analysis of hexane-extracted fibers show a higher degree of alignment as compared to soft-baked SWNT fibers (see Sec. 3.3.2). The polarized Raman measurements support this finding as well. Fibers were extruded from 6 wt% and 10 wt% hexane-extracted SWNTs in 102% sulfuric acid through 1” needles of varying orifice diameter.

Table 3.4 reports the polarized Raman ratio for each hexane-extracted SWNT fiber sample examined. The polarized Raman measurements show that the fibers have a very high degree of alignment and are, in fact, the highest aligned of any previously reported macroscopic neat SWNT object. Gommans et al. reported a ratio of ~5:1 for
electrically assembled SWNT fibers [47], while Fischer et al. have reported a similar ratio of ~5:1 for magnetic assemblies of SWNTs [86].

Table 3.4: Raman Results for Hexane-Extracted SWNT Fibers

<table>
<thead>
<tr>
<th>SWNT Concentration</th>
<th>Orifice Dia., [µm]</th>
<th>Needle Length</th>
<th>Coagulant</th>
<th>Raman Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt%</td>
<td>125</td>
<td>1”</td>
<td>Diethyl Ether</td>
<td>22 ± 2</td>
</tr>
<tr>
<td>10 wt%</td>
<td>175</td>
<td>1”</td>
<td>Diethyl Ether</td>
<td>28 ± 3</td>
</tr>
<tr>
<td>10 wt%</td>
<td>250</td>
<td>1”</td>
<td>Diethyl Ether</td>
<td>28 ± 3</td>
</tr>
<tr>
<td>10 wt%</td>
<td>125</td>
<td>1”</td>
<td>Water followed by Diethyl Ether</td>
<td>21 ± 1</td>
</tr>
<tr>
<td>6 wt%</td>
<td>125</td>
<td>1”</td>
<td>Diethyl Ether</td>
<td>19 ± 3</td>
</tr>
</tbody>
</table>

A couple of notable observations are apparent when the hexane-extracted fibers’ alignments are compared to the soft-baked fibers’. The two 6 wt% fibers possess the same alignment, as measured by polarized Raman. The 6 wt% fibers extruded from a 125 µm orifice showed a Raman ratio of 22 ± 3 and 19 ± 3 for the soft-baked and hexane-extracted SWNTs, respectively. The fact that SEM analysis shows notably different surface morphology for the two types of fibers suggests that, at 6 wt%, the differences in internal coagulation did not dramatically effect the alignment present in the initial coagulation skin. The surfaces of the fibers solidified efficiently in both cases.

However, the Raman ratio does not decrease with increasing orifice diameter for hexane-extracted fibers, whereas the soft-baked fibers show the opposite trend. Figure 3.27 plots the Raman ratio as a function of orifice diameter for 6 wt% soft-baked fibers extruded from 2” long needles as compared to 10 wt% hexane-extracted SWNT fibers extruded from 1” long needles. Admittedly, the concentration and needle length have not been kept constant, but the comparison is still interesting. The difference in behavior suggests that the liquid crystalline phase in the hexane-extracted SWNT / 102% sulfuric acid system is more easily influenced by the shear alignment than the soft-baked sample. Both fibers were extruded at approximately the same extrusion rate (~0.8 cm/sec) and
therefore experienced the same shear rate within the needle. Within a single phase liquid crystalline system of rods, the spacing between rods is inversely proportional to the concentration. Therefore, the ability to influence the orientation of a domain by a given shear flow will increase as well since such alignment is dictated by spatial interactions between neighboring molecules. In addition, the size of liquid crystal domains within the SWNT/acid system may very well increase with concentration, allowing additional geometric alignment during the extensional flow from the extrusion chamber into the needle. Both are likely and would explain the difference in behavior between the polarized Raman ratio and needle diameter for the two types of purified SWNT material.

![Figure 3.27: A plot of polarized Raman ratio vs. needle diameter for 6 wt% soft-baked fibers (red circles) and 10 wt% hexane-extracted fibers (blue squares). The relationship between the ratio and orifice diameter is different for the two systems.](image)

Finally, the 10 wt% hexane-extracted fiber extruded into water and transferred to ether shows the same degree of alignment (21:1) as its counterpart extruded directly into ether (22:1). Similar 6 wt% soft-baked SWNT fibers extruded into 10% aq. sulfuric acid and then transferred to ether possessed less surface alignment (14:1) than fiber extruded into ether (22:1). These results suggest that the more concentrated fibers were not as easily disrupted by inefficient coagulation. The higher concentration allows a more stable
outer skin to form while the internal structure solidifies more slowly. The lower concentration has a lower density of SWNT bundles and therefore, individual bundles are more easily disrupted by both the diffusion of internal solvent and destabilizing of the acid protonation. It is also possible that the uniformity of a fiber's internal coagulation may be more critical for slower coagulants and plays a role in this difference, but the role this variation would play is unclear at this time. Admittedly, the comparison made is between fibers produced from different starting purified SWNT material, but the qualitative observations are still useful.

Polarized Raman spectroscopy has proven itself a valuable analysis technique for exploring the alignment of neat SWNT fibers. Many of the results compliment the qualitative results provided by SEM. As is evident from discussions throughout the section, the effect of extrusion and coagulation variables on fiber alignment is a complicated one. Because of the frontier, exploratory nature of this research, a more controlled set of experiments was not possible. The role each of the variables play in the production and formation of neat SWNT fibers is surely to be the focus of future research projects.

3.3.4. Strength Characterization

While structural analysis of fibers is useful and interesting, ultimately it is the properties of a fiber that define its potential in real world applications. Ever since early research identified their impressive mechanical properties, SWNTs have been targeted as building blocks for the next generation of light-weight ultra-strong materials. Dalton et al. have had remarkable success at integrating SWNTs into composite fibers. Their fibers
boast an impressive array of mechanical properties: tensile strength of 1.8 GPa, strain-to-failure of 30%, Young's Modulus of 80 GPa [80]. However, the fibers are only 60 wt% SWNTs, with 40 wt% occupied by polyvinyl alcohol; their properties are over an order of magnitude lower than those of individual SWNTs. If the properties of individual SWNTs are to be successfully ported to macroscopic materials, neat SWNT products are the only viable option.

Macroscopic neat SWNT fibers produced in this research are an important first step towards realizing the ultra-performance SWNT materials. The fibers did not exhibit significant mechanical properties, but their creation is a difficult and crucial beginning. It is important to note that these fibers were not extruded under tension and were extruded at relatively low concentrations, as compared to other solution spun rigid rod polymer systems. The majority of the high strength of polymer fibers is acquired during the drawing and post-processing procedures, neither of which were explored in this research [57]. Most polymer fibers created using a wet-spinning technique are spun from dopant with 5 – 30 wt% polymer concentrations [18]. Higher concentrations will be explored in future SWNT fiber research, but have not been addressed here. Regardless, the mechanical properties of the first generation of neat SWNT fibers are an important milestone and provide for interesting conclusions.

Neat SWNT fibers produced from both soft-baked and hexane-extracted starting SWNT material were tested. Mechanical testing was performed using an Instron 5565 with a 50 N load cell. Pneumatic side action grips were used for soft-baked SWNT fibers, but were unavailable for hexane-extracted fibers; fixed clamps were used instead. Gauge lengths varied from 0.5 – 7”. Multiple fiber samples were tested and their ultimate loads
averaged for a given fiber type. Fiber diameters for the soft-baked fibers were obtained by averaging the width at six different locations under an optical microscope; hexane-extracted fiber diameters were obtained via SEM. Tensile strength for fiber samples was determined from the ultimate stress before breaking divided by the cross-sectional area of the sample. Young’s Moduli were obtained by fitting a line to the first linear region of the stress vs. strain curves.

Mechanical measurements for a variety of fibers are provided in Table 3.5. Unless otherwise indicated, fibers were extruded into diethyl ether in the manner described in Section 3.3.1. The soft-baked SWNT fibers exhibited a tensile strength of $\tau \approx 1$ MPa with a Young’s Modulus around $Y \approx 80$ MPa, while the hexane-extracted SWNT fibers possessed $\tau \approx 5$ MPa and $Y \approx 1$ GPa. These properties are poor compared to conventional fibers (see Sec. 2.2.5) and other SWNT composite fibers (see Sec. 2.3.1). However given the lack of extensional drawing and post-processing, there is still hope for the impressive properties of individual SWNTs. Interesting observations can also be drawn from these results that aid in understanding their formation and future analysis.

Table 3.5: Mechanical Properties of Neat SWNT Fibers

<table>
<thead>
<tr>
<th>Starting Sample</th>
<th>Needle Diameter [(\mu m)]</th>
<th>Fiber Diameter [(\mu m)]</th>
<th>Ultimate Load [mN]</th>
<th>Tensile Strength [MPa]</th>
<th>Young’s Modulus [MPa]</th>
<th>Raman Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 wt% soft-baked</td>
<td>125</td>
<td>71 ± 6</td>
<td>5.6 ± 0.2</td>
<td>1.4 ± 0.3</td>
<td>40 ± 20</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>6 wt% soft-baked</td>
<td>250</td>
<td>100 ± 10</td>
<td>13 ± 1</td>
<td>1.7 ± 0.4</td>
<td>130 ± 70</td>
<td>14 ± 2</td>
</tr>
<tr>
<td>6 wt% soft-baked</td>
<td>500</td>
<td>207 ± 15</td>
<td>28 ± 6</td>
<td>0.8 ± 0.3</td>
<td>80 ± 40</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>6 wt% hexane</td>
<td>125</td>
<td>36 ± 3</td>
<td>8.6 ± 1</td>
<td>8 ± 1</td>
<td>2300 ± 800</td>
<td>19 ± 3</td>
</tr>
<tr>
<td>10 wt% hexane</td>
<td>125</td>
<td>50 ± 2</td>
<td>7 ± 2</td>
<td>4 ± 1</td>
<td>1200 ± 600</td>
<td>22 ± 2</td>
</tr>
<tr>
<td>10 wt% hexane water/ether</td>
<td>125</td>
<td>50 ± 2</td>
<td>8.4</td>
<td>4.3 ± 0.5</td>
<td>500 ± 100</td>
<td>21 ± 1</td>
</tr>
</tbody>
</table>
One of the most interesting conclusions from the soft-baked fibers’ strength measurements is the correlation between tensile strength and intrinsic SWNT alignment. Figure 3.28 plots the tensile strength and polarized Raman ratio as a function of needle orifice diameter. Both properties follow a similar trend with respect to needle orifice diameter. The figure suggests that the tensile strength is inherently linked to the degree of SWNT surface alignment of a fiber. As SWNTs become more parallel with the fiber axis, the length of van der Waals tube-tube sidewall contact between individual SWNT bundles will increase. Therefore, it is reasonable to expect the strength to be related to the alignment.

![Graph](image)

**Figure 3.28:** A plot of tensile strength vs. needle orifice diameter (red circles) for soft-baked SWNT fibers. Scaled Raman ratio vs. needle orifice diameter data (blue squares) is provided for comparison.

In addition, Figure 3.29 shows an overall summary of Raman ratio as it relates to tensile strength, for both soft-baked and hexane-extracted SWNT fibers. The soft-baked fibers show strong indications of a linear proportionality between their Raman ratio and tensile strength. The hexane-extracted SWNT fibers do not exhibit such a relationship. These fibers also did not show a clear relationship between Raman ratio and needle
orifice diameter, while the soft-baked fibers showed a linear relationship (Fig. 3.27). The reason for these differences is not entirely clear. Most likely, the differences are related to coagulation behavior. For the soft-baked fibers, the larger proto-fibers were not as well coagulated, while the hexane-extracted fibers coagulated as effectively throughout the orifice range used (i.e. 125 – 250 μm).

![Graph showing tensile strength vs. Raman ratio](image)

**Figure 3.29:** A plot of average tensile strength vs. polarized Raman ratio for both soft-baked (blue circles) and hexane-extracted (red squares) SWNT fibers. The soft-baked fibers exhibit a linear relationship, while the hexane-extracted fibers do not.

In addition to tensile strength, values of Young’s Modulus were also obtained. Figures 3.30 and 3.31 depict stress/strain curves for typical 6 wt% soft-baked and 6 wt% hexane-extracted fibers, respectively. Plots from 10 wt% fiber testing were similar. Under a constant rate of extension (1 mm/min), the fibers experienced an initial stage where slack was removed and the load transferred to the fiber. Then, there was a region of elastic deformation, followed by plastic deformation just prior to failure. Fits to the elastic deformation data yielded Young’s Moduli for the fibers. Those values were averaged for each fiber type. Only one sample of the 6 wt% hexane-extracted SWNT fiber extruded into water and then transferred into diethyl ether was tested due to
availability. The uncertainty in its tensile strength was estimated from fluctuations in the testing data, while the other Moduli uncertainties were obtained from the fits. The effect of noise is notably more significant for the fixed clamps (Fig. 3.31) than the pneumatic side action grips (Fig. 3.30).

Figure 3.30: A stress vs. strain curve for a typical 6 wt% soft-baked SWNT fiber. The Young's Modulus is obtained from a fit to the linear portion of the curve (red dashed line).

Figure 3.31: A stress vs. strain curve for a typical 6 wt% hexane-extracted SWNT fiber. The Young's Modulus is obtained from a fit to the linear portion of the curve (red dashed line).
Neat SWNT fibers have been shown to possess marginal, but promising mechanical properties. They exhibited tensile strengths of $\tau \approx 1 - 5$ MPa with a Young's Modulus of $Y \approx 0.1 - 1$ GPa. The properties are comparable to those of SWNT buckypaper (see Sec. 2.3.2). However, these fibers have been produced with less than optimal coagulation of subnominal concentrations of SWNTs extruded without drawing. All of these conditions are known to drastically improve the mechanical properties of conventional fibers [57], and will be an important focus of future research.

### 3.3.5. Electrical Properties

In addition to their impressive mechanical properties, SWNTs have useful electrical properties as well. Depending on the type of nanotube (see Sec. 2.1.2), a SWNT can be either semiconducting or metallic. In addition, SWNTs have been shown to be ballistic conductors [7] and able to carry high current densities [100]. All of these facts make SWNT materials useful as electrically active components. This application is extremely useful with respect to conventional fibers due to the insulating nature of polymers [18].

Electrical resistivity measurements have been performed on the neat SWNT fibers produced in this research. The electrical resistivity research was not performed by this researcher. Instead, fiber samples were provided to the Fischer Group (University of Pennsylvania) and work was carried out there [21, 101, 102]. However, to provide a more complete picture of neat SWNT fiber properties, a summary of the work is included in this thesis.
Fischer et al. obtained electrical resistivity for various neat SWNT fiber samples using a 4-point DC measurement technique with current reversal averaging. Voltage probes were about 2 – 3 mm apart. It was necessary to sputter gold through a shadow mask to improve the quality of the contacts, presumably because the usual silver epoxies reacted with residual acid within the fiber samples. Low temperature measurements were performed in liquid helium and higher temperature measurements were made in vacuum. High temperature annealing was performed on samples by heating a fiber at 1150°C under vacuum for 2 hrs. Table 3.6 reports the room temperature resistivity for the various fiber samples, while Figures 3.32 and 3.33 provide the full resistivity vs. temperature behavior.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Needle Diameter (µm)</th>
<th>Green / Annealed</th>
<th>Resistivity at 300 K (mΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 wt% Soft-Baked</td>
<td>500</td>
<td>Green</td>
<td>0.6</td>
</tr>
<tr>
<td>8 wt% Soft-Baked</td>
<td>500</td>
<td>Annealed</td>
<td>8.1</td>
</tr>
<tr>
<td>6 wt% Soft-Baked</td>
<td>125</td>
<td>Green</td>
<td>0.3</td>
</tr>
<tr>
<td>6 wt% Soft-Baked</td>
<td>125</td>
<td>Annealed</td>
<td>2.6</td>
</tr>
<tr>
<td>6 wt% Soft-Baked</td>
<td>250</td>
<td>Green</td>
<td>0.5</td>
</tr>
<tr>
<td>6 wt% Soft-Baked</td>
<td>250</td>
<td>Annealed</td>
<td>5.5</td>
</tr>
<tr>
<td>10 wt% Hexane</td>
<td>125</td>
<td>Green</td>
<td>0.2</td>
</tr>
<tr>
<td>10 wt% Hexane</td>
<td>125</td>
<td>Annealed</td>
<td>2.8</td>
</tr>
<tr>
<td>6 wt% Hexane</td>
<td>125</td>
<td>Green</td>
<td>0.2</td>
</tr>
<tr>
<td>6 wt% Hexane</td>
<td>125</td>
<td>Annealed</td>
<td>3.4</td>
</tr>
</tbody>
</table>

The soft-baked and hexane-extracted fibers possessed similar electrical characteristics. The electrical resistivity measurements show the fibers to have exhibited semi-metal resistivities which increased after high temperature annealing. In general, the fibers possessed resistivities of $\rho \approx 0.3$ mΩ·cm at room temperature, which after annealing increased by an order of magnitude. This increase in resistivity after annealing is attributed to heavy p-doping from residual acid in the green fibers (i.e. as-spun) which
is removed upon annealing. Similar behavior was reported by Sreekumar et al. in their work with neat SWNT films from oleum dispersions (see Sec. 2.3.2). Thermopower measurements on green fibers suggest that the Fermi level was shifted by 0.55 eV into the valence band such that the semiconducting tubes were degenerately doped and contributed to electrical conductivity [21, 101]. In addition, it is believed that doping strongly improved the tube-tube electrical contacts, suppressing the low temperature upturn in resistivity. Similar behavior has been observed by Lee et al. in alkali-doped buckypaper samples [103]. The presence of residual acid is not surprising considering the relatively short coagulation dwell time used in the production of the neat SWNT fibers.

The electrical behavior of fiber samples as a function of temperature provides further information on the neat SWNT fiber system. The fibers possessed non-divergent resistivities with metallic behavior above 200 K. Resistivity data for acid-doped fibers fit well to the fluctuation-induced tunneling conduction mechanism [104, 105]. The resistivity was not divergent at low temperatures and can be described by

\[
\ln(\rho) \propto \frac{T_r}{T + T_s},
\]

(3.8)

with \(T_r \approx 10K\) and \(T_s \approx 20K\). These resistivities are two orders of magnitude lower than those reported for other SWNT fibers that involved polymers in their production process [12], but are on the same order as random mats of SWNTs [83].
Figure 3.32: Plots of electrical resistivity vs. temperature for a variety of unannealed (i.e. green) fibers. The fibers possessed non-divergent low temperature behavior and metallic behavior above 200 K.

Upon annealing the neat SWNT fiber samples, a non metallic low temperature behavior returned and the overall resistivity increased by an order of magnitude. Annealing simply evaporated away the bisulfate ions from within the fiber, leaving only SWNTs. Annealed fibers showed a divergent low temperature and a steadily decreasing resistivity above 200 K.
Figure 3.33: Plots of electrical resistivity vs. temperature for a variety of annealed fibers. The data shows non-metallic behavior.

Unlike mechanical properties, the soft-bake and hexane-extracted neat SWNT fibers possessed the same correlation between intrinsic alignment and electrical resistivity. In addition, both green and annealed fibers show a clear relationship between Raman ratio and resistivity (Fig. 3.34). The electrical resistivity is dependent on the length of tube-tube collinearity. The more aligned a fiber is, the easier it will be for electrons to find an uninterrupted electrical pathway from one point to another. The fact that both types of fibers showed a similar correlation suggests that the mechanical properties are more dependent on bulk alignment of the fiber, rather than localized “ideal” alignment necessary for transport properties.
Figure 3.34: A plot of room temperature (300 K) electrical resistivity vs. polarized Raman ratio for green (blue circles) and annealed (red squares) fibers. Both SWNT types show a linear relationship.

The Fischer Research Group, and in particular Juraj Vavro, have provided valuable research on the characterization of the electrical properties of neat SWNT fibers. The fibers were p-doped with residual acid which was removed upon annealing. Green fibers exhibited semi-metal resistivities, with a room temperature resistivity of $\rho \approx 0.3$ m$\Omega$-cm. Annealed fibers exhibited non-metallic divergent low temperature behavior with higher resistivities on the order of randomly aligned buckypaper. Because of this similarity, it is clear that neat SWNT fiber transport properties are not solely dependent on SWNT alignment, and are probably affected by other factors such as density, nanotube quality, bundle size, impurities, etc. Further research into improving the electrical properties through post-processing treatment or improved spinning conditions is surely a worthwhile endeavor.
3.3.6. Thermal Conductivity

In addition to electrical measurements, thermal conductivity measurements were performed on neat SWNT fiber samples. For the same reasons that transport of electrons is efficient along the length of a nanotube, phonon transport is also efficient. The theoretical thermal conductivity of SWNTs has been reported to be similar to that of in-plane graphite [8] and experimental work has shown ropes and mats of aggregated SWNTs to be on the order of 35 W/K·m [49]. Because of these reasons, neat SWNT materials have promising potential in thermal applications.

Like the research on electrical properties of SWNTs, the thermal conductivity measurements were not performed by this researcher. The work was done by Csaba Guthy from the Fischer Group at the University of Pennsylvania and is included here to provide a more complete understanding of the properties and potential applications of neat SWNT fibers. A more detailed discussion of the thermal properties of these neat SWNT fibers can be found elsewhere [21, 101].

Measurements of thermal conductivity were performed from 16 – 300 K using a comparative technique (Fig. 3.35) [106]. Heat is generated in a chip resistor and passed through a constantan rod. The heat is then transmitted through the sample, and finally through a second constantan rod, to a heat sink. Thermal conductance of the sample was measured by averaging the two ratios of temperature drops along constantan rods in series with the sample.
In general, the various annealed fibers all exhibited similar thermal properties. The thermal conductivity increased linearly with temperature and possessed a dependence similar to that of unaligned SWNTs [49]. The smooth dependence on temperature indicates the thermal conductivity is dominated by phonons, with more vibrational modes becoming occupied at higher temperatures. The 6 wt% fibers possessed room temperature conductivities of $\kappa \approx 20$ W/K:m, while the 8 wt% soft-baked fiber possessed a conductivity of $\kappa = 18$ W/K:m (Fig. 3.36). The first inclination is to attribute the lower conductivity of the 8 wt% fiber to a lower degree of alignment. However, the aligned fibers’ thermal conductivities are similar to those measured in mats of randomly oriented SWNTs [49] and magnetically aligned assemblies of SWNTs [86]. More likely, the 8 wt% fiber was not well extruded and possessed a greater void fraction. This fiber was one of the earliest produced in this research and the technique was not as well established. The sample was unavailable for SEM analysis and so this explanation is hypothetical but reasonable.
Figure 3.36: A graph showing thermal conductivity vs. temperature for a variety of neat SWNT fibers.

The Fischer Group, in particular Csaba Guthy, has measured the thermal conductivity of various neat SWNT fibers. The fibers possessed thermal conductivities similar to that of unaligned SWNT buckypapers $- \kappa \approx 20 \text{ W/K}\cdot\text{m}$. In addition, like their electrical transport properties, both the soft-baked and hexane-extracted fibers displayed similar thermal conductivities. The fibers’ properties are still far from the theoretically predicted thermal conductivity of individual SWNTs ($\sim 2000 \text{ W/K}\cdot\text{m}$). Like the electrical transport properties, these measurements indicate that additional factors, beyond SWNT alignment, are adversely affecting the thermal conductivity and deserve additional attention in the future.
3.3.7. X-Ray Diffraction Studies

Polarized Raman spectroscopy is a useful tool for probing the surface alignment of SWNT materials, but to obtain a measure of the internal bulk alignment within a SWNT fiber, one must turn to x-ray diffraction (XRD). XRD has been used to probe the structure of SWNT materials and composites for several years. Thess et al. used x-rays to examine the structure of SWNT ropes produced via pulsed-laser vaporization (PLV) synthesis [25]. Others have used XRD to characterize SWNT materials, such as magnetic assemblies of aligned SWNTs [86] and PBO/SWNT composite fibers [11].

Wei Zhou from the Fischer Group at University of Pennsylvania performed the XRD research described here [21, 102]. The work has been included to provide further understanding of the neat SWNT fibers. A multi-angle diffractometer equipped with Cu rotating anode, double-focusing optics, evacuated flight path, and 2D wire detector was used for x-ray scattering measurements. All samples were measured in transmission for 2 hours. Because of the small diameter of the fibers, several pieces were carefully assembled parallel to each other. Absorption by the samples was found to be negligible, so true background was directly subtracted from the fiber data.

XRD analysis of the fiber samples used a diffuse scattering technique which allowed for structural information from a pseudo-crystalline sample. For crystalline SWNT materials, Bragg diffraction peaks are observed in the range of $\sim 0.3 < Q < \sim 1.6$ Å$^{-1}$, where $Q$ is defined as $Q = \frac{\sin\theta}{\lambda}$ with $2\theta$ the angle between x-ray beam and detector, and $\lambda$ the wavelength of incident x-rays used. These peaks are from a triangular lattice plane normal to the aligned axis [25]. Unfortunately, the neat SWNT fibers were found to exhibit weak Bragg intensity. This is a result of the lower degree of crystallinity found in
HiPco SWNTs, as compared to diffraction of nanotubes produced from carbon arc or PLV synthesis [107]. Therefore, an analysis technique which included sources of diffuse small-angle scattering was utilized to obtain structural information on the neat SWNT fiber samples. Diffuse scattering could originate from isolated nanotubes, small and poorly crystallized large bundles, uncorrelated pores, impurity particles etc. However, the non-SWNT-related diffuse scattering is assumed isotropic, and the anisotropy of the scattering intensity is only from aligned nanotubes. The isotropic scattering will then include contributions from unaligned tubes and isotropic non-SWNT contaminants. Reliable distribution widths can be obtained from the x-ray data but no information pertinent to the aligned fraction of nanotubes. Zhou et al. have performed detailed polarized Raman spectroscopy on the neat SWNT fibers, which when coupled with the XRD analysis, indicate that the unaligned fraction is small (< 10%) [21].

The first X-ray scattering experiment performed was powder diffraactometry on neat SWNT fiber samples. Both neat and annealed samples were examined (Fig. 3.37). No Bragg peaks were detected from the neat fiber, but after annealing weak Bragg peaks were observed. These changes are attributed to the removal of residual acid and partial reorganization of SWNT bundles. Although vacuum annealing improved the crystallinity of the fibers, the main contribution to SWNT scattering remained diffuse.
Figure 3.37: Plots depicting x-ray scattering from green and annealed 8 wt% soft-baked SWNT fibers. The data shows weak Bragg peaks that marginally return upon annealing.

The second XRD experiment performed was an examination of the diffuse scattering signal of the neat SWNT fibers. Because of the fiber sample's orientation, the diffuse scattering will have a Gaussian distribution centered at azimuthal angles that coincide with the triangular lattice plane, namely 0° and 180°. Scattering intensity as a function of azimuthal angle was examined along a radial Q direction. Multiple 1° wedges were sampled in the range of the low angle weak Bragg peak and their intensities summed vs. azimuthal angle, \( \chi \).
Figure 3.38: Plots showing the background-subtracted x-ray scattering data for 8 wt% soft-baked SWNT fibers before and after annealing. The Gaussian fit is also shown. The fits show nearly identical mosaic angles.

In general, the XRD analysis shows the fibers to be highly aligned materials. Gaussian fits to the diffuse scattering (Fig. 3.38) produce mosaic angles of less than 70° for all samples. Table 3.7 summarizes the XRD results for various fiber samples. In addition, the fibers show little change in their mosaic angle before and after vacuum annealing, indicating that the annealment process does not disrupt the structural
alignment of the fiber. Not surprisingly, the XRD results agree with the relative
alignment of fiber types originally described by their polarized Raman ratios. The 8 wt%
soft-baked fiber has the largest mosaic angle and the lowest Raman ratio, while the
hexane-extracted fibers have the smallest mosaic angle and some of the highest Raman
ratios.

Table 3.7: XRD of Neat SWNT Fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Needle Orifice</th>
<th>Green / Annealed</th>
<th>FWHM</th>
<th>Raman Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 wt% Soft-Baked</td>
<td>500 μm</td>
<td>Green</td>
<td>63°</td>
<td>7 ± 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Annealed</td>
<td>64°</td>
<td></td>
</tr>
<tr>
<td>6 wt% Soft-Baked</td>
<td>250 μm</td>
<td>Green</td>
<td>55°</td>
<td>14 ± 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Annealed</td>
<td>54°</td>
<td></td>
</tr>
<tr>
<td>6 wt% Soft-Baked</td>
<td>125 μm</td>
<td>Green</td>
<td>45°</td>
<td>22 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Annealed</td>
<td>43°</td>
<td></td>
</tr>
<tr>
<td>6 wt% Hexane</td>
<td>125 μm</td>
<td>Annealed</td>
<td>31°</td>
<td>19 ± 3</td>
</tr>
<tr>
<td>10 wt% Hexane</td>
<td>125 μm</td>
<td>Annealed</td>
<td>31°</td>
<td>21 ± 1</td>
</tr>
</tbody>
</table>

X-ray diffraction analysis of the neat SWNT fibers, as performed by the Fischer
Group, has provided valuable information on the structure and alignment within the
fibers. While polarized Raman analysis allows a useful examination of the relative
alignment of fiber samples, it is limited to being a surface probe. In addition, because of
the diffuse scattering of the HiPco SWNT fibers, a combination of Raman analysis and
XRD is necessary for a complete picture of overall fiber alignment. Raman ratios over
20:1 and mosaic angles as low as 31° make these fibers the highest aligned neat SWNT
objects produced to-date.
3.4. Spinning Bob Mixer

The first generation of neat single-wall carbon nanotube (SWNT) fibers opened the door to a vast untapped field of research. These fibers were the highest aligned neat SWNT macroscopic material ever produced, and were produced from basic experimental techniques that barely scratched the surface of conventional fiber engineering knowledge and experimentation. The next logical step was to develop a robust laboratory apparatus that addressed the limitations of the Daca Spinning Method and allowed for more complete and in-depth research into the field of neat SWNT fibers.

The second major focus of this research was the development of the Spinning Bob Mixer (SBM). The experimental requirements necessary for the mixing and extruding of high concentrations of SWNTs in super acid presented a unique set of conditions that negated the possibility of using, or even modifying, an existing apparatus. The development of the SBM involved four important phases. The first involved identifying the problems associated with the Daca Spinning Method. Next, an integrated mixer/extruder that could meet all of the research requirements was designed and built from scratch. Then, the system was tested in a variety of experimental situations to identify and eliminate important engineering problems. Finally, the SBM, and all of its capabilities, were successfully used to produce large quantities of neat SWNT fibers.

3.4.1. Daca Spinning Limitations

Creating neat SWNT fibers required two critical steps. First, high concentrations of SWNTs had to be uniformly dispersed in 102% sulfuric acid. Second, the dispersion
needed to be extruded in a controlled manner. Initial experiments involved mixing in a Daca Double Helix Mixer for several days at elevated temperatures in an anhydrous environment (see Sec. 3.1.2). The sample was then transferred by hand to a stainless steel syringe inside a purged glove bag. The syringe was secured to a vertically mounted syringe pump and fiber extruded directly into a coagulant bath. The fact that the first ever neat SWNT fiber was created using this method is a definite milestone. However, these experiments highlighted several difficulties and limitations that would need to be addressed before further progress towards high quality neat SWNT fibers could be made. Specifically, the Daca Method possessed problems in three key areas: concentration limits, sample transfer & loading, and measurement/modularity.

The first limitation of the Daca Double Helix Mixer was its concentration limit. The mixer had difficulty mixing samples with concentrations above 6 – 8 wt% SWNTs in 102% sulfuric acid. The helical blade would struggle to start turning at the beginning of mixing and would often stall. In each experiment, the sample began as a plug of wetted granular material, the consistency of thick wet sand. The motor controlling the blade was just unable to homogenize concentrations above 8 wt%, and would have difficulty with concentrations above 6 wt%. As discussed in Section 2.2.3, typical polymer fibers are wet-spun at concentrations above 15 wt%. Higher concentrations were expected to yield greater extensibility and therefore, improved properties. The Daca mixing set-up used a 1/10 hp DC motor. A more powerful motor might have expanded the workable concentration range, but in light of the other problems present in the Daca Spinning Method, that avenue was not pursued.
The second complication encountered was sample transfer and loading. That process required mixing in one vessel, transferring to an anhydrous glove box, and then loading an extrusion syringe. All three steps involved loss of material, opportunities for moisture exposure, and inconvenient working environments. Typically, 15 mL of 102% sulfuric acid containing 6 wt% SWNTs was mixed in the Daca Double Helix Mixer. However, the mixer consisted of a narrow glass vessel (~1” ID, ~10” in length) and two intermeshing blades. Material would climb the blades, which could be minimized by adjusting the blade speed, but not fully eliminated. In addition, material would coat the inner glass walls and blades. Once transferred into the glove box, material would be scraped off the lower portion of the blades and loaded into the extrusion syringe. All of these steps resulted in a yield of ~50%. Secondly, the mixing and loading process had opportunities for error. Careful researchers could avoid moisture exposure, but the Double Helix Mixer and Glove Bag relied on positive pressure purging to prevent ingress of moisture and not air-tight seals. Finally, the mixing and loading process was simply messy and inconvenient. Handling the material and vessels required corrosion protection and left the loading environment messy from inevitable SWNT / acid exposure. A method for mixing and extruding the neat SWNT fibers was needed that was safe to operate, more efficient, and self-contained.

The third, and most important, problem with the Daca Spinning Method laid in its simplicity. The first experiments, while highly successful, were exploratory in nature. An efficient method for mixing and extruding neat SWNT fibers had not been established, and therefore several different methods involving relatively inexpensive supplies were attempted. In doing so, the resulting mixing and extrusion approach involved pseudo-
temporary set-ups involving off-the-shelf components. The set-up was unable to be easily modified or improved upon and did not possess any measurement capabilities. To reach the next stage in neat SWNT fiber spinning, an apparatus that had modularity in its operation and could monitor the mixing and extrusion processes was needed. This required the design of an integrated mixer/extruder from the ground up.

3.4.2. SBM Design & Construction

The Spinning Bob Mixer is a robust and powerful experimental apparatus for researching the mixing and extrusion of neat SWNT fibers. The apparatus is the next evolutionary step in the production of such fibers. The SBM concept began with a set of capabilities/criteria, which helped guide its design and construction. These requirements were as follows:

- Integrated mixer/extruder
- Resistant to 90 – 120 % sulfuric acid
- Capable of handling 1500 psi of pressure and 150° C
- Minimal mixing dead volume
- Ability to monitor mixing and extrusion processes
- Mixing and extrusion modularity
- Precision extrusion

The resulting apparatus meets all of these needs and includes additional features. The SBM has undergone several revisions and iterations since its inception. Notable design problems and how they were overcome are discussion in the next section (Sec. 3.4.3). In addition, complete mechanical drawings for the final state of the SBM can be found in
Appendix C. However, those drawings are far too detailed for a constructive discussion of the apparatus' operation. What follows is a general explanation of the various capabilities of the SBM.

The SBM is essentially a high performance apparatus consisting of a mixer integrated with an extruder. One of the key complications in the Daca Spinning Method was having the mixing apparatus separate from the extrusion apparatus. Building a machine that could seamlessly switch from mixing to extruding while maintaining an anhydrous environment, would allow the process to be better controlled and protected. To accommodate both modes of operation, while minimizing the transfer volumes involved, extrusion utilizes the same components as mixing, but with a minor diversion in flow. A step-by-step discussion of the mixing and extrusion operations is provided later.

Perhaps the most challenging aspect of designing the SBM was the environmental requirements. The apparatus needed to handle high pressures (1500 psi) and high temperatures (150°C), while resisting a highly corrosive environment (90 – 120 wt% sulfuric acids). The high pressure specification was addressed by insuring that all aspects of the apparatus could easily withstand over 1500 psi of pressure. This included material ratings, fastenings (flanges, tubing adapters, etc...), and o-ring seals. O-ring seals were designed using two readily available freeware gland design software programs – inPHorm (Parker Hannifin Corp.) and Kalrez® Application Guide (DuPont). In addition, all components of the SBM were chosen to handle 150°C with negligible wear or deformation. This criteria was easier to accommodate and was only a concern for plastic and rubber components.
The primary phenomenon that has enabled the production of neat SWNT fibers is their dissolution at high concentrations in super acids. Sulfuric acid is a highly corrosive solvent that can readily attack all metals, plastics, and rubbers. Given the resources invested in the design, construction, and implementation of the SBM it was critical that the system be able to handle sulfuric acid with negligible wear. In addition, the apparatus must not introduce significant metallic contaminants into SWNT samples. The system was designed to resist a range of sulfuric acid concentrations, 90 – 120 wt%. At the early stages of planning, the decision to focus entirely on 102% sulfuric acid had not yet been made. Both 102% and oleum (20 wt% excess SO₃) were considered viable solvents. Eventually, oleum was dropped over concerns of unwanted chemical oxidation effects. In addition, during disassembly and cleaning the 102% sulfuric acid would be exposed to ambient moisture and could be diluted to as low as 95 wt%, hence the lower limit.

The solution was exclusive use of known, corrosion resistant materials. The metal components were constructed from a special grade of stainless steel, Alloy 20cb3, and all seals were made with Teflon™ (PTFE) and/or Kalrez® components. Alloy 20cb3 is a high austenitic stainless steel with a typical composition of Fe₃₀.₂Ni₃₄Cr₂₀Cu₃.₃Mo₂.₅. “The 20-Type alloys are usually the first considered when an H₂SO₄ environment is too corrosive for the use of steel, 300-series stainless steels, or cast iron” [108]. In 102% sulfuric acid, 20cb3 is rated Excellent (< 2 Mils penetration / year) up to 40°C and Good (i.e. < 20 Mils / year) up to 150°C. In oleum, the metal rates Excellent at room temperature and Good up to 100°C [109]. Alloy 20cb3 provided the temperature range and corrosion resistance necessary for the SBM operational parameters.
The Spinning Bob Mixer is an elaborately engineered apparatus, but its operation is straightforward. A SWNT fiber experiment involves three steps: loading, mixing, and extrusion. A discussion of each part of the experiment and the relevant details follows. An overview of the SBM is provided (Fig. 3.39) and accompanied by a picture of the fully assembled apparatus (Fig. 3.40). Components of the SBM are referred to by name for simplicity. Schematics can be found through the List of Figures and in Appendix C.

**SBM Overview**

1. Central Bob
2. Extrusion Needle
3. Hydraulic Piston
4. Injection Port
5. Modular Mixing Elements
6. Pneumatic Gas Port
7. Pneumatic Piston
8. SWNT / Acid Mixture
9. Vacuum Port

Figure 3.39: A cartoon drawing of the Spinning Bob Mixer. The various components are listed and labeled. The drawing is not to scale and omits external connections.
Prior to loading, the SBM is prepared for sample injection. The apparatus is put together with both pneumatic pistons retracted, providing access to the injection and vacuum ports. The central bob is translated vertically, until the top of the bob touches the bottom of the upper support flange. The bob is rotated to bring the shaft mark inline with the axis of the apparatus. The positioning places the central bob’s thru-hole in line with the mixing path and seals the mixing from the extrusion region below. The SBM is evacuated for 6+ hrs at 100° C, or 12+ hrs at room temperature. The system is evacuated with a Phase 1 Scroll Pump (Varian, Inc.) and the vacuum pressure monitored with a 945 Pirani Gauge (MKS Instruments). The SBM internal vacuum reaches ~50 mTorr. If the experiment calls for elevated temperatures, the apparatus is heated with the heating shells at this time.
The SBM's temperature is controlled remotely with a simple, but effective method. Heater cartridges (200W, 120V; Omega Heater Co.) are slid into the central part of the SBM and into heating shells that bolt to the outside of the two side chambers. Thermocouples slide into the hull of the side and central chambers and provide feedback to a trio of CSC32 Benchtop Controllers (Omega Engineering, Inc.), which control the power supplied to the heater cartridges. The set temperature of the three regions is controlled remotely via computer. The result is a temperature feedback loop that can maintain the SBM's temperature to within ± 0.1°C.

Once the SBM has been fully evacuated, it is ready to accept a sample. The pre-mix syringe is connected to the right side port of the SBM and injected into the mixer while the mixing region remains under vacuum (Fig. 3.41). A plug valve is used in the path between the pre-mix syringe and the injection port to seal off the port after injection. Once the sample is inside the apparatus, the vacuum port is closed and the pneumatic gas is activated. Because of the internal vacuum, both pistons move forward, eliminating the free space. The SBM is now ready for mixing.
Figure 3.41: A drawing depicting the SBM being loaded with a SWNT / acid sample. The material is injected into the right with a pre-mix syringe and then the mixing region is sealed off by the pneumatics.

Mixing in the SBM is performed by pneumatically driven pistons that move material through internal mixing elements. A 4-way cross-over valve regulates the supplied pneumatic gas and is controlled by computer. The gas used is always pre-purified inert gas (e.g. nitrogen, argon) to minimize any residual moisture exposure. The two gas ports are connected to the two valve outputs, while one input is connected to a gas manifold and the other is connected to a check valve and silencer. In one position, the
left piston is pressurized with the pneumatic gas and the other piston is vented to the room through the check valve. The valve is then cycled, leaving the left piston vented and the right piston pressurized (Fig. 3.42). Because of a 20 psi check valve on the venting line, a positive pressure of inert, dry gas always exists behind the vented piston.

The internal mixing region is sealed against moisture ingress and sample leaks. On occasion, extended mixing resulted in a small amount of SWNT material to extrude past the piston o-rings to fill the piston circumference, and thereby reinforcing the seal. However, because the internal material is always at a significant positive pressure and dry, purified pneumatic gas is used on the other side of the piston, no moisture enters the sample.

The pressure cycling is used to move the sample through internal mixing elements. The SWNT / 102% sulfuric acid mixture is forced in one direction by a pressurized piston, passing through the mixing elements, and filling the opposite chamber. When the valve cycles, the opposite piston is pressurized, and the material is pushed back in the other direction. This process is repeated continually for extended periods of time, as needed for a given experiment.
Figure 3.42: A drawing depicting the mixing cycle of the SBM. One piston is pressurized with inert dry gas while the other is vented. The gas supply is then switched using a 4-way cross-over valve.
One of the features engineered into the SBM was an inherent modularity in operation. The internal mixing elements are removable. Experiments can be performed that utilize different types of mixing, whether to explore the efficacy of mixing or to change the type of mixing. Two mixing elements have been created to-date. Both have been successfully utilized to produce neat SWNT fibers with varying results.

The first kind of mixing element used in the SBM is a static mixer. Static mixers are used extensively in the chemical industry to mix a variety of samples. Their primary advantage is that the mixing components are static. The sample flow is used to drive the mixing. This allows static mixers to be used in difficult or hazardous applications, where moving parts would not be feasible. Figure 3.43 shows a bisection of the type of static mixer used and the mixing element during different kinds of mixing. The static mixer used in the SBM is a piece of 3/16" OD tubing with a blade change every ~0.3" of tubing length.

Figure 3.43: Images of a static mixer. The bisection of a static mixer (A) shows the helical alternating blades used to mix liquid flowing through it. Mixing action can be seen in different types of mixing: laminar blending (B), turbulent blending (C), and liquid-liquid dispersion (D).
The second mixing scheme used is the Rotating Shear Cell (RotCell). This mixing element installs on the left side of the SBM. It involves a rotating cylinder that provides high shear as SWNT material is pushed through it. Figure 3.44 provides an overview of its operation and Figure 3.45 depicts its installation in the SBM. SWNT material is pushed through an entrance disk with several small 1/16" holes. On the other side of the disk, the shear cylinder rotates. The spacing between the entrance disk and the shear cylinder is small (~100 μm). This region provides high shear as material passes through the entrance holes. The material then passes through channel grooves along the outer perimeter of the cylinder. Some material is also sheared by Teflon wipers on the shear cylinder that clean the ID of the RotCell housing. The material is sheared again as it passes from the rotating cylinder through holes along the perimeter of a fixed cone piece. The sample then undergoes extensional flow as it narrows down and out a single, axial 1/16" exit hole.

Figure 3.44: A cartoon depicting the Rotating Shear Cell in action. The red arrows indicate the flow path of sample material moving through the mixing component. The components in gray rotate while the other components are static.
Figure 3.45: Photographs showing the Rotating Shear Cell. (A) The components of the mixing element are laid out. (B) The internal shear cylinder with shaft is placed in the housing, followed by the entrance disk (C).

Figure 3.46: A cartoon depicting the RotCell installed in the SBM. The mixing element is used on the left side with the rotating shaft passing coaxial with the left piston’s shaft.
In addition to having modular mixing options, the evolution of an experiment’s mixing can be actively monitored. One of the most useful measurement capabilities of the SBM is the ability to monitor and record the linear velocity of the mixing pistons. A PL82 linear encoder (Sony Corp.) was installed on the left stabilizing piston along with a magnetic distance strip placed on the stabilizing housing. As it moves, this device measures magnetic marks within the strip. Knowing the calibration of the device allows for an in situ measurement of the piston’s velocity. This data is recorded during mixing and used to watch the evolution of the sample.

![SBM Linear Encoder Diagram]

Figure 3.47: A drawing depicting the linear encoder in use. The reader head measures a magnetic strip while the mixing piston moves, providing information of the piston’s motion.

The motion of the mixing piston will change during the course of sample mixing. At the start of mixing, the material is an inhomogeneous mixture of SWNTs soaked with sulfuric acid. The sample contains large chunks and aggregates. During the first stages of mixing, the sample is blended and homogenized with increasing amounts of SWNTs
truly solubilized by the super acid. Eventually, the sample will reach an equilibrium state of mixing. Throughout these mixing changes, the viscosity is a direct measure of the state of the system. In general, as the constituent entities become smaller due to mixing, interparticle colloidal effects become more important and cause the viscosity to increase [95]. So, as the SWNTs are homogenized and solubilized in the 102% sulfuric acid, the viscosity of the sample should increase, which will result in a decrease in piston velocity at a constant supplied pneumatic gas pressure. Additional changes in the system, such as chemical effects (e.g. oxidizing, cross-linking) or phase changes, might also be observable as a change in SWNT sample viscosity and therefore, the piston velocity. Specific experiments that utilized the velocity information are discussed in Section 3.4.4.

Once mixing is complete, the SBM is ready to extrude neat SWNT fibers. First, the mixing is stopped with the entirety of the SWNT sample in the right chamber. The left piston is locked in place in the forward position and the pneumatic gas is disabled. Note that at the beginning of the experiment, the right side of the SBM main body was assembled connected to the hydraulic chamber. The right piston shaft ends in a sealed piston head which can be pushed forward by a hydraulically pressurized piston. To retract the internal right piston, the hydraulic piston is refilled and pneumatic gas pressure is applied to the rear right piston. This elaborate connection scheme allows the right mixing piston to be driven pneumatically without any physical anchor to the hydraulic system. Then when it is needed, the hydraulics can be used to carefully control the forward motion of the right piston and therefore, fiber extrusion. The hydraulic system consists of a Harvard Apparatus HVP syringe pump with dual, center-line SS316 syringes connected to the hydraulic chamber. A high purity hydraulic oil is used as the movement fluid.
Before extruding the SWNT dopant, the SBM central bob must be set in place. The internal central bob consists of two primary components, a sealed thru-hole used in the mixing path and an internal filter setup. To extrude fiber, the bob is lowered all the way down until it touches the lower cone and is then raised back up to the desired gap setting. Marks around the perimeter of the upper translation housing allow a vertical positioning to an accuracy of ± 25 μm. Experiments typically used gaps of 125 – 625 μm. Figure 3.48 shows the SBM in its extrusion mode.

![SBM Extrusion](image)

**Figure 3.48: A drawing showing the extrusion mode of the SBM. The central bob is lowered, the left piston is locked forward, and the right piston is engaged by the hydraulic piston.**

During extrusion, the sample is moved in a controlled manner through the SBM and out the extrusion needle. The hydraulic syringe pump provides and extrusion accuracy as high as ±1% which allows for very controlled movement of material at a wide range of flow rates (0.44 μL/min to 5.9 mL/min). When extrusion is activated, SWNT material flows from the right chamber into the central bob region, filling up the free space. The flow continues inside the central bob, through an internal SS316 filter,
and back out (Fig. 3.49B). The filter removes contaminates just prior to fiber extrusion. Typically, a 40 μm mesh filter was used. The material then undergoes extensional flow down the cone and into the extrusion needle. The SWNT material extrudes from the needle as a proto-fiber and undergoes coagulation and collection.

In addition to computer controlled extrusion, the SBM has two additional features useful for neat SWNT fiber extrusion. The primary feature was a DLX422-3M melt pressure transducer (Dynisco) positioned in the plane of the inner chamber’s mixing holes (Fig. 3.49A). This provides in situ measurements on the pressure during extrusion. The pressure indicates the first stages of sample flow into the central chamber and then the subsequent internal state of extrusion. In addition, the pressure transducer provides a quick and easy method of monitoring the system pressure to insure that the upper pressure limits are not exceeded. The second useful feature is a gas port below the central bob (Fig. 3.49A). Inert, dry gas flows below the central bob throughout the mixing process to provide further redundancy against moisture ingress past the central thru-hole seals. Typically, the gas flow was stopped and the line closed off for extrusion just prior to moving the material forward with the hydraulics. Both of these features are further examples of the options engineered into the SBM.
Figure 3.49: A set of drawings showing the various features of the central bob region. (A) A melt pressure transducer and gas inlet port access the central bob region, while a internal filter (B) provides increased fiber quality.

The last capability engineered into the SBM apparatus is the rotating bob. At high concentrations, SWNTs in super acids have been found to be highly shear-thinning (see Sec. 3.2.2), as is expected for liquid crystalline systems. This characteristic can be taken advantage of during the extrusion of neat SWNT fibers. During shear-thinning, liquid crystalline domains align under shear, thus reducing the viscosity of the sample. The obvious first application of shear-thinning is the ability to extrude more viscous samples. The SBM apparatus has a maximum pressure that can be reliably maintained during extrusion. As the concentration of SWNTs in 102% sulfuric acid increases, the viscosity will also increase. Therefore, there is a maximum concentration (and extrusion rate) that can be handled by the SBM. By shear-thinning the sample prior to extrusion, the upper extrusion concentration should be able to be extended. A second possible use of shear-thinning is increased fiber properties.
While the shear-thinning of SWNT / super acid system has been experimentally verified, the orientation of SWNT liquid crystalline domains in a rotating shear field has not. Two possible situations could arise. The first involves the SWNT Spaghetti domains aligning parallel to the induced shear. This would result in concentric liquid crystalline domains around the rotating central bob (Fig. 3.50A). The second possibility is an orientation of the SWNT Spaghetti perpendicular to the shear along the vorticity direction (Fig. 3.50B). This type of shear alignment of rigid rod polymers is called “log rolling” [56]. However, its application to SWNT liquid crystalline domains would be a new phenomenon, and the result of the unique one-dimensional nature of SWNT Spaghetti. Some minor experimental evidence involving sheared microscope slides of SWNTs in super acid suggest that log rolling is a possibility. The exact orientational nature is unknown, but if the liquid crystalline domains aligned perpendicular to the applied shear, then they would also align parallel to the direction of extrusion. A rotating central bob may increase the size of the domains and therefore, increase the degree of alignment and continuity in the resulting fibers. All of this discussion is conjecture at this point. Nevertheless, the SBM is available for such possible future research.
Figure 3.50: A set of drawings depicting possible SWNT alignment from the rotating bob. The SWNT Spaghetti liquid crystalline domains will either align parallel to the shear (A) or parallel to the vorticity (B). Such shear-induced alignment may improve fiber properties.

All of the various features described enable and assist the spinning of neat SWNT fibers from the SBM. The apparatus has been designed to be a powerful laboratory machine. Not surprisingly, arriving at the final operational SBM had several challenges. However, the ability to spin and collect continuous lengths of neat SWNT fibers while monitoring both the mixing and extrusion processes was a strong motivating goal.

### 3.4.3. Challenges of the SBM

The SBM is an elaborate and powerful piece of laboratory equipment. However, arriving at a finished product that can successfully mix and extrude neat SWNT fibers in a controlled manner has had many challenges. The SBM has undergone several modifications and iterations during its development. A discussion of every small change is not necessary, but a treatment of the major hurdles that have been overcome is useful
in understanding the current state and operation of the SBM. In general, the SBM has faced six significant challenges during its design, construction, and testing – die plate limitations, elimination of central region dead volume, improvement of mixing elements, hydraulic mixing, pneumatic gas ingress, and internal metal wear.

The first SBM experiments had problems with die plate wetting. Instead of a Swagelok® extrusion needle, fibers were originally planned to be extruded from die plates. Industrial polymer fiber processes utilize such die plates and were the template from which many of the SBM designs originated. The die plate consisted of a conical well that ended in a fixed extrusion channel possessing low length to diameter (L:D) ratios. Orifices ranged from 125 – 500 μm and the die plate typically had a length to diameter ratio of 1 – 10. These die plates possessed two significant problems. The first is that because the extrusion channel is fixed and cannot be replaced during the experiment, a particulate would sometimes clog the experiment, and therefore end it. A replaceable needle configuration could always be swapped for a new needle. The second problem was lateral wetting.

The SWNT extrudate would wet the flat die plate face and spread laterally instead of extruding out as a fiber. Normally during polymer fiber spinning, the proto-fiber will swell upon exiting the spinneret due to internal pressures. Once threaded into the take-up system, the tension of the spin line will help eliminate excess lateral expansion [57]. However, because our system did not incorporate any tensioning, the fiber needed to extrude cleanly from the orifice on its own. The sulfuric acid in the dopant readily wet metal surfaces, like the 20cb3 die plate. The result was not a fiber, but a thick blob of SWNT material that would laterally wet the available die face and then start moving
outward (Fig. 3.51). Attempts were made to Teflon coat the face of the die plate, but the small orifices needed (e.g. 125 μm) were not maintained and the resulting die plates had flaps of coating disrupting the fiber extrusion.

![Image]

Figure 3.51: A photograph of die plate wetting. The SWNT material wets sideways and then starts moving out.

The second problem identified early in SBM testing was the existence of dead volume within the central bob region. The original design did not incorporate a sealed central hole passing through the bob and instead used the bottom cone of the bob to seal off the central region during mixing. If the middle volume below the side holes was not swept out during mixing, then inhomogeneities in mixing could occur. Poorly mixed portion of the sample would compromise the quality of the fibers or clog the extrusion orifice. The entire mixing volume needed to be swept out, or at least all of the volume that would “see” the extrusion orifice. Fiber experiments had frequent problems with particulate clogs and the fibers produced were of low quality. The solution was the introduction of the central thru-hole that directly connects the two sides of the apparatus to each other and leaves the region below the bob uninvolved in the mixing process (Fig.
3.42). Figure 3.52 depicts the SBM mixing configuration prior to the introduction of the central thru-hole.

![SBM No Thru Hole](image)

Figure 3.52: A drawing of the SBM prior to the central thru-hole. The SWNT material was mixed back and forth through the central bob region, but some material at the bottom was often poorly mixed.

The third major improvement was the design and implementation of the Rotating Shear Cell (RotCell). As was discussed in Section 3.4.2., the original mixing elements were a pair of static mixers. The RotCell provides several advantages over the static mixer. The primary advantage is the continuous high shear mixing that occurs within the component. A static mixer works by bisecting flow and under high pressure will break-up inhomogeneous aggregates on the millimeter size scale. However, it does not provide mixing on the micron-scale and instead must rely on thermodynamic and chemical effects to get complete mixing of SWNTs in acid. In the RotCell, material cannot avoid seeing two regions of high shear, during entering and exiting the RotCell. The spacing between the rotating shear cylinder and either the entrance disk or the fixed cone is 75 – 150 μm, with the central cylinder rotating at ~30rpm. This results in a shear of $\gamma \approx 200$ sec$^{-1}$ for material entering or exiting the RotCell.
The second advantage is the RotCell’s easy disassembly, cleaning, and modification. Because the static mixer elements consisted of enclosed tubing with internal blades, cleaning took several days of sonication and high pressure water jets. The possibility of a small lodged particle of SWNT matter remaining after cleaning was a concern. In contrast, all parts of the RotCell are removable and can be easily examined for unwanted corrosion or mechanical damage. In addition, the design allows for alternate shear cylinder geometries to be explored with no change to the housing or rotation components.

The fourth problem encountered in early SBM operation involved the approach used to drive the mixing pistons. The original set-up of the SBM utilized two Harvard Apparatus HVP syringe pumps for mixing in addition to extrusion. The syringe pumps could handle extended periods of continuous high pressure operation, but were limited to a volume flow rate of 11.8 mL/min, which equated to an approximate mixing cycle of 2 min for 12 mL of sample (typical volume). This mixing rate was far too low and was not imposing significant shear on the liquid flow. The solution was a shift from a fixed volume hydraulic system to a fixed pressure pneumatic system. As described in Section 3.4.2, the SBM utilizes a 4-way cross-over valve which supplies up to 500 psi of inert dry gas to the pistons. The result is an order of magnitude shorter mixing cycle, which means ten times the shear and ten times the mixing cycles for a given duration. Pneumatic operation resulted in a notable improvement in sample mixing and fiber production.

Soon after the transition to pneumatics in the SBM, inert gas was seen to occasionally bypass the piston o-ring seals and enter the sample region. The ingress was not a slow leak that would occur over days, or even hours, but was observed to occur in
short bursts immediately after cycling. When quickly switched from low to high pressure, a pressure shock wave of gas would enter behind the piston and often blow a little gas past the piston seals in addition to moving the piston (and sample) forward. Increasing the compression of piston o-rings had a small improvement, but even at high compressions, it did not solve the problem. The solution was a re-engineering of the mixing pistons to allow for bypassing gas to vent out of the SBM prior to entering the sample region. Once implemented, gas ingress was effectively eliminated. Figure 3.53 illustrates the gas vent pistons adopted in the final SBM design.

![Diagram](image)

**Figure 3.53:** A cartoon depicting a Gas Vent Piston. Pneumatic gas blows by the first o-ring, but vents out a central hole out the rear of the piston shaft.

The final challenge overcome during the testing of the SBM was internal metal wear. The internal components of the SBM withstood the high corrosive environment with minimal wear. The Alloy 20cb3 material was able to handle 102% sulfuric acid and no significant corrosion has been observed. However, in the first design of the RotCell,
significant wear on the small rotating metal components occurred. Strangely enough, this
wear occurred at rotating contacts between metal and plastic or rubber. Teflon and Kalrez
are both obviously less hard than a stainless steel alloy, but only at these contacts points
was the wear seen. Metal that was rotating, but not in contact with anything, did not
exhibit wear. The most plausible explanation is that in the super acid, Alloy 20cb3 forms
a passivated oxide layer. However, that oxide layer is soft enough to be worn away by
Teflon™, or prohibited from forming in the first place, thus exposing the metal to the
acid's corrosion. The solution was to use press fitted Teflon components at all of the
joints in question such that the only rotating points of contact were Teflon on Teflon. In
addition, the rotating shaft was coated with a PTFE-based coating, Fluorolon® 110
(Southwest Impreglon Sales, Inc.), that kept the rigidity of the metal, while providing the
lubrication and corrosive protection of PTFE. This fix solved the wear problem. Figure
3.54 shows pictures of the kind of wear observed in RotCell components prior to
Fluorolon® protection.

Figure 3.54: A series of photographs showing the metal wear caused by rotating metal / plastic or
rubber junctions. Distinct regions of wear existed on the fixed cone (A), both ends of the shear
cylinder (B, C), and the RotCell shaft (D).
3.4.4. SBM Experiments

After dealing with numerous engineering issues, the SBM was ready for experiments. A number of experiments were performed at various mixing and extrusion conditions. In addition to demonstrating the capabilities of the apparatus, the experiments allowed for preliminary exploration of the roles those conditions play in fiber spinning. In general, the SBM proved itself, meeting the design criteria set out in Section 3.4.1. Five different experiments were performed with the SBM and the results from those experiments showcase the versatility of the apparatus, while providing some further insights into neat SWNT fibers.

The first step in SBM fiber experiments was pre-mixing and loading. Hexane-extracted SWNT powder was dried thoroughly in a flask by evacuating at 100° C with a Phase 1 Scroll Pump for 6+ hrs. An appropriate amount of SWNTs for the desired concentration and sample volume (SWNT mass was not considered negligible compared to solvent mass) was then dried overnight in a vacuum oven at 80° C, along with the pre-mix syringe components. The dry items were transferred into an anhydrous glove box along with freshly prepared 102% sulfuric acid. The SWNTs were poured into a small crystallization dish and the appropriate amount of acid added to the vessel. The SWNTs were left to soak up the acid for 6+ hrs, occasionally stirring with a glass rod to insure all dry SWNT material was wetted with acid. Finally, the SWNT / acid mixture was transferred into the pre-mix syringe.

Once pre-mixed, the SBM was used to mix and extrude samples as outlined in Section 3.4.2. The pre-mix syringe was connected to the apparatus and injected into the
evacuated central chamber. The pistons sealed off the mixing region and the mixing began. Pneumatic pistons, controlled by valve cycling, mixed the material back and forth inside the SBM. The evolution and behavior of the SBM mixing was monitored by a linear encoder and recorded via computer. Once mixing was completed, the SBM was shifted to extrusion mode by securing the left piston and lowering the central bob. Fiber was then extruded. The resulting fibers were collected and characterized. The details of the five experiments are provided in Table 3.8. All experiments used 102% sulfuric acid as a solvent and were extruded into and collected from columns of diethyl ether (see Sec. 3.4.2).

**Table 3.8: SBM Experiment Details**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>SWNT Concentration (wt%)</th>
<th>Mixing Element</th>
<th>Duration (days)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>Static Mixers</td>
<td>3</td>
<td>Room Temp.</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>RotCell</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>RotCell</td>
<td>4.5</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>RotCell</td>
<td>5.5</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>RotCell</td>
<td>2</td>
<td>Room Temp.</td>
</tr>
</tbody>
</table>

The SBM experiments provided information on the general operation of the apparatus. The SBM was able to mix and extrude well under a variety of conditions. The monitoring components integrated into the design proved invaluable. The pressure transducer located in the central region (see Fig. 3.49) provided information on the flow of material during the initial stages of extrusion, pressures used for extrusion through various needle lengths and orifice diameters, and feedback on the use of the rotating bob as a tool for shear-thinning. The linear encoder used to track the piston velocity resulted in very interesting information on the evolution and behavior of the SWNT samples during mixing.
When an extrusion experiment was first started, the hydraulic piston was moved forward at a moderate pace to engage the right pneumatic piston. Once the SWNT sample started moving into the central region, the transducer’s pressure would start to increase, allowing the researchers to adjust the extrusion rates and disable the flow of gas below the central bob. This prevented sample from being wasted in uncontrolled extrusion or travel into the gas flow line.

The second use for the central pressure transducer was monitoring extrusion pressures. The pressure drop, $P$, over a length of tubing, $L$, and radius, $R$, for a power law fluid is proportional to [95]:

$$P \propto \frac{LQ}{R^{1+3n}}, \quad (3.9)$$

where $Q$ is the volume flow rate and $n$ is the power law index of the fluid. For SWNTs in 102% sulfuric acid, the pressure drop should be linear with tubing length and inversely proportional to the radius to the 1.6 power ($n = 0.2$, see Sec. 3.2.2). The needle pressures measured for a couple of experiments are included in Table 3.9. Note that the pressure measurements are taken above the internal bob filter and therefore are not solely measurements of the pressure drop across the needle. A pressure drop across the filter and around the central bob is included in the measurements.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Concentration (%)</th>
<th>Length (in)</th>
<th>Orifice Dia. (µm)</th>
<th>Extrusion Rate (mL/min)</th>
<th>Gap (µm)</th>
<th>Pressure (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>2</td>
<td>125</td>
<td>0.04</td>
<td>625</td>
<td>365</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>1</td>
<td>175</td>
<td>0.04</td>
<td>625</td>
<td>185</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
<td>1</td>
<td>250</td>
<td>0.02</td>
<td>625</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>0.5</td>
<td>125</td>
<td>0.01</td>
<td>125</td>
<td>218</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>1</td>
<td>125</td>
<td>0.01</td>
<td>125</td>
<td>318</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>2</td>
<td>125</td>
<td>0.01</td>
<td>125</td>
<td>840</td>
</tr>
</tbody>
</table>
The pressure drop across the extrusion needles increases with length and decreases with radius. However, the relationships predicted by Equation 3.9 do not seem to track in this preliminary data. One would expect a more dramatic increase in pressure with changing radius, but Experiment 1 shows a pseudo-linear relationship. However, a linear relationship is expected with changing length, but when the needle length was reduced from 2" to 1" in Experiment 5, the pressure decreased by more than 50%. While a detailed exploration of this relationship was not explored, pressures were found to depend on both of these variables. The SBM demonstrated itself sufficient to perform experiments focused on extrusion pressures.

The central pressure transducer is also the key probe used to explore the operation of the central rotating bob. The rotating bob was engineered into the SBM as a unique tool for SWNT fiber research. Unfortunately, as the complexity of the SBM grew, the focus of neat SWNT fiber research shifted away from the rotating bob and towards a more practical goal of successfully testing the SBM as a mixer and extruder. However, in several experiments the rotating bob was utilized during fiber production. Shear-thinning of SWNT dope was confirmed in several experiments by a drop in the extrusion pressure when the bob was rotated. For example, Experiment 1 saw a 10% drop in pressure when extruding a 6 wt% sample through a 125 μm, 1" needle with a gap setting of 625 μm.

Preliminary results exploring the rotating bob as a tool for improving fiber alignment were performed in several experiments. Fiber samples were produced at various gap settings with the bob rotation on (30 rpm) and off. Polarized Raman analysis suggests interesting conclusions about this feature.
Table 3.10: Effect of the Rotating Bob of Fiber Alignment

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Orifice Dia. (µm)</th>
<th>Needle Length (in)</th>
<th>Extrusion Rate (mL/min)</th>
<th>Gap (µm)</th>
<th>Rotation</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>125</td>
<td>2&quot;</td>
<td>0.04</td>
<td>625</td>
<td>N</td>
<td>2.5 ± 0.5</td>
</tr>
<tr>
<td>1</td>
<td>125</td>
<td>2&quot;</td>
<td>0.04</td>
<td>625</td>
<td>Y</td>
<td>4.3 ± 0.7</td>
</tr>
<tr>
<td>2</td>
<td>175</td>
<td>2&quot;</td>
<td>0.04</td>
<td>125</td>
<td>N</td>
<td>9 ± 3</td>
</tr>
<tr>
<td>2</td>
<td>175</td>
<td>2&quot;</td>
<td>0.04</td>
<td>125</td>
<td>Y</td>
<td>6 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>175</td>
<td>2&quot;</td>
<td>0.04</td>
<td>250</td>
<td>N</td>
<td>8 ± 3</td>
</tr>
<tr>
<td>2</td>
<td>175</td>
<td>2&quot;</td>
<td>0.04</td>
<td>250</td>
<td>Y</td>
<td>4 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>175</td>
<td>2&quot;</td>
<td>0.04</td>
<td>500</td>
<td>N</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>2</td>
<td>175</td>
<td>2&quot;</td>
<td>0.04</td>
<td>500</td>
<td>Y</td>
<td>11 ± 3</td>
</tr>
<tr>
<td>5</td>
<td>175</td>
<td>2</td>
<td>0.04</td>
<td>125</td>
<td>N</td>
<td>9 ± 3</td>
</tr>
<tr>
<td>5</td>
<td>175</td>
<td>2</td>
<td>0.04</td>
<td>125</td>
<td>Y</td>
<td>6 ± 2</td>
</tr>
<tr>
<td>5</td>
<td>175</td>
<td>2</td>
<td>0.04</td>
<td>250</td>
<td>N</td>
<td>8 ± 3</td>
</tr>
<tr>
<td>5</td>
<td>175</td>
<td>2</td>
<td>0.04</td>
<td>250</td>
<td>Y</td>
<td>4 ± 2</td>
</tr>
<tr>
<td>5</td>
<td>175</td>
<td>2</td>
<td>0.04</td>
<td>500</td>
<td>N</td>
<td>5 ± 1</td>
</tr>
<tr>
<td>5</td>
<td>175</td>
<td>2</td>
<td>0.04</td>
<td>500</td>
<td>Y</td>
<td>11 ± 3</td>
</tr>
</tbody>
</table>

In three different experiments, when the gap was set to 125 or 250 µm, the polarized Raman ratio was found to decrease with the introduction of rotation. This data suggests that the shear of the bob temporarily disrupted the SWNT Spaghetti domains, thus decreasing the alignment in the resulting fibers. However, with a 500 or 625 µm gap, the opposite effect was observed. One possible explanation is that the size of the SWNT Spaghetti domains is on the order of ~250 µm. At smaller gap settings, the domain effectively occupies the entire volume and is therefore disrupted more easily by the shear at the walls of the rotating region. At a gap setting of 500 µm, there is still room for an individual domain to grow, and so the shear assists in aligning the existing domain as well as increasing its size. Another explanation is that different shear rate regimes have notably different alignment behavior. The alignment is improved when subjected to the moderate shear rates present in 500 – 625 µm gaps, but that the higher shear rates of 125 – 250 µm gaps disrupt the alignment. Regardless, the rotating bob does appear to have an effect, although a seemingly complicated one. The fact that this trend was observed in three different experiments at two different concentrations and with different mixing
schemes suggests that some interesting sample behavior is occurring and that the rotating bob is a useful tool for such investigations.

The second valuable feature of the SBM is the ability to monitor the sample evolution and behavior during mixing. The linear encoder provided interesting information during Experiments 3 – 5, but was not fully operational for the earlier two experiments. The encoder measured the velocity of the left pneumatic piston during mixing and recorded the data to a local computer. That data was then used in two ways. The first way was an examination of the velocity profile of the mixing piston during a single stroke. The reader head provided position vs. time information for each mixing stroke. An examination of this plot provided information on any irregularities in the piston movements, either from mixing/sample behavior, or mechanical irregularities. The position vs. time data for multiple cycles was then used to provide an average velocity over time for the overall mixing behavior of the experiment. Sample changes could be observed in this plot and could be used to determine the appropriate time for fiber extrusion.

Initially, SBM experiments were mixed as long as possible. As described in Section 3.4.2, the hypothesis was that the viscosity of the sample would increase over time as the SWNTs were homogenized and solvated by the super acid. Eventually, the nanotubes would be as mixed as possible by the mixing elements and conditions of the experiment. The piston velocity, and therefore the sample viscosity, would level off at some equilibrium state. Experiments 3 & 4 utilized this philosophy to mix 10 and 8 wt%, respectively. The linear encoder enabled the point when the mixing behavior stopped changing to be determined. Figure 3.55 plots the average piston velocity for both
Experiment 3 and 4 during the latter stages of mixing at different fixed pneumatic gas pressures. Note that early mixing was unable to be recorded, and that the plot shows the last half of mixing only. The initial mixing velocity was seen to increase dramatically at first, reaching a steady state, followed by the behavior in Figure 3.55. Both samples displayed a non-linear increase in viscosity (i.e. decrease in velocity). The behavior appeared to follow the predicted model of mixing previously described.

![Graph showing mixing time vs. velocity for Exp. 3 and 4.]

**Figure 3.55:** A plot of pneumatic piston average velocity vs. mixing time. The origin does not mark the beginning of the experiment. The 10 wt% sample (red circles) and 8 wt% (blue squares) both show a non-linear decrease in velocity during the later stages of mixing.

Unfortunately, both of these experiments produced samples with such high viscosities, that fiber samples were very difficult to extrude and collect. It was believed that either the apparatus was incapable of handling “fully mixed” 8 – 10 wt% samples, or that some kind of oxidative chemical reaction had occurred that changed the sample (e.g. cross-linking of individual SWNTs) during the latter mixing. For comparison, the next
experiment used the same mixing conditions as Experiment 4, but was mixed for a shorter amount of time. The piston velocity was monitored during the early stages of mixing, and once the first steady-state plateau was reached, fiber was extruded. Comparisons of the fibers produced from Experiments 4 and 5 will be discussed later.

![Graph of piston velocity vs. mixing time for 8 wt% SWNTs in 102% sulfuric acid. The plot shows a steadily increasing velocity that approaches an asymptotic equilibrium state. The origin is the start of the experiment.](image)

**Figure 3.56:** A graph of piston velocity vs. mixing time for 8 wt% SWNTs in 102% sulfuric acid. The plot shows a steadily increasing velocity that approaches an asymptotic equilibrium state. The origin is the start of the experiment.

In addition to monitoring the evolution of sample mixing, the linear encoder allowed the individual piston strokes to be recorded. During the extended mixing in Experiments 3 & 4, a nonlinear feature was observed in the piston velocity (see Fig. 3.58). The piston moved forward in a jerky fashion of alternating slow and fast speeds. This phenomenon is in fact observed in some viscoelastic polymer samples, such as polyethylene (see Fig. 3.57), and is known as *stick-slip*. Stick-slip flow is not well understood, but is believed to be unstable flow caused by surface effects at the walls of
the channel [95]. One theory is that under certain conditions the polymer system adheres to the wall more readily, stretches, and then releases, producing stick-slip behavior [61]. Stick-slip is avoided in commercial fiber spinning because the instabilities result in rough, uneven fibers with inferior properties. The SWNT / 102% sulfuric acid samples did not exhibit this phenomenon during the early stages of mixing, and the behavior was not seen at all in the entirety of mixing during Experiment 5. The development of stick-slip may be indicative of a substantial change in the composition of the SWNT sample.

![Graph showing shear stress vs. shear rate](image)

**Figure 3.57:** Shear stress vs. shear rate for a high density polyethylene melt. The flow is instable and displays stick-slip behavior [95].
Figure 3.58: A plot showing the distance vs. time for the mixing piston. Experiment 3 (red solid line) displays stick-slip behavior, while Experiment 5 (blue dashed line) does not.

SEM analysis of fiber samples produced from Experiments 4 & 5 provide further insight into the difference between long and short mixing durations. Both fibers were extruded from 8 wt% SWNTs in 102% sulfuric acid. Experiment 4 was mixed for more than twice as long as Experiment 5. In addition, Experiment 4 was mixed at 100°C, while Experiment 5 was mixed at room temperature. Figure 3.59 depicts a fiber from Experiment 4. The images show a very rough fiber with no alignment. The surface is granular and reminiscent of the compromised fiber of Figure 3.21. Bundles of SWNTs are not easily distinguishable until viewed at high magnification. No trace of a substructure of large SWNT bundles appears to exist. Stick-slip during mixing and extrusion could have contributed some to the poor fiber surface. For all intents and purposes, this fiber is a failure.
Figure 3.59: Scanning electron micrographs of an 8 wt% SWNT fiber from Experiment 4. (A, B) The fiber is very rough with no alignment. (C, D) SWNT ropes cannot be easily distinguished until viewed at high magnification.

In contrast, Experiment 5 was very successful in producing fibers. The fibers were extruded in large quantities and were easily collected. SEM analysis of these fibers reveals a dramatic difference in morphology from those produced in Experiment 4. Although coagulation resulted in a collapsed, flattened fiber, even at low magnifications it is evident that an inherent bulk alignment of SWNTs exists (Fig. 3.60A). Examination at increasingly higher magnifications continues to show this overall alignment (Fig. 3.60B, C) and reveals the tell-tale substructure of large SWNT bundles that was observed in Daca-spun fibers (Fig. 3.60D). These fibers are obviously of better quality than the
previous fibers. The extended mixing duration at elevated temperatures appears to have damaged the SWNT / 102% sulfuric acid sample in some way. The contribution of temperature to these results is not clear, it certainly accelerated any chemical effects. Future experiments that explore intermediate mixing durations at elevated and room temperatures will provide additional insight into this aspect of neat SWNT fiber spinning. The SBM’s ability to monitor the mixing evolution of a sample to facilitate differences in fiber engineering was successfully demonstrated.

Figure 3.60: Scanning electron micrographs of an 8 wt% SWNT fiber produced during Experiment 5. (A, B) The fiber displays overall bulk alignment of SWNTs at low magnifications and (C, D) reveals a substructure of large SWNT bundles at high magnifications.
In addition to the important active capabilities of the SBM, one of the main
criteria of the apparatus was the ability to withstand the corrosive effects of super acids at
high temperatures. As discussed in Section 3.4.1, Alloy 20cb3 was selected as the
primary material used to build the body and parts of the SBM. Corrosion of the internal
components is unacceptable for both the life time and performance of the apparatus, as
well as the properties of resulting fibers. Metal contaminants will act as defect sites for all
physical fiber properties. Thermogravimetric Analysis (TGA) was used to measure the
effects of corrosion. Samples were mixed to their entirety and then collected from the
SBM for analysis. TGA in argon was performed at 500°C to determine the final solid
mass concentration (SWNTs + contaminants) in the sample. The inert high temperature
environment allowed the sulfuric acid, and any water absorbed from the atmosphere
during handling, to evaporate. After that, the same sample was subjected to TGA in air at
800°C to obtain the concentration of metal impurities. The high temperatures pyrolized
away the SWNTs and leave ash. The ash is assumed to be oxidized metal in the form of
Fe₂O₃. As discussed in Section 3.1.1, SWNTs samples used in the experiments were
previously purified to an ash content of < 6 wt%. Table 3.11 shows the results of TGA
from the five experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Starting Concentration (wt%)</th>
<th>Ending Concentration (wt%)</th>
<th>Final Ash Content (wt%)</th>
<th>SWNT Mass Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>6.0</td>
<td>15.7</td>
<td>-10%</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>6.5</td>
<td>25.1</td>
<td>-14%</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>12.4</td>
<td>37.3</td>
<td>-17%</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>6.9</td>
<td>4.8</td>
<td>-13%</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>6.9</td>
<td>13.3</td>
<td>-20%</td>
</tr>
</tbody>
</table>
The TGA results should provide a clear picture of the oxidative effects of the 102% sulfuric acid during the SBM experiments. The final ash content should be a direct indication of any increase in metal from corrosion of the SBM. Four of the five experiments reveal a notable increase in metal content, with Experiment 4 showing no increase. All of the experiments were performed after the RotCell metal wear problem was solved (see Sec. 3.4.3). Experiment 4 was performed over 5.5 days of mixing at 100°C, while Experiment 5 mixed for only 2 days and at room temperature. And yet, Experiment 4 showed no increase in metal content and Experiment 5 showed a significant increase. Experiment 1 was mixed at 100°C and Experiment 2 at room temperature for the same duration, with Experiment 1 resulting in less uptake in metal than Experiment 2. In addition to metal content, the combination of final sample concentration and ash content can provide information on any changes in SWNT mass during mixing. SWNTs that have had their ends opened via intense sonication have been shown to shorten in length when exposed to certain strong acids [30]. It is feasible that, even without sonication, some nanotubes have exposed ends from the purification process and may be shortened during mixing in 102% sulfuric acid. Table 3.11 also shows the loss of SWNT mass for each experiment, assuming a starting ash content of 6 wt%. Note that it is possible for an experiment that shows both an increase in final concentration and an increase in metal content to not result in any SWNT loss. All five experiments showed notable losses in material. However, Experiment 4 again resulted in a lower change than Experiment 5, as did Experiment 1 vs. Experiment 2. These TGA results are counter intuitive and suggest that either the execution of sample collection and/or TGA approach is flawed, or that the interpretation of the results is incorrect. Either
way, additional experiments with repeated TGA measurements are necessary to answer this question. Analysis of blank tests involving only 102% sulfuric acid under the same mixing conditions were planned, but unfortunately not performed during this research. Such tests would provide simpler results without the added involvement of SWNTs.

In addition to explorations into the effects of mixing duration, experiments were performed with two different mixing elements and the resulting fibers compared. Experiment 1 involved mixing with static mixers and Experiment 2 involved mixing with the Rotating Shear Cell (RotCell). The mechanisms involved in each method are discussed in Section 3.4.2. The RotCell was believed to provide improved mixing of SWNTs in 102% sulfuric acid due to an active high shear mixing. Fibers were produced in both experiments and probed via SEM and polarized Raman spectroscopy.

SEM analysis of fibers produced from the static mixing of Experiment 1 showed less than ideal fibers. At low magnification, the fiber is rough and uneven. Moderate magnifications, however, do reveal some inherent alignment and a substructure of large SWNT bundles. High magnification shows that the alignment is not ideal, with many regions of unaligned aggregations of bundles, similar to buckypaper. In general, the fibers are mediocre. They do appear to possess some alignment and substructure, but have defects.
Figure 3.61: Scanning electron micrographs of a 6 wt% SWNT fiber from Experiment 1. The sample was mixed with static mixers and possesses mediocre alignment. Scale bars were unavailable, magnifications are provided instead.

In comparison, SEM images of fibers produced from Experiment 2 show better alignment. The fibers are not dramatically better than those of Experiment 1, but the fibers appear to possess more aligned SWNT bundles with better surface density and morphology. At low magnifications, the two fibers have similar surface morphology, but a qualitative sense of alignment is more readily apparent in the RotCell fiber. At higher magnifications, the SWNTropes are better defined with less surface contaminants and regions of unaligned nanotubes.
Figure 3.62: Scanning electron micrographs of a 6 wt% SWNT fiber produced from Experiment 2. The sample was mixed with the RotCell. The fiber possesses minor improvements in alignment over the static mixer fiber of Experiment 1.

Access to the cross-sections of the fibers was provided by Wang et al. using their special microtoming technique [22]. SEM analysis shows the fibers to both possess collapsed structures, indicative of dense, rigid skin formation during coagulation. Neither fiber appears to contain substantially more or less voids than the other. The less symmetric shape of Experiment 1’s fiber is not relevant without further data on coagulation. In general, the fibers appear to have coagulated along similar paths.
Figure 3.63: Scanning electron micrographs showing the cross-sections of fibers produced from (A) Experiment 1 and (B) Experiment 2. Both fibers are 6 wt% SWNT extruded into diethyl ether.

Polarized Raman analysis was also performed on fibers produced from the two experiments. Table 3.12 lists comparative results. Unfortunately, insufficient attention was paid towards keeping all extrusion variables constant, but qualitative comparisons can still be made. The results suggest a possible improvement in fiber alignment from the RotCell over the static mixer elements. The first two fibers show the RotCell sample to have a significantly higher Raman ratio, even though the extrusion rate was significantly lower. The effect of the SBM gap without rotation at 500 – 625 μm is not expected to be significant given the much smaller needle orifice diameter of 125 μm. The second two fiber samples do not support a significant improvement, however. The fiber samples have about the same alignment.

Table 3.12: Raman Comparison of Static Mixers vs. RotCell Fibers

<table>
<thead>
<tr>
<th>Mixing Element</th>
<th>Orifice Dia</th>
<th>Needle Length</th>
<th>Extrusion Rate (mL/min)</th>
<th>SBM Gap (μm)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>RotCell</td>
<td>125</td>
<td>2&quot;</td>
<td>0.004</td>
<td>500</td>
<td>6 ± 2</td>
</tr>
<tr>
<td>Static Mixer</td>
<td>125</td>
<td>2&quot;</td>
<td>0.04</td>
<td>625</td>
<td>2.5 ± 0.5</td>
</tr>
<tr>
<td>Static Mixer</td>
<td>175</td>
<td>1&quot;</td>
<td>0.04</td>
<td>625</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>RotCell</td>
<td>175</td>
<td>2&quot;</td>
<td>0.04</td>
<td>500</td>
<td>5 ± 1</td>
</tr>
</tbody>
</table>
In addition to direct analyses of fiber samples, RotCell mixing was qualitatively better than the static mixers. The extrusion was cleaner and more uniform. More importantly, during the extrusion of the RotCell sample, no needle became clogged. The static mixer experiments always resulted in contaminants which would clog extrusion needles multiple times during the experiment. The needles would have to be changed out with new ones. Admittedly, Experiment 2 mixed at 100°C compared to room temperature for Experiment 1, but the notable results of Experiment 5 support the theory that the RotCell is an effective mixing method.

In addition to experiments demonstrating the various abilities of the SBM, characterization of fibers produced from Experiment 5 show the fibers to be similar to those produced from earlier research. The SBM was designed as a robust apparatus capable of picking up where the Daca Spinning Method left off and surging forward into the next generation of neat SWNT fibers. Experiment 5 proved very successful and allowed for the production of large quantities of neat fibers and preliminary explorations into some extrusion variables previous unexplored. Fiber extrusion was not performed at room temperature, but instead from the SBM heated to 100°C. In addition to extrusion into the standard room temperature column of diethyl ether, fiber samples were also extruded into chilled diethyl ether (~0°C). Finally, fiber samples were successfully extruded using a ~1 cm air gap into both room temperature and chilled diethyl ether. Full characterization of every fiber was not performed due to time limitations. Structural characterization of fiber samples was performed with SEM, polarized Raman spectroscopy, and XRD. The electrical resistivity and strength of select fiber samples
were also measured. Unless otherwise specified, characterization was performed on fibers extruded without an air gap into room temperature diethyl ether.

SEM analysis of Experiment 5 fibers showed the fibers to be well aligned with uneven surface morphology. The surface composition and alignment of fibers from Experiment 5 have already been discussed in the context of varying mixing durations. The fiber possessed a rough collapsed surface, but appeared relatively well aligned with a substructure of SWNT bundles. In addition, the cross-section of several fiber samples was exposed by Wang et al. Two fiber samples produced during Experiment 5 are shown in Figure 3.64. Both fibers possessed a collapsed, uneven shape due to coagulation. On the positive side, the fibers do appear to have coagulated into dense fiber structures lacking significant voids.

![Figure 3.64: Scanning electron micrographs of 8 wt% fibers produced during Experiment 5.](image)

Polarized Raman analysis was performed on all of the fiber samples produced during Experiment 5. As mentioned previously, additional extrusion conditions were attempted during this experiment. Raman analysis was the only characterization able to be applied to each of the fiber samples. Table 3.13 lists the Raman results for the various
fibers. Several observations can be drawn from these results. Not surprisingly, an increase in extrusion rate increased the resulting fiber alignment. The Raman Ratio increased from $3.8 \pm 0.5$ to $8 \pm 2$ as the extrusion rate increased by a factor of five. Also not surprising is that, in the absence of drawing, the fiber alignment decreased with the introduction of an air gap. The extrusion environment was not kept dry. Ambient moisture was taken in by the extruding fiber, disrupting alignment. The most interesting result is the improvement of alignment with the inclusion of a cold bath. Commercial solution spinning involves low temperature coagulation baths to optimize the tensioning and coagulation rate of fiber spinning [18]. Colder coagulation baths result in slower diffusion rates, thus allowing the skin to play a lesser role in the fiber shape. With the future introduction of tensioning during spinning, the effects of cold baths will certainly be even more pronounced.

Table 3.13: Experiment 5 Raman Results

<table>
<thead>
<tr>
<th>Orifice Dia. (μm)</th>
<th>Needle Length</th>
<th>Extrusion Rate (mL/min)</th>
<th>Coagulation Method</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>2&quot;</td>
<td>0.002 – 0.008</td>
<td>RT Ether</td>
<td>3.8 ± 0.5</td>
</tr>
<tr>
<td>125</td>
<td>2&quot;</td>
<td>0.02</td>
<td>RT Ether</td>
<td>8 ± 2</td>
</tr>
<tr>
<td>125</td>
<td>2&quot;</td>
<td>0.02</td>
<td>RT Ether w/ Air Gap</td>
<td>4.9 ± 0.7</td>
</tr>
<tr>
<td>125</td>
<td>2&quot;</td>
<td>0.002 – 0.02</td>
<td>Cold Ether</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>125</td>
<td>1&quot;</td>
<td>0.01</td>
<td>Cold Ether</td>
<td>4 ± 1</td>
</tr>
</tbody>
</table>

Further characterization of fibers produced during Experiment 5 was provided by collaborators at the University of Pennsylvania. Two fiber samples were examined. Both fibers were extruded directly into a diethyl ether column, one into a room temperature (RT) bath and the other into a cold ether bath. These results demonstrate the SBM’s ability to extrude fibers of equal quality as Daca-spun fibers, while providing additional data on recent neat SWNT fibers.
XRD analysis was performed by Wei Zhou using the experimental technique described in Section 3.3.7. Both fibers possessed a full-width half-maximum (FWHM) mosaic angle of $\varphi = 31^\circ$, the same as the 6 & 10 wt% Daca-spun hexane-extracted neat fibers. This is a direct measure of the degree of bulk alignment within the fibers, and indicates that although the fibers display a collapsed ribbon-like shape (Fig. 3.60A), the bulk alignment is as good as the cleanly circular hexane-extracted fibers.

Next, Juro Vavro performed electrical characterization of the same fibers. Electrical resistivity measurements were performed on as-spun (i.e. green) fiber samples in the manner described in Section 3.3.5. Figure 3.65 displays the two fiber samples’ resistivity as a function of temperature. The fibers possessed resistivities similar to the earlier Daca-spun fibers, with room temperature values of $\rho = 0.20$ m$\Omega$-cm and $\rho = 0.34$ m$\Omega$-cm for RT and cold baths, respectively.

![Figure 3.65: A plot of the resistivity vs. temperature for 8 wt% fibers extruded into room temperature ether (blue circles) and cold ether (red squares). The fibers possess similar resistivity behaviors.](image)
Finally, Reto Haggenmueller performed mechanical testing on the same kinds of fiber samples. Testing was similar to the method described in Section 3.3.4. An Instron apparatus with a 10 N load cell was used. Samples were mounted on a paper frame (gauge length = 1") and tested using clamp fixtures. Cross-head speed was kept constant at 1 mm/min. The steepest initial slope in the Stress-Strain plot (Fig. 3.66) was taken as the elastic modulus. A cross-sectional area of 900 μm² was obtained from SEM images and used to calculate the stress. Multiple lengths of each fiber type were tested and the results averaged. Table 3.14 lists the extrusion conditions and resulting average mechanical properties.

<table>
<thead>
<tr>
<th>Orifice Dia. [μm]</th>
<th>Needle Length</th>
<th>Extrusion Rate [mL/min]</th>
<th>Coagulation Bath</th>
<th>Elastic Modulus [GPa]</th>
<th>Tensile Strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>125</td>
<td>2&quot;</td>
<td>0.02</td>
<td>RT Ether</td>
<td>21 ± 1</td>
<td>90 ± 9</td>
</tr>
<tr>
<td>125</td>
<td>2&quot;</td>
<td>0.002 – 0.02</td>
<td>Cold Ether</td>
<td>7 ± 1</td>
<td>41 ± 3</td>
</tr>
</tbody>
</table>

Figure 3.66: Two example Stress vs. Strain plots for 8 wt% SWNT fibers extruded into room temperature ether (blue circles) and cold ether (red squares).
A couple of interesting developments are seen in the mechanical testing of these fibers. The main observation is that these fibers are notably stronger than their Daca-spun hexane-extracted counterparts. The earlier hexane-extracted SWNT fibers possessed a tensile strength of $\tau \approx 5$ MPa and an elastic modulus of $Y \approx 1$ GPa; both properties for the RT fibers from Experiment 5 are 20 times higher. These values are only a factor of 3 away from being considered "average" by conventional fiber mechanical standards (see Sec. 2.2.5), and without any extensional drawing or post-processing. The second interesting observation is that the fibers spun into the cold ether bath exhibited lower mechanical properties. The same fibers showed the opposite during Raman analysis – the cold bath fiber possessed a higher Raman ratio. This trend is the opposite seen in earlier fibers, which indicated that the Raman ratio was proportional to tensile strength. However, only two data points are represented here and other extrusion conditions were different. Regardless, the mechanical testing shows the fibers to be better than the Daca-spun fibers.

The SBM experiments have successfully demonstrated the SBM’s role as a robust apparatus for neat SWNT fiber spinning. Because of the frontier nature of neat SWNT fiber research, the ability to perform a wide variety of experiments is essential. The various features engineered into the design of this system allow for tremendous flexibility in monitoring, measuring, and performing mixing and extrusion experiments. Modular mixing elements allow for mixing experiments to explore the efficacy of different mixing strategies, while continuously monitoring the sample evolution with the piston’s linear encoder. The central bob has revealed an interesting behavior within SWNT / 102% sulfuric acid samples and will allow future research to explore the effects of shear-
thinning fiber spinning as well as shear-assisted alignment experiments. Finally, characterization of fiber samples have demonstrated the basic ability of the SBM to continue where the Daca Spinning Method left off, further exploring the properties and science behind neat SWNT fibers.
4. Conclusion

The future of technology is nanotubes. A decade after their discovery, single-wall carbon nanotubes (SWNTs) continue to impress scientists with their myriad of amazing properties. Individual SWNTs have mechanical properties greater than high performance steel at 1/6 the weight, electrical conductivity better than copper, and thermal conductivity to rival diamond. Most of these properties have been experimentally verified. SWNTs' resume as the ultimate molecular entity is remarkable. However, the future of nanotubes will be limited to nanometer and micrometer scale applications unless macroscopic materials are developed that successfully display these properties.

The ultimate SWNT material will be a macroscopic fiber consisting of no polymer or surfactant substructure, a truly neat SWNT fiber. The anisotropic properties of SWNTs lend themselves to fiber spinning. Their mechanical, electrical, and thermal properties are all superior along their axis. Macroscopic aligned, crystalline fibers consisting of only SWNTs will translate bulk materials into the ultimate properties observed on the nanometer scale. Composite fibers of SWNTs and polymers will serve a useful intermediary role as appetizers to the neat fibers, but will never fully realize the potential of SWNTs. The most promising route to bulk SWNT materials is neat fibers. The road to such neat macroscopic SWNT fibers will be a challenging one, but one that requires a steady progression of SWNT fiber research to be successful.

This thesis reports the successful creation of the first ever macroscopic neat SWNT fiber. The research involved three main focuses, each building upon the discoveries of its predecessor. Conventional fiber engineering of rigid rod polymers was
used as a template to guide the development of SWNT fiber spinning. Like rigid rod polymers, SWNTs were found to readily dissolve at high concentrations in super acids. The nanotubes self-assembled into a nematic lyotropic liquid crystalline phase. The phase behavior and rheology of SWNTs in 102% sulfuric acid was explored. These samples were then spun using a wet-jet solution spinning technique into diethyl ether. The resulting fibers were characterized and showed links to the original liquid crystalline phase as well as interesting physical properties. Finally, the Spinning Bob Mixer, a robust laboratory mixer / extruder, was designed and tested.

One of the main challenges of SWNT research has always been the dispersion of individual nanotubes at high concentrations. SWNTs were found to readily disperse in 102% sulfuric acid at high concentrations (6 – 10 wt%). The nanotubes followed the traditional phase behavior of rigid rods – isotropic, biphasic, and single phase liquid crystal, but displayed a unique one-dimensional liquid crystalline phase (SWNT Spaghetti). Rheology experiments showed that the system is very viscous with strong shear-thinning and power law type behavior.

The first macroscopic neat SWNT fibers were spun from this concentrated liquid crystalline state. Fibers were created by wet-jet solution spinning into a diethyl ether coagulation bath with no extensional drawing. The technique produced continuous lengths of neat SWNT fibers. Scanning electron microscopy (SEM) analysis of the fibers showed them to be highly aligned, devoid of surface contaminants. High resolution images revealed a substructure of large SWNT bundles of the same size as the SWNT Spaghetti domains. Cross-sectional images of the fibers confirmed the spaghetti structure. Neat SWNT fibers were produced from both soft-baked and hexane-extracted purified
nanotubes and were found to produce fibers with different morphologies. Soft-baked SWNTs formed dense, rigid skins during coagulation which caused them to collapse into irregular, flattened fibers, while hexane-extracted material formed softer skins and coagulated into uniform circular fibers.

In addition to a fascinating hierarchical structure, as revealed by SEM, quantitative characterization of the neat SWNT fibers was performed. Polarized Raman spectroscopy, combined with x-ray diffraction (XRD) analysis, showed the fibers to be the highest aligned neat SWNT material produced to-date. Polarized Raman ratios as high as $28 \pm 2$ and XRD full-width half-maximum mosaic angles as low as $31^\circ$ were measured for the neat fibers. Physical characterization of the neat SWNT fibers was also performed. The neat SWNT fibers were found to be p-doped by residual acid and possessed room temperature semi-metal resistivities around $\rho \approx 0.3 \text{ m}\Omega\cdot\text{cm}$ which increase by an order of magnitude upon removal of the acid by high temperature annealing. The thermal conductivity of the neat fibers increased linearly with temperature, with a room temperature conductivity comparable to unaligned SWNT buckypaper. Unfortunately, mechanical testing of the neat SWNT fibers resulted in poor properties. The soft-baked SWNT fibers exhibited a tensile strength of $\tau \approx 1 \text{ MPa}$ with a Young's Modulus around $Y \approx 80 \text{ MPa}$, while the hexane-extracted SWNT fibers possessed $\tau \approx 5 \text{ MPa}$ and $Y \approx 1 \text{ GPa}$. However, all of the properties of these first SWNT fibers are promising given the basic laboratory techniques used and the lack of drawing during spinning.

The first generation of neat SWNT fibers emphasized the need for a controlled, robust laboratory apparatus designed to handle the requirements of SWNT mixing and
extrusion. To answer these limitations and provide the modularity and measurement capabilities necessary to truly address the production of high quality neat SWNT fibers, a custom apparatus was built. The Spinning Bob Mixer (SBM) was engineered to facilitate the next generation of fibers. The SBM is an integrated mixer and extruder capable of continuously mixing viscous, corrosive samples at temperatures up to 150°C and pressures up to 1500 psi. In addition, the apparatus has a number of features which empower research of neat SWNT fibers.

The SBM was successfully tested as a valuable tool for investigating the production of neat SWNT fibers. Multiple experiments were performed under a variety of mixing conditions. A rotating bob in the central extrusion region was successfully tested and revealed a distinct correlation between rotation and resulting fiber alignment. The rotating bob was shown to be a potentially valuable and unique tool for exploring alignment in liquid crystalline SWNT samples. Modular mixing elements were used to mix SWNTs in 102% sulfuric acid. The resulting fibers provided preliminary information on the efficacy of different mixing schemes as well as demonstrating the modularity designed into the SBM. In addition, the evolution of SWNT / 102% sulfuric acid samples during mixing was monitored through measurements of the piston velocity. The viscosities of SWNT samples were found to transition through multiple stages and resulting fibers showed distinct differences in quality. The SBM demonstrated itself a useful tool for exploring the effects of mixing on fiber properties. Finally, large quantities of continuous macroscopic neat SWNT fibers were extruded and shown to be equivalent to the first generation fibers. The mechanical properties of the SBM fibers, however, were found to be more than an order of magnitude better than their earlier counterparts.
Overall, the SBM proved itself a powerful laboratory apparatus capable of enabling the next stage of neat SWNT fiber research.

This thesis is a notable milestone in neat SWNT fiber research. The first ever macroscopic neat SWNT fibers have been produced using a solution spinning technique from a super acid nematic liquid crystal. The fibers are the highest aligned neat SWNT material produced to-date. Whereas the physical properties are not impressive yet, the fact that such a fiber has been produced without any extensional drawing is a worthy accomplishment. The first generation of neat SWNT fibers has been created and a critical foundation of experimental understanding developed. The road to the ultimate fiber will continue to be challenging, but armed with powerful research apparatuses, like the Spinning Bob Mixer, success is inevitable.
Appendix A. HiPco SWNT Purification

A.1. Standard Soft-Baked Purified SWNTs (method 1)

1. Soft-Baking
   a. Fill a clean, dry beaker with 20 – 30 g of raw HiPco nanotubes and cover with aluminum foil. Use aluminum tape to secure the cover to the beaker. Make sure to not cover tightly, but instead provide some space above the beaker, otherwise the cover can break and spill SWNT into the oven.
   b. Record the mass of the beaker + NT + foil
   c. Use an oven which is connected to a heated reservoir of water.
   d. Heat the water reservoir until lightly boiling.
   e. Heat the oven at 225°C for 15hrs (time defined as start of heat ramping to start of oven cooling).
   f. Remove the beaker and record the mass. This is the soft-bake weight loss.

2. Acid Cleaning
   a. Add to the same beaker, 1 L of concentrated HCl. Stir the material with a Teflon rod to make sure all of it has been wet.
   b. Place a large (~2” length) magnetic stir bar in the mixture and set it stirring. The slurry should be visibly stirring, but not vigorously.
   c. Allow to stir for ~12 hrs (i.e. overnight) at room temperature in a closed fume hood.

3. Neutralization
   a. Stop the stirring. Pour 1L of deionized water into the HCl slurry.
b. Set up the slurry filtering using a large ceramic Buchner funnel, Whatman filter paper, and a filter flask.

c. Use a peristaltic pump and a DI water reservoir to refill the slurry at the same rate that it is filtering. It is critical that these flow rates be equilibrated to avoid spilling over or dropping the water line below the solid slurry.

d. Leave the system in a constant filtering set-up. For the first 4 – 8 hrs the filtrate will have a yellowish color from the dissolved iron. Then it will become clear.

e. Check the pH of the filtrate. If it is not neutral, continue to filter for another 2 – 4 hrs and then sample again. Stop only after it is neutral.

4. Methanol Dried Nanotubes

a. Disconnect the peristaltic pump system.

b. Filter 2L of HPLC methanol through the nanotubes.

c. Transfer the SWNT material to a crystallization dish. Cover with perforated aluminum foil.

d. Allow to dry naturally for ~12 hrs (i.e. overnight).

5. Check Purity

a. Perform TGA in air at 800°C on dry purified SWNTs to obtain purity level.

b. If ash content is not below 6 wt%, repeat A.1.2 – 4.
A.2. Hexane Extracted SWNTs (method 2)

1. Soft-Baking (same as A.1.1.)

2. Acid Cleaning
   a. Add to the same beaker, 100 - 125 mL of 36.5% aq. HCl. Stir the material with a Teflon rod to make sure all of it has been wet.
   b. Place a large (~2" length) magnetic stir bar in the mixture and set it stirring. The slurry should be visibly stirring, but not vigorously.
   c. Allow to stir for ~12 hrs (i.e. overnight) at room temperature in a closed fume hood.

3. Hexane Extraction
   a. Transfer the HCl slurry to a large separation flask.
   b. Add 50 mL of HPLC hexanes.
   c. Shake the flask vigorously by hand. The nanotubes will migrate to the upper hexane layer.
   d. Drain out the water; be careful not to loose any nanotubes.
   e. Add 300 mL of deionized water to the flask.
   f. Repeat steps c – f twice more.
   g. Drain out the water, careful not to loose any nanotubes.
   h. Transfer the hexane-NT slurry to a crystallization dish. Cover with perforated aluminum foil.
   i. Allow to dry naturally overnight.

4. Check Purity
a. Perform TGA in air at 800°C on dry purified SWNTs to obtain purity level.

b. If ash content is not below 6 wt%, repeat A.2.3 – 4.
Appendix B. SWNT Sample Characteristics

B.1. Weight / Volume Concentration Conversions

The concentration of single-wall carbon nanotubes in a liquid medium is typically characterized by either the weight or volume percentage. Conversion from one to the other requires only the densities the SWNTs and the solvent involved. Samples in this research were usually prepared using weight percentages, \( \text{wt}\% \), given by

\[
\frac{m_{NT}}{m_{\text{acid}} + m_{NT}} \times 100 = \text{wt}\%, \tag{B.1}
\]

with \( m_{NT} \) and \( m_{\text{acid}} \) the masses of the SWNTs and acid. In addition, the SWNT volume concentration, \( \text{vol}\% \), of the sample is

\[
\frac{Vol_{NT}}{Vol_{\text{acid}} + Vol_{NT}} \times 100 = \text{vol}\%, \tag{B.2}
\]

where \( Vol_{NT} \) and \( Vol_{\text{acid}} \) are the volumes of SWNTs and sulfuric acid, which can also be written in terms of their masses and densities, \( \rho \):

\[
\frac{m_{NT}}{\rho_{NT}} = Vol_{NT} \quad \text{and} \quad \frac{m_{\text{acid}}}{\rho_{\text{acid}}} = Vol_{\text{acid}}. \tag{B.3}
\]

The volume concentration can therefore be written solely in terms of the densities and the weight concentration. Equation B.1 can be rewritten in terms of the acid mass:

\[
\frac{m_{NT} \left( 1 - \frac{\text{wt}\%}{100} \right)}{\frac{\text{wt}\%}{100}} = m_{\text{acid}}. \tag{B.5}
\]
Then, Equation B.3 & B.4 can be substituted into Equation B.2 for the volumes,

\[
\left( \frac{m_{NT}}{\rho_{NT}} \right) \times 100 = \text{vol} \%, 
\]  
\( (B.6) \)

and Equation B.5 can be substituted into the result for the acid mass:

\[
\left( \frac{m_{NT}}{\rho_{NT}} \right) \times 100 = \text{vol} \%, 
\]  
\( (B.7) \)

this simplifies to an equation to translate between weight and volume concentrations:

\[
\frac{\rho_{\text{acid}} \text{wt}\%}{(100 - \text{wt}\% \rho_{\text{NT}} + \rho_{\text{acid}} \text{wt}\%)} \times 100 = \text{vol} \%. 
\]  
\( (B.8) \)

Note that the density of isotropic SWNTs in solution and for solid, aggregated SWNTs is significantly different due to unavoidable void spaces within the hexagonal close-packing structure. The density of 102% sulfuric acid is \( \rho_{\text{acid}} = 1.88 \text{ g/cm}^3 \) [110], and the approximate density of HiPco SWNT material is \( \rho_{\text{bundle}} = 1.32 \text{ g/cm}^3 \) for close-packed nanotubes and \( \rho_{\text{ind}} = 1.69 \text{ g/cm}^3 \) for individual HiPco SWNTs in solution (see App. B.2).

### B.2. SWNT Density

Based on the structure of a given SWNT type, the mass density for that nanotube in solution and in a hexagonal close-packed bulk form can be calculated. From Sec. 2.1.2, a SWNT is defined by its chiral vector, \( C_h \). The chiral vector is defined as
\[ C_h = n\vec{a}_1 + m\vec{a}_2, \]  

(B.9)

where \( \vec{a}_1 \) and \( \vec{a}_2 \) are unit vectors and \( n \) and \( m \) are integers. The diameter of a given SWNT with indices \((n, m)\) can be determined from the chiral vector. Fig. B.1 depicts the chiral vector and the corresponding SWNT molecular geometry.

![Graphene sheet diagram](image)

Figure B.1: A graphene sheet is shown depicting the chiral and translation vectors of a SWNT. The vectors for a \((6, 2)\) semiconducting nanotube are shown as an example.

The length of the chiral vector can be determined by the law of cosines,

\[ C_h^2 = (na_1)^2 + (ma_2)^2 - 2(na_1)(ma_2)\cos\left(\frac{2\pi}{3}\right). \]  

(B.10)

From the geometry of the carbon hexagon, the magnitude of the unit vectors can be substituted into the equation:

\[ C_h^2 = (\sqrt{3}a_{c-c})^2(n^2 + m^2) - 2nm(\sqrt{3}a_{c-c})(\sqrt{3}a_{c-c})\left(-\frac{1}{2}\right), \]  

(B.11)

which simplifies to

\[ C_h = \left(\sqrt{3}a_{c-c}\right)(n^2 + nm + m^2)^{1/2}. \]  

(B.12)

Since the chiral vector defines the circumference of the SWNT, the diameter is given by
\[ d_\pi = \frac{C_h}{\pi} = \frac{\sqrt{3}a_{\text{c-c}}}{\pi}, \]  
\[ \text{where } a_{\text{c-c}} \text{ is the bond length between carbon atoms. The bond length from } C_{60} \text{ is an appropriate value, } a_{\text{c-c}} = 0.144 \text{ nm [27].} \]

To determine the unit cell of a given nanotube, the translation vector must be determined next. This vector is more complicated, but was worked out by Dresselhaus \textit{et al.} in their research involving SWNT symmetry groups [27]. The vector can be written as

\[ \bar{T} = [2m + n\bar{a}_1 - (2n + m)\bar{a}_2] / d_R \]  
\[ \text{with a length of} \]

\[ T = \frac{\sqrt{3}C_h}{d_R} \]  
\[ \text{where the length of } C_h \text{ is given by Equation B.12 and } d_R \text{ is the greatest common denominator of } (2m + n) \text{ and } (2n + m). \]

With the translation and chiral vectors defined, the mass per unit cell can be determined. The total number of hexagons in a given unit cell, \( N \), is simply the product of the vector’s lengths divided by the volume of a hexagon:

\[ N = \left[ \frac{\sqrt{3}C_h}{d_R} \right] \left[ C_h \right] \left( \frac{3\sqrt{3}}{2} a_{\text{c-c}}^2 \right) = \frac{2}{3d_R} \frac{C_h^2}{a_{\text{c-c}}^2}, \]

\[ \text{which simplifies to} \]

\[ N = \frac{2}{d_R} \left( n^2 + nm + m^2 \right). \]  
\[ \text{Since each hexagon contains 2 carbon atoms, the total mass per unit cell, } m', \text{ is given by} \]

\[ m' = m_{\text{Carbon}} N A \frac{2}{d_R} \left( n^2 + nm + m^2 \right). \]
The final step in calculating the mass density of an individual SWNT or a SWNT bundle is determining the appropriate volume. In both cases, the diameter calculated using Equation B.13 needs to be modified to take into account the van der Waals radius (Fig. B.2). At atomic distances, dipole-dipole interactions repel molecules, limiting how close two molecules can approach each other. In SWNTs, like graphite, this distance has been experimentally determined to be \( d_{VDW} = 0.344 \text{ nm} \), in effect increasing a nanotube’s diameter by that amount.

Figure B.2: A cartoon depicting the volume of a SWNT bundle vs. that of an individual SWNT. The dark circles represent SWNTs, while the light circles represent their van der Waals radius. The hexagon is the cross section used in determining a bundle’s density.

For an individual SWNT, the density is simply the mass of the nanotube divided by the volume occupied by the nanotube. Assuming a nanotube of length, \( L \), and ignoring the end effects of a nanotube, that density is

\[
\rho_{\text{ind}} = \frac{\frac{L}{T}m'}{\frac{L\pi}{4}(d_i + d_{VDW})^2} = \frac{4m'}{T\pi(d_i + d_{VDW})^2}, \tag{B.19}
\]

with \( d_i \) and \( m' \) given by Equation B.13 and B.18, and \( d_{VDW} = 0.344 \text{ nm} \).
For SWNTs in a bundle, the volume can be defined by a hexagonal cross-sectional area shown in Fig. B.2 and a bundle length, $L$. This cross sectional area is given by

$$A_{hex} = \frac{3\sqrt{3}}{2} (d_i + d_{VDW})^2,$$  \hspace{0.5cm} (B.20)

which leads to a density of

$$\rho_{bundle} = \frac{3 \left( \frac{L}{T} \right) m'}{L^3 \sqrt{3} \left( d_i + d_{VDW} \right)^2} = \frac{2m'}{T \sqrt{3} \left( d_i + d_{VDW} \right)^2}$$  \hspace{0.5cm} (B.21)

with $d_i$ and $m'$ given by Equation B.13 and B.18, and $d_{VDW} = 0.344$ nm. Note that for a given SWNT type, the density of an individual is greater than a bundle of the same nanotube. For HiPco material, the average nanotube diameter is 0.93 nm [111], which corresponds closest to a (9, 4) nanotube. The density of packed (9, 4) SWNTs is $\rho_{bundle} = 1.32$ g/cm$^3$ and the density of an individual (9, 4) SWNT is $\rho_{ind} = 1.69$ g/cm$^3$. 
Appendix C. Spinning Bob Mixer Schematics

The Spinning Bob Mixer (SBM) has evolved into an elaborate and powerful laboratory apparatus. The machine has been designed as an integrated mixer / extruded capable of handling corrosive mixtures at high temperatures. Because it was designed and built from the ground up, complete machine drawings are provided as a reference for thesis discussions and for future research involving the SBM. Although the SBM has undergone several iterative modifications and improvements, only the final design state is included here. A discussion and analysis of the design and use of the SBM, including how it is assembled and operated, can be found in Sec. 3.4.2. Unless otherwise specified, part numbers refer to Swagelok products. O-ring information is provided with the relevant SBM component. O-rings are defined by a code: “116 V90”. The first number (e.g. “116”) is the o-ring size, the second code describes the compound with “V” for Viton and “K” for Kalrez™ and the durometer rating. Typical o-rings used in the SBM were V747-75, V709-90, K6375-75, and K3018-91. In addition, the following abbreviations are used throughout the schematics:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Text</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>Counter Bore</td>
</tr>
<tr>
<td>D</td>
<td>Diameter</td>
</tr>
<tr>
<td>DP</td>
<td>Depth</td>
</tr>
<tr>
<td>ID</td>
<td>Inner Diameter</td>
</tr>
<tr>
<td>L</td>
<td>Length</td>
</tr>
<tr>
<td>OD</td>
<td>Outer Diameter</td>
</tr>
<tr>
<td>W</td>
<td>Width</td>
</tr>
</tbody>
</table>
Figure C.1: SBM Main Body, Overview
Main Body, Right (20cb3, Q: 1)

Tap 1/2"-18

0.190"

3.563"
3.000"

0.375"

1.750" 1.250" 1.688"

0.645"

Drill 0.125" w/ 0.295" CB to 0.25" DP

2.750"

Drill 0.093" 0.312"

0.939" 1.000"

O-Ring Groove

1.449" OD
1.095" ID
0.102" DP

Tap 1/4"-28 on 2.25" BC

Other Parts

VCO Tube Weld, 316L-4-VCO-1A x1
O-ring, 217 V75 x1

Figure C.2: SBM Main Body, Right
Main Body, Left (20cb3, Q: 1)

O-Ring Groove
1.449" OD
1.095" ID
0.102" DP

Drill 0.125" w/ 0.295" CB to 0.25" DP

2.750"

Tap 1/4"-28 on 2.25" BC

1/8" Locator Pin Holes on 2/25" BC

Other Parts
VCO Tube Weld, 316L-4-VCO-1A x 1
O-ring, 217 V75 x 1

Figure C.3: SBM Main Body, Left
Figure C.5: SBM Upper Support Flange
Upper Support Flange Parts (Q: 1)

Gas Inlet Collar (Teflon)

Teflon Support

Top Flange (SS304)

Clear #8 on 0.875" BC

Figure C.6: SBM Upper Support Flange Parts
Translation Housing, Lower (SS304, Q: 1)

40 threads per inch along 1" length

Tap for #4-40 on BC 1.062" to depth of 0.2" (two sets of 4 tap holes)

#4-40 Taps Described Above

Clearance for 1/4-28 on BC 2.5"

Other Parts
Linear Bearing, LMB-2 (WM Berg) x2
Needle Bearing, NRB-65 (WM Berg) x2

Figure C.7: SBM Translation Housing, Lower
Translation Housing, Upper (SS304, Q: 1)

Tap thru for #6-32

Tap thru ¼-28 on BC 2.5"

Chamfer 45deg

Clear for 1.75"

Other Parts
Thrust Bearings x2

Figure C.8: SBM Translation Housing, Upper
Translation Housing, Other (SS304)

Sm. Bearing Flange (Q: 2)

1.312" 0.125" 0.712"

Clear for #4-40 on 1.062" BC

Lg. Bearing Flange (Q: 1)

3.00" 0 1/4" 1.50"

Clear for 1/4"-28 on 2.5" BC

Thrust Bearing Spacer (Q: 1)

1.63" 0.75" 0.250"

Figure C.9: SBM Translation Housing, Other
Translation Housing, Other (SS304)

Positioning Shaft (Q: 1)

Tap 1/4"-20
1.875" Close fit to 3/8" shaft
0.500"

Thread 5/8"-18

Close fit to thrust bearings
1.125"

Retaining Ring (Q: 4)

0.062" 0.812" Close Fit to 0.625"

Figure C.10: SBM Translation Housing, Other pt. 2
Central Bob, Bottom (20cb3, Q: 1)

Thread
3/4"-20

0.375"

0.500"

0.801"

1.375"

0.825"

0.062"

45deg

0.187"

0.060"

0.250"

0.188"

0.985"

Filter Support (20cb3, Q: 1)

0.280"

0.688"

0.125"

0.188"

0.188"

0.125"

0.496"

Other Parts
Inline Filter (40um), SS-4F-K4-40 x1
O-ring, 013 K75 x1

2:1 Scale

Figure C.11: SBM Central Bob, Bottom
Central Bob, Top (20cb3, Q: 1)

Press fit 3/8" shaft

Drill thru 1/16" w/ expanded openings

O-ring Groove
0.273" OD
0.145" ID
0.058" DP

Thread 3/4"-20

0.500"-0.560"

0.800"

2:1 Scale

Other Parts
O-ring 007 K91 x2

Figure C.12: SBM Central Bob, Top
Central Bob, Shaft (SS304, Q: 1)

1/4" Set Screw Groove

Mark to track angular position of bob

#4 Set Screw Groove

2:1 Scale

0.375"

Figure C.13: SBM Central Bob, Shaft
Lower Extension Body (20cb3, Q: 1)

O-Ring Groove
1.117" OD
0.993" ID
0.075" W

1/8" Locator Pins on 2.625" BC
0.750"
3.000"
0.993"

O-Ring Groove
1.449" OD
1.095" ID
0.102" DP

1/8" Locator Pin Holes on 2.625" BC

Drill 0.093" thru on 2" BC, 30deg

Clear 1/4" on 2" BC

30 degrees

Drill 0.260" thru on 2.75" BC

Other Parts
O-ring 217 V75 x1
O-ring 022 K91 x1

Figure C.14: SBM Lower Extension Body
Needle Plate (20cb3, Q: 1)

O-ring Groove
0.800" OD
0.564" ID
0.077" DP

Drill 0.210" thru
Tap 1/4"-28
to 0.335" DP

Clear 1/4"
w/ 0.40 CB
to 0.27" DP

Other Parts
Needle Adapter, SS-100-1-1 w/ NPT end
threaded to 1/4"-28 x1
1/16" SS Pre-cut Tubing (Upchurch Scientific) x1
O-ring, 114 K75 x1 (optional)

Figure C.15: SBM Needle Plate
Die Plate (20cb3, Q: 3)

Clear 1/4" w/ 0.40 CB to 0.125" DP on 2" BC

1/8" Locator Pins on 2.625" BC

Drill 0.260" thru on 2.75" BC

0.312"  0.125"  0.938"
45deg

0.375"  0.062"

0.093" dia face

Bottom face coated with 0.003 - 0.005" of Fluorolon 110, a PTFE-based coating, by [Southwest Impreglon Sales, Inc (Houston, TX)]

Extrusion Orifice x3
0.005" L : 0.005" D
0.025" L : 0.025" D
0.020" L : 0.025" D

Figure C.16: SBM Die Plate
Figure C.17: SBM Rt. Port Flange
Rt. Flange Spacer (SS304, Q: 1)

Clear 1/4"
2.250" BC
O-Ring Groove
1.449" OD
1.085" ID
0.104" DP

Other Parts
O-ring, 217 V75 x1

---

Hydraulic Piston Shafts (SS304, Q: 1/ea)

Thread 1/4"-28
0.56"

Polish
0.311"

Position Shaft
3.80"

Connecting Shaft

0.320" 0.650" 0.250"

3.410"

Thread 1/4"-28

---

Figure C.18: SBM Rt. Flange Spacer

Figure C.19: SBM Hydraulic Piston Shafts
Hydraulic Pistons (SS304)

Hydraulic Fluid Piston (Q: 1)

Tap 1/4"-28 to 0.380" DP

Tap 1/4"-28 to 0.309" DP

0.871" O-ring Groove
0.759" ID
0.935" OD
0.142" W

0.935" Other Parts
O-ring, 116 V90 x2

Connector Piston (Q: 2)

Tap 1/4"-28 to 0.309" DP

0.217" O-ring Groove
0.759" ID
0.935" OD
0.142" W

0.925" Other Parts
O-ring, 116 V90 x1
Teflon Split Ring x1
(0.759" ID, 0.937" OD, 0.140" W)

Figure C.20: SBM Hydraulic Pistons
Figure C.21: SBM Hydraulic Cylinder
Figure C.22: SBM Hydraulic Port Flange
Figure C.23: SBM Hydraulic Syringe
Clear 1/4" on one side,  
Tap 1/4"-28 on other  
both on 2.250" BC

1/8" Locator pin holes

2.750"

Cut sides away to reveal bare

0.250"  

1.250"  

1.750"

5.500"

0.250"

Figure C.24: SBM Lt. Piston Support Housing
Lt. Port Flange (SS304, Q: 1)

Drill 0.125" to 1.000" DP then drill perpendicular with 0.15" dia to intersect

Tap #4-40 on 7/8" BC 1/4" DP

Clear for 1/4" on 2.25" BC

1/8" Locator Pins on 2/25" BC (both sides)

Weld VCO Adapter to top port

Flange (SS304, Q: 1)

Clear #4-40 on 0.875" BC

Other Parts
O-ring, 014 V90 x1
VCO Adapter, 316L-4-VCO-1A x1

Figure C.25: SBM Lt. Port Flange
Figure C.26: SBM Lt. Rotating Bearing Shaft
Left Stabilizing Piston (SS304, Q: 1)

Tap #4-40
0.25" DP on
0.625" BC

Flange (SS304, Q: 1)
Clear #4-40
on 0.625" BC

Other Parts
Teflon Split Ring (1.00" ID, 1.248" OD, 0.375" W) x1

Figure C.27: SBM Lt. Stabilizing Piston
Figure C.28: SBM Lt. Rotating Bearing Housing
Figure C.30: SBM Gas Vent Piston Parts
Figure C.31: SBM Gas Vent Piston, Static
Figure C.32: SBM Gas Vent Piston Shaft, RotCell
Figure C.33: SBM Gas Vent Piston Shaft, Right
Static Mixer Elements (SS316/20cb3, Q: 2)

Thread 1/2"-20

Press fit
Kenics Model# 0.19 Tube 17
SS316 Static Mixer and cut to length

2:1 Scale

Figure C.34: SBM Static Mixer Elements

RotCell Entrance Disk (20cb3, Q: 1)

Drill 0.0625" holes on 0.4375" BC

Clear for #4-40 on 0.650" BC

Two slots 0.062" deep

2:1 Scale

Other Parts
O-Ring, 010 PTFE x1

Figure C.35: SBM RotCell Entrance Disk
Figure C.36: SBM RotCell Shear Cylinder
Figure C.37: SBM RotCell Fixed Cone
**Figure C.38: SBM RotCell Housing**
Figure C.39: SBM RotCell Housing Cap
RotCell Shaft (20cb3, Q: 1)

Inner Shaft

Thread for #10-32

Tap #6-32

4.500"

0.375"

0.500"

Gray region coated with
0.003 - 0.005" of Fluorolon 110,
a PTFE-based coating, by
[Southwest Impreglon Sales, Inc (Houston, TX)]

Outer Shaft

5.625"

0.375"

0.244"

2 Flats
90deg apart

Figure C.40: SBM RotCell Shaft
Figure C.4.1: SBM RotCell to Static Mixer Adapter

45deg
0.062" DP
0.093" W
Four angled slots

0.875"
0.931"
1.732"
0.320"
0.560"
0.200"
0.494" ID
0.805" ID
0.932" OD
0.806" ID
0.256" W
0.125" W

Groove for Split Teflon

Thread 3/4"-24
Top 1/2"-20

Grove for Split Teflon

Grove for Split Teflon
Lower Bob Gas Port (20cb3, Q: 1)

1.000" 0.187" 1.000" 0.250"

Thread 3/8"-24 Knurl Surface 0.062" 0.250"

0.147"

Other Parts
O-Ring, 007 PTFE x1
Elbow Ball Valve, SS-43S4-A x1

Pre-mix Syringe Flange (SS316, Q: 1)

0.500" 0.313"

Clear #10-32 on 1.80" BC
O-Ring Groove 0.487" OD
0.313" ID
0.142" DP

Drill 0.74" from edge at 60deg angle to meet tap

0.262"

Tap 5/16"-24 on 0.75" BC

0.25" DP

0.125" DP

2.188"

Other Parts
O-ring, 109 V90 x1
Swagelok to O-Seal Adapter, SS-200-1-2ST x1

Figure C.42: SBM Lower Bob Gas Port

Figure C.43: SBM Pre-mix Syringe Flange
Pre-mix Syringe Bore (SS316, Q: 1)

O-Ring Groove
- 1.085" ID
- 1.449" OD
- 0.104" DP

Tap #10-32 x4 on 1.80" BC

Other Parts
- O-ring, 217 V75 x1
- Plug Valve, SS-4P4T-KZ

Figure C.44: SBM Pre-mix Syringe Bore
Pre-mix Syringe Plunger (SS316, Q: 1/ea)

Shaft
- 0.400" to 0.311"
- 3.750"
- Thread 1/4-28
- Tap #6-32 to depth of 3/16

Handle
- 2.000"
- Clear #6-32
- Sink for Flathead screw
- 0.250"

Plunger
- 0.625"
- Tap 1/4"-28 to 0.375" DP
- O-Ring Groove x2
- 0.925" OD
- 0.737" ID
- 0.120" W

O-Ring Plate
- 0.062"
- Clear for #4-40 on 0.75" BC
- 1.000" x 0.313"

Other Parts
- O-ring, 116 K91 x2

Figure C.45: SBM Pre-mix Syringe Plunger
Heating Shell (Al, Q: 2)

Cut 1/4" x 1/4" 1/4" notch
Cut into two pieces
Drill 0.125"
  w/ 0.260" CB
to 2.50" DP
on 2.250" BC

Clear #8

2.625"

Make one of each set

2.750"

Drill 0.125" thru
Tap #4-40
to 0.250" DP

Figure C.46: SBM Heating Shell
Blind Testing Flanges (SS304, Q: 1)

Filler Flange
Clear 1/4" on 2" BC

Flat Flange
Clear 1/4" on 2" BC

Figure C.47: SBM Blind Testing Flanges
Figure C.48: SBM External Adapter
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