I, Anli Wang, hereby submit this original work as part of the requirements for the degree of Master of Science in Mechanical Engineering.

It is entitled:
Spinning Methods for Carbon Nanotube Fibers

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Spinning Methods for Carbon Nanotube Fibers

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Abstract

Carbon nanotubes (CNTs) have excellent properties along the tube axis. Although the material has fantastic properties at nano scale, it has proven difficult to assemble CNTs into macro-scale products that retain these properties. This thesis investigates different methods for spinning short CNTs into continuous fibers.

The first part of the thesis concentrates on the study of dry spinning techniques. CNT fibers can be produced from spinnable arrays. It is found that CNT length plays an important role in the strength of CNT fibers. However, long CNT arrays are usually not spinnable. Alternative ways to spin long CNTs into fibers were exploited. One way is to assemble these long CNTs with the aid of liquid. The obtained fiber has high electrical conductivity by using annealed CNTs but low strength. Another way explored is to make a long CNT array spinnable by binding the ends of CNT bundles in the array.

Besides dry spinning, wet spinning methods were also applied to spin CNT fibers. One way of wet spinning to produce CNT fibers is through coagulation of CNT dispersions in a polymer bath. Parameters involved in the spinning process and post treatments were studied. A possible mechanism of the coagulation was given. Process of another method is to add CNTs in a polymer solution and wet spin the polymer. Polyvinyl alcohol (PVA) is used as the matrix polymer and several baths were investigated. Addition of CNTs in PVA solution improves strength of the fiber when CNT are well dispersed. Properties of these fibers were dominated by the polymer.
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Chapter 1  Introduction

Carbon nanotubes (CNTs) have received great research interests since their discovery by Iijima in 1991 [1]. This is primarily due to their unique structure that exhibits significantly superior material properties as compared to existing materials, for instance, enhanced mechanical strength, high electrical and thermal properties. These superior properties have been widely validated by theoretical and experimental investigations by a great number of researchers [2–7]. However, the key challenge is to make macro-scale products with these unique advantages.

Numerous efforts have been directed to study and exploit these superior properties of CNTs. For example, high current density of CNTs has been validated by experiments [8], which made CNTs a promising candidate of interconnect in microelectronics [9]. Idea of designing smart nano-actuator using the CNTs was demonstrated [10]. Application of CNTs as an oscillator was proposed by Zheng et al., which can operate efficiently up to frequency range of gigahertz due to the low friction coefficients of CNTs [11]. Furthermore, CNT based macroscopic materials have been investigated extensively. Both neat and composite CNT products have been made in forms of fibers, films and aerogel [12–17]. CNT film based touch screen [18] and speaker [19] have been demonstrated. CNT fibers as electrical wires is promising as they are lighter and stronger compared with copper wires.

Recently, CNT fibers have been an active research area. CNTs have the great potential to yield fibers with superior electrical and thermal properties, as they has high aspect ratio, high tensile strength and stiffness, and low density. Spinning is an important technique in making long CNT fibers using relatively short CNTs, which needs to be investigated systematically. The objective of this thesis is to develop several spinning techniques that can be applied to make CNT
fibers with super mechanical properties. The spinning techniques should be scalable so that they can be potentially employed in making large quantity of CNT fibers for fabricating CNT composites. In the following section, a literature review on CNT properties and several spinning techniques for CNT fibers is given.

1.1 Synthesis of CNTs

Three main methods of synthesizing CNTs have been developed, namely, arc discharge, laser ablation, and chemical vapor decomposition (CVD) [20]. Arc discharge and laser ablation use high temperature and thus produce CNTs with fewer structural defects. CVD techniques are inexpensive and produce large quantities of high yield and purity, compared to the other two methods [21].

Arc discharge is a high temperature synthesis method. For a common arc discharge method, DC arc discharge is used between two graphite electrodes. Then they are put in a chamber filled with inert gas. Single-wall carbon nanotubes (SWNTs) can be produced with transition metal catalysts, and multi-wall carbon nanotubes (MWNTs) are usually produced without the present of catalysts.

Laser ablation is similar to arc discharge excerpt that laser provides the energy to the mixture of graphite and catalysts. SWNTs grown from laser ablation have high quality and high purity.

CVD techniques have dominated the production of CNTs. Nanoparticle catalysts with diameter smaller than 3 nm can be used to synthesis SWNTs. Larger catalysts promote the growth of MWNTs. Catalysts can be either put on a substrate or sprayed into the furnace. High pressure carbon monoxide (HiPco) process is one of CVD techniques that produce high quality SWNTs.
1.2 Structure of CNTs

A CNT has the shape of a hollow cylinder with caps on each end. It can be considered as a cylinder made by rolling up several layers of graphite. The layer is often called the wall of a CNT. As shown in Figure 1-1, CNTs can be divided into different types in terms of the number of their walls, for example SWNTs, double-wall carbon nanotubes (DWNTs), triple-wall carbon nanotubes (TWNTs) and MWNTs. Typically, the tube diameter is a couple of nanometers for SWNTs and tens of nanometers for MWNTs. The length of CNTs varies from nanometer to centimeter. Aspect ratios of CNTs are usually very high.

![TEM images of (a) a DWNT and (b) a MWNT.](image)

Figure 1-1. Transmission electron microscope (TEM) images of (a) a DWNT and (b) a MWNT. Inter-wall distance is about 0.34 nm [22].

The direction of rolling up the graphite layer determines the structure of a SWNT. An illustration of rolling direction is shown in Figure 1-2. The direction can be represented by the chiral vector $\mathbf{C}_h$. The beginning and end of the vector $\mathbf{C}_h$ join together when the graphene sheet is folded into a CNT. Based on the chiral vector, SWNTs are classified to be armchair, zigzag, and
chiral. A SWNT behaves as a conductor if it has the armchair structure and it will behave as a semi-conductor for other structures [23]. However, it has been shown that curvature of small diameter CNTs could induce re-hybridization of electron orbital and may change the type of conductance [24].

Figure 1-2. Illustration of rolling direction for CNTs [20].

1.3 Properties of CNTs

As we are interested in CNT fibers, it is important to know the properties of CNTs that constitute the fiber. Many studies on mechanical, electrical and thermal properties of CNTs have been reported in the last twenty years. Studies on CNT properties are reviewed here.

1.3.1 Mechanical Properties

Measurement of individual CNTs has proved challenging due to extremely small size of CNTs. At first, individual CNT properties were estimated by testing small CNT bundles under
scanning electron microscope (SEM) [25,26]. Tensile properties of individual CNTs was first measured by Yu et al. [27]. Figure 1-3 illustrates their method. A CNT is deposited between a soft atomic force microscope (AFM) cantilever and a rigid AFM cantilever. By calibrating the force constants of the soft AFM cantilever, breaking force of a CNT can be derived from the deformation of the soft AFM cantilever. Later a direct force measurement setup was developed [28]. In Nanoworld Lab at the UC, average strength of 2.4 GPa for small twisted CNT bundles were obtained using force measurement system under SEM [29]. However, testing on individual CNT has not been achieved yet.

It was found that CNTs have two main failure modes in the tests. One is clean breakage. The other is sword-in-sheath type [31]. These two failure modes are illustrated in Figure 1-4. It was reported that the clean breakage usually happens in low-quality tubes, while high-quality CNTs tends to have sword-in-sheath type failure [32].

Figure 1-3. Illustration of CNT strength measurement with ATM cantilevers [30].
Numerous research efforts were driven to measure the tensile strength of individual CNTs [27,28,30,31,33–36]. Findings by previous researchers are collected and analyzed here. Note that strengths reported in literature are usually effective strengths, which are calculated from the area of walls. Engineering strength of individual CNTs uses the whole cross section as the area. Table 1-1 gives an overview of mechanical properties of CNTs from the literature. From the table we can see that engineering strength is much lower than effective strength. Effective and engineering strengths of individual CNTs are shown in Figure 1-5 and Figure 1-6, respectively. From the two figures, we can see clearly that engineering strength is lower, especially for larger diameter CNTs. Effective strengths are in the range of 10 – 140 GPa with a mean value of 46 GPa, while engineering strengths have a mean value of 16 GPa. In addition, effective strengths show low correlation of the diameter, but engineering strength of CNTs decreases with the diameter. CNTs with diameter larger than 10 nm typically have strength lower than 10 GPa.
Table 1-1. Mechanical properties of individual CNTs measured experimentally in the literature

<table>
<thead>
<tr>
<th>CNT type</th>
<th>Effective Strength&lt;sup&gt;a&lt;/sup&gt; (GPa)</th>
<th>Engineering Strength (GPa)</th>
<th>Young’s Modulus (GPa)</th>
<th>No. of Samples</th>
<th>Synthesis method</th>
<th>Year/Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT</td>
<td>33</td>
<td>2.1</td>
<td>−−</td>
<td>7</td>
<td></td>
<td>2000 [27]</td>
</tr>
<tr>
<td>MWNT</td>
<td>−−</td>
<td>150</td>
<td>910</td>
<td>1</td>
<td>arc grown</td>
<td>2002 [28]</td>
</tr>
<tr>
<td>MWNT</td>
<td>110</td>
<td>−−</td>
<td>−−</td>
<td>26</td>
<td>CVD</td>
<td>2005 [37]</td>
</tr>
<tr>
<td>MWNT</td>
<td>16</td>
<td>0.2</td>
<td>−−</td>
<td>1</td>
<td></td>
<td>2005 [36]</td>
</tr>
<tr>
<td>MWNT</td>
<td>24</td>
<td>3</td>
<td>955</td>
<td>14</td>
<td>arc grown</td>
<td>2007 [30]</td>
</tr>
<tr>
<td>MWNT</td>
<td>108</td>
<td>8</td>
<td>1048</td>
<td>3</td>
<td>arc grown</td>
<td>2008 [31]</td>
</tr>
<tr>
<td>DWNT/TWNT</td>
<td>28</td>
<td>13</td>
<td>1070</td>
<td>11</td>
<td></td>
<td>2009 [34]</td>
</tr>
<tr>
<td>SWNT</td>
<td>79</td>
<td>45</td>
<td>−−</td>
<td>12</td>
<td></td>
<td>2010 [33]</td>
</tr>
<tr>
<td>MWNT</td>
<td>−−</td>
<td>48</td>
<td>−−</td>
<td>−−</td>
<td></td>
<td>2011 [35]</td>
</tr>
</tbody>
</table>

<sup>a</sup>: the area for effective strength is calculated using the equation \( A = \frac{\pi}{4} (OD^2 - ID^2) \). In literature it is calculated by the equation \( A = t \cdot \pi \cdot OD \). Results of the two calculation methods have large difference in small diameter CNTs. Here \( OD \) stands for outer diameter, \( ID \) is the diameter of inner tube, and \( t = 0.34 \text{ nm} \) is the wall thickness.

Figure 1-5. Effective strength of individual CNTs (data from Refs: [27,30,31,33,34]).
Effective strengths of majority individual CNTs in literature are not as strong as that ideally expected. One reason for low strength is the defects on the walls of CNTs. It was reported that defects reduced the effective strength [38]. Chirality of CNT also plays a significant role in the strength. Simulation results show that an armchair SWNT is about 20% stronger than a zigzag SWNT [38,39]. Experiment conditions could also have contributed to the low strength. Electron beams in SEM/TEM may induce heating in the testing environment and may damage the wall of CNTs [40].

As for low engineering strength, one important reason is that MWNTs tend to have sword-in-sheath failure [31], due to weak interactions between the walls. Force needed to extract inner walls of MWNTs was measured be 3~5 $nN$ [41–43], while average force to break a SWNT is 183 $nN$ [33]. Figure 1-7 (b) shows that the relation between the extraction force and the distance. Irradiation can be used to connect walls of MWNTs and enhance the interactions between walls, and thus improve the engineering strength of CNTs [31].
1.3.2 Electrical Properties

Individual CNTs have good electrical properties such as high electrical current density and superconductivity. Current density of a CNT is determined by electrical breakdown of the CNT. The electrical density of SWNT was reported to be up to $10^9$ A/cm$^2$ [8]. Defective MWNTs are reported to have a resistivity of order of $10^{-4}$ Ω · m, which is much lower than copper, but they have a maximum electrical density up to $10^6$ A/cm$^2$, which is comparable to that of a copper [44]. CVD-grown MWNTs have electrical density in the order of $10^7$ A/cm$^2$ both in the air and vacuum [45]. The ability to carry high electrical density makes CNTs a great potential to be used as interconnects in microelectronics.

Experimental studies show that metallic SWNTs and some MWNTs superconductivity with transition temperatures at 15~18 K [46–48]. Ballistic transport in axial direction of CNT was experimentally observed in short CNTs [6]. However, large contact resistance of CNTs remained a hinder to exploit electrical conductivity of CNTs [9]. Typically neat CNT fibers have electrical resistivity on the order of $10^{-5}$Ω · m. To date the best electrical conductivity of CNT fibers
reported is $2 \times 10^{-7} \Omega \cdot \text{m}$ [49], which is one order of magnitude lower than that of copper ($1.7 \times 10^{-8} \Omega \cdot \text{m}$).

### 1.3.3 Thermal Properties

CNTs have an anisotropic structure. Thermal conductivity along the tube axis is very high. SWNTs were theoretically predicted to have high thermal conductivity (6600 W/mK for armchair SWNTs, 950 W/mK for armchair SWNT bundles) [3,5]. While thermal conductivity is much lower in the direction perpendicular to the tube axis (theoretically calculated to be $\sim 5$ W/mK) [5].

The measurement of thermal conductivity of CNTs along the axis was first realized on CNT bundles. Thermal conductivity of a SWNT bundle was reported to be around 30 W/mK, and for MWNT bundles it was only 10 W/mK [50]. CNT bundles have a lower thermal conductivity than individual CNT because of the boundary phonon scattering between CNTs in the bundles [50]. In contrast, individual MWNT was found to have a thermal conductivity of $\sim 740$ W/mK (at 296 K) by the $3 - \omega$ method at a room temperature [51]. While another group reported a value of 300 W/mK for individual MWNT using a similar method [52]. To eliminate the influence of thermal contact resistance, Raman shift method was developed to measure thermal conductivity of individual CNTs. And it was obtained that the thermal conductivity of SWNTs and MWNTs are 1813 W/mK (effective value: 2400 W/mK) and 1400 W/mK, respectively [7]. Inner walls of MWNTs do not contribute to the thermal conductivity as much as the outmost wall, so the thermal conductivity is lower than that of SWNTs [7].

Although individual CNTs have super high thermal conductivity, recent research work shows that thermal conductivity of CNT fibers were relatively low (typical value is around 20 W/mK [49,53,54]). This is probably due to the defects on the walls of CNTs and high thermal
contact resistance between CNTs. So far CNT fibers that are composed of high quality SWNTs have the best thermal conductivity, that is, 380 W/mK [49].

1.4 CNT Fibers

The production of CNT fibers has been a study of interest recently. Here fiber is used to represent all one-dimensional CNT products. The interest in CNT fibers is motivated by the potential to produce fibers with outstanding mechanical, electrical, and thermal properties. Techniques to produce CNT based fibers are often divided into two categories, dry spinning and wet spinning. Figure 1-8 presents a classification of spinning methods that have been applied to produce CNT fibers.

![Classification of spinning methods for CNT fibers](image)

1.4.1 Dry Spinning

Dry spinning of CNTs is developed based on aligned CNT arrays synthesized by a CVD method. CNT arrays from which a continuous web can be drawn are called spinnable arrays. Figure 1-9 presents SEM images of spinnable arrays. Fan et al. first reported that CNT web was able to be pulled out from a CNT array in 2002 [55]. Later it was found that fibers can also be spun during growth of CNT in the CVD furnace without the need of growing spinnable arrays [56]. This
method is usually called direct spinning. Direct spinning is achieved by using a floating catalyst CVD method. Figure 1-10 (a) shows the process of producing fibers directly from the furnace. Structure of direct spun CNT fiber is shown in Figure 1-10 (b). Fibers produced by direct spinning have a same yarn structure as fibers spun from spinnable arrays.

![Figure 1-9. SEM images of (a) a spinnable CNT array and (b) the spinning process [57].](image)

![Figure 1-10. Direct spinning. (a) Illustration of direct spinning process and (b) SEM images of CNT fibers made by the direct spinning [56].](image)

In the development of dry spun CNT fibers, lots of efforts have been put on improving the tensile strength of the CNT fibers. Properties of fibers made by dry spinning are listed in Table
1-2. From the table, we can see that strength of fibers varies in a wide range. Mechanism of spinnability has been investigated to better understand structure of CNT fibers. In addition, several post treatments approaches have been applied to improve properties of dry spun CNT fibers such as twisting, densification, stretching, heat treatment, polymerization and cross-linking.

Table 1-2. Properties of CNT fibers produced by dry spinning methods.

<table>
<thead>
<tr>
<th>Year</th>
<th>Method/treatments</th>
<th>CNT wt%</th>
<th>Strength GPa</th>
<th>Modulus GPa</th>
<th>Electrical $10^{-5} \Omega \cdot m$</th>
<th>Thermal $W/mK$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Spinning from spinnable arrays</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2007[59]</td>
<td>Twist; $d$: 13μm</td>
<td>100</td>
<td>0.17</td>
<td>89</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Re-spin $d$: 10μm</td>
<td>100</td>
<td>0.41</td>
<td>241</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Twist $d$: 4 μm</td>
<td>100</td>
<td>0.85</td>
<td>275</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Re-spin $d$: 3 μm</td>
<td>100</td>
<td>1.91</td>
<td>330</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2007[60]</td>
<td>Twist</td>
<td>100</td>
<td>1.9</td>
<td>195</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>100</td>
<td>3</td>
<td>205</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2007[54]</td>
<td>Twist</td>
<td>100</td>
<td>--</td>
<td>--</td>
<td>3.3</td>
<td>26</td>
</tr>
<tr>
<td>2009[62]</td>
<td>Twist</td>
<td>100</td>
<td>~0.5</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Twist + tension + heat</td>
<td>100</td>
<td>1~1.3</td>
<td>--</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2009[63]</td>
<td>Twist</td>
<td>100</td>
<td>0.6</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010[64]</td>
<td>Twist</td>
<td>100</td>
<td>1.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Twist + densification;</td>
<td>80</td>
<td>1.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010[65]</td>
<td>Twist</td>
<td>100</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010[66]</td>
<td>Twist; $d$: 20μm</td>
<td>100</td>
<td>0.3~0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Twist; $d$: 4.5 μm</td>
<td></td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Twist + polymer(polystyrene)</td>
<td>90</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010[67]</td>
<td>Twist</td>
<td>100</td>
<td>0.4~0.6</td>
<td>1.1~2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Twist + densification</td>
<td>100</td>
<td>0.6~1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Year</td>
<td>Method/treatments</td>
<td>CNT wt%</td>
<td>Strength GPa</td>
<td>Modulus GPa</td>
<td>Electrical $10^{-5} \Omega \cdot m$</td>
<td>Thermal $W/\text{mK}$</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------</td>
<td>---------</td>
<td>--------------</td>
<td>-------------</td>
<td>----------------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td></td>
<td><strong>Spinning from spinnable arrays</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010[68]</td>
<td>Twist</td>
<td>100</td>
<td>0.4 $- 1$</td>
<td>10 $- 18$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010[70]</td>
<td>Twist</td>
<td>--</td>
<td>2</td>
<td>120</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>2011[71]</td>
<td>Twist+tension+heat+polymer(PU\textsuperscript{1})</td>
<td>70$- 80$</td>
<td>1.6$- 2$</td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011[14]</td>
<td>Polymer (PVA\textsuperscript{2}) (sheet)</td>
<td>65</td>
<td>1.74</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011[72]</td>
<td>twist</td>
<td>100</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>twist + infiltration</td>
<td>--</td>
<td>0.91</td>
<td>65</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>twist + infiltration +crosslinked</td>
<td>--</td>
<td>2.2</td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>further crosslinked</td>
<td>--</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012[73]</td>
<td>Twist</td>
<td>100</td>
<td>0.7</td>
<td>44</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Twist + polymer (Resin)</td>
<td>--</td>
<td>1.2</td>
<td>62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012[74]</td>
<td>Twist; polymer (PVA)</td>
<td>100</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012[15]</td>
<td>Twist</td>
<td>53</td>
<td>1</td>
<td>70</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>2012[53]</td>
<td>Twist</td>
<td>100</td>
<td>--</td>
<td>--</td>
<td>1.2$- 2.5$</td>
<td>25$- 60$</td>
</tr>
<tr>
<td><strong>Direct spinning</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2007[61]</td>
<td>Twist</td>
<td>100</td>
<td>0.3$- 1.9$</td>
<td>89$- 330$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1\textit{mm} gauge; maximum</td>
<td>100</td>
<td>8.8</td>
<td>357</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010[58]</td>
<td>Twist</td>
<td>100</td>
<td>1$- 1.5N/tex$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010[69]</td>
<td>Twist</td>
<td>100</td>
<td>0.4$- 1.25$</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012[75]</td>
<td>Twist</td>
<td>100</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{1}: Polyurethane (PU); \textsuperscript{2}: polyvinyl alcohol (PVA).

**Mechanism of spinnability**

Mechanism of spinnable arrays is investigated to improve properties of dry spun fibers. In spinning of cotton yarns, friction between cotton fibers plays an indispensable role. For CNTs van
der Waals force between bundles is believed to be crucial [76]. Entanglements at the top and bottom of the array was speculated to bond the CNT bundles [76]. This speculation was disproved by the fact that etching the top and bottom of an array did not change the spinnability [70]. Gilvaei et al. found that the force needed to pull out a web from a spinnable array was more uniformly distributed along height of the array than that from an unspinnable array, which also indicated that entanglement at the top and bottom of an array was not related to spinnability [77]. Zhu et al. proposed that entanglement of CNT bundles during pulling provided the force to connect CNT bundles [78]. Another group established a similar model to explain the reason of spinnability. They believe interconnections between bundles bind bundles together and therefore bundles can be continuously pulled out [79]. Although explanations of detailed mechanism are different, studies pointed to a common result that alignment and density of the array are two most important factors.

**Methods for strength improvement**

Twisting is introduced in the production of CNT fibers shortly after the discovery of spinnable arrays. Dry spun CNT fibers have the same structure as traditional staple yarns which are also made by short one-dimensional elements [58]. As two important factors in yarn structure, twisting angle and diameter of CNT fibers have been studied to optimize the strength [63,66–68,80]. Twist angle has a great impact on the strength of CNT fibers. However, there is no consensus on the optimum twist angle. One reason is that sample numbers in some literature is quite limited, and thus the result has little statistical significance. The other reason is that properties of fibers are strongly dependent on properties of spinnable arrays, such as alignment of bundles, length, and density. Diameter is another factor that influences the strength of CNT. Some found
that strengths of fibers increase as diameters decrease [67]. Others reported that fibers of larger
diameter have higher strength [68].

Another way used to improve strength is densification by a solvent [67,69,81]. Illustration
of the process is shown in Figure 1-11. Diameter of fibers can be effectively reduced and load
transfer between bundles can be enhanced. A wide range of chemicals can be used to densify CNT
fibers such as acetone, water, ethanol and N-methylpyrrolidinone (NMP). In general, densification
can increase the strength to several times that of as-spun fibers.

![Illustration of densification of CNT fibers](image)

Figure 1-11. Illustration of densification of CNT fibers [67].

Polymers are infiltrated into CNT fibers to enhance mechanical properties [15,66,70,71].
Figure 1-12 shows a comparison of cross sections of CNT fibers before and after infiltration. From
the figure we can see that the cross section of CNT fibers is more condensed after polymer
infiltrated. Polymers act as binders and increases load transfer between CNT bundles. Further
improvement of strength can be achieved by cross-linking CNT and infiltrated polymer [72].
Although polymer infiltration is effective in strength enhancement of the CNT fiber, thermal and
electrical properties are usually decreasing [15,71].
Figure 1-12. Cross section of (a) a neat CNT fiber and (b) a PU-CNT fiber [71].

Other post processing approaches to improve strength have also been studied. High temperature annealing was applied to CNT fibers but did not effectively improve tensile strength of dry spun fiber for annealing at 1700°C [9], although individual CNTs are reported to become stronger after annealing [32]. Inspired by irradiation of individual MWNTs [31], Pierlot et al. applied gamma irradiation to CNT fibers and strength improvement is observed [83].

A point to note is that strain rate and gauge length affect tensile values, similar to traditional spun yarn [84]. In direct spinning method, gauge length is reported to have a significant impact on strength. High strength is obtained at short gauge length (1 mm) [61]. When the gauge increases to 20 mm, the distribution of the strength becomes stable and the strength is much lower than strength tested at small gauge length. Different gauge lengths (1~20 mm) do not have much impact on the tensile properties of fibers spun from spinnable arrays [74].

1.4.2 Wet Spinning

Wet spinning has been used for producing polymer fibers for decades [85]. It is the first method applied to CNT fibers production. The key issue in the wet spinning of CNT fibers is the dispersion of CNT at high concentration. Dispersion of CNTs is also a major concern in
reinforcement with CNTs of polymers, metals, and ceramics [86,87]. It is critical to disperse CNTs as desired and improve the interfacial force between CNTs and matrix. Poor dispersed CNTs usually weaken rather than reinforce CNT based composites. Tensile strength of pristine CNT enforced solids could be either slightly increased [88–90] or decreased [91–96]. In contrast, CNTs with surface modification have a better interaction with the matrix and contribute to both modulus and strength of solids [95,97,98].

**Dispersion**

Many research efforts have been directed towards dispersing CNTs in solvents. Attractive interactions among CNTs are high, as CNTs have high aspect ratios and thus large surface areas. This inherent bundling effect makes dispersion of CNT extremely hard. Dispersion is highly related to CNT types. Reducing CNT with Li or Na works better on arc grown SWNTs than HiPco SWNTs in respect to dispersion in water [99]. Super acids are found to have better performance on dispersion of HiPco SWNTs than that of arc grown SWNTs [100]. In general SWNTs are harder to disperse than MWNTs. Figure 1-13 presents methods that are applied to disperse CNTs.

![Dispersion methods classification](image)

**Figure 1-13. Classification of dispersion methods.**
(A) Mechanical dispersion

Mechanical dispersion includes shearing, ball milling, sonication, and centrifuge. Shearing is a mild way to disperse particles in liquid [101]. Size of the propeller and mixing speed are the key to dispersion quality. Extensive shearing will exfoliate the CNT bundles and shorten CNTs [102]. Ball milling can break materials into small particles because of the high pressure generated by collision of small rigid balls [103]. Ball milling combined with chemicals is used to functionalize CNTs while breaking them down [104]. It is easy to operate and ready to be industrialized. Milling time, rotation speed and size of balls are factors that govern the separation of CNTs. Sonication is mostly used in laboratory. It is achieved using a sonic bath or a sonic probe. Probe sonication is more effective to disperse CNTs in a liquid compared to bath sonication. Probe sonication damages CNTs with aggressive or prolonged treatment [105,106]. Scission of CNTs is governed by the sonication energy [107]. Figure 1-14 shows the relation between input energy and CNT length. Centrifuge and filtration are also used to help obtain well dispersed CNTs [108]. CNT dispersion is a colloidal system, so centrifuge and filtration can be used to remove bundled CNTs.

Figure 1-14. CNT length and sonication energy [107].
(B) Surface modification

Surface modifications improve CNT dispersion by changing the surface of CNTs through two ways: covalent functionalization and non-covalent modification [86]. Covalent surface modifications introduce functional groups to side walls or ends of CNTs [109]. A typical way to functionalize the tubes is through reaction with molecules of high chemical reactivity. These molecules can then be replaced by functional groups [110]. Functional groups can also be attached to the sidewalls of CNTs through defects, as defective sites have high activity [111]. In covalent functionalization process, defects are inevitably created on the walls of CNTs and usually result in deteriorated mechanical properties and transport properties of CNTs. An alternative way is using non-covalent surface modifications by polymers and surfactants [112]. Polymers enhance the dispersion of CNTs by pi-pi stacking interactions [113], and surfactants prevent aggregates of CNTs by attaching to surface of CNT and thus reducing surface tension of CNTs [114]. One drawback is that surfactants or polymers on surface of CNTs are difficult to remove.

(C) Solvents

It is found that CNTs can be dispersed in some solvents without the need of surface modification. Chlorosulfonic acid (CSA) is found to be a good solvent for high quality CNTs [49].

**Spinning methods**

Wet spinning has been used to produce polymer fibers for decades. Recently, it is found that wet spinning can be applied to CNT fiber production. Ways to spin CNTs can be roughly divided into three categories: CNT based spinning, liquid crystal spinning, and polymer based spinning. Properties of CNT fibers made by wet spinning are listed in Table 1-3.
Table 1-3. Properties of CNT fibers produced by wet spinning methods.

<table>
<thead>
<tr>
<th>Year</th>
<th>Dispersant-bath</th>
<th>CNT type</th>
<th>CNT wt%</th>
<th>Strength $GPa$</th>
<th>Modulus $GPa$</th>
<th>Electrical $10^{-5} \Omega \cdot m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CNT based spinning</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000[115]</td>
<td>SDS$^1$-PVA</td>
<td>SW</td>
<td>60</td>
<td>0.14</td>
<td>15</td>
<td>100</td>
</tr>
<tr>
<td>2002 [116]</td>
<td>SDS-PVA</td>
<td>SW</td>
<td>--</td>
<td>0.15</td>
<td>15</td>
<td>--</td>
</tr>
<tr>
<td>2002[117]</td>
<td>SDS-PVA</td>
<td>SW</td>
<td>--</td>
<td>0.2</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2003[118] [119]</td>
<td>LDS$^2$-PVA</td>
<td>SW</td>
<td>60</td>
<td>1.8</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2005[120]</td>
<td>SDS-PVA</td>
<td>SW</td>
<td>--</td>
<td>1.8</td>
<td>45</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MW</td>
<td>--</td>
<td>1.4</td>
<td>35</td>
<td>--</td>
</tr>
<tr>
<td>2005[121]</td>
<td>SDS-glycerol/glycol in ethanol</td>
<td>SW annealed</td>
<td>100</td>
<td>--</td>
<td>--</td>
<td>150</td>
</tr>
<tr>
<td>2005[122]</td>
<td>LDS,SDBS$^3$,CTAB$^4$-PEI in methanol</td>
<td>SW</td>
<td>--</td>
<td>0.09$^a$</td>
<td>6$^a$</td>
<td>5~10</td>
</tr>
<tr>
<td></td>
<td>Triton x100- PEI in methanol</td>
<td>SW</td>
<td>--</td>
<td>0.05$^a$</td>
<td>--</td>
<td>30~100</td>
</tr>
<tr>
<td>2005[123]</td>
<td>LDS-37%HCl</td>
<td>SW/MW</td>
<td>100</td>
<td>0.065$^a$</td>
<td>12$^a$</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>-annealed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-PVA</td>
<td></td>
<td></td>
<td>0.77$^a$</td>
<td>8.9$^a$</td>
<td>5,000</td>
</tr>
<tr>
<td>2006[124]</td>
<td>Functionalized CNT - PVA+HCl</td>
<td>MW</td>
<td>--</td>
<td>0.5</td>
<td>4~10</td>
<td>3,000~8,000</td>
</tr>
<tr>
<td>2007[125]</td>
<td>LDS-PVA</td>
<td>SW</td>
<td>--</td>
<td>0.1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Hot drawing</td>
<td></td>
<td></td>
<td>1.8</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2012[126]</td>
<td>SDS-PVA</td>
<td>MW</td>
<td>--</td>
<td>0.4~1</td>
<td>1.4~5</td>
<td>170</td>
</tr>
<tr>
<td>2012[127]</td>
<td>SDBS,graphene-PVA</td>
<td>SW</td>
<td>--</td>
<td>0.5</td>
<td>2</td>
<td>650</td>
</tr>
<tr>
<td>2012[128]</td>
<td>SDS-sodium alginate</td>
<td>MW</td>
<td>≤ 2.4</td>
<td>0.14~0.25</td>
<td>4~7</td>
<td>4~7 × 10$^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23</td>
<td>0.14~0.25</td>
<td>4~7</td>
<td>300</td>
</tr>
<tr>
<td>liquid crystal spinning</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2004[129]</td>
<td>102% sulfuric acid-diethyl ether/water/aqueous sulfuric acid</td>
<td>SW</td>
<td>100</td>
<td>0.1</td>
<td>120</td>
<td>0.2</td>
</tr>
<tr>
<td>2004[130]</td>
<td>102% sulfuric acid-ether</td>
<td>SW</td>
<td>100</td>
<td>--</td>
<td>--</td>
<td>0.25~8</td>
</tr>
</tbody>
</table>

$^a$ denote the results are not clearly marked.
In this category, CNTs participate in the coagulation process. Vigolo et al. applied wet spinning to SWNT fiber production in 2000 [115,117]. They dispersed SWNTs with a surfactant, injected the dispersion into PVA solution, and obtained SWNT-PVA composite fibers. Figure 1-15 shows the scheme of the spinning process. CNT types affect the coagulation in this method. It was found that HiPco SWNTs were easier to coagulate than arc grown SWNTs [135] and that arc grown SWNTs coagulated while purified arc grown SWNTs did not [135]. Dalton et al. upgraded the setup to a semi-continuous process and obtained much higher production speed [125]. Miaudet
et al. first made MWNT-PVA fibers using this method [120]. Properties of MWNT-PVA fibers are not as good as those of SWNT-PVA fibers. Hot drawing is a major way to improve the tensile strength and modulus of CNT-PVA fibers by improving the alignment of CNTs and PVA molecules in the fibers [118,120]. Shearing stress during extrusion also contributes to alignment of CNTs and thus properties of fibers [126].

![Illustration of wet spinning process](image)

Figure 1-15. Illustration of wet spinning process [115].

Other composite and neat CNT fibers were developed using a similar process. Other than PVA bath, spinning of CNT dispersion can be achieved in bathes such as alginate [128], ethanol-glycol [121], polyethylenimine (PEI)-methanol [122]. Functionalized CNTs can be well dispersed in water and can be spun directly into PVA and acid solution [124]. Composite CNT fibers have relatively low electrical conductivity due to the existence of polymer. Conductive polymer such as PEI were used as the bath, and the produced SWNT-PEI composite fibers have a high conductivity but low strength. Neat CNT fiber was obtained by injecting surfactant dispersed CNTs into acid
or base bath [123]. The formation of fiber is achieved by flocculation due to PH change. Fibers spun in this way have good electrical conductivity but low strength.

(B) **Liquid crystal spinning**

Liquid crystal spinning is a special case of CNT based spinning. It has been used in production of high performance fibers such as Kevlar (a para-aramid synthetic fiber). CNTs have a rod-like structure. There are three states for rod-like structures in solvent: isotropic, biphasic, and nematic. Illustration of each state is shown in Figure 1-16. In nematic liquid crystal, CNTs are aligned in one direction in local. CNT dispersions in CNT based spinning have an isotropic state, while dispersion used in liquid crystal spinning has a nematic state.

![States of rod-like molecules in solvents: (a) isotropic, (b) biphasic, and (c) nematic liquid crystal](image)

Figure 1-16. States of rod-like molecules in solvents: (a) isotropic, (b) biphasic, and (c) nematic liquid crystal [136].

Liquid crystal state was achieved in 102% sulfuric acid for SWNTs [129]. Neat SWNT fibers can be produced by injecting SWNT dispersions into diethyl or water bath [130]. Alignment of SWNTs in the fiber is important to thermal and electrical properties of such a fiber. With CSA as the solvent, CNT fibers with high thermal and electrical conductivities were produced [49]. Liquid crystal spinning can also be applied for MWNTs [131]. Properties of MWNT fibers are not as good as SWNT fibers.
(C) Polymer spinning

CNTs can be added to polymers as fillers. In both wet and melt spinning process, CNTs can be added into polymer solution such as PVA [133,134], Polyacrylonitrile (PAN) and regenerated cellulose [137]. Electrospinning has also been investigated to produce CNT reinforced nanofibers [138]. Addition of CNT is found to increase strength and modulus of the fiber. This is because CNTs reinforce the matrix and facilitate formation of crystalline structure in PVA [12].

Drawing is the crucial step in production of polymer fibers. Addition of CNTs keeps the high drawing ratio of polymer [133,134]. Drawing of the fiber aligns both the PVA molecules and CNTs and improves the strength of the composite fibers [139]. With same drawing ratio, PVA-CNT fibers have higher strength than pure PVA fibers if CNTs are well dispersed in the matrix [134].

1.4.3 Other Spinning Methods

Other novel ways to spin CNT fibers are reported in literature. Cotton-like DWNT was produced using a floating catalyst CVD method and the cotton-like DWNTs can be twisted into fibers under heating [140]. Cotton-like CNT can also be produced by adding foaming chemicals to substrate used in synthesis of CNT arrays. The obtained cotton CNT can be spun into fibers [141]. In general cotton-like CNTs do not have good alignment and it is hard to obtain fibers with uniform structure. Another way to produce CNT fiber is by rolling CNT film into a cylinder and condensing the cylinder. CNT fibers produced in this way have a compact structure [142].

Small scale CNT fibers are produced in pursuit of good alignment. CNTs are dispersed in liquid crystal in order to take advantage of the alignment [143]. A continuous CNT fiber can be pull out from this CNT liquid crystal, which is shown in Figure 1-17. It is possible to remove large
part of liquid crystal material from the fiber. Dielectrophoresis can also be used to produce well aligned short CNT fibers [144]. The produced fibers have small diameters (less than 1μm) and short lengths (from 1 μm to 1 cm). These small scale fibers have potential applications in making CNT based probes and electron field emitters.

![Figure 1-17. A liquid crystal-CNT composite fiber](image)

1.5 Summary

In this chapter, properties of individual CNTs are reviewed. Experimental results show that the strength of individual CNTs varies from 3~150 GPa. According to the tensile tests on individual CNTs, CNTs with fewer walls are stronger and are more preferable to produce strong CNT fibers. Individual CNTs also have good electrical and thermal conductivity.

Methods that have been used in production of CNT fibers are reviewed. These methods can be divided into two kinds, dry spinning and wet spinning. In dry spinning technique, CNTs are spun into fibers from spinnable arrays or directly from the synthesis furnace. Continuous production of CNT fibers can be achieved in direct spinning methods. In contrast, CNTs are
dispersed in solvent and then coagulate into fibers in wet spinning. Good alignment of CNTs can be obtained in wet spinning and thus neat CNT fibers have better electrical properties than most dry spun fibers.
Chapter 2  Dry Spinning of CNT Fibers

In order to fully utilize the unique properties of CNTs, it is necessary to assemble CNTs into macro-scale products. One way to assemble CNTs is to twist individual CNTs into continuous fibers. This process is very similar to that for fabricating textile. Numerous methods have been developed to achieve this goal, where dry spinning is one of them. The dry spinning is a process of making CNT fibers from spinnable arrays, which is a well-established method. The key of this method lies in the synthesis of spinnable arrays. In particular, long CNT arrays should be used as the basis for spinning a long and super strong CNT fiber. In this chapter, several ideas of spinning long CNTs are presented and analyzed. Since it is generally known that strong interactions between CNTs bundles are required in order to assemble them into fibers, one possible way of using certain liquids is adopted to increase the interaction between bundles. Another possibility is to bind ends of CNT bundles in a CNT array so that these bundles can be pulled out continuously.

2.1 Spinning from Spinnable Arrays

2.1.1 Experimental Setup and Procedure

Two different machines have been designed and manufactured for spinning CNT fibers from spinnable arrays, that is, the low speed machine and the high speed machine, as shown in Figure 2-1. In both setups there are two motors used in the spinning machines. The draw motor is used to pull the CNT web from spinnable arrays, while the twist motor is to twist the CNT web. The high speed spinning machine is newly developed in NanoWorld lab at UC, which has a superior performance than the low speed machine. Here, the rotation speed can be well controlled to guarantee the speed accuracy. Also it can reach a much higher speed up to 3000 rotation per
minute (RPM). Moreover, the whole structure has been optimized to avoid mechanical vibration that might affect the spinning performance during the process.

Figure 2-1. (a) Low speed spinning machine and (b) high speed spinning machine.

The spinning procedure for the spinning machines is consisted of following steps:

1) Prepare a spinnable array attached to the silicon substrate and fix the substrate onto the holder with double sided tape. In this study, the arrays are synthesized on silicon substrates by a catalyst CVD method.
2) Cut the array with a razor blade and pull the blade away from the array. Repeat this process until CNT web from the full width of the array are attached to the blade. Then attach the CNT web to the bobbin for collecting CNT fibers.

3) Turn on the twist motor and then the drawing motor. Twist degree of fibers can be controlled by adjusting rotation speeds of the two motors.

In this chapter, several tests have been conducted using above test procedure to spin different CNT fibers. The results and discussion will be presented in the following section. In order to better evaluate the performance of this dry spinning technique, mechanical property of these spun fibers are measured and analyzed. In addition, several promising post-processing methods are adopted to improve the tensile strength.

2.1.2 Results and Discussion

Following the spinning procedure shown above, different CNT fibers have been made. SEM is used to characterize CNT arrays and fibers. Figure 2-2 (a) and (b) show SEM images of a spinnable array. The array has a height of 244 μm and is composed of well-aligned CNT bundles. Figure 2-2 (c) shows a CNT web pulled from the array. The CNT web can be twisted into a CNT fiber. Figure 2-2 (d) presents a CNT fiber that has a cylindrical shape. The degree of twisting can be characterized by the surface twist angle $\theta$. Here $d$ is the diameter that is used to calculate the areas of fibers. Effects of twisting angle and diameter on the fiber’s strength will be discussed in the following subsection.
Figure 2-2. SEM image of (a) a spinnable array, (b) CNT alignment of the spinnable array, (c) CNT web pulled from the spinnable array, and (d) a dry spun fiber.

In order to evaluate tensile properties, the dry-spun CNT fibers are tested using the tensile strength testing machine Instron 5948 as shown in Figure 2-3. The preparation of test samples is shown in Figure 2-4 [145]. It is hard to put the CNT fibers directly to the test grips. Therefore, a piece of paper is used to hold the CNT fiber. Two layers of double sided tape are used to eliminate slippery during testing. The sides of paper are cut after the sample is put to the grips. Figure 2-5 shows the stress-strain curve for three as-spun samples. It can be determined that the maximum tensile strength is about 250 MPa.
Figure 2-3. Testing machine Instron 5948 [145].

Figure 2-4. (a) Sample preparation process [145], and (b) a sample in testing.
It should be noted that the dry-spun CNT fibers are produced from short CNT bundles. These fibers have a similar structure to staple yarns in textile [146] that have been extensively studied. Hence, similar strength analysis methodology can be applied to that of CNT fibers. It has been reported that the strength of a twisted yarn was primarily governed by the short fibers that constitute the yarn [147]. Normally, the strength of yarns is far below that of fibers. Sasser et al. reported that the strength of cotton yarns was about 31% (rotor spun) and 37% (ring spun) of the cotton fiber’s strength [148]. One reason was due to the variation in the load carried by individual fibers [149]. Also, inclination of the fiber to the yarn axis decreased the load transfer ability of the fiber in the axial direction. In addition, slippage of fibers, especially in outer layer [147], reduced the strength transition coefficient from fibers to yarns. In the following section, several key factors affecting the maximum strength of yarn has been analyzed, such as twisting angle, fiber length and fiber friction. Furthermore, different post-processing treatments were applied to improve the strength of CNT fibers, such as post twisting and thermal annealing.
**Twist angle and diameter**

The twisting process plays an important role on compressing short CNT bundles into a continuous strong fiber. In Figure 2-6, strengths of 40 as-spun fibers made from different arrays are plotted with respect to the twisting angle. It can be seen that it seems there is no obvious correlation between the strength and twist angle. It was reported that the process of twisting could compress the structure, which to certain degree may enhance the load transfer ability between CNT bundles [73]. Also, the twisting will lead to certain decrease of the diameter of spun fibers, which contributes to the tensile strength of these fibers. On the other hand, higher twisting degree makes CNT bundles more inclined to the axial direction, which is adverse to load transfer of CNT bundles along the fiber axis. According to above analysis, there exists an optimum twist angle that gives the maximum tensile strength [57,66]. However, in our current tests, we do not see this particular trend. This is probably due to the inconsistence of the raw spinnable arrays. While the relationship between diameter and strength, as shown in Figure 2-7, shows that the strength of fibers increases when the diameter is decreased. Study of fibers spun from the same array may better reveal the relations.
Figure 2-6. Strength and twist angle of fibers spun from different arrays.

Figure 2-7. Strength and diameter of fibers spun from different arrays.

Figure 2-8 shows the SEM image of CNT fibers with low twist and high twist. It can be seen that fibers of low twist angle have a loosely packed structure and compact for a highly twisted fiber. These two different structure densities will have different mechanical strengths. Figure 2-9
shows a typical breakage of twisted fibers. The failure mode is similar to that of traditional yarns [147]. Slippage between CNT bundles and breakage happens in the same time.

Figure 2-8. SEM images of (a) a low-twisted fiber and (b) a high-twisted fiber.

Figure 2-9. Failure modes of CNT fibers (a) twist angle 11° and (b) twist angle 50°.

Post twisting

Post twisting has been used to improve the strength of CNT fibers. In the tests, two fiber samples spun from different arrays were post twisted. The post twisting is in the same direction as the original twisting. Figure 2-10 compares the SEM image of as-spun fiber and post twisted fiber and it shows that CNT fiber after post twisting have a smoother surface and smaller diameter. Some CNT fibers become non uniform, as shown in Figure 2-10 (c). This distortion may be caused
by high twisted as spun yarn and excess post twisting. Table 2-1 lists properties of fibers and it shows that the post twisting can lead to reduced diameter and enhanced breaking force of the fiber. We can see that the post twisting improves the maximum tensile strength by about 100%. The strength improvement is not as significant as that reported in the literature [59,150] where post twisting increased strength by 300% – 400%. More statistical samples might be required for better representation of this relationship. In general, it has been demonstrated the effectiveness of post-twisting of the spun fibers for further enhancing the mechanical property.

![SEM images](image.png)

Figure 2-10. SEM image of (a) an as-spun fiber, (b) a post twist fiber, and (c) non-uniform structure due to post twist.

Table 2-1. Effect of post twist on properties of dry spun fibers.

<table>
<thead>
<tr>
<th>Label</th>
<th>Treatment</th>
<th>Twist angle (°)</th>
<th>Diameter (µm)</th>
<th>Force (N)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-spun</td>
<td>11.2</td>
<td>18.4</td>
<td>0.032</td>
<td>120</td>
</tr>
<tr>
<td>Sample 1</td>
<td>Post twist 1</td>
<td>13.5</td>
<td>15.1</td>
<td>0.038</td>
<td>211</td>
</tr>
<tr>
<td></td>
<td>Post twist 2</td>
<td>13.4</td>
<td>14.3</td>
<td>0.040</td>
<td>250</td>
</tr>
<tr>
<td>Sample 2</td>
<td>As-spun</td>
<td>20.1</td>
<td>20.4</td>
<td>0.083</td>
<td>254</td>
</tr>
<tr>
<td></td>
<td>Post twist</td>
<td>23.4</td>
<td>18.2</td>
<td>0.120</td>
<td>461</td>
</tr>
</tbody>
</table>
**CNT length and strength**

The ability of load transfer between bundles of CNTs is also a key factor to improve the strength of CNT fibers. The relation between the strength of CNT fibers and CNT length is shown in Figure 2-11. Strengths of CNT fibers spun from six arrays were tested. The CNT length is estimated by measuring the array height, which is in the range of 200 – 550 μm. To reduce effects of twist angle, the fibers were divided into two groups according to the twist angle. We can see from the figure that the strength of fibers increases with the CNT length. This relation is consistent with results in the reference [64]. Increasing the length of these CNT bundles enhances the load transferring ability. This is because for a longer CNT bundle the contact length is increased, which will lead to more interactions with other CNT bundles. Unfortunately, long CNT arrays have relatively low spinnability [151]. To fully understand relation between CNT length and strength, it is desired to control other parameters of CNT arrays such as alignment, density, and diameter of CNTs, which may be realized during the synthesis of CNT arrays.

![Figure 2-11. Relation between CNT length and the strength of CNT fibers. Small twist angle: 10-30 degree; large twist angle: 40-50 degree.](image-url)
**Thermal treatment**

High temperature thermal treatment of CNTs can also improve the structure and thus influence the interactions between CNT bundles [152]. Thermal annealing was done on the same dry spun fiber under two conditions, 2000°C and 2700°C, for 1 h under argon atmosphere. Acetone densification is applied to both as-spun fibers and annealed fibers. For each thermally treated spun fiber, the tensile test was conducted similar to that introduced above. Figure 2-12 and Figure 2-13 show stress-strain curves of CNT fibers after annealing and acetone densification. The black solid line is the spun fiber without any post-treatment, the red dotted line is that after annealing only, the purple dashed line is for the spun fiber with densification and the blue dash dotted line is for that with annealing and densification. It can be seen from Figure 2-13 that the maximum strength is significantly increased after annealing at 2700°C. However, it shows certain degreasing when the temperature is at 2000°C.

![Stress-strain curves of CNT fibers](image)

**Figure 2-12. Typical stress-strain curves of CNT fibers annealed at 2000°C.**
To better understand the performance of post thermal treatment on the tensile strength, more samples were prepared and the results are shown in Table 2-2. We can see that the tensile strength shows a little decreasing when the fibers were treated by annealing at 2000℃. On the other hand, the strength is increased when the annealing temperature is at 2700 ℃. It has been shown in Nanoworld that high temperature (> 2600℃) annealing significantly improves G/D ratio of CNTs, while lower temperature is less effective. Therefore, the increase of strength is likely resulted from the improved structure of CNTs and fewer impurities.

Acetone densification is applied to the as-spun and annealed fibers. The fiber is soaked in acetone for about 1 min, then it is dried in air. It is noticed that the densification significantly improve the Young’s modulus of samples annealed at 2000 ℃ compared to as-spun samples. Figure 2-14 shows the surface morphologies of fibers before and after densification. It can be seen that the fiber has a more compact surface after the densification. The failure mode for both is dominated by slippage. Diameter reduction is observed for both samples. Annealed samples have
less reduction than that of as-spun samples. This is probably because CNT bundles become stiff after annealing.

Table 2-2 Effects of thermal annealing at 2000°C on CNT fibers.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sample</th>
<th>Force (mN)</th>
<th>Diameter (μm)</th>
<th>Strength (MPa)</th>
<th>Modulus (GPa)</th>
<th>No. of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-spun</td>
<td>82.80(7.07)</td>
<td>33.43(3.81)</td>
<td>94.35</td>
<td>3.47(0.92)</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Densified</td>
<td>86.99(16.43)</td>
<td>26.92(1.28)</td>
<td>152.91</td>
<td>5.46(0.70)</td>
<td>9</td>
</tr>
<tr>
<td>2000°C</td>
<td>Annealed</td>
<td>64.61(6.02)</td>
<td>36.64(0.81)</td>
<td>61.31</td>
<td>2.90(0.29)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Annealed-densified</td>
<td>81.11(9.56)</td>
<td>30.30(0.98)</td>
<td>112.53</td>
<td>11.85(1.30)</td>
<td>6</td>
</tr>
<tr>
<td>2700°C</td>
<td>Annealed</td>
<td>89.60(21.27)</td>
<td>27.78(2.83)</td>
<td>147.90</td>
<td>8.45(3.74)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Densified-Annulled</td>
<td>88.89(6.65)</td>
<td>24.89(1.77)</td>
<td>182.78</td>
<td>8.07(1.69)</td>
<td>6</td>
</tr>
</tbody>
</table>

Numbers represent: mean (standard deviation).

Figure 2-14. SEM image of (a) an as-spun fiber, (b) failure mode of an as-spun fiber, (c) a densified fiber, and (d) failure mode of a densified fiber.
2.2 Spinning from Fluffy CNT

The tests discussed above show that spinning long CNTs has a great potential to obtain super strong CNT fibers. Fibers spun from longer CNTs spinnable arrays have higher strength [64]. However, long CNT arrays produced in Nanoworld Lab at UC are not easy to spin when directly applying the dry-spinning process shown in above section. Hence, a new method has been made to spin these long CNT bundles into continuous fibers, which is spun from the fluffy CNT.

It has been proposed to spin long CNT bundles using the way as that for spinning cotton fibers. However, CNT bundles have much low coherence than cotton fibers. They are different from cotton fibers in terms of fiber properties including length, fineness, strength, crimp, and cross section. Compared to cotton fibers, CNT bundles are shorter and much thinner. It has been shown that short cotton fibers put a high requirement on spinning and are detrimental to cotton yarn properties [153]. Therefore, it is crucial to increase the length of CNT bundles. Besides geometry differences, the friction between fibers is very important in producing staple yarns [154]. Friction of fibers is the force that holds fibers together during the drafting (a process used to align fibers). Also, friction is the key factor to transfer fiber strength to yarn strength. CNT bundles normally exhibit a low friction force since it is composed of carbons. Hence, it is necessary to enhance the interactions between CNT bundles. One way to achieve higher interaction is by dispersing CNT bundles in a solvent. Attractions between bundles allow assembly of bundles into a continuous fiber. The loosely bonded CNT bundles can be enhanced by inserting twist.

2.2.1 Experimental Procedure

This section gives a brief description of the spinning procedure directly from fluffy CNTs. In those tests, it is required to prepare the CNT arrays first, which were synthesized on steel films.
The height of those arrays is approximately 1~5 mm. As shown in Figure 2-15, a grinder is used to shear the CNT arrays. Through this grinding process, the CNT arrays were tore into small bundles by the shearing force. It can be seen that volume of these smeared CNTs is expanded after shearing, thus we call them fluffy CNTs. Then, those fluffy CNTs were put into a solvent such as water and ethanol. Surfactant sodium dodecyl sulfate (SDS) and triton X100 were used to separate the CNT bundles in distilled water. No surfactant is needed for ethanol as it has a strong ability to separate CNT bundles as compared to water. Sonication was used to help disperse CNT bundles. Sonication time depends on the amount of solution and the type of surfactant. A pair of tweezers is used to pick up a small amount of CNT bundles. These lifted bundles will attract bundles in solution once their ends are attached. A fiber can be produced by keep dipping its end to the bundles in the solution. Twist is inserted to the fiber to enhance the connections between bundles.

2.2.2 Results and Discussion

Shearing in air is effective in breaking down CNT arrays into small bundles. Larger quantity of CNT arrays can induce larger shearing force. The volume of CNTs increases to ten
times of the original volume after 10~60 sec shearing. While the length of these CNT bundles shows no significant change and Raman G/D ratio remains the same after shearing. This implies that the shearing only breaks the CNT bundles into small bundles without cutting CNTs.

Sonication can separate these CNT bundles from each other when immersing in a solvent. Figure 2-16 (a) shows a dispersion that is ready to assemble. If the mixture is over sonicated, CNT bundles are shortened and are entangled to form lager bundles as shown in Figure 2-16 (b). Here, the aggregations of bundles are not wanted, which might affect the spinning ability.

![Figure 2-16. Suspension of CNT bundles that are (a) separated and (b) over sonicated.](image)

Figure 2-17. Spinning process of fluffy CNT.
In this method, manual effort is required to attach the end of fiber to bundles in the solvent. Figure 2-17 shows the process of drawing the CNT fiber out of the solvent. It is noted that arbitrary long fiber can be produced. However, the fiber has a non-uniform structure, as can be seen from Figure 2-18 (a). The diameter of a 3 cm long fiber varies from 53 μm to 80μm with a mean value of 75 μm. Similarly, the tensile tests were conducted to measure the strength of spun fibers, and it shows strength of about 20 MPa. In comparison, this strength is far below that obtained by dry-spinning. This is possibly due to the lower connection between the CNT bundles. Figure 2-18 (b) shows the breakage end. From the figure we can see that the failure is dominated by slippage between CNT bundles. On the other hand, when the spun fiber was immersed in water for 3 days to remove the SDS, the electric resistivity shows an increase from $3.56 \times 10^{-5} \Omega \cdot m$ to $1.43 \times 10^{-5} \Omega \cdot m$. The fibers have electrical properties that are comparable to fibers spun from spinnable arrays.

Figure 2-18. Microscope image of (a) a non-uniform CNT fiber and (b) failure of the fiber.
2.3 Ni Coating on Unspinnable Arrays

When pulling from a spinnable array, CNTs (or small bundle of CNTs) always go through the whole length of the array and pick up neighboring CNTs at the ends. This phenomenon inspires the modification on those unspinnable arrays. The idea here is to bind ends of CNT bundles in the CNT arrays, such that these bundles in non-spinnable arrays, especially in long CNT arrays, can be pulled out one by one. Illustration of the process is shown in Figure 2-20. It is also observed that long CNT arrays usually have entangled top or bottom. It is necessary to remove the entangled part and make sure that ends of CNT bundles appear on the surface as shown in Figure 2-21. Nickel is used as the binder to enhance the ends, as it has good compatibility with CNT and can be easily deposited on CNT [155]. To improve lateral interactions between CNT bundles, heating can be used to melt nickel particles so that nickel binds nearby CNT bundles. Steps in nickel spinning way include removing entangled CNTs, coating nickel particles on top and bottom of the CNT array, spinning, and heat treatments.

Figure 2-19. Residual SDS on the surface of a CNT fiber.
2.3.1 Remove Entangled CNTs

It is found that some arrays have clean surface after high temperature annealing. However, high temperature annealing is not always able to clean the surfaces of CNT arrays. Electrical heating of the array in air is proposed to remove the highly entangled surfaces. This proposal is based on the finding that top and bottom of CNT arrays have the highest temperature due to entanglement when CNT arrays are applied with voltage in vacuum. In air, the entangled CNTs have the highest temperature and can be burned before other parts start burning. Therefore the entanglement CNTs can be removed from the array.
In the experiment, copper wires were used to support the CNT array. However, point discharge was observed at the contact surface between the wire and the array when voltage was applied. In order to obtain smooth current path, silver paint is used to obtain large contact between CNT array and wires. Figure 2-22 shows illustration of the experiment. A pair of glass slides painted with silver is used to support the CNT array. Two sides of the CNT array are attached to silver paint. Note that voltage is applied to the sides rather than the top and bottom of an array.

![Illustration of electrical heating on a CNT array.](image)

As the voltage increases, the center of top and bottom surface turns to dark red. Thermometer is used to test the temperature. Dark red color indicates that the temperature is around 600°C. In most cases, it is the top and the bottom of an array that have largest resistance in the array and therefore has the highest temperature. The resistance of the array increases sharply once the part of large resistance is burned. Electrical heating can be done within several minutes. However, SEM images show that electrical heating does not remove all of the entanglement part if any. The problem is that there are usually cleavages inside CNT arrays. The cleavage of an array has the largest resistance and nearby CNTs will be burned instead of top or bottom of the array. Electrical heating may work on arrays with uniform structure.

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Plasma oxidation is a more controllable way to remove a thin layer of CNT arrays. Plasma in the clean room is successfully applied to CNT arrays. The ends of CNT bundles are visible under SEM. Figure 2-23 shows the top of an array after plasma etching.

![Figure 2-23. The top of a CNT array after plasma etching.](image)

2.3.2 Nickel Coating

Electroplating is used to coat nickel particles to the top and bottom of CNT arrays. The process is illustrated in Figure 2-24. A DC power supply provides a stable voltage. A nickel wire is attached to the cathode, and a CNT array to the anode. Both the nickel wire and the top of a CNT array are put in watts nickel solution. The watts nickel solution is heated to about 55°C. In experiments, constant voltage is applied to the array and nickel wire. Voltage and coating time are set as parameters that control coating amount. Voltage of 1~3 V is applied. Coating time varies from 1~5 s. Current varies from 7~13 mA for different arrays.
Figure 2-24 Illustration of nickel electroplating on CNT arrays

Figure 2-25 shows SEM images of nickel coating. These images show that some of the CNT arrays are successfully coated. Figure 2-25 (a) represents thick nickel layer coated on the top of a CNT array. From the image we can see that the coating is not uniform. Some parts are coated with a thick layer, while other parts are coated with small particles as shown in Figure 2-25 (b). With lower voltage applied, large nickel particles are observed on the top of a CNT array in Figure 2-25 (c). A close view in Figure 2-25 (d) shows that these particles glue the CNT bundles together. When high voltage (10 V) is applied, thick nickel layer is coated shown in Figure 2-25 (e). Breakage of the array is observed on the part coated with nickel. This is because the array shrinks in the solution and is then coated by nickel. When the array is dried, it returns to original shape but the nickel layer restrains its expansion. Therefore the expansion force breaks the nickel layer. Figure 2-25 (f) shows that nickel layer is coated on tips of the CNT bundles. From the SEM images of nickel coating (Figure 2-25 (a) 1V and (f) 5V), we can see that nickel layer under high voltage is more uniform.
Figure 2-25. Nickel coating on the top of CNT arrays.
Ends of six long CNT arrays are coated at 5~10 V to obtain relatively uniform nickel layers. Two of the arrays (array1 and array2) are annealed at 2600 °C for 4 h by Air Force. It is not clear if the other four arrays are post treated. Pulling is applied to the arrays before and after coating. Figure 2-26 shows results of the pulling of array1 and array2. The blue arrow indicates the connection of CNT bundles and the red arrow points to the final breakage. Before coating, it is noticed that one end of array1 is pullable, and the other is not, as shown in Figure 2-26 (a). The array1 was pulled for seven times with the same observation. After nickel coating, two out of six pulling give longer fibers shown in Figure 2-26 (b). During the other trials, CNT bundles either broke at the start of pulling or could not grab nearby bundles at the end. Similar result is observed for array2. It is also noticed that inside part of array2 behaves different from the outer layer. The outer layer is not pullable at both ends. The results presented are from the middle part of array2. The other four arrays tested are not pullable at both ends either before or after nickel coating. Based on these results, it seems nickel coating may help to bind the CNT bundles and enhance the spinnability of CNT arrays.

![Figure 2-26 Pulling of (a) array1 before nickel coating and (b) array1 after nickel coating](image)
2.4 Summary

In this chapter, dry spinning techniques for making CNT fibers from spinnable arrays are investigated. Parameters governing fiber structure have been studied such as twist angle, fiber diameter, and CNT length. For CNT fibers from different arrays, strength of CNT fibers has no obvious correlation with twist angle but seems to decrease with diameter. It is found that CNT fibers strength increases with CNT length. Post treatments such as post spinning, heat treatment and densification are applied to enhance the mechanical property of spun fibers. Post twisting and densification are effective in both increasing the load transfer between CNT bundles and reducing fiber diameters. Heat treatment at 2000°C in argon does not improve the performance of the CNT fiber. When temperature increases to 2700°C, both tensile strength and modulus of CNT fibers are improved.

The spinning approach for fluffy CNTs is studied in pursuit of spinning long CNTs. Long CNT arrays are sheared into small CNT bundles. The bundles are manually assembled into a continuous fiber through a solvent. For such a fiber, connections between CNT bundles are weak and thus the fiber is weak. In addition, the nickel coating method is proposed to enhance the connections of CNT bundles in long CNT arrays. Preliminary results of nickel coating on CNT arrays are obtained.
Chapter 3    Wet Spinning of CNT Fibers

In this chapter, various wet spinning methods that have been applied to spin CNT fibers using different types of CNTs are reported. The basic concept of wet spinning is to disperse CNTs with one solution, and then inject it into another solution in which part of the injected solution is dissolved and other part coagulates into fibers. First, the dispersion of CNTs is introduced, which is very important for the wet spinning technique. Then two different categories of wet spinning processes are presented, including CNT-based wet spinning and Polymer-based wet spinning. For each spinning approach, different types of CNTs are studied and compared using these two spinning techniques to evaluate the spinning performance.

3.1 Dispersion

Dispersion of CNTs into a solution is the key for performing wet spinning for making CNT fibers. Normally, mechanical approaches are adopted to disperse CNTs, including shearing, bath sonication and probe sonication. In addition, chemicals such as surfactants, polymers, and others are used along with mechanical methods. In the following section, various types of CNTs are tested, such as CNTs synthesized with catalyst on silicon substrate in Nanoworld Lab at UC, CNTs synthesized on steel film by General Nano, and CNT synthesized by HiPco process from Carbon Nanotechnology Incorporated (CNI). Treatments such as functionalization, purification, and annealing are applied to those CNTs.

3.1.1 CNT Types and Properties

This section gives a categorization of different CNTs applied in the study in terms of types and properties. One of the efficient approaches is using Raman spectroscopy, which has been
widely applied to determine the quality of CNTs as well as the diameter of SWNTs. Figure 3-1 (a) and (b) show the Raman spectra of SWNTs and MWNTs, respectively. We can see from Figure 3-1 (a) that SWNTs have peaks at frequency from 100 to 500 cm$^{-1}$, which is called the radial breathing mode (RBM). This mode is primarily dependent on the diameters of SWNTs. It has been reported that the diameter of SWNTs can be calculated by the equation $d$ (nm) = $A$/cm$^{-1}$, where $A$ is a constant that equals to 248 nm/cm [156]. Also, as seen in Figures 3-1(a) and (b), the peak at $\sim$1350 cm$^{-1}$ is called D-band which indicates certain defects of the CNTs. The high peak with frequency of 1582 cm$^{-1}$ is called G-band showing the active mode of graphite. Here, the ratio of the intensities of D-band and G-band (G/D ratio) is usually adopted as an indicator of the structural quality of CNTs.

![Figure 3-1. Raman spectra of (a) SWNTs and (b) MWNTs.](image)

Properties of CNTs used in this study are listed in Table 3-1. The functionalized SWNTs (F-SWNTs) are characterized by setting the RAMAN spectroscopy with 514 nm laser. Diameters are calculated to be 0.93 nm and 1.36 nm. Similarly, the diameters of DWNTs are 1.55 nm. G/D
ratios of different CNTs are listed in Table 3-1. It is noted that SWNTs have a G/D ratio of 20 and FSWNT has a lower value due to increased number of defects on sidewalls of tubes. G/D ratio of MWNTs provided by General Nano is 1.97 for pristine materials and 5.08~9.66 for that after annealing at 2600°C in argon. Plasma functionalization decreases the G/D ratio to 1.05~1.18 due to defects produced on the wall of MWNTs.

Table 3-1. CNT types and properties.

<table>
<thead>
<tr>
<th>CNT</th>
<th>Provider</th>
<th>CNT description</th>
<th>Raman G/D ratio</th>
<th>G/D ratio (nm)</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>CNI</td>
<td>-- functionalized SWNT</td>
<td>19.49, 16.76</td>
<td>0.92, 1.36</td>
<td>1~2 μm</td>
</tr>
<tr>
<td>DWNT</td>
<td>CNI</td>
<td>--</td>
<td>12.46</td>
<td>1.55</td>
<td>1~2 μm</td>
</tr>
<tr>
<td>MWNT</td>
<td>General Nano</td>
<td>2600°C argon</td>
<td>5.08~9.66</td>
<td>~20</td>
<td>0.1~5 mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>335°C air</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plasma functionalized</td>
<td>1.05~1.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWNT</td>
<td>Nanoworld</td>
<td>--</td>
<td>1.32</td>
<td>~10</td>
<td>0.3~0.5 mm</td>
</tr>
</tbody>
</table>

3.1.2 Surfactant Aided Dispersion

Mechanical methods have been used in dispersion of CNTs such as shearing, bath sonication, probe sonication (Figure 3-2), and filtration. The microscope images of dispersion by different methods are shown in Figure 3-3. The dispersion contains 0.15wt% CNT, 1wt% surfactant SDS, and distilled water. Total mass of dispersions shown in this section is 31 g unless notified otherwise. It can be seen that the shearing breaks CNT arrays into small bundles and there
is no obvious cutting effect of shearing. The size of CNT bundles decreases after long time of shearing. The dispersion was inhomogeneous and large bundles can be seen after 3 h shearing. To enhance the dispersion of these CNT bundles, bath sonication is then used along with the shearing. Clearly, we can see that the bath sonication exfoliates the CNT bundles and makes the CNT bundles fluffy. It should be noted that bath sonication is not very effective. Here, probe sonication is applied and has been considered as the most effective method to disperse CNT bundles. In this process, all these CNTs were cut into short pieces and CNT bundles break into small CNT aggregations. In our tests, the length of CNTs are reduced to less than 100 μm from 300 μm after 4 h probe sonication.

Figure 3-2 Photo of (a) shearing machine, (b) bath sonifier, and (c) probe sonifier
Figure 3-3. Dispersion of CNTs at Nanoworld. The dispersion contains 0.15% CNT, 1% SDS, and distilled water.
Then, similar dispersion procedure was applied to other types of CNTs. Note that same concentration of surfactant SDS is used. The CNTs collected from spinnable arrays are hard to achieve homogenous dispersion since these CNTs are highly entangled, while the adoption of prolonged probe sonication can achieve nearly homogeneous dispersion as shown in Figure 3-4 (a) and (b). Note that the mass of this dispersion is 10 g. Obviously, small CNT bundles can be seen after the sonication. SEM image shows that CNTs are surrounded by SDS. Although CNT arrays provided by General Nano has a height of 1~5 mm, the dispersion is easier than that of CNTs at Nanoworld which is 0.3~0.5 mm in length. Figure 3-4 (c) and (d) compare the dispersion quality of the two types. Higher concentration of CNTs from General Nano subjected to shorter sonication shows better quality of dispersion. SWNTs are short and have small diameters. They can be dispersed well with SDS. No noticeable aggregation is observed with microscope.
Figure 3-4. Dispersions of different CNT types. The dispersion contains CNT, 1 wt% SDS and distilled water.
Functional groups attached to walls of CNTs can facilitate the dispersion of CNTs in water. Plasma is used to functionalize the CNTs. To achieve a uniform functionalization, CNTs is sonicated in the acetone and dried into a thin layer. Acetone is used as a solvent because it has a stronger ability to wet CNTs than water and evaporates quickly. After the functionalization, CNTs are dispersed in water along with the SDS. Figure 3-5 shows the microscope image of the dispersion. We can see that the CNTs are better dispersed after functionalization. Furthermore, annealing is used to improve the structure of MWNTs provided by General Nano. After the annealing, the MWNTs is dispersed and sonicated. Figure 3-6 shows the dispersion quality. Annealing does not change the quality of dispersions.

![Image](image.png)

**Figure 3-5.** Dispersion of (a) pristine CNTs and (b) functionalized CNTs. The dispersion contains 0.15% CNT, 1% SDS, and distilled water.
Figure 3-6. Dispersion of 5 mm annealed MWNTs. The dispersion is filtered by P8 filter.

3.2 CNT Based Wet Spinning

3.2.1 Experimental Procedure

In this section, several wet spinning tests are introduced by using the in-house developed spinning device, as shown in Figure 3-7. The CNT dispersion prepared in the above section will be placed into a syringe, and the red box in the left is syringe pump controlling the injecting speed of the CNT dispersion to a bath. The CNT fibers are formulated in the bath. Also, there is a long needle connecting the syringe to the bath. The bath is placed on top of a fixer that rotates along with the injecting process. The rotating speed of the bath can be tuned by an electrical motor. The test procedure is as following, the first step is preparation of CNT dispersion as introduced in the above section. Here, the F-SWNT is purchased from CNI Company. A 10g mixture was prepared, which contains 0.1 – 0.4 wt% F-SWNTs, 1 wt% surfactant, and distilled water. The surfactant used is the SDS. The mixture was sonicated for at least 2 h by probe sonifier. The tip of the sonifier is 5 mm in diameter and it was put 10 mm or less below liquid surface. Otherwise materials near the surface may not be well sonicated. The output energy was set to level 3 (3~5 W). The mixture
was put in a bottle with the diameter of 20 mm. The bottle was put inside an acetone-water bath to keep the mixture from overheat. After the sonication, the mixture turned to be a stable homogenous CNT suspension.

![Experimental setup for wet spinning.](image)

Next, we need to prepare the bath solution. In this test, bath of 5% PVA solution was prepared by adding the PVA powder to distilled water and then kept it at 90℃ while stirring it until fully dissolved. The PVA solution was put away for 24 hours or bath sonicated for 4 hours to remove bubbles.

Then, the CNT dispersion is extruded into the PVA bath through a steel needle. The needle size varies from 0.2 \( \text{mm} \) to 0.5 \( \text{mm} \). The dispersion coagulates in the PVA bath and forms a continuous CNT fiber. The coagulated fibers are weak at the time of forming and require careful handling. Next, the fiber is transferred into a water container to remove the remaining PVA. Finally, the CNT fiber is dried in air after washing in water.
3.2.2 Results and Discussion

To better understand the fiber production process, parametric studies were performed to investigate the effect of each parameter on the performance of wet-spun fibers. The CNT dispersion quality is the key factor in the coagulation process. The first step is to find out minimum sonication time to disperse CNTs. A 10 ml sample with 0.2 wt% F-SWNT and 1 wt% SDS is prepared. The sample is subjected to the sonication and is injected into a PVA bath following the experimental procedure. Three different coagulation results are observed with the increase of sonication time, as shown in Figure 3-8. The dispersion has large amount of sediment with 15 min sonication, and the dispersion dissolves in the bath slowly when it is injected into the PVA bath. When sonication time was increased to 1 h, the dispersion has less sediment. However, the formulated gel fiber is too fragile to allow any handling. As the sonication time was increased above 2 h, the dispersion is nearly homogeneous. A well-formed CNT fiber is formulated as can be seen from Figure 3-8(c). Then, the tensile strengths of these CNT fibers were measured and the results are shown in Figure 3-9. Effect of sonication on the strength of CNT fibers is not obvious. The two series show different trends. Sonication facilitates exfoliation of CNT bundles which can improve strength. In the meantime, it shortens the CNTs. The cutting of CNT is adverse to the strength of the fiber.
Then three dispersions with different concentrations of F-SWNT are investigated, that is, 0.1 wt%, 0.2 wt%, and 0.3 wt%. The dispersions have same SDS concentration of 1 wt%. Average strength is listed in Table 3-2. It is found that the dispersion with 0.2 wt% F-SWNT
produced fibers of the highest strength. Aggregation of CNTs may happen in dispersion with 0.3% CNT and thus reduce the fiber strength.

Table 3-2. Strength and concentration of F-SWNT.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Concentration in dispersion (wt%)</th>
<th>Avg. tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>98.6</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>105.5</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>72.3</td>
</tr>
</tbody>
</table>

**Coagulation**

The coagulation is an important step in the fiber formation. In all those tests, it was found the coagulation rate of CNT and PVA is slow, and the time required for coagulation is typically about 1 min. Also, the prolonged coagulation time has no obvious effect on the strength. Hence, the coagulation time is set at 2~3 min in the following experiments. Long coagulation time is a major hurdle for the process to be continuous. Either a long channel for flowing bath or a low flow speed (production rate) is required. The following relation must be satisfied for making this spinning process continuous: Length of bath channel = flow speed × coagulation time. A 2.4 m channel for bath is required for continuous fiber production if flow speed of bath is 0.04 m/s which is currently used.

Morphological features of the fiber are influenced by coagulation conditions. Here four solutions of different PVA concentration were prepared, that is, 1 wt%, 3 wt%, 5 wt%, and 8 wt%. The same CNT dispersion was injected to these baths. The dispersion contains 0.2wt% CNT and 1 wt% SDS and was subjected to 4.5 h probe sonication. Gel fiber formed when by
injecting CNT dispersion to 1 wt% PVA solution. However, it was too fragile to be moved out of the PVA solution. The fiber produced from 3 wt% PVA was also weak but was transferred to water. The fiber was fully solidated after two days immersing in water. The 8 wt% PVA has high viscosity and the solution sticks to the coagulated fibers. Figure 3-10 shows that strengths of dried fibers are related to PVA concentration. Fiber produced from lower concentration PVA solution has higher strength. This is due to low coagulation rate for a low concentration PVA bath. In general, low coagulation rate yields dense fiber [157]. Large amount of water in the bath is actually solvent for CNT dispersions, which decreases the coagulation rate. It is noted that the optimum bath is the 5 wt% of PVA solution considering the strength and coagulation time.

Figure 3-10. PVA concentration and strength.

Effect of molecule weight of PVA on coagulation and strength of fibers is evaluated. In our current tests, two kinds of PVA are used. One has a molecule weight of 88,000 g/mol, and the other is 143,000 g/mol. PVA solutions that contain 5 wt% solid PVA were prepared. It is noted that a DWNT dispersion that does not coagulate in the low PVA solution coagulates in the high
PVA solution. Here results of FSWNT-PVA fibers are listed in Table 3-3. Fibers spun from the higher molecule weight PVA have tensile strength of 98.7MPa, which is stronger than the strength (84.9Mpa) using light weight PVA.

Table 3-3. Effects of PVA molecule weight on strength of fibers.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Tensile strength (MPa)</th>
<th>Modulus (GPa)</th>
<th>Elongation (%)</th>
<th>PVA Avg. M.W. (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>84.9</td>
<td>4.6</td>
<td>5.4</td>
<td>88,000</td>
</tr>
<tr>
<td>2</td>
<td>98.6</td>
<td>4.9</td>
<td>9.6</td>
<td>143,000</td>
</tr>
</tbody>
</table>

**Injection parameters**

The injection parameters such as injection rate, rotating speeding, and needle size are also studied. It is found that these parameters have quite a large range as long as relations between them are satisfied. The first thing is to make sure the bath flow is laminar. This is satisfied for all the rotating speed of the setup used. Needle size is related to the dispersion quality. For well dispersed SWNTs, gauge 30 (0.255 mm inner diameter) can be used. For most dispersions, gauge 25 (0.455 mm inner diameter) is used. For a given needle size, uniform fibers can be made with a proper injection rate. If the injection rate is too high, the fiber is found to have a bamboo-like structure, as shown in Figure 3-11. This is likely caused by bundles in dispersion. The bundles clogged the needle and accumulated pressure of the flow pushed them out. Rotating speed of the bath is adjusted according to injection rate. Low rotating speed will make the injected CNT dispersion stack near the needle. As a result, the fiber is wavy. High rotating speed will break the fiber into pieces. The appropriate rotating speed is slightly higher than injection rate so that the
shearing force is able to stretch but not break fibers. Figure 3-12 and Figure 3-13 show effect of injection rate and rotating speed on strength, respectively. Thicker fibers tend to be stronger. This is likely because thicker fibers have fewer defects. The key is to keep the fiber uniform so it is easy to carry out post treatments.

![Figure 3-11. Fibers with poor structure.](image)

![Figure 3-12. Injection rate and strength. Rotating speed is 7RPM. Off center distance is 5cm.](image)
3.2.3 Post Treatments

*Dry process and drawing*

The wet spun fiber is dried by hanging one end and leaving the other end attached to water. The ribbon-like fiber collapses into a dense fiber with semi-circular cross section during the dry process. This collapse is caused by surface tension force. The dried fiber has a rugged surface shown in Figure 3-14. These wrinkles cannot be eliminated by drawing. It is also noted that several wet fibers can collapse into a single fiber (plied fiber) in the dry process as shown in Figure 3-15. The plied fiber has good stability in water, similar to as-produced fibers.

Figure 3-13. Rotating rate and strength. Injection rate is 0.8ml/min.
Then, drawing test was conducted to study the elasticity of wet fibers before and after the drying process. As can be seen from Table 3-5 and 3-6, the wet fibers have better elasticity than dried fibers. Elongation of wet fiber depends highly on the extension rate. Under a low extension rate, wet fibers have maximum extension of about 36% (The fiber is manually drawn). Fibers drawn in the room temperature have similar strength to as-spun fibers, though elongation rate is
reduced after drawing. The strength of plied fibers increases by 11% in average, but the increase has no statistical importance.

Table 3-4. Maximum elongation of wet fibers.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Length in water</th>
<th>Length after drawing</th>
<th>Drawing elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35</td>
<td>49</td>
<td>0.40</td>
</tr>
<tr>
<td>2</td>
<td>32</td>
<td>46</td>
<td>0.44</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>130</td>
<td>0.30</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>62</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 3-5. Effect of drawing on fiber strength (10~15 specimens).

<table>
<thead>
<tr>
<th>Fiber</th>
<th>treatment</th>
<th>Strength(MPa)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>As-produced</td>
<td>74.37</td>
<td>15.60</td>
</tr>
<tr>
<td>2</td>
<td>drawn</td>
<td>72.20</td>
<td>6.97</td>
</tr>
<tr>
<td>4</td>
<td>Ply drawn</td>
<td>80.21</td>
<td>3.36</td>
</tr>
</tbody>
</table>

Hot drawing was performed by drawing the fiber on top of a heater, as shown in Figure 3-16. The temperature is non uniform along the surface of the heater, so a block of steel is put on top of the heater. Top surface of the metal has a temperature of 80 – 90 °C when the heater temperature is set to 300°C. Tensile strengths of drawn fibers are listed in Table 3-6, which shows that hot drawing increased the strength of fibers. The reason is that the inner molecular chains become more oriented to the fiber axis as the fibers were drawn. Strength improvement by drawing under higher temperature is more significant. This is because higher temperature allows higher draw ratio and better rearrangement of PVA molecules and CNTs. Note that elongation of CNT
fibers is calculated by the average change of length while in fact the center of the fiber is drawn most. Further strength improvement is expected if the fiber is uniformly drawn under higher temperature.

![Diagram of hot drawing process](image)

Figure 3-16. Illustration of hot drawing process.

Table 3-6. Effect of hot drawing on strength of fibers (Pull rate: 1cm/min).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>Set temperature-real temperature (°C)</th>
<th>Drawing elongation (%)</th>
<th>Diameter (μm)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>none</td>
<td>0</td>
<td>0</td>
<td>47.21</td>
<td>91.46</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>130-40</td>
<td>47.37</td>
<td>37.53</td>
<td>146.56</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>160-40</td>
<td>17.98</td>
<td>41.60</td>
<td>143.00</td>
</tr>
<tr>
<td>0</td>
<td>none</td>
<td>0</td>
<td>0</td>
<td>46.09</td>
<td>73.22</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>300-85</td>
<td>73.47</td>
<td>43.17</td>
<td>131.70</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>300-85</td>
<td>--</td>
<td>36.6</td>
<td>167.78</td>
</tr>
</tbody>
</table>

**Low temperature heat treatment**

Heat treatment with a lower temperature in air is applied to remove the PVA in CNT fibers. Two samples of CNT-PVA fibers were kept in an oven at 100°C and 310°C for 3 h in air, respectively. Table 3-7 shows the results of low temperature heating in air. After heating at 100°C, the electrical resistivity of the fiber is reduced and the strength remains the same. Also, the fibers
do not swell as much as the as-produced fibers when they are put in water. Thermal treatment at 100℃ involves mainly loss of physically absorbed water in the fiber [158]. In contrast, heating at 310℃ causes partial dehydration of PVA and formation of polyene. The electrical resistivity of CNT fibers is improved to the order of dry-spun CNT fibers, but the strength drops to 7.64 MPa. This is because the PVA has a melting point of 230℃ and it decomposes rapidly above 200℃. Figure 3-17 shows cross sections of fibers before and after the heat treatment at 310℃. More CNT bundles are observed after the heat treatment. Failure mode of the fiber does not change too much. Unlike as-produced fibers, these fibers have good stability in water.

![Figure 3-17. SEM image of (a) an as-produced fiber and (b) a fiber after 310℃ annealing in air (scale bar: 500 nm for both).](image)

Table 3-7. Properties of CNT fibers that are heated in air.

<table>
<thead>
<tr>
<th></th>
<th>Treatment</th>
<th>Resistivity (Ω · m)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample1</td>
<td>none</td>
<td>$6.8 \times 10^{-3}$</td>
<td>73.22</td>
</tr>
<tr>
<td></td>
<td>100℃ 3h</td>
<td>$8.5 \times 10^{-4}$</td>
<td>71.34</td>
</tr>
<tr>
<td>Sample2</td>
<td>none</td>
<td>$1.2 \times 10^{-3}$</td>
<td>109.31</td>
</tr>
<tr>
<td></td>
<td>310℃ 3h</td>
<td>$4.8 \times 10^{-5}$</td>
<td>7.64</td>
</tr>
</tbody>
</table>
3.2.4 Spinning of MWNTs and Coagulation Mechanism

It is noted that MWNTs produced by a CVD method cannot be wet spun into strong fibers by CNT based spinning methods. Compared to MWNTs, F-SWNTs have higher Raman G/D ratio, functional groups, shorter length, and smaller diameter. Efforts have been devoted to the spinning of MWNTs provided by General Nano. MWNTs is thermal annealed at high temperature in order to improve CNT structure. Annealing is done at 2600°C in argon. Raman G/D ratio of 9 for MWNTs is obtained after annealing, which is considerably high. However, structure improvement and removal of impurities of MWNTs show no obvious help in dispersion or spinning. Plasma functionalization is used to oxide walls of MWNTs which is verified by Raman spectra. Functional groups on sidewalls of MWNTs may contribute to dispersion, but do not make MWNTs dispersion into fibers. Oxidation in air is tried in order to remove amorphous carbon and produce defects on CNTs, which turned out to be useless.

As sonication helps coagulation of FSWNT in PVA bath, MWNT dispersion was sonicated for up to 16 h. Annealed 5 mm MWNTs provided by General Nano did not coagulate in PVA bath. The dispersion contains 0.7 wt% of MWNT and 1 wt % SDS. After sonication, the dispersion is filtered by a filter paper (qualitative grade: P8, Particle Retention: > 20µm, purchased from fisher scientific). The MWNT dispersion provided by Arvind did coagulate in PVA bath after about 10 h sonication. The dispersion contains 0.13 wt% of MWNT and 1 wt % SDS. However, the coagulated fiber has a porous structure and the formed gel is weakly bounded together (Figure 3-18).
After a long time of sonication, the difference between dispersions of MWNTs and that of SWNTs is not obvious when light microscope is used to detect bundles. Small bundles are spotted in both dispersions. It is noticed that crystallization pattern of SDS/SWNT dispersion is different from SDS/MWNT dispersion (Figure 3-20). SWNTs induce SDS to form triangular shape crystal, while MWNTs do not influence SDS crystal pattern. The diameter of CNTs is likely to be the reason.
Depletion interactions might be the main reason for the formation of fibers when CNT dispersion is injected into PVA solution. When macromolecules are added to a stable colloid, they cannot occupy the space between nanoparticles if the distance between nanoparticles in the colloid is smaller than the size of the macromolecules. An osmotic pressure arises to eliminate the region of no macromolecules. The force induced by osmotic pressure is called depletion attraction [159–161]. Figure 3-21 shows an illustration of depletion attraction for rod-like particles. PVA has a size of tens of nanometers. Mean diameter of MWNTs provided by General Nano is 20 nm, which is similar to the size of PVA, while SWNT has a diameter of 1 nm. SDS also has a rod-like structure and is about 1 nm in length. When SWNT dispersion is added into PVA bath, space between SWNTs are small and cannot be occupied by PVA and thus is pressed together. On the other hand,
MWNTs have similar size to PVA molecule and tend to diffuse into PVA bath. Using a similar method, spinning of MWNTs of $10\, nm$ diameter has been reported in literature [124,133].

![Illustration of coagulation induced by depletion attraction](image)

Figure 3-21. Illustration of coagulation induced by depletion attraction [160].

### 3.3 Polymer Based Wet Spinning

#### 3.3.1 Experimental Procedure

In this set of experiments, CNT is first dispersed in distilled water or Dimethyl sulfoxide (DMSO, purchased from Sigma-Aldrich). The dispersion was subjected to up to 4 h bath sonication or probe sonication. PVA powder is then added to the dispersion. PVA is used as matrix because it has the potential to be high performance fiber and can be easily processed [162,163].
The mixture is heated to 90℃ and is kept stirred to facilitate the dissolve of PVA. The dispersion is then extruded into different baths.

### 3.3.2 Results and Discussion

**Ethanol as bath**

Ethanol is a coagulant for PVA solution. DWNT dispersion contains 0.35 wt% DWNT (CNI, 1 \( \mu m \)) and 10 wt% PVA. MWNT dispersion has 0.5 wt% CNT (General Nano, 100 \( \mu m \)) and 9 wt% PVA. The dispersions are subjected to 15 min probe sonication. Another MWNT dispersion is prepared to study enhancement of strength, which contains 0.5 wt% CNT (General Nano, 100 \( \mu m \)) and 5 wt% PVA. Neat PVA sheet is produced as the control group. Boric acid is added in order to crosslink PVA. The amount of boric acid is 0.3 wt% of solid PVA. The dispersion is subjected to 5 min probe sonication and 80 min bath sonication.

Dispersion of CNT and PVA coagulates into ribbon-like fibers when it is injected into ethanol. The fiber coagulates fully in seconds. The strength of the produced composite fibers is low for both DWNT and MWNT as listed in Table 3-8. Fibers with DWNT as filler have a stronger strength than that of MWNTs. This is likely due to the better dispersion of CNTs in fibers. As the fibers have irregular cross section, sheet is produced to help obtain accurate tensile results. A piece of sheet is shown in Figure 3-23. Micro pores are observed on the surface of the fiber (Figure 3-22). These pores are responsible for the low strength. CNT bundles are seen on the cross section of the fibers (Figure 3-22). The fiber is insulator though it contains about 2.6 wt% CNTs. No improvement in strength of fiber is achieved by adding CNTs into PVA solution. Adding of boric acid does not improve strength effectively.
Table 3-8. CNT types and treatment on strength of CNT fibers.

<table>
<thead>
<tr>
<th>Type</th>
<th>CNT</th>
<th>PVA</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber</td>
<td>0.35 wt% DWNT</td>
<td>10 wt%</td>
<td>62.50</td>
</tr>
<tr>
<td></td>
<td>0.5 wt% MWNT</td>
<td>9 wt%</td>
<td>43.52</td>
</tr>
<tr>
<td>sheet</td>
<td>none</td>
<td>10 wt%</td>
<td>12.13</td>
</tr>
<tr>
<td></td>
<td>0.5 wt% MWNT</td>
<td>10 wt%</td>
<td>12.64</td>
</tr>
<tr>
<td></td>
<td>0.5 wt% MWNT</td>
<td>10 wt% with boric acid</td>
<td>13.76</td>
</tr>
</tbody>
</table>

Figure 3-22. SEM image of (a) micro pores observed on surface of a CNT-PVA fiber (b) CNT bundles at the cross section of a fiber.

Figure 3-23. A piece of CNT-PVA sheet.
**Sodium sulfate solution as bath**

Sodium sulfate solution bath is commonly used in production of PVA fibers in industry. Saturated sodium sulfate solution at 40°C is used. Coagulation rate is fast. Unlike other methods, the produced fibers have circular cross sections. Fibers with 6.7 wt% CNT are produced in this way. The produced fiber is fragile after drying. The tensile strength is measured to be 5 MPa. One problem of this method is that the injected coagulates into semi solids and stick to needle (see Figure 3-24).

![Figure 3-24. Clog of the dispersion in extruding process.](image)

**Methanol as bath**

The third bath used is methanol. Dispersions of different F-SWNT concentrations are prepared. PVA concentration is 15 wt% for all the dispersions. Ratios of F-SWNT to solid PVA are 0, 8 %, and 20 %. In the experiment, hot dispersion (about 70°C) of high concentration of PVA (15 wt%) is injected into cold methanol bath at 5 – 8 °C. Hot drawing is applied to all the fibers.

It is found that the dispersion does not coagulate in methanol at room temperature. Also, dispersion of low PVA concentration only partly coagulates. Therefore high concentration of PVA solution is needed. Figure 3-25 shows the strength distribution of 20 % fibers. As-produced fibers
with smaller diameter tend to have stronger strength. This is probably because thinner fibers keep the alignment better during the injection process.

![Graph showing effective strength vs. diameter for PVA-CNT fibers.](image)

Figure 3-25. Strength distribution of as-produced 20% CNT fibers.

Mechanical properties of PVA-CNT fibers are listed in Table 3-9. From the table we can see that neat PVA fiber has the highest strain, while fibers with 8% CNT have the highest strength. Aggregation of CNTs may happen in 20% CNT-PVA fibers and cause low strength. Temperature of hot drawing is at the range of 80~100°C. These fibers can be drawn to several times of its original length. For fiber with 20% CNT concentration, the strain increases by hot drawing. This is likely caused by rearrangement of CNT and PVA molecular alignment due to the heat energy. Strengths are in the range of 30~70 MPa for as-produced fibers and fibers drawn in room temperature. After hot drawing, the strength is improved to 200~300 MPa. Figure 3-27 shows a typical stress-strain curve for fibers before and after hot drawing.
Table 3-9. Effect of hot drawing on PVA-CNT fibers.

<table>
<thead>
<tr>
<th>F-SWNT/PVA</th>
<th>Treatment</th>
<th>Strength (MPa)</th>
<th>Strain (mm/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>--</td>
<td>49.23</td>
<td>184.50%</td>
</tr>
<tr>
<td></td>
<td>Hot drawing</td>
<td>220.42</td>
<td>51.23%</td>
</tr>
<tr>
<td>8 wt%</td>
<td>--</td>
<td>56.13</td>
<td>61.50%</td>
</tr>
<tr>
<td></td>
<td>Hot drawing</td>
<td>312.54</td>
<td>48.12%</td>
</tr>
<tr>
<td>20 wt%</td>
<td>--</td>
<td>44.73</td>
<td>14.25%</td>
</tr>
<tr>
<td></td>
<td>Hot drawing</td>
<td>215.48</td>
<td>49.23%</td>
</tr>
</tbody>
</table>

Figure 3-26. Comparison of strength of PVA-CNT fibers.
Stability of fibers was tested at room temperature. As-produced fibers soften and gradually dissolve in water. After hot drawing, fibers coil as soon as it contacted water and eventually dissolve in water. The electrical resistance of fibers before and after hot drawing is out of the range of four probe method. These fibers are insulator despite large concentration of CNTs in the fiber.

3.4 Summary

Several methods have been tried to wet spin CNT fibers. Results of each method applied to CNTs are listed in Table 3-10. Coagulation happens in most cases. However, not all coagulated fibers are strong. Some of the coagulated fibers are so weak that they break when moved out of bath, which is noted as ‘weak’ in the table.
Table 3-10. Summary of wet spinning methods used in making CNT fibers.

<table>
<thead>
<tr>
<th>CNT type</th>
<th>Surfactant/polymer</th>
<th>Bath</th>
<th>Coagulation</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT based spinning</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-SWNT SWNT DWNT</td>
<td>SDS</td>
<td>PVA solution</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>High M.W. PVA solution</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ethanol/acetone</td>
<td>Yes</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37% HCl solution</td>
<td>Yes</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td>SDS, PVP</td>
<td>5% PVA solution</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>MWNT</td>
<td>SDS</td>
<td>PVA solution</td>
<td>Yes</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td></td>
<td>High M.W. PVA solution</td>
<td>Yes</td>
<td>Weak</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37% HCl solution</td>
<td>Yes</td>
<td>Weak</td>
</tr>
<tr>
<td>Polymer based spinning</td>
<td>PVP</td>
<td>5% PVA solution</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PVA</td>
<td>Na$_2$SO$_4$ solution</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PVA</td>
<td>Ethanol</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PVA, boric acid</td>
<td>Ethanol and KOH</td>
<td>Yes</td>
<td>Ribbon</td>
</tr>
<tr>
<td></td>
<td>PVA, boric acid</td>
<td>Methanol</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PVA, boric acid</td>
<td>Acetone</td>
<td>Yes</td>
<td>Stick to needle</td>
</tr>
<tr>
<td></td>
<td>PVA, DMSO</td>
<td>Methanol (cold)</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

Coagulation of CNT dispersions in PVA bath is studied. This approach is dependent on CNT types. Purchased SWNT, DWNT, and F-SWNT can be spun into fibers, while MWNTs produced in Nanoworld and General Nano cannot be spun into fibers. F-SWNT produces the strongest fiber among the four types. Spinning of F-SWNT-PVA fiber is studied. Uniform fibers can be obtained by controlling needle size, injection rate, and flow speed. The long coagulation time makes it hard to be a continuous process. Also, it is hard to control the amount of CNT in
fiber. Hot drawing of the fiber is used to improve strength. Low temperature annealing in air removes part of PVA in fiber and improves electrical properties. However, the annealed fiber has low tensile strength.

CNTs can be added as fillers in polymer spinning. Properties of such a CNT-PVA composite fiber are dominated by polymer PVA. These fibers are insulators and they dissolve in water. CNTs can enhance the strength of polymer when they are well dispersed in the polymer. CNTs of high concentration tend to aggregate and thus decrease the strength. Hot drawing improves the strength of the CNT-PVA fibers.
4.1 Conclusion

In this thesis, spinning techniques for CNT fibers have been studied. Firstly spinning from spinnable arrays is introduced. Novel techniques are proposed for spinning long CNTs. Wet spinning methods are also investigated.

Spinning from spinnable arrays is a well-established method. Here parameters governing fiber structure have been studied such as twist angle, fiber diameter, and CNT length. For CNT fibers from different arrays, strength has no obvious correlation with twist angle but seems to decrease with diameter. Strength of the majority CNT fibers is in the range of 100~300 MPa. It is found that strength of CNT fibers increases with CNT length. Post treatments such as post spinning and heat treatment are applied to enhance the mechanical property of spun fibers. Post twisting is effective in both increasing the load transfer between CNT bundles and reducing fiber diameter. Heat treatment at 2000℃ in argon does not improve the performance of the CNT fiber. When temperature increases to 2700℃, both tensile strength and modulus of CNT fibers are improved.

Study on spinnable arrays shows that longer CNT produce stronger CNT fibers. Therefore, novel spinning approaches for long CNTs are investigated. The spinning of fluffy CNTs is introduced. Long CNT arrays are sheared into small CNT bundles. These bundles can be manually assembled into a continuous fiber through a solvent. Electrical resistivity of such a fiber is 1.43 × 10⁻⁵ Ω · m, which is comparable to fibers spun from spinnable arrays. However, strength is only 20 MPa due to weak connections between CNT bundles. Another proposed approach to spin long
CNT is the nickel coating method. In this method, nickel is electroplated to the top and bottom of long CNT arrays in order to bind the ends of bundles. Preliminary results of nickel coating on CNT arrays are obtained.

Wet spinning methods are also investigated. One method is the coagulation of surfactant dispersed CNTs in PVA bath. This approach is found to depend on CNT types. Spinning of FSWNT-PVA fiber is studied. Uniform fibers can be obtained by controlling needle size, injection rate, and flow speed. The fibers have strength of $80 \text{ MPa}$ and electrical resistivity of about $6.8 \times 10^{-3} \Omega \cdot \text{m}$. The fibers swell but do not dissolve in water. Hot drawing of the fiber improves strength to $140 \text{ MPa}$. Low temperature annealing in air removes part of PVA in fiber and improves electrical resistivity to $4.8 \times 10^{-5} \Omega \cdot \text{m}$. However, the annealed fiber has low tensile strength. In this method, long coagulation time is required which makes it hard to be a continuous process. Also, it is hard to control the amount of CNTs in the fiber.

The other wet spinning method studied is adding CNTs into a polymer solution as fillers. Addition of CNTs improves the strength of polymer when CNT concentration is low. High concentration CNT tends to aggregate and thus decrease the strength. Hot drawing improves the strength of the CNT-PVA fibers from $56 \text{ MPa}$ to $310 \text{ MPa}$. However, properties of such a CNT-PVA composite fiber are dominated by polymer PVA. These fibers dissolve in water and are insulators despite of the high concentration of CNTs.

4.2 Future Work

The challenge in this research is to assemble CNTs into continuous fibers that preserve properties of individual CNTs. A variety of research directions need to be pursued further to make strong CNT fibers feasible.
1) Study of thermal annealing on CNT fibers is a possible direction, as it gives promising results for developing neat CNT fibers with good mechanical and electrical properties. In addition, thermal annealing may benefit the investigation of interactions between CNT bundles, since annealing can provide different interfaces between CNT bundles by improving CNT structures and reducing impurities.

2) Synthesis of long spinnable SWNT arrays would be an ideal approach, based on the findings that individual SWNTs shows much higher strength than MWNTs and that CNT fibers spun from longer CNT arrays are stronger.

3) For current unspinnable long CNT arrays, it is necessary to improve the structure uniformity and strength of CNT bundles. In respect to spinning, a small twisting setup may be considered to twist the CNT bundles and thus enhance their coherence.

4) For wet spun composite CNT fibers, further study may include improving alignment of CNTs in fibers and interfacial bonding between the matrix and CNTs.
Bibliography


