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Processing, Spinning, and Fabrication of Continuous Fibers of Single-Walled Carbon Nanotubes

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ABSTRACT

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Single-walled carbon nanotubes (SWNTs) show great promise for use in a wide range of applications. One of the most promising avenues for attaining these applications is the dispersion of SWNTs at high concentrations in superacids and processing into macroscopic articles such as fibers or films. Fibers spun from SWNT/superacid dispersions indicate that the morphology of the starting SWNT material influences the final morphology of the as-spun fiber. Here, we describe a method (termed disentanglement) of dispersing SWNTs in superacids and treating them using a high-shear, rotor/stator homogenizer, followed by coagulation to recover the solid SWNT material for use in fiber spinning. Several lines of experimental evidence (rheology and optical microscopy of the SWNTs in solution, scanning electron microscopy (SEM) of the coagulated material, and SEM of fibers spun from the coagulated material) show that this disentanglement treatment radically improves the degree of alignment in the SWNTs’ morphology, which in turn improves the dispersibility and processability. Raman microscopy and thermogravimetric analysis (TGA) before and after homogenization show that the treatment does not damage the SWNTs. Although this
technique is particularly important as a pre-processing step for fiber spinning of neat SWNT fibers, it is also useful for neat SWNT films, SWNT/polymer composites, and surfactant- or polymer-stabilized SWNT dispersions.

Macroscopic neat SWNT fibers were successfully produced and characterized. Studies on coagulated fiber morphology suggest that slow acid removal is crucial to minimizing voids. Better SWNT coalescence and alignment were obtained by using appropriate coagulant and dope concentration. SWNTs were disentangled and dissolved at high concentrations (8 - 10 wt%) in 102% sulfuric acid. Fibers were subsequently extruded by dry-jet wet spinning into ice water and polyvinyl alcohol (PVA) / ice water. Drawing the fiber continuously while spinning further aligned the SWNTs within the fiber. The use of PVA (< 1%) in the coagulant slowed acid removal allowing better SWNT coalescence without damaging the SWNT electrical properties. The resulting combination of pre-processing and fiber drawing shows a threefold improvement in fiber tensile strength.
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1 Introduction

Nanoscale science and technology has introduced building blocks to create nearly perfect macroscale objects. Two such building blocks were discovered in the last decade of the 20th century: multi-wall carbon nanotubes (MWNTs) were discovered in 1991 [Iijima, 1991] followed by single-walled carbon nanotubes (SWNTs) in 1993 [Bethune et al., 1993, Ebbesen et al., 1992]. These extraordinary, molecularly perfect macromolecules have received great interest in the scientific world with their unique mechanical [Krishnan et al., 1998, Walters et al., 1999, Yu et al., 2000], electrical [Tans et al., 1997], and thermal [Che et al., 2000] properties, making SWNTs the most desirable building block for new multifunctional material.

If these superior properties of carbon nanotubes are to come to fruition, SWNTs must be incorporated fully into macroscopic neat materials. The preferred application for SWNTs is fibers, due to their anisotropic geometry and properties. Rigid-rod macromolecules spun from a concentrated liquid crystalline phase tend to align in a clearly defined direction generating noteworthy anisotropic fiber properties [Gupta et al., 1997]. Researchers have been highly successful over the past few years in creating composite SWNT fibers. Several polymer systems have also been marginally improved in their mechanical, electrical, and thermal properties through the use of nanotubes [Andrews et al., 1999, Haggenmueller et al., 2000, Kumar et al., 2002, Vigolo et al., 2000]. In contrast to composite SWNT fibers, neat SWNT fibers comprised exclusively of SWNTs takes full advantage of individual SWNT properties. Researchers are creating
neat SWNT fibers using solid-state [Kim et al., 2004] and solution spinning [Ericson et al., 2004] techniques.

Neat SWNT fibers pose a challenge in production, as the process involves two key steps:

1. In order to form a liquid crystalline phase, SWNTs require dispersion as individual units at high concentrations.
2. The resulting liquid crystal must be spun in a controlled manner using durable equipment that can withstand the process fluids.

Fibers comprised of rod-like polymers produced by traditional spinning techniques are solution spun at 5 - 45 wt% concentrations [Gupta et al., 1997]. However, SWNT’s van der Waal forces cause them to aggregate hindering adequate dispersion at high concentrations. Treating SWNTs with organic solvents [Bahr et al., 2001], aqueous surfactants [Vigolo et al., 2000], and polymer wrapping [O’Connell et al., 2001] allow SWNTs to disperse at elevated concentrations. Unfortunately, these suspending agents necessitate removal either during or after the production of the fiber. Lars Ericson’s thesis [Ericson, 2003] proposed preparing SWNT fibers employing conventional rigid rod polymer engineering methods involving superacids.

Rigid rod polymer fibers such as poly p-phenylene terephthalamide (PPTA) are spun at high concentrations by using superacids such as 100% sulfuric acid. In the case of SWNTs, these powerful acids protonate the rod-like SWNTs [Ramesh et al., 2004]. Protonation provides strong electrostatic repulsion that counters the van der Waals forces, allowing the SWNTs to separate and dissolve in the superacid. Thus, superacids have
been proven to disperse SWNTs at high concentrations forming a distinct liquid crystalline phase [Davis et al., 2004].

Neat SWNT fibers spun by Drs. Lars Ericson [Ericson, 2003] followed by Hua Fan [Fan, 2007] utilized conventional rigid-rod spinning techniques and are used as a baseline for this thesis. During their experiments, it was discovered that alignment of the individual SWNTs within the fiber proved to be a challenge. The spun fiber morphology was affected by the original starting material, which was typically entangled bundles. This thesis provides a solution to the alignment problem by:

1. Disentangling the SWNT bundles encouraging alignment of individual SWNTs within larger ropes.
2. Employing dry-jet wet spinning techniques drawing the fiber as it is spun.

The entangled, purified HiPco SWNT (P-SWNT) was pre-processed prior to spinning by immersing them with 120% sulfuric acid into a flask and homogenizing with a rotor/stator. This disentangled the SWNT creating larger rope bundles which were then coagulated and thoroughly dried. Disentangled SWNT (D-SWNT) was added to 102% sulfuric acid at 8 wt% concentration. This sulfuric acid was allowed to intercalate the D-SWNT ropes overnight then mixed thoroughly with a mixer, all within a water-free environment. The sample was then transferred to a stainless steel syringe and spun using a dry-jet wet spinning technique and extruded into ice water and polyvinyl alcohol (PVA) (< 1%) / ice water and collected on a steel drum.

This reproducible process revealed neat SWNT fibers with highly organized, thick structures with a threefold improvement in fiber tensile strength. Supplemental
experiments using various methods and conditions were conducted in order to classify
and compare the resulting fibers.

1.1 Carbon Nanotube Background

Sumio Iijima of NEC Corporation is credited with the initial discovery of carbon
nanotubes in 1991 [Iijima, 1991]. Within an argon environment, high voltage was applied
between two carbon electrodes. Examination by transmission electron microscopy
revealed carbon needles on the negative electrode. These graphitic carbon microtubules
shaped like concentric hollow cylinders consisting of multiple shells, were given the
name “carbon nanotubes.”

1.1.1 Nanotube Synthesis

Multi-wall nanotubes (MWNTs), the first such nanotubes produced and studied,
were discovered by accident in the soot around a carbon arc apparatus, equipment used to
produce carbon whiskers with the application of high voltage between carbon electrodes.
While this device has been in use since the 1950s, it recently produced $C_{60}$, the
nanotube’s predecessor [Ebbesen, 1996]. Single-wall carbon nanotubes (SWNTs) were
discovered a year later, when two independent research groups added transition metals
(e.g., cobalt, nickel, iron) to the process [Bethune et al., 1993, Ebbesen et al., 1992]. Still
popular today, this arc-discharge method produces nanotubes with few structural defects,
while its only apparent flaw is a small batch yield ($\sim 100$ mg / day) [Journet et al., 1997].

Three additional methods for SWNT synthesis exist, each of which has both
advantages and disadvantages:
1. Chemical Vapor Deposition (CVD) [Hafner et al., 1998]: high quality, cost-effective, most common method with low batch yields (~30 mg / day).

2. Fluidized Bed CVD (FBCVD) [See et al., 2007]: good quality, high diameter selectivity, scalable cost-effective process producing high batch yields [Resasco et al., 2002].

3. Pulsed Laser Vaporization (PLV) [Thess et al., 1996]: higher batch yields (~1 g / day) [Rinzler et al., 1998] compared to CVD.

4. High Pressure Carbon Monoxide (HiPco): highest batch yields (>10 g / day) of high-purity SWNTs [Bronikowski et al., 2001].

The HiPco process, pioneered and mass produced at Rice University, provides our neat SWNT fiber project the necessary large amount of high-quality SWNTs. HiPco SWNTs are developed with a high-pressure (30 - 50 atm), high-temperature (900 - 1100 °C) gas-phase CVD process. Iron particles are added to flowing CO gas creating Fe(CO)\textsubscript{5}. The heated Fe(CO)\textsubscript{5} decomposes, condensing the iron atoms into catalytic clusters upon which SWNTs nucleate and grow.

1.1.2 General Properties of Carbon Nanotubes

A carbon nanotube can be thought of as a sheet of graphite rolled into a long, narrow cylinder. Nanotubes vary in length (100 - 1000 nm) and are approximately 1 nm in diameter. Nanotubes, like graphite, are composed of interconnected hexagons of carbon atoms which span their full surface. The spatial orientation of the hexagon in relation to nanotube’s axis has produced three chirality classifications as illustrated in Figure 2.1: (1) armchair; (2) zigzag; and (3) chiral. The first two types of nanotubes are named after their exposed patterns in their cross-sections; the third type represents all
other nanotubes with varying twists along the nanotube axis. As chirality changes, so does the nanotube’s conductive properties. The most conductive chirality is armchair, whereas others vary between semi-conducting and conducting.

![Figure 1.1: Three chirality classifications of carbon nanotubes. The three chirality classifications of carbon nanotubes: a) armchair, b) zigzag, and c) chiral. Note the varying orientation of the hexagons with respect to the nanotube axis [Dresselhaus et al., 1996].](image)

SWNTs display another characteristic behavior by aggregating themselves into ordered structures. The SWNT’s smooth tubular surface has significant van der Waals binding energy between tubes [Girifalco et al., 2000, Thess et al., 1996] causing the SWNT to aggregate into bundles (or ropes) of 10 – 20 nm in diameter and several microns in length [Liu et al., 1998].
The ultimate research goal is to isolate the properties of individual SWNTs. However, suspending individual nanotubes in a stable suspension is very difficult because of the inherent bundles created by their van der Waals forces. The approaches tried thus far to separate nanotubes from these bundles are: organic solvents [Bahr et al., 2001], aqueous surfactants [Vigolo et al., 2000], and polymer wrapping [O’Connell et al., 2001]. Unfortunately, however, no high concentrations (> 0.5 wt%) of individual SWNTs have been produced through any of these methods.

### 1.1.3 Raman Spectroscopy

Raman spectroscopy, an instrument used to probe molecular structures, is used to identify SWNT batch characteristics and to determine overall alignment of SWNTs within neat SWNT fibers. Several distinct bands originate from various aspects of the nanotube within a SWNT Raman spectrum (Fig. 1.3) and these serve as valuable indicators of the type, size, and orientation of SWNTs:

1. First band (frequency at 100 - 300 cm\(^{-1}\)): The Radial Breathing Modes (RBM) of the SWNTs originate from an out-of-plane radial vibration of the nanotube and
are directly dependent on SWNT diameter [Dresselhaus et al., 2003, Kukovecz et al., 2002].

2. Second band: D-band (disorder peak at 1350 cm⁻¹) and its second order G'-band (2700 cm⁻¹) are highly dispersive indicating disorder in the electronic states of SWNTs. The D-band intensity has been experimentally attributed to SWNT defects [Khare et al., 2003] and chemical side-wall functionalization [Bahr et al., 2001, Mickelson et al., 1999].

3. Third band: G-band (1582 cm⁻¹) is the active mode of graphite. This band is composed of two peaks: (1) G⁺ peak related to the in-plane axial carbon atom vibrations; and (2) G⁻ peak related to the in-plane circumferential vibrations. The G⁺ peak is dependent on the relative orientation between the excitation source polarization vector and nanotube axis, due to the high anisotropic polarizability of SWNTs [Saito et al., 1998], resulting in an increased intensity of the peak when the incident polarized laser light is parallel to the nanotube’s axis rather than perpendicular [Gommans et al., 2000, Saito et al., 1998].
Figure 1.3: Raman spectrum for a SWNT bundle. Raman peaks showing (RBM) Radial Breathing Modes, (D) D-band disorder peak, (G) G-band graphite peak. The inset shows the two G-band peaks associated with axial (G$^+$ peak) and radial (G$^-$ peak) in-plane molecular vibrational modes [Ericson, 2003].

Polarized Raman spectroscopy has proven to be a valuable tool for macroscopic samples, allowing the examination of the orientation of individual SWNTs within the bulk [Casavant et al., 2003, Gommans et al., 2000, Poulin et al., 2002]. The overall degree of alignment in a sample may be determined by comparing the ratio of the maximum G$^+$ peak intensity to the minimum intensity as the laser polarization orientation is rotated. Probing with the same excitation laser wavelength can also produce comparisons between samples.

1.2 Fiber Background

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. These anisotropic requirements are suited to polymers. Fiber spinning involves the following interdependent four steps:
1. Preparing the fiber-forming polymer,
2. Preparing the liquid sample (i.e., dope),
3. Extruding the fiber,
4. Conducting post-processing treatments.

Polymer fibers include polymers that are either rigid or flexible depending upon application. Because of their rigid anisotropic nature, SWNTs are modeled as rigid rod polymers and this research modeled our approach after tested rigid rod fiber spinning techniques.

Fiber-forming dope can be either a melt or a solution. The process of melt spinning requires melting the polymer sample, pressure-driving the extrusion, and cooling it into a solid. However, due to the fact that single-wall carbon nanotubes decompose prior to melting (around 750 °C in air and 2000 °C in an inert environment), melt spinning in not an option. The only viable option is solution spinning. Consequently, this thesis focuses on the solution spinning of SWNT liquid crystals while examining the four steps for SWNT fiber creation.

### 1.2.1 Liquid Crystalline Polymer

Liquid crystals lack the full three-dimensional positional order of a solid but possess the fluidity of a liquid while maintaining long-range molecular orientational order (i.e., they point in the same direction along a common axis, called the director). Molecules which comprise liquid crystals tend to possess some rigidity, while taking either an oblate (disk-like) or prolate (cigar-like) shape. Figure 1.4 outlines the three basic types of liquid crystal systems - nematic, smectic, and cholesteric.
Liquid crystalline polymers are either thermotropic or lyotropic. Thermotropic, as the name suggests, denotes polymers that transition from isotropic fluids to liquid crystals upon temperature changes. As such, thermotropic polymer fibers are melt spun. The liquid crystals in this research are lyotropic, like rigid rod polymers, dissolve in a solvent. Lyotropic polymers are solution spun into fibers.

At high concentrations, rigid rod lyotropic liquid crystalline polymers organize themselves into aligned domains due to their anisotropic geometry and spatial constraints. The rods align parallel to each other minimizing their interactions and increasing their packing density. In most systems, there exists a range of concentrations where two phases coexist. This biphasic system consists of an isotropic phase and a liquid crystalline phase. Some of the rods are in aligned domains while others are in non-aligned domains. Reorientation of the rods can be achieved through elongational or shear flow [Donald et al., 1992].
Polymeric liquid crystalline systems have a distinctive viscosity behavior as a function of applied shear rate. A three-region viscosity vs. shear rate curve is illustrated in Figure 1.5. As the shear rate increases, the viscosity of the liquid crystalline system decreases. At low shear rates, there is strong shear-thinning followed by a region where shearing ceases to influence orientation (a Newtonian plateau). At high shear rates, region III, the molecules become more aligned, greatly packed, and internal friction between molecules is reduced. The viscosity at this region is described by a power law:

\[ \eta = m \gamma^n, \]

where \( \eta \) is the viscosity, \( \gamma \) is the applied shear rate, and \( m \) and \( n \) are constants.

Figure 1.5: Liquid crystalline polymer viscosity vs. shear rate three-region model. Regions I) high shear-thinning; II) Newtonian plateau; III) power law.

Birefringence is a second common characteristic of liquid crystals and is a common first indicator of a liquid crystalline system. A polarized optical microscope reveals that incident polarized white light is transmitted through the liquid crystal sample at different intensities; liquid crystal samples appear as light and dark regions, representing different liquid crystalline domains with various orientations.
Valuable information for fiber spinning can be obtained from the phase diagram for polymeric liquid crystals (Figure 1.7). Understanding the unique rheological and phenomenological characteristics discussed previously, including the *biphasic chimney* which separates the isotropic from the single phase liquid crystal, an appropriate dope can be formulated for fiber spinning from single-phase, well-aligned liquid crystalline samples.

**Figure 1.7: Rigid rod liquid crystal phase diagram.**
Typical phase diagram showing temperature vs. volume concentrations of a rigid rod 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 [Donald et al., 1992].
1.2.2 Fiber Spinning

In order to produce industrial quantities of neat SWNT fibers, solution spinning is the only fluid-based feasible process. Two basic methods for spinning lyotropic liquid crystalline polymers into fibers include pressure-driven extrusion of the dope through varying size orifices (typically 50 - 250 μm in diameter) [Gupta et al., 1997] and are defined by the method of solvent removal and fiber coagulation:

1. Dry-spinning: coagulates fiber by solvent evaporation during fiber spinning in a heated chamber; slower process and spinning speeds achieved than melt-spinning; dopes are typically 15 – 45 wt% polymer solids.

2. Wet-spinning: coagulates emerging fiber filaments in precipitation bath as solvent leaves fiber by diffusing into bath and solidifying fiber; slower extrusion speeds and lower polymer concentrations in dope (5 – 30 wt%).

![Figure 1.8: Three types of fiber spinning.](image)

a) melt spinning, b) dry solution spinning, and c) wet solution spinning [Griskey, 1995].
A modified wet-spinning method, which greatly improves the fiber properties, has been developed for some modern high-performance aromatic polyamide fibers, including aramid fibers like poly p-phenylene terephthalamide (PPTA) and poly p-phenylene benzobisoxazole (PBO). A short air gap between the spinneret and the coagulant surface allows for a low temperature coagulant bath that does not freeze the spinning solution; because the dope can be maintained at higher temperatures, a higher concentration can be spun at reasonable pressures. This modified dry-jet wet spinning process produces PPTA fibers possessing half the strain-to-failure and twice the modulus as wet-jet wet-spun PPTA fibers [Gupta et al., 1997]. The advantage of dry-jet wet spinning is greater alignment among polymer molecules from elongational flow prior to coagulation.

![Figure 1.9: Dry-jet wet spinning technique used to produce aramid fibers.](Gupta et al., 1997)

Solidification by coagulation during wet-spinning is a complicated, critical stage in fiber formation, involving several complex factors, including the polymer type, solvents used, coagulant bath temperature, flow rates, and orifice diameter. The specific coagulant is chosen based on its ability to mix with the dope's solvent, while being incompatible with the polymer (i.e., poor solvent, low diffusion rate); this allows the
coagulant to solidify the constituents which remain after the solvent has drained from the fiber. This mass transfer phenomenon of coagulation, during which the solvent from the dope diffuses into the coagulant bath, creates a skin around the fiber during the extrusion process slowing coagulation of the fiber’s core. Structural stability is thus provided as the skin increases radially during exposure, allowing the application of tension to the fiber line.

\[2\zeta^*\]

**Figure 1.10:** A skin being created around the core of the fiber during coagulation. [Ziabicki, 1976]

The diffusion of the solvent outward from the fiber and the coagulant inward determines the final shape of a fiber’s cross-section. The solvent’s high miscibility with the coagulant and moderate diffusivity out of the fiber [Ziabicki, 1976] creates three potential scenarios as shown in Figure 1.11.
Tension during extrusion is a crucial step toward uniform alignment of a fiber’s internal structure. Known as drawing a fiber, the tension helps align the crystalline structure prior to coagulation. Once a fiber is no longer in its “wet,” deformable stage and is coagulated in a “dry” stage, further alignment of internal molecules is very difficult. Fiber densification is also promoted by drawing the fiber as the solvent leaves improving the fiber’s overall properties.

1.2.3 Fiber Post-Processing

Post-processing of the fiber is the final and key step in enhancing the fiber’s properties. Despite the tension during coagulation, the fiber still possesses internal stresses which will relax over time and weaken the fiber. The fibers are heated in tension in order to relax these internal stresses locking the internal molecules in place to maintain their uniformity and high degree of alignment.
1.2.4 Conventional Fibers

High performance fibers are used in applications requiring superior mechanical, electrical, and thermal properties. Multifunctional fibers which possess two or all three characteristics are the current focus of fiber engineering due to the reduction of costs and space, as well as the improved versatility represented by their implementation. Fibers with high mechanical strength and low weight are desirable for aerospace and security applications. Polymer fibers are inherently good electrical insulators, but can be manipulated with conductive fillers or chemically doped to add conductive properties. Improving thermal properties of a fiber is difficult, but carbon fibers have been identified to be useful in temperature sensitive applications. Ultimately, the cost to benefit ratio is the primary concern when creating or choosing a fiber for a specific application. SWNTs, given their high mechanical, electrical conductivity, and thermal conductivity, are the primary candidate to enhance conventional fibers.

1.2.5 Composite SWNT Fibers

Composites are comprised of two categories of constituent materials: matrix and reinforcement. In all composites, the main development challenges are: a homogenous dispersion of the reinforcement within the matrix; and the surface interaction between the matrix and the reinforcement (load transfer). Developing composites using SWNTs as the reinforcement is particularly difficult because of SWNTs inherent tendency to aggregate due to van der Waals forces [Sandler et al., 1999, Sennett et al., 2003]. Secondly, SWNTs are smooth hydrophobic molecular entities that do not covalently bond to the polymer
matrix limiting the load transfer from the matrix to the individual SWNT [Ajayan et al., 2000, Cooper et al., 2002].

The most notable composite fiber involved SWNTs and polyvinyl alcohol (PVA) was developed by Vigolo et al. [Vigolo et al., 2000]. The SWNTs were dispersed in an aqueous solution of sodium dodecyl sulfate (SDS) via sonication. The SWNT / PVA fibers were produced via a gel-spinning technique, which included extruding the suspension into a 5 wt% PVA (MW 7000) co-flowing stream. The fibers demonstrated intriguing mechanical properties, including: tensile strength, $\tau \approx 150$ MPa; elastic modulus, $Y \approx 9-15$ GPa; and strain-to-failure of 3%. The first generation of SWNT / PVA fibers could also be tied into knots without sustaining damage and possessed an electrical resistivity of $\rho \approx 0.1 \ \Omega \cdot \text{cm}$.

The process continues to garner improvements, such as the post-processing fiber treatment developed by Vigolo et al. which incorporated steps of rewetting and drying under tension [Vigolo et al., 2002], improving both the mechanical properties and internal alignment of SWNTs. Tensile strength doubled ($\tau \approx 300$ MPa) and the elastic modulus of stretched fibers increased to $Y = 40$ GPa.

Dalton et al. [Dalton et al., 2003] have also improved recently the fiber engineering process for SWNT / PVA fibers. The ensuing SWNT / PVA fibers proved to contain less contaminants that those produced by Vigolo et al. although measuring at only 60 wt% SWNTs. On the other hand, the tensile strength of $\tau = 1.8$ GPa and elastic modulus of $Y = 80$ GPa are striking, as are the results that these new and improved SWNT fibers have extraordinary electroactuation and supercapacitance.
1.2.6 Neat SWNT Fibers

In order for SWNT's full properties to be realized on the macroscale, materials and fibers need to be made exclusively from SWNTs and not a constituent of a composite. Composite SWNT fibers, although very promising and applicable to certain situations, are a stepping stone to neat SWNT fibers. The main hurdles of a neat SWNT fiber are availability of starting material and nanoscale manipulation. Although the HiPco process yields a large amount of material, there are problems with differences in batch properties and characteristics. The second hurdle is lack of knowledge regarding handling, modification, and manipulation of individual SWNTs and SWNT bundles in order to acquire the functional neat objects.

Neat SWNT material include buckypaper (tangled mat of randomly oriented large SWNT bundles [Smith et al., 2000]), films [Sreekumar et al., 2002], and fibers. Although studies on neat SWNT buckypaper and films have garnered insight into individual SWNT behavior and manipulation, the resulting materials fall short of providing the mechanical strength and capabilities of a neat SWNT fiber.

Neat nanotube fibers have been produced by two methods: solid-state and solution spinning. Solid-state spinning is similar to the production of yarn and have produced the best mechanical properties for nanotube fibers to date [Kim et al., 2004]. Nanotubes are grown vertically on a substrate (carpet grown) and spun while twisting the nanotube yarn [Zhang et al., 2004]. Although carpet grown nanotubes are longer, and introduce less overall endpoint defects, the individual nanotubes do not coalesce as well with each other as do solution spun nanotubes. Solution spun nanotubes are solubilized in either a surfactant or super-acid and then coagulated into a fiber. Although consisting of
shorter nanotubes compared to solid-state spinning, the solution spun fibers process is readily scalable for industry adaption.

Figure 1.12 illustrates the relationship between longer SWNTs (high aspect ratio) and neat SWNT fiber tensile strength. Perfectly packed fibers consisting of long SWNT (10 \( \mu \text{m} \) in length with 1nm diameter) are estimated to attain the potential failure strength of an individual SWNT [Yakobson et al., 2000]. Solid-state spun fibers produced with long carpet grown SWNTs have high tensile strength but low interbundle connectivity and poor alignment [Kim et al., 2004, Motta et al., 2007]. Solution spun fibers consisting of short SWNT have improved morphology (alignment and packing) but have resulted in low tensile strength [Fan, 2007]. If solution spun fibers consisted of longer constitutive nanotubes, it is logical to conclude that they would have improved morphology and higher tensile strength. This thesis illustrates our attempt to solution spin long HiPco SWNT producing fibers with high tensile strength with improved packing and alignment.
Figure 1.12: Tensile strength of different nanotube fibers as a function of their aspect ratio. A slope of 1 has been drawn through each data point to indicate how tensile strength will scale with nanotube length [Yakobson et al., 2000]. Fiber morphology and coalescence is compared independently from the aspect ratio of the constituent nanotubes [Behabtu et al., 2008].
2 High-Shear Disentanglement of SWNT Bundles

2.1 Introduction

Individual single-walled carbon nanotubes (SWNTs) possess remarkable properties with a Young’s modulus of 1000 GPa [Krishnan et al., 1998], tensile strength above 30 GPa [Walters et al., 1999, Yu et al., 2000], electrical conductivity better than copper (in the case of armchair SWNTs) [McEuen et al., 2002, Tans et al., 1997, Thess et al., 1996], and thermal conductivity comparable to that of diamond [Che et al., 2000, Hone et al., 1999]. Potential SWNT applications span a wide range, from transistors [Seidel et al., 2004] to chemical sensors [Besteman et al., 2003] and, notably, mechanical reinforcement as neat materials [Dalton et al., 2003, Ericson et al., 2004, Vigolo et al., 2000] or polymer composites [Kobashi et al., 2007, Kumar et al., 2002, Moniruzzaman et al., 2006]. The properties of individual nanotubes have not yet been fully realized in neat SWNT materials as well as polymer-SWNT composites, primarily due to inadequate control of the SWNT structure in terms of alignment and packing (for neat materials) or dispersion (for composites), which in turn affect stress transfer in the material [Ericson et al., 2004]. To fully exploit SWNTs’ microscopic properties in neat macroscopic articles, the SWNTs must be processed into a dense, aligned state with good contact between SWNTs; in composites, the SWNTs must be dispersed individually (or nearly so). Here, we describe a pre-processing treatment, termed disentanglement, that facilitates subsequent dispersion of SWNTs into fluid phases. This processing step yields improved and more consistent alignment in acid-spun neat SWNT fibers. The disentanglement process is useful for pre-treating SWNTs for any process involving dispersion in acids.
(such as dispersion in polymer composites). Disentanglement is also a critical step in the formation of uniformly cut ‘ultra-short’ SWNTs for dispersion in polymer composites [Chen et al., 2006] and may be useful for SWNT films [Wu et al., 2004], dispersion in surfactants [Huang et al., 2004], or even dispersion via polymer wrapping [O'Connell et al., 2001, Star et al., 2002, Star et al., 2001].

Due to their high aspect ratio and the strong van der Waals attractions between them, individual SWNTs tend to aggregate into dense, robust, entangled networks of ropes [Liu et al., 1998], usually 10-20 nm in diameter and several microns in length, limiting their solubility and alignment. As such, SWNTs cannot be easily dispersed without some kind of chemical or physical surface modification to prevent this aggregation. Surfactants have been used to help separate and disperse individual SWNTs [Islam et al., 2003], but their use requires sonication and centrifugation at highly dilute concentrations (below 100 mg/L); moreover, fully removing surfactants from the final solid SWNT material is difficult. Superacids such as fuming sulphuric acid and chlorosulphonic acid have been used to disperse SWNTs at high concentrations (over 10 wt%). This technique is successful because the SWNTs become protonated and form charge-transfer complexes of individual nanotubes surrounded by sulphuric acid [Ramesh et al., 2004]. At low concentration, SWNT-acid mixtures are biphasic mixtures of a dilute isotropic phase of well-dispersed SWNTs in equilibrium with liquid crystalline domains with spaghetti-like morphology [Davis et al., 2004, Rai et al., 2005]. At sufficiently high SWNT concentration, these mixtures are liquid crystalline [Davis et al., 2004] and can be spun into continuous fibers [Behabtu et al., 2008, Ericson et al., 2004, Wang et al., 2005] and cast into films [Sreekumar et al., 2002].
SWNTs are wet spun by homogeneously mixing a high concentration of SWNTs into a strong acid, extruding this viscous mixture (termed ‘dope’) through a needle-like orifice into a non-solvent (or ‘coagulant’) where the solvent is removed and the SWNT dope solidifies into a fiber. A similar technique is used to process rod-like polymers such as poly (p-phenylene terephthalamide) PPTA in sulphuric acid into Kevlar fibers [Jiang et al., 1993]. Ericson et al. [2004] mixed 8 wt% SWNTs in 102% sulphuric acid (2 wt% excess SO₃), extruded the SWNT/acid dope through a needle (125-250 μm diameter), and coagulated the dope in water to arrive at a solid neat SWNT fiber. That article and related work [Ericson, 2003] reported that the morphology of the starting SWNT material affects the morphology of the as-spun fiber (Figure 2.1). Specifically, if the starting SWNT ropes are highly entangled prior to mixing in acid and spinning, the spun fibers typically do not attain a well aligned, packed morphology. SWNTs packed into entangled ropes have little mobility, and this hinders their mixing into superacids - possibly yielding a non-equilibrium entangled gel of swollen SWNT ropes rather than a liquid crystal. This structure can hamper reorientation and alignment during fiber spinning. Here we present a scalable disentanglement process that promotes alignment of the SWNTs at the microscale and improves the properties of the resulting macroscopic fiber.
2.2 Experimental Section

SWNTs were produced by the HiPco process [Bronikowski et al., 2001] and purified by multistep gas-phase oxidation in the presence of SF$_6$. The material was then washed in 6M HCl to remove catalyst and non-SWNT carbon [Xu et al., 2005]. This purification method essentially removes all non-SWNT carbon and lowers the metal content of the sample to less than 3 wt%. The purified SWNTs were dispersed at 0.25 wt% in 520 mL of 120% H$_2$SO$_4$ (Alfa Aesar, 20% SO$_3$, density 1.925 g/mL) in a tri-neck round bottom flask and homogenized at high speed (3500 rpm) with a rotor/stator immersion blender for 72 h. To prevent possible shear-induced heating of the SWNTs and potential high-temperature reactions with the acid, the entire mixing apparatus was wrapped with a cooling system that kept the solution at room temperature or below. The system was sealed to prevent SO$_3$ from escaping, with the exception of one flask port connected to a bubbler to release any pressure build-up. After 72 h of homogenization,
the SWNTs were precipitated by coagulating the SWNT/acid solution into ice in a 4L Erlenmeyer flask. This aqueous acidic mixture was thoroughly washed with deionized water and vacuum filtered onto a 5 µm Millipore Durapore® membrane until neutral to remove residual acid. Care was taken to remove all residual acid in the system to prevent potential SWNT oxidation during the subsequent high-temperature vacuum drying. After the filtration, the neutralized SWNTs were immersed in methanol and then diethyl ether in order to remove any residual water from the material; this water-removal step is critical for successful mixing and fiber spinning, since residual water could compromise SWNT protonation and dispersion. The SWNTs were then removed from the filtration apparatus and further dried in a vacuum oven at 85 °C.

During homogenization, samples were taken at progressive time increments (i.e. 5 min, 1 h, 3 h, etc.) up to 72 h, and rheological measurements, optical microscopy, and scanning electron microscopy (SEM) were performed to characterize each sample. Rheological characterization was performed on an ARES (TA Instruments) strain-controlled rotational rheometer [Davis et al., 2004]. Parallel plate fixtures (50 mm diameter) made of Hastelloy C were used to prevent corrosion. An anhydrous environment was maintained by blanketing the sample with a continuous flow of argon in addition to covering the sample surface with an inert, low-viscosity fluid, 25 mPa·s silicon oil. Optical microscopy was performed on a Zeiss Axioplan optical microscope. The SEM samples were water coagulated, neutralized, and placed in a vacuum oven at 85 °C. SEM measurements were performed on a JEOL 6500F thermal field emission electron microscope.
2.3 Results and Discussion

Figure 2.2 shows the effects of the disentanglement process. As-produced (raw) HiPco SWNTs consist of entangled networks (Figure 2.2(a)) of fine, randomly oriented ‘primordial’ ropes 10-20 nm in diameter. This randomly entangled network persists in the purified SWNTs (Figure 2.2(b)) but in a more compact morphology. After disentanglement and coagulation, the SWNTs are locally aligned in ‘super ropes’ of 50 nm or more in diameter (Figure 2.2(c)).

After disentanglement, the SWNTs are readily dispersed into fuming sulphuric acid without the aid of sonication. Figure 2.3 shows a side-by-side comparison of experiments where raw, purified, and disentangled SWNT powders are dusted into 120% sulfuric acid with minimal mixing in an anhydrous atmosphere. After 18 h, the raw and purified SWNTs aggregate whereas the disentangled does not. The presence of iron catalyst particles and fullerenes in the raw sample explains the difference in color between raw and purified. Although the disentangled sample appears lighter in color, it contains the same amount of SWNTs as the other samples.
Immediately After 18 h

Figure 2.3: Raw, purified, and disentangled HiPco SWNT dispersed in oleum. Two photographs of 70 ppm of (a) raw, (b) purified, and (c) disentangled HiPco SWNTs immediately after immersion in 120% sulphuric acid (left) and the same vials after 18 h (right). Both the raw and purified SWNTs aggregate whereas the disentangled SWNTs show uniform dispersion.

The effects of the rotor/stator disentanglement process are compared to a control mixing method where the SWNTs are dispersed at the same concentration and simply stirred with a stir bar rather than being homogenized by the rotor/stator. The difference in morphology between samples disentangled by these two methods is shown in Figure 2.4, which shows SEM images of the coagulated solution. Purified SWNTs are dispersed in 120% H₂SO₄ and homogenized at high speed with a rotor/stator immersion blender for 5 min (Figure 2.4(a)), an hour (Figure 2.4(b)), and 24 h (Figure 2.4(c)). After 5 min (Figure 2.4(a)), the SWNT morphology resembles the morphology of purified SWNT presented in Figure 2.2(b), but the SWNTs are beginning to form larger ‘super ropes’. After 1 h, disentangled super ropes dominate and start to form aligned regions. After 24 h, the
images show large regions of aligned ropes. This is in stark contrast to the simple stir-bar method which results in a morphology (Figure 2.4(d)) that still resembles purified SWNT (Figure 2.2(b)) even after 24 h of stirring.

Figure 2.4: Comparison between stir-bar and rotor/stator methods.
SEM images of coagulated solution samples showing the dramatic change in morphology during disentanglement using the high-speed rotor/stator between (a) the first 5 min and (b) 1 h later. Within the first few minutes of disentanglement, larger rope structures are forming but are still entangled. After an hour, the SWNTs form larger, less entangled continuous ropes. (c) After 24 h, these large rope structures show local alignment. (d) For comparison, instead of the rotor stator, we performed the same experiment with mixing via stir bar for 24 h. The simple stir-bar method does not adequately break up the tightly entangled SWNT aggregates, nor create larger ropes, whereas the rotor/stator method does. The scale bar at the bottom of each image is 100 nm.

Optical microscopy of the two samples (stir-bar method versus rotor/stator method) after 24 h is compared in Figure 2.5. The stir-bar method (Figure 2.5(a)) leaves undispersed material and large aggregates (up to 5 mm) whereas the rotor/stator breaks
up all aggregates and helps to align and coalesce the SWNT domains (Figure 2.5(b)). Birefringence of the rotor/stator sample (Figure 2.5(d)) clearly illustrates large regions of aligned domains as compared to the stir-bar method (Figure 2.5(c)), which shows very little alignment.

Figure 2.5: Optical microscopy images comparing stir bar and rotor/stator disentangled SWNT. Optical microscopy images of HiPco batch 188.3 after 24 h of disentanglement using (a) a stir bar and (b) a high-speed rotor/stator. The sample homogenized by the stir bar appears dispersed but is still entangled, containing visible aggregates and undispersed material. The sample homogenized by the rotor/stator contains aligned thread-like liquid-crystalline ‘spaghetti’ domains and no aggregates. Images (c) and (d) are images under cross polars of (a) and (b) respectively. The scale bar at the bottom of each image is 20 µm.

Rheological measurements confirm a rapid drop in viscosity of the SWNT/acid dispersion associated with the rotor/stator method as compared to that associated with the stir-bar method. After 12 h, the rotor/stator-mixed sample reached a steady state whereas
the viscosity of the stir-bar-mixed sample was four times that of the rotor/stator-mixed sample (Figure 2.6) and remained so even after ten days. The inset of Figure 2.6 illustrates the shear rate in relation to viscosity for the 12 h sample. This representative sample illustrates SWNT shear thinning, a result of the individual SWNT’s high aspect ratio and their arrangement into thread-like, aligned liquid-crystalline domains (dubbed ‘spaghetti’ [Davis et al., 2004]).

![Figure 2.6: Rheological data comparing the stir bar and rotor/stator disentanglement methods. Rheological data (viscosity at a shear rate of 1 s⁻¹ as a function of total disentanglement time) comparing the two disentanglement methods (rotor/stator versus stir bar). The viscosity of the solution homogenized by the rotor/stator method (red) quickly decreases and reaches a steady state after 12 h. The inset illustrates shear thinning of the 12 h sample. Because of their high aspect ratio, SWNTs exhibit shear thinning at all measured shear rates. The viscosity of the solution homogenized by the stir bar method (blue) is four times higher, decreases at a much slower rate, and never achieves the same low viscosity as that of the sample homogenized by the rotor/stator method. The inset shows the shear-thinning behavior of the solution homogenized by the rotor/stator method and is consistent with the formation of liquid-crystalline domains which align with increasing shear rate.](image-url)
Figure 2.7 depicts SEM of fibers spun from the stirbar sample and rotor/stator sample. Again, the morphology of the fiber spun from the disentangled SWNT material shows a substructure composed of much larger SWNT ropes.

![Figure 2.7: SEM images comparing stir bar and rotor/stator fibers.](image)

SEM images of HiPco batch 188.3 after spinning into a fiber [Ericson et al., 2004] using SWNT from the (a) stir bar mixed sample and (b) rotor/stator-mixed sample. Alignment measurements from Raman spectroscopy show a ratio of 5:1 for the stir bar and 13:1 for the rotor/stator. The scale bar at the bottom images (a) and (b) is 100 nm, and the inset scale bar is 30 μm.

Raman spectra are obtained on a Renishaw RamaScope with 785 nm diode laser for the raw, purified, and disentangled SWNTs and are shown in Figure 2.8. The results show that these are undoubtedly pristine single-walled carbon nanotubes with the SWNT-unique radial breathing mode (RBM at 100–300 cm$^{-1}$), the disorder mode (D-band at around 1300 cm$^{-1}$), and the characteristic tangential mode (G-band at 1590 cm$^{-1}$). For all the samples, the intensity ratio (D/G ratio) was less than 1/20, indicating that the SWNT sidewalls were pristine. This suggests that the disentangled SWNTs were neither damaged nor functionalized during the high-shear disentanglement process. (The G-band shifts in the presence of acid; this process is reversible if the acid is removed because the acid imparts a delocalized positive charge rather than covalent functionalization.)
Figure 2.8: Raman spectra of raw, purified, and disentangled SWNT.
Raman spectra (785 nm laser) of raw, purified, and disentangled HiPco batch 188.3 showing that the use of fuming sulphuric acid does not functionalize the nanotubes. Spectra are normalized to the graphite band (G-band at 1590 cm\(^{-1}\)). If the SWNTs were functionalized, the defect band (D-band at 1300 cm\(^{-1}\)) would increase relative to the graphite band. The D/G ratios are less than 1/20, indicating that the SWNT sidewalls are pristine (raw 0.028; purified 0.038; and disentangled 0.024).

Thermo-gravimetric analysis (TGA) also shows typical weight loss associated with purified and disentangled nanotubes (Figure 2.9). There were negligible amounts of water (100 °C) and sulphuric acid (290 °C) as indicated by no significant weight loss at the temperatures associated with these compounds. As stated before, the presence of water hinders protonation of the SWNT and successful fiber spinning, so the elimination of water is critical.
Figure 2.9: TGA of purified and disentangled SWNT.
Thermo-gravimetric analysis (TGA) illustrating weight loss of purified and disentangled SWNT.
Disentangled SWNT used for fiber spinning contained negligible amounts of water (100 °C) and sulfuric acid (290 °C) as indicated by no significant weight loss at these temperatures.

The mechanism of the disentanglement process works as follows. As the rotor spins (Figure 2.10), it draws the SWNTs axially into the dispersion head and creates radial flow through the slots of the rotor/stator arrangement. It is this extensional force, along with the cross forces in the shear gap, that progressively eliminate SWNT entanglements and promote the alignment and coalescence of SWNT domains into larger, aligned structures. This occurs for the following reasons: when SWNT material is placed in fuming sulphuric acid, the acid rapidly diffuses into the ropelike structures, intercalates between the SWNTs, and creates threadlike ‘spaghetti’ liquid-crystalline domains [Davis et al., 2004]; this rapid diffusion process has previously been observed in fiber-swelling experiments [Ericson et al., 2004]. The motion of the nanotubes is mainly restricted to the lengthwise direction of these domains. In the case of purified SWNT samples dispersed
in fuming sulphuric acid, these domains are highly restricted in their relative motion owing to the entanglements, so there is little chance for the domains to disentangle, disperse, align, or coalesce. Thus, little to no change in morphology is observed (as in Figure 2.4(d)). In the case of SWNT samples that are disentangled using the rotor/stator set-up, the kinetics of the liquid-crystalline domains are no longer hindered because the strong viscous forces pull on the spaghetti domains, facilitating the breakup of entanglement points. This not only aids in dispersion, but it also allows the liquid-crystalline domains to reorient, flow-align, and coalesce. When this disentangled sample is coagulated, the morphology shows super ropes that are much larger in diameter than the ropes observed in the starting material, as shown in Figure 2.4. Also, in the purified SWNT material dispersed without disentanglement, optical microscopy shows the presence of densely packed SWNT aggregates; the viscous forces of the disentanglement process breaks these aggregates apart and allows acid to intercalate and disperse the SWNTs. These aggregates are caused by the purification process and can lead to major problems in fiber spinning, so their elimination is essential.

Figure 2.10: Rotor/stator schematic. The high-speed rotation of the rotor automatically draws the SWNTs axially into the dispersion head, forcing them radially through the slots of the rotor/stator arrangement. The flow in the small gap between the rotor and the stator produces strong shearing forces that promote dispersion and alignment of the SWNTs.
2.4 Conclusions

We have developed a treatment method for SWNT material in which the SWNTs are dispersed in superacid and homogenized using a high-shear rotor/stator. Our results show significant changes in the sample morphology without damage to the SWNTs. The high-shear forces align the SWNT liquid crystalline domains in the local direction of flow, allowing for domain coalescence. When coalesced and quenched, the solid SWNT morphology consists of large SWNT ropes; this morphology is reflected in better order and coalescence in fibers spun from the homogenized material. This change in morphology is beneficial for SWNT fibers because improved alignment and improved frictional contact between the constituent SWNTs improve the mechanical properties of the fiber. This technique can also be used to pre-treat SWNTs for processing of SWNT/superacid dopes into aligned films and to aid in the production of ultra-short SWNTs [Chen et al., 2006]. It may also prove useful for the production of surfactant- or polymer-stabilized SWNT dispersions and SWNT/polymer composites.

2.5 Experimental Contributions

My contribution to this work was SWNT purification, disentanglement, coagulation, chemical and physical drying, sample collection, and subsequent fiber formation. Additionally, I designed and tested the apparatus, performed SEM, TGA, and Raman on the SWNTs before, during, and after the experiment and set up the stir-bar experiment. A. Nicholas G. Parra-Vasquez performed rheological measurements whereas Natnael Behabtu performed optical microscopy. Micah Green collected samples; Hua Fan spun D-SWNT fiber; Colin Young collected samples and prepared the apparatus.
3 Fiber Spinning

SWNTs have extraordinary thermal, mechanical, and electrical properties at the nanoscale. If these properties are to be fully utilized, individual SWNTs must be assembled into macroscale products such as fibers and films. In order to cost effectively transfer this technology to market, conventional methods using current industry infrastructure and techniques are explored. A conventional dry-jet wet spinning approach was employed to extrude liquid crystalline SWNTs/superacids solutions into fibers. SWNTs from different High Pressure Carbon Monoxide (HiPco) batches were purified, disentangled, dispersed into a superacid, thoroughly mixed, extruded into a coagulant and dried. Each of these processes had multiple parameters that were isolated and repeated ultimately producing one of the strongest solution spun SWNT fibers.

3.1 Experimental Section

Improved mixing of SWNTs in 100+% H₂SO₄ has necessitated trying different mixing methods, including designing and building a custom-made apparatus (a combination of a mixer and an extruder shown in Appendix B: Mixer Schematics). In order to further explore the fiber spinning process, multiple features were built into the mixing apparatus, and optimal conditions for mixing and spinning were determined through a series of experiments and examination of the resulting fibers. In consideration of a comprehensive assessment of traditional dry-jet wet spinning methods for fiber production, this present study can be divided into several major sections:

1. Pre-processing – includes HiPco conditions, purification, and disentanglement.
2. Mixing conditions – includes concentration of SWNT in sulfuric acid, concentration of super-acid, pre-mixing, and static mixing.

3. Extrusion conditions – includes spinneret choices, drawing, and different coagulants.


3.1.1 Pre-processing

This research exclusively used SWNTs produced via the HiPco process. The properties of each HiPco batch can be adjusted by varying the Fe catalyst flow rate. HiPco batch 187.3 intentionally used half the ordinary amount of Fe catalyst flow rate creating overall longer nanotubes (1 μm) [Carver et al., 2005]. As discussed in Chapter 1, we desire longer SWNTs for fiber spinning to lower the overall endpoint defects.

Raw SWNT material contains considerable amounts of amorphous carbon, metal catalyst particles, and giant fullerenes (> 30 wt%) [Nikolaev et al., 1999]. Chiang et al. [2001] first developed a “soft-baking” process which was designed to remove the metal catalysts and other non-SWNT particles. This old purification process left behind approximately 20% of the metal catalysts. This amount of purified SWNTs, with the catalysts primarily clinging to the side walls of SWNT bundles, didn’t significantly impede the fiber spinning process. However, a large amount of catalysts could potentially prevent SWNT bundles from coalescing to form bigger bundles, which is necessary for the fiber to achieve superior mechanical and electrical properties. Xu et al. [2005] established another purification method for HiPco raw SWNTs, which produced a better carbon yield and lower impurities in the final product (< 4%) through a controlled multi-step oxidation process. Increasing the temperature during this oxidation process may
breakdown and eliminate shorter and smaller diameter SWNT leading to a purified material comprised mostly of long SWNTs. TGA performed on the purified 187.3 batch shows 6.25% ash consisting of oxidized metal in the form of Fe₂O₃.

The fundamental cause for the difference between batches has yet to be discovered. One finding, however, did conclude that the individual purification process has no bearing on the morphological differences. Current beliefs maintain that it is the SWNT growth conditions of the HiPco reactor (i.e., catalyst flow rate and the designs of the reactors) which have the most potential impact on the SWNT Fiber Spinning project's starting material.

SWNTs from different HiPco batches were discovered to be morphologically different from one another when examined by Scanning Electronic Microscopy (SEM). In most of the batches, the SWNT bundles proved to be rather entangled which impeded fiber spinning at high concentrations due to lack of adequate dispersion. In order to properly initiate the fiber spinning process, the purified SWNTs required disentanglement as explained in the previous chapter. Figure 3.1 shows two SEM images comparing purified SWNT to disentangled SWNT of the same HiPco batch, 187.3.
3.1.2 Mixing Conditions

The groundwork by Ericson [Ericson, 2003], Davis et al. [2004], and Fan [Fan, 2007] ascertained that current HiPco SWNT forms a liquid crystalline phase at concentrations between 8 – 10 wt%. Fan was able to spin fibers with SWNT concentrations between 4 – 14 wt% showing that higher concentrations of SWNTs produce better fibers, similar to fibers produced using high concentration liquid crystalline polymers. Higher concentrations also produced fewer defects on the skin of the fiber during coagulation because less acid had to be removed from the fiber during coagulation. Research also conducted by Fan concluded that optimized H$_2$SO$_4$ concentrations were between 102 – 105%. In February 2004, Fan spun HiPco batch 125.4 + .5 (a mixture of batches 125.4 and 125.5) at 8 wt% with 102% H$_2$SO$_4$ resulting in the best solution spun SWNT fibers to date [Ericson et al., 2004].

Premixing 8 wt % SWNT with the 102% H$_2$SO$_4$ prior to introducing it into the static mixer is an important step for homogeneity. Titration was performed on the
superacid prior to premixing to ensure an accurate value of excess SO₃ concentration. In early experiments, the acid and SWNTs were loaded on opposite sides of the static mixer. However, this method did not evenly disperse the acid with the SWNTs; half the SWNTs would be oversaturated with acid whereas the other half would be free of acid. Premixing overnight allowed the acid to intercalate the SWNTs. The SWNT paste during premixing and static mixing was always kept in a portable glove bag with positive pressure from anhydrous gas (Ultra-High Purity Nitrogen) to minimize exposure to moisture. Moisture introduced into the SWNT / acid system could create alewives, discrete entities, hindering coalescence of SWNT bundles during fiber extrusion [Davis et al., 2004].

Figure 3.2 illustrates the static mixer. The premixed SWNT dope was injected into one reservoir and pressed through the static mixer housing into the opposing reservoir. The entire system had a minimal amount of moisture: the reservoirs were oven dried at 100 °C prior to use; the pistons were driven with anhydrous gas; the entire system was sealed in a portable glove bag with positive pressure from anhydrous gas. The dope was mixed thoroughly until mixing pressure reached a steady value (on average, 18 hrs totaling 4500 cycles).
Figure 3.2: Overview of fiber spinning mixer and extruder set-up.
A smaller, simplified version of Fan's "Refined Mixer" [Fan, 2007] and Ericson's "Spinning Bob Mixer" [Ericson, 2003] which uses less SWNT material and less parts for potential moisture exposure. a) Photograph of the static mixer removed from its housing showing length of 1.25 in. b) Cutaway overview drawing of the mixing setup - two axisymmetric piston sections facing each other with a static mixing section in between. c) Close-up cutaway drawing of the static mixer. The mixing section is linked to the piston section via a ball valve used to prevent moisture contamination during extrusion. d) Photograph of extrusion set-up showing a pneumatic valve (top of photo) pushing the SWNT dope through a capillary into a coagulant bath.

3.1.3 Extrusion Conditions

A small extrusion orifice is ideal to promote a uniform coagulation and improved alignment [Ericson, 2003]. We experimented with three types of spinnerets: an extrusion die, a glass capillary, and a stainless steel needle. The extrusion die provided the smallest orifice but would readily become obstructed requiring too much extrusion pressure causing the dope to leak out the sides of the die. A glass capillary was tapered to encourage elongational flow but had a variable orifice leading to inconsistent fiber
diameters. For consistency, we settled on the stainless steel needle with inner diameters of 175 and 250 μm. To aid in uniform coagulation, we used the smaller, 175 μm needle as much as possible. However, this small orifice would become easily clogged requiring that we use the larger diameter 250 μm needle.

The majority of fiber spinning experiments were wet spun by immersing the spinneret directly into the coagulant. However, for batch 187.3, we were able to achieve a dry-jet wet spinning with an air gap up to 7 in. Figure 3.3 illustrates our dry-jet wet fiber spinning into an ice water bath. The purpose of the dry-jet is to create a slowly coagulating region where the fluid filament can stretch promoting fiber alignment. Figure 3.3(d) shows a close-up of the fiber with beads of sulfuric acid accumulating on the surface of the fiber. Slow coagulation and tension on the fiber are ideal environmental conditions to encourage alignment of the internal molecules, whether they are rigid rod molecules or SWNTs.

High quality poly(p-phenylene terephthalamide) (PPTA) fibers spun from sulfuric acid possess better properties at slower coagulations [Rakas et al., 1989]. Wet-spinning had previously shown that defects occur during the exchange of the solvent and coagulant. Slowing down the coagulation process causes the entire fiber to coalesce at a uniform rate. During extrusion, solvent molecules (sulfuric acid) diffuse faster at higher temperatures, which significantly increase the exchange rate. When coagulation is too fast, a skin quickly forms over the wet fiber upon contact with the coagulants; conversely, the inner part of the fiber remains soft due to entrapped acids. As the acid continues to leave the fiber, the skin shrinks and easily distorts the soft interior during coagulation forming a “dog bone” shape [Ziabicki, 1976]. Thus, increased temperatures during
extrusion in the coagulation bath proved to be detrimental to neat SWNT fibers [Fan, 2007]. In contrast, lower temperatures resulted in a slower, more even coagulation process, both internally and externally. This allowed researchers to exercise more control during the extrusion process and resulted in improved fiber alignment and mechanical properties.

Figure 3.3: Fiber spinning with air gap.
a) Disentangled HiPco batch 187.3 8wt% in 102% $\text{H}_2\text{SO}_4$ coagulated in ice water. The dope could withstand enough tension to allow for a long air gap (up to ~7 in air gap). b) The whole fiber was in continuous tension for ~1 min. c) While spinning into ice water, the extruder was stopped and the fiber could hang for ~10 min. d) The sulfuric acid absorbed moisture in the air, squeezing out of the coagulating fiber, forming beads along the surface of the fiber.

Attempts to collect the fiber on a spool were tried after we successfully spun a neat SWNT fiber from a dry-jet. Attaching the fiber’s end to a spinning drum, we drew the fiber as it was extruded at a maximum of 1% draw as shown in Figure 3.4. The fibers from batch 187.3 were drawn continuously for a great length indicating that the SWNT dope was homogeneous.
Figure 3.4: Dry-jet wet spinning of 8 wt% SWNT in 102% H\textsubscript{2}SO\textsubscript{4} into 1% PVA / H\textsubscript{2}O. This fiber was extruded from a 1 in. long spinneret with a 175 \textmu m orifice coagulated in less than 1% PVA / H\textsubscript{2}O solution near 0 °C (ice was removed to not interfere with fiber). This fiber was also drawn at 1% onto a 6 in. metal drum (a) with a 7 in. air gap (c). c) The air gap partially coagulated the fiber from the moisture in the air. The ice cold 1% PVA / H\textsubscript{2}O coagulant provided structural support and slowed down the removal of acid from the SWNT fiber. b) The fiber took a 90° turn when it was fully coagulated.

Various coagulants were used in these experiments including: water, diethyl ether, diluted sulfuric acid, and diluted polymer solutions. The most promising coagulants were ice water and a diluted polyvinyl alcohol (PVA) solution / ice water. Poulin’s group [Vigolo et al., 2000] conducted experiments using PVA solutions (< 0.5 wt%) as a coagulant for extruding high quality neat SWNT fibers with ~40% PVA.

In our experiments, after coagulation, the SWNT fibers were coated with a thin layer of polymer on the surface. There was no noticeable difference in morphology between the PVA-coagulated and water-coagulated fibers. Heating the fibers at 250 °C in
a tube furnace within in inert environment was sufficient to remove the PVA from the SWNT fiber without oxidizing the SWNTs themselves. Correct coagulation conditions yielded low porosity in the fibers, while good alignment united small SWNT bundles, increasing the likelihood for coalescence into larger bundles.

3.1.4 Post-extrusion Processes

After extrusion and coagulation, neat SWNT fibers were collected from the coagulation bath and dried under tension in a vacuum oven at 85 °C for a couple of hours in order to remove residual water from inside the fiber. The quality of the SWNT fiber was confirmed through Scanning Electronic Microscopy (SEM), which provided a qualitative measure of a fiber's overall shape, as well as its degree of alignment along the surface of a fiber. Raman spectroscopy quantitatively measured the alignment of the SWNTs along the fiber axis. A DC 2-point probe was used to measure electrical resistivities for various neat SWNT fiber samples.

3.2 Results and Discussion

SWNT processing (solubility, mixing, and extrusion) appeared to be sensitive to:
(a) initial differences among HiPco tubes across batches; (b) overall morphology of nanotube bundles; and (c) the average tube length. The majority of neat SWNT fibers produced by wet spinning were mechanically weak. However, some HiPco batches produced strong fibers (comparatively). These batches were 125.4 +.5 (a mixture of two batches – some long tubes with short tubes) and 187.3 (half as much catalyst flow rate yielding longer tubes). We also used batch 183.6, which is considered a normal HiPco run with a standard catalyst flow rate.
Among the project's most important challenges was interpreting the morphological changes during the overall fiber spinning process. Different HiPco batches revealed great variations in the morphology of SWNTs directly influencing the spinning conditions and impacting the quality of the fiber. Figure 3.5 compares the morphology between two HiPco batches, 183.6 (unsuccessful spinning) and 187.3 (successful spinning). Batch 183.6 has a very wispy, loose morphology able to form bundles whereas batch 187.3 is entangled and doesn't form large bundles. Although disentanglement and mixing are difficult with longer SWNT, longer SWNT is imperative to making a strong, highly conductive fiber.

Figure 3.5: Comparison of purification, disentanglement, and final fiber between two HiPco batches. SEM images comparing HiPco batch 183.6 (a-c) and 187.3 (d-f). Batch 183.6 was considered a regular HiPco run whereas 187.3 contained half the catalyst flow rate resulting in longer nanotubes. a) Purified 187.3 showed a “wispy” morphology. b) After disentanglement of 183.6, the bundles were several hundred nanometers across. c) The final fiber of 183.6 showed highly aligned bundles but lacked overall coalescence and large voids between bundles. d) Purified highly entangled batch 187.3. e) Disentangled 187.3 was less successful compared to 183.6 resulting in smaller bundles that were more entangled. F) Final fiber of 187.3 shows an overall smoother surface and greater coalescence between individual SWNT bundles. All images were at the same magnification with a scale bar of 100 nm.
Fan spun strong fiber [Fan, 2007] attributing his success with the “wispy” morphology of the HiPco starting material shown in Figure 3.6(a). We spun a fiber with similar characteristics but the morphology of the starting material is greatly different than Fan’s. Although we disentangled batch 187.3 (as shown in Figure 3.5(e) at X 50,000), the overall morphology at a lower magnification (X 10,000) is very entangled as shown in Figure 3.6(b). The longer tubes of batch 187.3 have lower solubility; therefore, disentanglement is difficult and results in the entangled starting material of Figure 3.5(e). Although entangled, this starting material was processed with the proper amount of excess SO₃ (2%) allowing enough solubility to be thoroughly mixed. The excess SO₃ was not raised further to avoid violent reactions during coagulation, which hinder coalescence of the SWNT during fiber production.

Figure 3.6: SEM images comparing two different HiPco batches.
SEM images of two different HiPco batches of starting material used for fiber spinning. a) Purified HiPco batch 125.4 + .5 Dr. Fan used for February 2004 fiber spinning. Note the wispy, untangled morphology of the SWNT. b) Disentangled HiPco batch 187.3. Note that D187.3 did not produce large bundles as compared to the previous batch of D186.3. The scale bar in both images is 1 μm.

Figure 3.7 shows a side-by-side comparison of the spun fiber from HiPco batches 125.4 + .5 and 187.3. Batch 125.4 + .5 showed great mechanical strength (47 MPa) but the morphology of the fiber contained small, aligned fibrils containing a large amount of
voids and little overall coalescence (Figure 3.7 a and b). Batch 187.3 showed great coalescence (Figure 3.7(c)) but poor alignment at higher magnification (Figure 3.7(d)). Longer nanotubes, and the entanglement of these nanotubes, contributed to this particular fiber’s mechanical strength.

Figure 3.7: SEM comparison between two neat SWNT “good” fibers. SEM images comparing HiPco batches 125.4 + .5 (a and b) to that of 187.3 (c and d). a) Dr. Fan’s fiber contained 8 wt% SWNT in 102% H$_2$SO$_4$ extruded through a stainless steel needle 125 μm (12 February 2004). b) The fiber’s morphology contains large, uncoalesced bundles of SWNTs aligned along the axis. c) This fiber also contained 8 wt% SWNT in 102% H$_2$SO$_4$ extruded through a stainless steel needle with an orifice of 175 μm (5 March 2008). Although this fiber was extruded through a larger orifice, its diameter is similar to the 125.4 + .5 fiber. This particular fiber was drawn during extrusion compressing the SWNT bundles together giving a similar diameter compared to 125.4 + .5. d) Magnification of the fiber shows a uniform appearance with few voids but little coalescence and alignment.

The fiber’s tensile strength and Young’s Modulus were determined using an Instron 1000 with a 10N load cell. The results are listed in Table 3.1 below. The fiber’s
strength is limited by the presence of localized defects and voids making the modulus a better indicator of mechanical performance. It is important to note that these fibers were not annealed. In Fan’s thesis [Fan, 2007], he annealed this particular fiber in H₂ / Ar at 850 °C at 1 atm for 1 hr and again at 1100 °C in vacuum. This annealing increased 125.4 + .5 fiber’s tensile strength from 47 MPa to 116 MPa and a Young’s Modulus from 30 GPa to 120 GPa. Generally, annealing has led to approximately four times increase in modulus and three times increase in strength. The strongest 187.3 fiber we tested had a tensile strength of 375 MPa which is an eight times improvement over Ericson’s Science paper [Ericson et al., 2004]. Additionally, the Young’s Modulus of this same fiber is twice an improvement (64.5 GPa vs. 30 GPa) of Ericson’s Science paper. It is important to note that these fibers were dried in a vacuum oven under tension; not annealed. In previous experiments, annealing has led to an increase in a factor of three in strength and an increase in a factor of four in modulus. In comparison, laboratory-grade PBO fibers possess a tensile strength of 2.6 GPa and a Young’s modulus of 138 GPa [Kumar et al., 2002].

<table>
<thead>
<tr>
<th>Fiber: dope, coagulant, needle size (non-annealed)</th>
<th>Tensile Strength (MPa)</th>
<th>Young's Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 wt% Sulfuric, Ice Water, 175 μm</td>
<td>131.8</td>
<td>22.5</td>
</tr>
<tr>
<td>8 wt% Sulfuric, 1% PVA in Ice Water, 175 μm</td>
<td>375</td>
<td>64.5</td>
</tr>
<tr>
<td>8 wt% Sulfuric, 1% PVA in Ice Water, 175 μm</td>
<td>283.4</td>
<td>46.8</td>
</tr>
<tr>
<td>8 wt% Sulfuric, 1% PVA in Ice Water, 175 μm (ave)</td>
<td>329.2</td>
<td>55.7</td>
</tr>
<tr>
<td>125.4 + .5 8 wt% Sulfuric, Ice Water, 125 μm</td>
<td>47</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 3.1: Mechanical Properties of Neat SWNT Fibers.
Mechanical properties of spun fiber using different conditions (solvent, coagulant, and spinneret size). Except were noted, all fibers used the same HiPco batch 187.3 and were as-spun (non-annealed). The tensile strength and Young’s modulus of the PVA coagulated fibers were double that of ice water coagulated fibers. The strongest fiber in this experiment was 8 wt% 102% H₂SO₄ in diluted (< 1%) PVA / Ice Water using a 175 μm needle. This fiber (187.3) had eight times the tensile strength and twice the modulus of HiPco batch 125.4 + .5 (in red) as reported in Science [Ericson et al., 2004].
SEM images were taken of each fiber’s failure points revealing the internal morphology (Figure 3.8). Fan’s 125.4 +.5 fiber shows large internal voids but generally good alignment of SWNT. The 187.3 fiber shows fewer voids but better overall alignment. Both fibers are circular and exhibit fiber pullout morphology with no clean breaks.

Figure 3.8: SEM comparison between two neat SWNT fibers failure points. SEM images of the fiber’s failure point during tensile testing for HiPco batch (a) 125.4 +.5 and (b) 187.3. a) The 125.4 +.5 fiber is circular compared to other fibers during this period which were dog bone shaped (coagulated in diethyl ether). Although most SWNT bundles are going in the same direction, there are a lot of voids on the surface and internally. b) The 187.3 fiber was also circular with the SWNTs going in the same direction. However, this fiber had fewer voids and was more compact than 125.4 +.5. The scale bar for both images is 10 µm.

The 187.3 fiber was coagulated not only in ice water but also in a diluted (< 1%) PVA / ice water bath. SEM images reveal similar morphological characteristics between the two coagulants at high magnification (X 50,000). Figure 3.9 shows ice water coagulated fiber (a and c) and PVA / ice water coagulated fiber (b and d). The fiber at the macroscale (X 1,500) showed greater voids in the PVA coagulant (b) than the ice water coagulant (a). This is probably a result of how the fiber was drawn during coagulation more than the actual coagulation bath. The ice water coagulated fiber may have been drawn at a specific rate resulting in the current morphology compared to the PVA
coagulated fiber. Logically, the PVA should slow down the coagulation rate resulting in fewer voids. Both fibers were dried under tension in a vacuum oven at 85 °C. Most of the PVA that coated the fiber was burned off during this drying process. It is important to note that the PVA / ice water coagulant did not drastically affect the fiber’s resistivity as noted in Table 3.2. The resistivity of the PVA coated fiber was only a factor of three higher than the water coagulated fibers.

Figure 3.9: SEM comparison between fibers that were coagulated in H₂O and PVA. SEM images of a fiber from the same batch (187.3) coagulated in ice water (a and c) and diluted PVA / ice water (b and d). a) This fiber was drawn prior to and during coagulation in ice water. This fiber’s skin has very smooth morphology. b) The diluted PVA / ice water fiber was not drawn during this experiment resulting in a wrinkled fiber with many voids. The scale bar for both a and b is 10 μm. c) Ice water coagulated fiber magnified (X 50,000) shows a similar morphology to the diluted PVA / ice water fiber shown in (d). The scale bar for both c and d is 100 nm.
Raman spectroscopy was used to compare the ratio of the maximum G+ peak intensity to the minimum intensity on each fiber. This measurement is used to gauge the overall alignment of SWNTs in the fiber. Table 3.2 lists the Raman ratio for each fiber. Although the 187.3 fiber was mechanically strong, its Raman ratio was surprisingly low compared to the 125.4 + .5 fiber. This information, as well as the SEM images, leads me to believe that the individual SWNTs were entangled causing the mechanical strength.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Raman Ratio</th>
<th>Resistivity (mΩ-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 wt% Sulfuric - Drawn in Water 65 °C</td>
<td>5.7</td>
<td>0.94</td>
</tr>
<tr>
<td>8 wt% Sulfuric - Dry-Jet Wet Draw in Ice Water</td>
<td>4.0</td>
<td>0.87</td>
</tr>
<tr>
<td>8 wt% Sulfuric - Ice Water</td>
<td>3.0</td>
<td>2.96</td>
</tr>
<tr>
<td>8 wt% Sulfuric - Drawn in RT Water</td>
<td>4.5</td>
<td>1.1</td>
</tr>
<tr>
<td>8 wt% Sulfuric - PVA Drawn in RT water; Stretched</td>
<td>4.4</td>
<td>3.12</td>
</tr>
<tr>
<td>125.4 +.5 8 wt% Sulfuric, Ice Water, 125 µm</td>
<td>28</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 3.2: Alignment and Resistivity Measurements. Raman spectroscopy and resistivity measurements were taken for various fibers. All fibers are from batch 187.3 unless otherwise indicated. Although strong, the Raman ratio of the recently spun fibers was significantly lower compared to the 125.4 +.5 fiber indicating poor SWNT alignment of the 187.3 fibers. The resistivity of the PVA coagulated fiber was not significantly greater than the other water coagulated fibers. We conclude that PVA coagulation, in addition to drying to remove the PVA, did not drastically negatively impact the resistivity of the SWNT fiber.

Dr. Duque performed experiments determining the luminescence properties of individual SWNTs [Duque, 2009]. In these experiments, Dr. Duque confirmed that a HiPco batch with twice as much Fe catalyst flow rate (187.4) contains SWNTs with smaller diameters than SWNT from batches with an average catalyst flow rate. This is also consistent with results from Carver et al. [Carver et al., 2005]. In contrast, the batch that we used for our fiber experiments (187.3) had half the catalyst rate of an average batch presumably making longer tubes with larger diameters that were ultimately less soluble. Longer tubes with greater surface area coalesce better because of their length which contributed to the difficult disentanglement and stronger fibers.
3.3 Conclusion

Three parameters that greatly influence the quality of neat SWNT fibers are: properties of specific HiPco batch; concentration of SWNTs in the superacid; and the superacid concentration. HiPco batch 187.3, produced with a low Fe catalyst flow rate, had a longer than average SWNT length resulting in entangled SWNTs promoting mechanical strength in the fiber. These longer nanotubes influence the solubility of the batch as a whole impacting the SWNT concentration and superacid concentration parameters needed to produce a strong fiber. Although we believe that a SWNT concentration of 8 – 10 wt % and a superacid concentration of 102 – 105% H₂SO₄ are the optimal ranges, further studies are necessary to determine the exact parameters for a given HiPco batch.

3.4 Experimental Contributions

My contribution to this work was SWNT purification, disentanglement, coagulation, chemical and physical drying, sample collection, and subsequent fiber formation. Additionally, I designed and tested the apparatus, performed SEM, TGA, and Raman on the SWNTs before, during, and after the experiment. Hua Fan assisted in original fiber spinning and design. Natnael Behabtu performed tensile testing; Colin Young assisted in preparing the samples and fiber spinning.
4 Conclusion

This thesis presents two processes that improve neat SWNT fiber spinning: disentanglement and dry-jet wet spinning. Disentanglement increased SWNT mobility and alignment into large SWNT bundles. These larger aligned bundles improved SWNT processing into fibers as well as SWNT films and uniform SWNT cutting techniques. The neat SWNT fiber project combined novel materials with traditional processing techniques. A dry-jet wet spinning technique used to spin rigid-rod polymers into fibers was applied to SWNTs greatly improving the neat SWNT fiber's mechanical properties.

Disentanglement shows significant changes in SWNT morphology without damaging individual SWNTs. Two dramatic morphological changes occur after the disentanglement process: SWNT bundle sizes increase tenfold; and SWNT alignment is improved. Aligned primordial ropes coalesce into larger bundles, an energetically favorable, automatic process. The high-shear forces of the disentanglement rotor/stator align the SWNT liquid crystalline domains in the local direction of flow, allowing for domain coalescence. This change in morphology is beneficial for SWNT fibers because improved alignment and improved frictional contact between the constituent SWNTs improve the mechanical properties of the fiber. Increased bundle size eases dispersion allowing for uniform cutting when applied to the production of ultra-short SWNT [Chen et al., 2006]. Disentangled SWNT may also allow for greater dispersion when applied to aligned SWNT films and SWNT/polymer composites.

Dry-jet wet spinning neat SWNT fibers resulted in a threefold improvement in tensile strength over previous wet spun neat SWNT fibers. Drawing the fiber prior to coagulation to assist in improving morphology (alignment and packing) is a great
development. This proved that SWNTs could continue to be treated as a rigid-rod polymer and solution spun into a fiber. A PVA / ice water (< 1%) coagulant also improved the fiber’s mechanical strength without dramatically affecting the fiber’s electrical properties.

The quality of the SWNT fiber is largely dependent upon HiPco starting material and varied between HiPco batches. Continued refinement of the HiPco process is needed in order to create reproducible starting material consisting of mostly long SWNT. Further experiments need to be designed to determine optimal HiPco batch characteristics. The motivation in designing these experiments is the long turn around time for spinning fibers. It takes approximately one month for each fiber spinning consisting of purification of raw HiPco SWNT, disentanglement, fiber spinning, and characterization. Experiments designed to identify ideal HiPco starting material should be a priority in order to cut down turn around time and eliminate variability in HiPco SWNT. One such experiment is measuring the solubility of the HiPco SWNTs in a particular superacid. Generally, the higher the solubility, the better the SWNT mobility resulting in a highly aligned neat SWNT fiber.

Although not extensively studied for this thesis, it is my observation that both the concentration of the SWNTs in the superacid (8 - 10 wt%) and the superacid concentration (102% H₂SO₄) play important roles in coagulation and resultant quality of the fiber morphology and mechanical strength. I believe there to be an optimal SWNT concentration and superacid concentration specific to each HiPco batch which provides enough SO₃ protonation to allow for adequate SWNT mobility and slow enough coagulation to produce highly aligned, densely packed neat SWNT fibers. Additionally,
individual SWNT diameters, defect density, and average SWNT lengths may also play a part in how SWNTs interact during fiber formation. However, it is unclear at this point to what extent these variables affect the final fiber.

Post-processing experiments involving drawing and annealing the SWNT fiber are the next logical steps in improving the fiber's mechanical strength. The dry-jet wet spinning and fiber collection under tension were the first steps in drawing the fiber. Drawing the fiber continuously while spinning further aligned and densely packed the SWNTs within the fiber. Future experiments could include increasing the draw ratio during collection. Annealing the fiber under tension at high temperatures in an inert atmosphere to remove residual water and acid has shown to quadruple the Young's Modulus but has little impact on the tensile strength [Fan, 2007]. Annealing also improves the crystallinity of the SWNT bundles inside the fibers.

The successful reproducible demonstration of dry-jet wet spinning neat SWNT fibers makes us closer to achieving a highly conductive, mechanically strong, atomically perfect fiber. As the discovery of nanotubes approaches the 20 year mark, we are closer to fully understanding their characteristics and finding suitable applications to improve our lives. The work in this thesis contributes to one application that could greatly impact aerospace materials, law enforcement protection, and energy distribution.
Appendix A. Rotor / Stator Schematics

The rotor / stator design was based upon commercially available homogenizers. We modified certain parts to increase performance and lower costs. The material used was a noncorrosive stainless steel (SS 316) which withstood the high SO₃ concentration of our superacid +100% H₂SO₄. Commercial motors that we initially attached to our rotor / stator had a short lifespan due to the corrosive, acidic environment as well as the long usage time. We finally settled on an enclosed AC motor.

Figure A.1: Rotor / stator’s head diagram.

Figure A.2: 3-D representation of the rotor / stator’s head.
Figure A.3: Rotor shaft.

Figure A.4: Stator shaft.
Figure A.5: Flask cap for rotor / stator.

Figure A.6: Photograph of rotor / stator a) disassembled and b) assembled.
Figure A.7: a) Assembled apparatus in round bottom flask. b) Rotor / Stator head.

Figure A.8: Assembled apparatus attached to AC motor in a cooling bath.
Appendix B. Mixer Schematics

This mixer design is a simplified, smaller extension of both Ericson’s [Ericson, 2003] and Fan’s [Fan, 2007] designs. Instead of Ericson’s multifunctional Spinning Bob Mixer (SBM), we kept this design inline through a single static mixer (Figure B.5), a mixer typically used in the chemical industry for its safe use in hazardous conditions. This mixer is also a third the size of Fan’s mixer using less starting material allowing for more experiments with different conditions. The mixer and parts were SS316 to resist corrosion by the high concentration sulfuric acid.

Viton® O-Rings were used on both static and dynamic parts of the mixer providing a good seal of the system in light of the caustic acid. The spinneret was 1 in. long needles created from Upchurch Scientific tubing with an inner diameter varying from 175 and 250 μm. The smallest tube was generally chosen for three reasons: 1) to maximize the length of the extruded fiber; 2) to provide high shear rate on the dope; and 3) to promote a uniform coagulation (i.e. the acid could leave the inside of the fiber easier if there was less distance to the surface).

Alewives, discrete entities formed when acid suspended SWNTs are exposed to water, hinder coalescence of SWNT bundles weakening fiber properties. To combat this problem, the SWNT paste during mixing was always kept in a portable glove bag with positive pressure from anhydrous gas, minimizing the chance of being contaminated by moisture.
Figure B.1: Photo of static mixer (approximately 1.25 in) along with flow diagram. [http://www.admix.com/admixer_how.htm]

Figure B.1: Mixer reservoir schematic.

Figure B.2: Mixer piston schematic.
Figure B.3: Reservoir end cap schematic.

Figure B.4: Reservoir end cap and static mixer housing schematic.
Figure B.6: 3-D images of entire assembled mixer.

Figure B.7: Photo of operating mixer sealed in an inert environment.
5 References


