Mechanical behaviour of carbon nanotube fibers spun from vertically aligned arrays

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**MECHANICAL BEHAVIOR OF CARBON NANOTUBE
FIBERS SPUN FROM VERTICALLY ALIGNED ARRAYS**

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

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Summary

Due to their unique structure, carbon nanotubes (CNTs) have excellent properties including high thermal conductivity, high current capacity, and superior mechanical and chemical properties, which make them excellent one-dimensional materials with potentially wide applications. In order to utilize these properties, nano-scale CNTs must be prepared into macro-scale assemblies. CNT fibers, notably the fibers spun from vertically aligned CNT arrays, have therefore attracted great attention in recent years. Although these fibers have the inherent potential of leveraging on the excellence of CNTs, the individual fiber's properties strongly depend on their structures and morphologies. The strength of the best fibers is still much lower than the theoretical and experimental results from individual CNTs or small CNT bundles. Moreover, up to now, no attention has been paid to the influence of test condition, specifically strain rate effects on mechanical performances of CNT fibers.

The goal of this research is to investigate the structural properties of CNT fibers, and study the strain rate dependent failure mechanisms and its relation to the fibers' structure and morphology of failure. CNT fibers were directly spun from vertically aligned CNT arrays. The mechanical behaviors of CNT fibers were investigated for a wide range of tensile strain rates employing several characterization techniques, including static/dynamic tensile tests, polarized Raman spectroscopy, and fiber fracture surface observations. From these systematic studies, the failure mechanism of CNT fibers was analyzed and their relation to fibers' structures was deduced. The

results could be divided into the following sections:

Firstly, the general properties of CNT fibers that were spun from CNT arrays were provided. The mechanical strength and electrical conductivity of CNT fibers were measured statistically. The structural properties of CNT fibers were characterized by Raman spectroscopy and non-uniform twisting was found inside the fiber. It was found that once the spinning process was fixed, the uniformity of fibers' mechanical strength and electrical conductivity was fixed. Based on these systematic experiments, a fixed fiber spinning process was determined for the follow-on studies.

Then, CNT fibers were tensile tested in a wide range of strain rates. It was found that the mechanical response of CNT fibers exhibited a strain rate strengthening effect, and two different failure mechanisms dominated at high and low tensile strain rates, respectively. The key factors, inter-tube slippage and CNT alignment, that limited the mechanical properties of current CNT fibers were then discussed and possible failure mechanisms were proposed based on fibers' mechanical behavior and the observations of fracture surfaces by scanning electron microscopy (SEM).

Mechanical behavior and reliability of CNT fibers were then studied in detail under low strain rates. Static mechanical test and electrical measurement, combined with an in situ Raman spectroscopy, were used to monitor the load transfer and failure process. The morphology of CNTs in the fibers was characterized by transmission electron microscopy (TEM). The results further confirmed that the performance of CNT fibers at low strain rates was determined by slippage and breakage between

nanotubes or small tube bundles. An improvement approach was proposed and studied by introducing a second element with a 3-D network structured polymer to improve the load transfer efficiency between CNTs (or small CNT bundles) inside the fibers. It was demonstrated that the CNTs in the fiber could be effectively constrained, resulting in more effective load transfer.

Comparatively, at high strain rates, the structure dependent mechanical performance of the CNT fibers was investigated. A facile approach was applied to improve the alignment of CNTs by re-wetting, swelling, and re-drying the CNT fibers in a dilute HCl solution. The alignment of CNTs and its influence on fibers were examined. The mechanical behaviors of CNT fibers before and after post-treatment were compared as well. It was found that the alignment of CNTs showed significant influence on fibers' mechanical strength.

Finally, statistical methods employing modified Weibull models was developed to analyze the distribution of mechanical strength and failure mechanisms of fibril materials, was introduced to examine the breaking mechanisms under different strain rates. Variation of fibers' strength and its dependence on fibers' diameters and strain rates were investigated. Based on statistical analysis of our experimental data, further mathematical evidence could be deduced to support the failure mechanisms proposed for low and high strain rates.

Chapter 1 Introduction

The introduction chapter provides some background information about Carbon nanotube (CNT) fibers and recent progress in the failure mechanism analysis of CNT fibers. The research objectives, detailed scope of this research and outline of this thesis are documented.

1.1 Background of CNT fibers

CNTs have been reported to have ultra-high tensile strength (11 GPa to 60 GPa) and Young's modulus (0.5 TPa to 5 TPa), which are much higher than all other materials [1-3]. At the same time, they exhibit high stiffness, low density, good chemical stability, and high thermal and electrical conductivities [4-8]. These superior and unique properties make CNTs very attractive for many structural applications and technologies, such as aerospace structures, body armors, and sporting goods. However, due to their small size, it is difficult to utilize them in practical applications [9-11]. Comparably, assembling CNTs into macroscale articles is one promising approach to push CNTs into practical applications. Early studies focused on CNT-reinforced nanocomposites showing that CNTs were effective fillers to enhance the mechanical properties of polymer matrices, but the reinforcement was limited by the quality of dispersion, CNT alignment, and load transfer efficiency at the interface between CNT and polymer matrices [12].

CNT fibers spun from vertically aligned arrays, which was firstly reported in

2002 [13], received more and more attentions in the recent years [13-18]. They inherit excellent mechanical strength, and at the same time possess excellent electrical and thermal conductivity, which make them ideal building blocks for high performance engineering materials and lead to large scale applications possible due to the simplicity in fiber spinning process. For example, high electrical conductivity of pure CNT fibers in the range of 300 to 600 S cm⁻¹ has been demonstrated, which is much higher than that of buckypapers and CNT-based composites. Their mechanical strengths were measured in the range of 0.25-3.3 GPa. Combined with their light weight, the specific mechanical strength in GPa (g cm⁻³)⁻¹ of CNT fibers is even higher than that of commercialized carbon fibers.

1.2 Mechanism concern of fibers' mechanical failure

As fibers are assembled by interconnected individual CNTs and small bundles, fibers' microstructures have significant influence on their mechanical performances. At the same time, test condition, for instance strain rate, has always been considered to have great influence on mechanical behavior of tested materials. Until now, only a few studies have been reported to quantitatively relate the structure of CNT fibers, which were spun from different processes, to their mechanical behaviors. In the case of fibers directly spun from chemical vapor deposition (CVD) furnace, both Li and Windle have found that serious sliding exists when fibers are under tension [19-21]. By using Raman scattering as nondestructive monitoring tool, Xie investigate the structural deformation process of single-walled CNT (SWNT) networks and their

derivation, SWNT fibers [22]. They also found that the sliding exists and the strengths of CNT fibers are determined by the strength of inter-bundle junctions.

Comparably, in recent years, much effort has been paid to improve the mechanical strength of CNT fibers spun from vertically aligned arrays, including different post-treatment, morphology control of CNT arrays, spinning process improvement and modification of CNT fibers [4, 23-27]. Up to now, significant progresses have been achieved on strength improvement. Unfortunately, a systematic study and a comprehensive understanding on strain rate dependent mechanical property and failure mechanism of CNT fibers spun from vertically aligned arrays still lack. Meanwhile, the microstructures of CNT fibers are strongly spinning process dependent. Thus, the strain rate dependent failure mechanisms and their relationship to fibers' microstructures together with a statistical analysis subject to test conditions and scale effect are the research interests investigated and reported in this thesis.

1.3 Objectives

The objective of this study is to develop experiments and analyses to fill the research gaps in:

- 1) To develop fiber spinning process and study the structural properties of as-spun CNT fibers;
- 2) To investigate strain rate dependent mechanical behavior of CNT fibers and strain rate dependent failure mechanisms; correlate the mechanical behavior

of CNT fibers with their structures;

- 3) To develop statistical models to capture the different impacts of strain rate and diameter on fibers' mechanical strength, thus then mathematically analyze the failure mechanisms of CNT fibers.

The research outcome is to develop:

- 1) A methodology for spinning CNT fibers and characterizing fibers' properties;
- 2) Deeper understanding of strain rate dependent mechanical behavior of CNT fibers and their correlation to fibers' microstructures;
- 3) A modified Weibull model to include the influence of strain rate and diameter and give mathematical evidence to failure mechanisms proposed in this study.

1.4 Scope

The detailed scope of this study involves the following six categories:

1) *To synthesize spinnable CNT arrays and prepare fiber samples for mechanical tests.* The growth process of vertically aligned CNT arrays by CVD method and the spinning process of CNT fibers from vertically aligned arrays were briefly introduced. The quantitative description of spinnability of CNT arrays was defined. And the preparation of fiber samples for mechanical and electrical tests were detailed described.

2) *To investigate the general properties of CNT fibers.* Capillary induced

densification and twisting, which are believed to enhance the interfacial interaction between individual CNTs inside the fibers, were employed during spinning process. The mechanical stress-strain behavior and electrical conductive properties of CNT fibers were measured. Then the structural property of as-spun CNT fibers was characterized by depth-profile Raman Spectroscopy.

3) *To study the effects of test conditions (strain rates) on mechanical behaviors of CNT fibers.* It is well known that the strain rate, among other test conditions, has great influence on mechanical behavior of tested materials. The comparative studies of mechanical strength, strain and Young's modulus of CNT fibers tested at different strain rates were performed. SEM was extensively employed to characterize the morphologies of fiber fracture surfaces. The failure mechanism was then proposed from the strain-rate dependences as well, together with the results from fiber's fracture morphology.

4) *To investigate the failure mechanism of CNT fibers under low strain rates and correlate failure mechanisms to fibers' microstructures.* Mechanical behavior of CNT fibers was examined under low strain rates. Static mechanical test, electrical measurement and Raman spectroscopy were utilized to in-situ monitor the load transfer and failure process. Transmission electron microscopy (TEM) was employed to characterize the microstructure of CNT fibers. The correlation between fiber failure mechanism and CNT arrangements was discussed. Finally, the concept of introducing a 3-D net-work polymer was demonstrated to improve the load transfer at the

interface, and the mechanical behavior of resultant fibers was fully characterized.

5) *To examine the failure mechanism of CNT fibers at high strain rates and the influence of CNTs' alignment on fiber mechanical strength.* Alignment of CNTs inside the fibers has always been considered as an important factor that will improve fibers' mechanical performances. In order to examine the influence of CNTs alignment on fibers mechanical performance, a post-treatment approach was introduced by rewetting CNT fiber in weak acid solution. The morphology of CNTs inside the fibers was characterized by SEM and polarized Raman spectroscopy. Mechanical performance of resultant CNT fibers was tested accordingly.

6) *To analyze the variation of fiber strength and failure mechanisms by modified Weibull models.* The effect of strain rates on mechanical behaviors of CNT fibers was examined by a mathematical approach. The distributions of fiber strength were evaluated by taking into account strain rates and fiber diameters. Through developing modified Weibull strength distribution models by adopting strain rate and fiber diameter as variants, correlations between strain rate effects on ultimate strength in a power law breakdown frame-work and failure mechanisms were built up.

1.5 Outline of the thesis

This thesis is organized into eight chapters. Chapter 1 and 2 are the introduction and literature review chapters in order to provide background information about the research topic, highlight the state of progress, find out technical challenges/issues, and

define research directions. Chapter 3 is experimental details, in which the sample preparation/characterization, experimental setups and test procedures are detailed. Chapters 4 to Chapter 6 are the main parts of this thesis, including individual illustration of experiments, results, data analysis, discussion and summary in each chapter. Chapter 7 is the conclusion. Finally comes Chapter 8 which is recommendation for future work.

Chapter 2 Literature Review

CNTs are much stronger than any other engineering materials. Their tensile strength is about 11-63 GPa for individual multi-walled CNTs (MWNTs) and 13-52 GPa for individual SWNTs [1-3, 28]. They are also good conductors for electricity and heat [5, 7, 29-34]. However, the ultra small size makes them difficult to handle in practical applications. In order to utilize their extremely high strength, CNTs must be assembled into larger size assemblies, such as macroscopic CNT fibers. Recent progresses [4, 14, 15, 17, 24, 35, 36] in CNT fibers demonstrate the possibility to retain CNT's excellent properties at larger scale and more practicable level.

In this section, the properties of CNT fibers were briefly reviewed including different fabrication methods, structure dependent mechanical performances resulted from different fabrication approaches, and the effects of test conditions on fibers' mechanical behavior. Following that, various characterization methods, such as static/dynamic tensile test and in-situ electrical measurement during tension and polarized Raman spectroscopy & their capabilities in in-situ monitoring stress transfer and structural changes of CNT fibers, were introduced. These methods could be utilized to characterize stress relaxation, load transfer and failure evolution processes. Finally, a statistical model based on Weibull distribution and its applications in predicting failure mechanism in a mathematical way were depicted.

2.1 Properties of CNT fibers

2.1.1 Fabrication of CNT fibers

Numerous methods have been developed to assemble CNT fibers [10]. Generally, these techniques could be divided into two groups: solution-spinning methods [37-41] and solid-spinning techniques [13, 14, 35, 42, 43]. In solution-based spinning, CNTs need to be dispersed into a liquid first, and then spun into fibers, by a process similar to that used for polymeric fibers. In solid-spinning processes, CNT fibers could be spun from cotton-like CNT mats [35, 43], from an aerogel of CNTs formed in CVD reaction zone [42, 44], or from vertically aligned CNT arrays [14, 17]. The microstructures and performances of CNT fibers are strongly dependent on processing methods and detail process parameters. In this part, several key spinning techniques will be briefly introduced.

2.1.1.1 Solution-based spinning

CNT fibers could be produced by using “solution-spinning” method, just like most synthetic fibers created from a concentrated viscous liquid. These processes consist of dispersing CNTs in solution and then re-condensing the CNTs in a stream of another solution, which serves as coagulant [38, 39, 45, 46]. CNTs are inert in pristine state, and tend to bundle together due to the strong van der Waals interactions, making them difficult to disperse uniformly in aqueous or any organic solvents. Therefore, the first critical challenge in development of this method is the difficulty of

processing CNTs in a liquid state. Some methods have been utilized to overcome this problem through oxidation and grafting with different functionalities [9, 47-51], but these methods normally destroy CNT's intrinsic structures and properties. Thus, they are not favored for fiber spinning. Shaffer *et al.* [52] have previously suggested that CNTs can be viewed as analogous to high-aspect ratio, rigid-rod polymers. According to this analog, CNTs are supposed to be applicable to two types of solution-based spinning methods: coagulation spinning and liquid-crystal solution spinning.

2.1.1.1.1 Surfactant-based coagulation spinning

Generally, the principle of the “coagulation spinning” used for synthetic fiber processing could be depicted as: when a polymer solution is extruded through a thin capillary tube and injected into a bath that contains a second liquid in which the solvent is soluble but the polymer is not, the polymer will condense and form a fiber due to phase separation. Employing this “coagulation spinning” method for CNT fiber fabrication, the CNTs need to be dispersed into a liquid solution at an almost molecule level so that they could be manipulated and aligned well. Surfactants are widely utilized for this purpose because of their ability to adsorb/wrap at the surface of individual CNTs and prevent them from re-bundling. This spinning approach was initially adopted by Vigolo [39].

In their fabrication process, as shown schematically in Figure 2.1, arc-discharge-produced SWNTs were firstly dispersed in an aqueous solution by using sodium dodecyl sulfate (SDS) as surfactant, then injected into a rotating bath of

aqueous PVA solution, which serves as coagulant. During this process, PVA displaced the surfactant, causing CNTs collapse and forming ribbon-like elastomeric gel-fibers. These fragile fibers were pulled from the coagulation bath at a rate of about 1 cm min⁻¹ in order to form solid fibers. Such fibers were washed by immersing in successive water container in order to remove excess PVA and surfactant residues, and then dried by pulling them out of water bath.

Figure 2.1 Schematic of the experimental setup used to make SWNT ribbons. The capillary tip was orientated so that the SWNT injection was tangential to the circular trajectory of the polymer solution. (Reference [39])

It is found that one critical parameter to obtain a good dispersion of CNTs is the amount of SDS. When the concentration of SDS is too low, large and dense clusters of

the CNTs will still exist in solution even after sonication, which means that the amount of surfactant is too low to produce an efficient coating and induce enough electrostatic repulsion that could counterbalance van der Waals attractions. On the other hand, when the concentration of SDS is too high, the osmotic pressure of the excess micelles causes depletion-induced aggregation. They found that an optically homogeneous solution could be formed with 0.35 wt% CNTs and 1 wt% SDS for CNTs with particular diameter and length. Flow-induced alignment could lead to a preferential orientation of the CNTs in fibers, and has a close relationship to relative flow rate between injection solution and coagulant solution, as shown in Figure 2.2. The coagulant must flow faster than the gel-fiber in order to stretch the fiber along the axis direction and promote alignment of CNTs in the fiber. This could be accomplished by rotating the coagulant container [10, 39].

Figure 2.2 (a) When the coagulation bath doesn't flow or flows slower than injecting rate, a net compressive force acts on the gel-like fiber, compromising the alignment. (b) When the coagulant

flows along the extruded fiber and faster than the injecting rate, a net stretching force will be resulted to increase the alignment. (Reference [10])

This coagulation-based fiber spinning technique is exciting because of its simplicity and ability to produce fibers with very high CNT loadings (60 wt. %). The final CNT/PVA composite fibers exhibit a tensile strength in the order of 0.1 GPa and a Young's modulus varying between 9 and 15 GPa. In contrast to most ordinary carbon fibers, CNT fibers (shown in Figure 2.3) can be heavily bent and even tightly tied without breaking. However, there are some challenges existing in this method, including dispersion of SWNTs at high concentrations, low processing rate, and the poor fiber mechanical performance.

Figure 2.3 (a) A dry ribbon deposited on a glass substrate (The black arrow indicates the main axis of the ribbon, which corresponds to the direction of the initial fluid velocity). (b) A CNT fiber.

(c) Knots reveal the high flexibility and resistance to torsion of the CNT microfibers. Scale bars: 500 nm and 25 μm for A and B. (Reference [39])

2.1.1.1.2 Liquid-crystal-based solution spinning

Spinning from lyotropic liquid-crystalline solution of rigid-rod molecules is another important method used for fiber production. It can be seen in Figure 2.4 that MWNTs could be viewed as high-aspect ratio, rigid-rod polymers and have been shown to exhibit liquid crystallinity by Song [53, 54]. Ericson *et al.* [55] first successfully produced well-aligned macroscopic fibers composed solely of SWNTs from lyotropic solutions in super acids. Fuming sulfuric acid charges SWNTs and promotes them to order into an aligned phase with individual mobile CNTs surrounded by acid anions. This ordered dispersion was then extruded into a coagulant bath (either diethyl ether, 5% sulfuric acid, or water) to form continuous macroscopic CNT fibers.

Figure 2.4 SEM images of a dried MWNT film. (a) The director fields around a pair of disclinations of topological strength $+1/2$ and $-1/2$ and (b) the region toward the edge of the film which is free of disclinations. (References [53, 54])

The possible mechanism, that very high CNT concentrations in the spinning

solutions are possible for this superacid spinning, is the repulsive interaction between CNTs generated in superacids (100+% sulfuric acid) due to formation of charge-transfer complexes: individual positively charged CNTs surrounded by a finite number of sulfuric acid anions. At very low concentration, such charged tube-anion complexes behave as Brownian rods. At higher concentration, as shown in Figure 2.5, the CNTs coalesce and form ordered domains, behaving similarly to nematic liquid crystalline.

Figure 2.5 A model illustrating the swelling of SWNT ropes in sulfuric acid. (a) A cartoon of SWNTs in van der Waals contact within a neat fiber. (b) The same SWNT fiber after re-exposure to sulfuric acid. (Reference [55])

The CNT fibers spun by such a process have interesting structural and physical properties, including high orientation, good electrical and thermal conductivities, and reasonable mechanical properties. The alignment of CNTs within these fibers is within $\pm 15.5^\circ$. The strength is 116 ± 10 MPa, and the Young's modulus approaches 120 ± 10 GPa. However, some protonation of the material occurs because of prolonged

contact with the sulfuric acid. The CNT/acid system is very sensitive to water, thus the introduction of even minimal moisture causes phase separation and precipitation of discrete needle-like crystal solvates. And superacid route is also found not effective for MWNTs. To address the last problem, S. J. Zhang *et al.* [38] developed a new coagulation process, by which they spun MWNTs from a liquid-crystalline ethylene glycol dispersion. The MWNT fibers have a Young's modulus of 69 ± 41 GPa and a yield strain of 0.3%. Fracture occurred typically at strains below 3% and stresses of 0.15 ± 0.06 GPa. However, the dispersion of CNTs is still the critical issue and the mechanical performances of these fibers are far behind expectation.

2.1.1.2 Solid spinning

In order to eliminate the dispersion problem existing in solution-based spinning methods, spinning CNT fibers directly from as-grown CNT materials seems to be a more convenient way. In the following, two main solid spinning approaches will be described: spinning CNT aerogel from CVD reaction zone and spinning from vertically aligned CNT arrays [14, 42].

2.1.1.2.1 Spinning fibers from aerogel of CNTs

Zhu *et al.* [56] have first reported the formation of a 20-cm-long CNT thread after the pyrolysis of hexane, ferrocene, and thiophene. This work shows the possibility of direct fiber formation in a furnace. Based on this phenomenon, a totally different fiber spinning method was developed by Li [42, 57]. They were able to spin neat CNT fibers directly from an aerogel of CNTs formed in CVD reaction zone, as

shown in Figure 2.6. The precursor materials include liquid hydrocarbon feedstock, ferrocene which forms the iron nanoparticles that act as nucleation sites for the growth of CNTs, and thiophene which is an established rate enhancer for vapor grown carbon fibers [58]. The key requirements for continuous spinning are the formation of CNT aerogel and removal of the product from reaction zone. These were realized through the appropriate choice of reactants, control of the reaction conditions, and continuous withdrawal of the products with a rotating spindle used in various geometries.

Figure 2.6 (a) Schematic of the direct spinning process. The liquid feedstock, in which small quantities of ferrocene and thiophene are dissolved, is mixed with hydrogen and injected into the hot zone, where an aerogel of CNTs form. This aerogel is captured and wound out of the hot zone continuously as a fiber or film. (b) SEM image of a fiber. (c) Well-aligned MWNTs within the fiber. (Reference [42])

Recently, systematic studies of this method have been carried out [59, 60]. From the view of reactants and growth conditions, the continuous spinning process is possible with a range of oxygen-containing carbon sources. Aromatic-hydrocarbons lead to the deposition of carbon particles, thick fibers, or both, but cannot enable a

continuous spinning process unless they are mixed with another oxygen containing source. Thiophene is found to be a necessary additive. It was used as an established rate enhancer for vapor grown carbon fibers [42, 58], but its actual role played in CNT aerogel generation is still open to discussion. It is well accepted that sulfur, another additive, plays a major role in promoting carbon-hydrocarbon reactions, especially when associated with iron [58]. Through carefully controlling the growth conditions, the length and diameter of CNTs in aerogel could be tuned, and it is found that lower concentrations of iron lead to a greater proportion of SWNTs and DWNTs which are favorable for high-performance fibers. For example, it is found that the large diameter double wall CNTs may collapse within fibers, leading to an increase in friction between individual CNTs, which is beneficial to the mechanical performance of CNT fibers [25]. Regarding the processing parameters, it is found that CNT alignment, the density and microstructures of fibers can be controlled by drawing/winding rate and post-processing methods. The degree of alignment could be manipulated by adjusting the winding rate as there is a tension introduced into this winding process, which supply a force to align CNTs in the fiber. By introducing the wetting and evaporation of volatile organic liquids such as acetone, the condensation of the CNTs in fibers is greatly increased. However, up to now, only two groups could realize fiber spinning by using this method [42, 57].

2.1.1.2.2 Spinning fibers from vertically aligned CNT arrays

CNT arrays have their own unique structure in which all CNTs are aligned in the vertical direction. The first preparation of a CNT array was reported by Li [61], which

provides an opportunity to develop both highly ordered and high surface area materials. Shortly after that, massive growth of patterned CNT arrays was reported by Fan [62]. The mechanisms of nanotube growth and self-orientation were demonstrated. However, the length of CNTs is still at nano/micron scale. Until 2002, a breakthrough was made by Jiang [13] by simply drawing a neat CNT yarn from a vertically super-aligned CNT array. They found that CNTs could be self-assembled into yarns of up to 30 cm in length. Following that, M. Zhang *et al.* [14, 63] produced highly orientated, free-standing CNT transparent sheets using a similar method, and further assembled CNTs into fibers by using a draw-twisting spin method [14]. The typical SEM images of fiber spinning processes are shown in Figure 2.7.

Figure 2.7 SEM images showing the structures formed during the draw-twist process. (Reference [14])

In order to realize their practical applications, some key issues need to be resolved in advance. Currently the growth of CNT arrays is easy, but not all CNT

arrays could be spun into yarns or fibers. X. B. Zhang *et al.* [36] found that strong van der Waals interactions existed between individual CNTs within super-aligned arrays, and this van der Waals force makes the CNTs join end to end, thus forming a continuous yarn during pulling. Meanwhile, M. Zhang *et al.* [14] claimed that the formation of yarn was due to the disordered regions at the top and bottom of the CNT arrays, which entangled together forming a loop. Kuznetsov developed a structural model to describe the fiber spinning process [64]. The key element in their model is a network of individual carbon nanotubes or small bundles interconnecting the array of main large-diameter CNT bundles of the forest as shown in Figure 2.8. They concluded that the drawing mechanism for CNT sheet formation involves two principal processes that reconfigure the interconnection network: 1) unzipping by preferentially peeling off interconnections between the bundles in the forest and 2) self-strengthening of these interconnections by densification at the top and bottom of the forest during draw-induced reorientation of the bundles. In the view of growth conditions, Zhang *et al.* demonstrated that by controlling catalyst pretreatment conditions, the degree of spinnability of CNTs is closely related to the morphology of CNT arrays [18]. They found that shortest catalyst pretreatment time lead to CNT arrays with the best spinnability, while prolonged pretreatment resulted in coarsening of catalyst particles and nonspinnable CNTs. By controlling the calescence of catalyst particles, they demonstrated the CNT arrays can be tuned from well-aligned, spinnable forests to uniformly wavy, foam-like films. Jia *et al.* studied the influence of carbon sources on spinnability of CNT arrays [65]. They found that C_2H_4 is superior

to C_2H_2 as the carbon source for the growth of mainly double- and triple- walled CNTs and the spinning of high-strength fibers. Several other groups have also paid attentions to the growth of spinnable CNT arrays and great progress has been achieved [24, 66-71].

Figure 2.8 Sequence of consecutive SEM images, given by panels from (a) to (d), of the side view of the CNT forest during the pulling-out process. Red circles show the sequence of points where a pulled-out bundle started pulling the next bundle. Blue circles show the rupture of two adjacent bundles. (Reference [64])

From the above description, it is found that fibers produced by the wet spinning process, showed an encouraging stiffness of 120 GPa but only modest strengths on the order of 0.1 GPa [10]. Meanwhile, the dispersion of CNTs remains difficult to achieve due to its inert nature. Comparatively, a “solid” fiber-spinning method is more attractive, especially spinning fibers from vertically aligned CNT arrays.

2.1.2 Structural dependent mechanical properties of CNT fibers

CNT fibers, no matter which fabrication methods were used, are assembled with millions of individual CNTs and small CNT bundles in either well aligned or non-uniformly distributed manner. The length and diameters of CNTs vary depending on processing approaches. Thus, the mechanical performances of CNT fibers, including strength, strain, Young's modulus, toughness, and even the failure mechanisms, are strongly depending on their microstructures, for examples, the alignment of CNTs in the fiber, the diameter & length of nanotubes, and the morphology of nanotubes (straightness/waviness).

It is well accepted that CNTs in the fiber in a well aligned manner will give good mechanical performance. For the fibers spun from coagulation method, Poulin *et al.* demonstrated that alignment of CNTs in a fiber should be mainly fixed during the drying stage (when the mesh is collated) and is not fixed during the initial coagulation process. Further treatments of the fibers are thus required and could be used to improve their properties. When the coagulated CNT-PVA fibers rewetted, swollen, and re-dried vertically under a tensile load with a weight attached to the end of the fiber, its mechanical strength could be improved. The fibers could be stretched up to 160%. Young's modulus and tensile strength are substantially higher for the stretched fibers. They are, respectively, of about 10 GPa and 125 MPa for the as-spun fibers and 40 GPa and 230 MPa for the stretched fibers. The results are shown in Figure 2.9. Furthermore, the author employed a hot-drawing treatment to improve the properties

of nanotube-PVA fibers. This treatment yields a crystallinity increase of the PVA and an unprecedented degree of alignment of nanotubes [40, 72]. Windle's group also measured the mechanical properties of coagulation-spun polymer-CNT composite fibers. The effects of nanotube content and orientation on the mechanical properties of those composite fibers were studied. Raman measurements showed that Herman's orientation parameter to increase with drawing, indicating that the nanotube alignment occurs [73]. They found that both the fiber modulus and strength scale linearly with volume fraction till a maximum value after which these properties remain constant.

Figure 2.9 (a) SEM image of a raw fiber, (b) SEM image of a stretched CNT fiber, and (c) Stress-strain curve of a raw and a stretched fiber made from the same batch of CNTs. (Reference [72])

Except alignment, it is well known that interfacial friction plays a crucial role in the mechanical properties of CNT based fibers, composites, and devices. Zhang used molecular dynamics simulation to investigate the pressure effect on the friction within CNT bundles [25]. Figure 2.10 shows the volume-pressure relation during the

pressure loading up to 1.2 GPa and unloading down to 0 GPa for the $16 \times (23, 0)$, and $16 \times$ random chirality bundles, respectively. The bundles show step-by-step structural transition and the transition pressures are mainly radius dependent. They found that collapsed CNT bundles under atmospheric pressure are possible and the clear experimental evidence of collapsed nanotubes was recently reported by Motta.

Figure 2.10 Volume vs pressure for the $16 \times (23, 0)$ and $16 \times$ random chirality bundles. V_0 is the volume at zero pressure. The bundles show step-by step structural transition, shown in filled circles and squares. By unloading the pressure (open circles and squares), the bundles remain collapsed until the return pressure below which the bundles expand to the initial structure. Insets a-d: Snapshots of the $16 \times (23, 0)$ bundle during the pressure loading up to 0.5, 0.7, 0.8 and 1.0 GPa, respectively. (e) Collapsed structure is remained when the $16 \times (23, 0)$ bundle is unloaded down to 0.05 GPa. (f) Collapsed $16 \times$ random chirality bundle at 0.2 GPa. (g) Larger tubes as the $16 \times (40, 0)$ remain collapsed even under zero pressure. Here, $T = 300$ K (Reference [25])

Vilatela *et al.* proposed a model for the strength of pure CNT fibers spun directly from CVD furnace [20]. The model points to the parameters of the subunits that must be optimized in order to produce improvements in the strength of macroscopic CNT fibers, primarily nanotube length and shear strength between CNTs. Based on their analysis, it is revealed that fiber strength originates from resistance to nanotube pull-out and is proportional to the nanotube-nanotube interface contact area and shear strength, where the contact area is determined by their degree of collapse.

Figure 2.11 Structure of the fiber product. (a) SEM image of knotted fiber. (b) HR-TEM image of a bundle close to a fiber fracture revealing that the bundles consist, predominantly, of collapsed double-wall nanotubes greater than 5 nm. (Reference [60])

Motta *et al.* [60] described improvement in mechanical strength and relate the performance to unique aspects of fiber microstructure with knotted shape (shown in Figure 2.11). They have also shown that the mechanical properties of the fibers are directly related to the type of CNTs, which in turn, can be controlled by the careful adjustment of process parameters. From the observation of the “dog-bone” cross

section of double- and triple-wall nanotubes with equivalent diameter larger than 5 nm, the nanotubes are seriously collapsed in radial direction and compressed, which will lead to an increased interface and an enhanced mechanical strength.

For the CNT fibers spun from vertically aligned CNT array, the influences of twisting, nanotube length and straightness were also studied [4, 14, 17, 24]. Similar to traditional cotton spinning process, by downsizing this ancient technology Zhang *et al.* [14] demonstrated the fabrication of single, two-ply, four-ply and knitted CNT fibers as shown in the Figure 2.12. They achieved fiber strength greater than 460 MPa by introducing twist during spinning of CNTs from CNT forests. They emphasized that the load can be transferred effectively between CNTs because of the twisting. In a twisted fiber, individual CNTs are inclined at an angle θ with respect to the fiber axis, generating transverse forces which lock the fibers together as a coherent structure. They also found these twisted yarns deformed with cyclic hysteresis over large strain ranges from 0.5% to 8%, providing up to 48% energy damping. These yarns could also retain their strength and flexibility even after being heated in air at 450 °C for an hour or being immersed in liquid nitrogen. Furthermore, Li and her coworkers [23] observed a double-peak behavior of the tensile properties as a function of twist angle, which is different from the single peak of traditional fibers [74]. On the other aspect, since their first discovery in 2002, Jiang and his coworkers [36] have tried to expand the synthesis process to a larger scale at low pressure for commercial CVD systems, which may give rise to a higher degree of uniformity. By the time of 2006, they have achieved a 4-in. wafer scale synthesis of super-aligned CNT arrays and found that the

strength of their yarns could be improved with a mechanical strength of around 600 MPa after being heated at high temperatures (2000 K) [36].

Figure 2.12 SEM images of (a) singles, (b) two-ply, and (c) four-ply MWNT fibers, as well as (d) knitted MWNT fibers. (Reference [14])

Instead of using post-spinning treatment, Zhang *et al.* [4, 5, 15, 17] found that mechanical properties can be significantly improved by using longer CNT arrays. The tensile strength and stiffness of their fibers spun from a 1-mm-long CNT array were measured in the range of 1.35-3.3 GPa and 100-263 GPa, respectively, which are many times stronger and stiffer per weight than the best existing engineering fibers and CNT fibers reported previously. It is obvious that the strength of CNT fibers increased with increasing CNT array length which yields a much larger friction between CNTs. Longer CNTs will also introduce fewer mechanical defects (like the

ends of CNTs) per unit fiber length [65, 66, 75-78]. Other factors like structure, purity, density, alignment and the straightness of CNTs have all been investigated [4, 24]. For instance, in order to get dense packed CNT fibers, surface-tension-driven densification [36, 79] was employed during fiber spinning. Zhang *et al.* found that after the CNT yarn was pulled through droplets of ethanol, the several centimeters wide yarn shrank into a tight fiber typically 20-30 μm in diameter and the strength of the CNT yarn was dramatically improved [14]. Zheng *et al.* have observed a strong correlation between the array morphologies (the straightness of CNTs) and the fiber properties: well-aligned arrays yield high performance, while wavy arrays give poor performance. Figure 2.13 summarizes the influence of several parameters on fibers' mechanical performances [24].

Figure 2.13 (a) As-spun and post-twisted small-diameter CNT fibers spun from a 650 μm array. (b) A comparison of fiber strengths at different array height. The black line shows that the strength of CNT fibers increases with the array height, and marks shows the strength dependence on array morphology (the dot ● represents the data from oxygen-assisted growth that shows poor CNT alignment, the square ■ represents the data from the normal growth, and the triangle ▲ represents the data from the hydrogen-assisted growth that shows good CNT alignment). (Reference [4, 24])

Except post-treatment of CNT fibers and morphology control of CNT arrays, the

spinning process and modification of CNT fibers have all been employed to improve fiber's mechanical performance. Tran [80, 81] introduced a modified process for the dry spinning of CNT fibers. They introduced a tensioning rod system in order to improve the microstructure of CNT fibers and thus their mechanical properties. They found by using this modified spinning process, the mechanical strength has been increased around twofold from 500 MPa to around 1.1 GPa. Another way to modify the spinning process is to introduce a secondary phase such as polymers [27, 82, 83]. As the strength of CNT is much higher than the shear force between CNTs, a small amount of polymer may function as adhesive element to improve the load transfer between CNTs inside the fiber.

Thus, it could be concluded that the characterization and improvement of load transfer between CNTs in the fibers, which actually is structure dependent, is the concern in all these studies.

2.1.3 Test condition dependent mechanical properties of CNT fibers

If fabrication conditions are maintained the same, where the CNT fibers were all spun from the same vertically aligned arrays, test conditions, for instance temperatures and strain rate, have always been considered to have great influence on the mechanical behaviors of tested materials. Until now, only one study has been performed [14]. When the CNT fibers were post-treated, Baughman *et al.* found that CNT yarns can retain their strength and flexibility after heating in air at 450 °C for an hour or when immersed in liquid nitrogen.

Strain rate strengthening effect was previously observed in metals and polymer fibers [84, 85]. For examples, the effects of strain rate on mechanical behavior of Kevlar fiber bundles was studied by Wang and co-workers [86]. The stress-strain curves of Kevlar aramid fiber bundles under both quasi-static and high rate loading were obtained. A bimodal Weibull distribution statistical model of strain rate dependences of fibers and a test method of determining mechanical properties and Weibull parameters of fibers from fiber bundle test were developed to investigate the fracture modes in Kevlar fibers. The effects of temperature and strain rate on the tensile behavior of unfilled and talc-filled polypropylene were also studied [87, 88]. Both the elastic modulus and yield strength of polypropylene were found strain rate dependent and decreased with increasing temperature and increased with increasing strain rate. CNT fiber spun from vertically aligned arrays was assembled by interconnected individual CNTs and small bundles in end-to-end manners. Their microstructures are similar to polymer fibers with linear, long-chain molecular. So, it is expected that CNT fibers may exhibit strain rate dependent mechanical properties. Unfortunately, no study has been reported in this area.

In summary, great effort has been paid to enhance mechanical strength of CNT fibers and up to now, significant progress has been achieved in this aspect. It has been reported that the tensile strength of CNT fiber spun from vertically aligned arrays scattered in the range of 0.25 to 3.3 GPa, while the test conditions are not well defined. Regarding the intrinsic properties of CNT fibers, especially those tested under different conditions, there are further research spaces to be filled. Strain rate, among

other testing conditions, has a major effect on the measured fiber properties [85, 89, 90]. Moreover, different mechanical behavior of CNT fibers may be required in different applications. Thus, more tasks need to be done to further investigate the intrinsic mechanical properties of CNT fibers tested under different conditions, specifically different strain rates, and their morphology dependent mechanical behaviors.

2.2 The characterization methods

As indicated in the above section that the mechanical performance of CNT fibers strongly depend on strain rate and their microstructures which are originated from fabrication process, the characterization of fibers' structures with a direct/indirect method is essential for both ex-situ and in-situ measurements. For the CNT fibers spun from vertically aligned arrays, nanotubes are connected in an end-to-end manner. In order to investigate its strain rate dependent mechanical behaviors, different characterization methods, underlying principles and their capabilities in characterizing CNT fibers were introduced in the following two sections: 1) static/dynamic tensile tests, and 2) Raman spectroscopy.

2.2.1 Static/dynamic tensile tests (including in-situ measurements)

Except direct stress-strain tensile tests, the static/dynamic mechanical tests and in-situ electrical measurement under tension are widely applied to characterize the mechanical behavior of materials.

Load relaxation tests were usually employed for providing information on the inelastic deformation behavior [91]. Hart and Solomon are the first to adopt load relaxation test to determine material properties for modeling after a critical analysis of the phenomenology of plastic deformation [92]. Krempl studied the characteristic relaxation of ductile metals and alloys at room and high temperature showing a scaling relation derived from Hart's theory [91, 93]. Subsequent testing with servo-controlled testing machines and strain measurement on the gauge length showed that an increase of prior strain rate also increased the average relaxation rate. For relaxation tests starting in the flow stress region, it is found that the relaxation curves can be independent of the stress and strain at the start of the relaxation tests.

Cyclic loading/unloading tension was an effective method to verify the permanent deformation in strain. For CNT fibers spun directly from CVD furnace, Li used this method by stretching the fiber to a strain of 4.4% (stress of 0.23 GPa), then unloading till to zero stress, and finally reloading until the fiber broke [19]. There is a residual strain of 3.4% after completely unloading. Upon reloading, the elastic limit (yield strength) of the fiber increases by 50% and the elastic modulus increases slightly. The residual strain was attributed to the slippage among CNTs and the unrecoverable part of the CNT alignment during the strengthening stage. Windle's group also used a cyclic loading/unloading to study the stress transfer in the CNT fibers [21]. The fiber was first strained up to 2% of its original length, then unloaded back to a small pretension ($<0.01 \text{ GPa SG}^{-1}$) and then strained back again up to fracture. The stress strain curve shows an initial, approximately linear region of

mostly elastic deformation, followed by yield at the onset beyond which plastic deformation begins to become dominant. For the fibers spun from vertically aligned arrays, Zhang used this method to demonstrate hysteretic stress-strain curves of their CNT fibers when subjected to loading/unloading cycles [14]. They found complete unloading did not return the fiber to its original length, but the initial hysteresis loop was essentially unshifted on subsequent cycles as shown in Figure 2.14. Depending on initial strain, the observed energy loss per stress-strain cycle of a two-ply CNT fiber was 9 to 22% for cycle strain of 0.5%, 24 to 28% for cycle strain of 1.5%, and 39 to 48% for the maximum reversible cycle strain (2 to 3% for total strains up to 8%). Within a hysteresis loop, the effective modulus on initial unloading and initial reloading was much larger than for the final parts of the unloading and reloading steps. Also relevant for applications, the failure strength of CNT fiber (singles and two-ply) was unaffected by 50 loading/unloading cycles over a stress range of 50% of the failure stress.

Figure 2.14 Hysteretic stress-strain curves (strain rate $1\% \text{ min}^{-1}$) observed on unloading and reloading a two-ply fiber over a 1.5% strain range after differing initial strains. (Reference [14])

For in-situ characterizations, utilizing electrical techniques has been established as a noninvasive way to monitor damage in carbon-fiber-reinforced composites under static and dynamic loading conditions [94-97]. Because carbon fibers are conductive, fracture of fibers will result in changes in electrical resistance. Some groups have attempted to locally modify electrical properties of glass fiber yarn bundles through coating with carbon powder/CNTs and utilizing them for damage sensing [94, 98-104]. Wang and Chung monitored the static/fatigue damage and dynamic strain in cross-ply carbon fiber polymer matrix composites using direct current measurement techniques [94]. Kupke performed measurements of both direct current and alternating current electrical properties for the detection of damage in carbon fiber composite specimens during testing [105]. Their results showed that it is possible to monitor the strain and to identify the different composite failure mechanisms using electrical methods. Chou developed this approach by processing glass fiber-epoxy composites and utilizing CNTs dispersed in the epoxy phase as distributed sensors to evaluate the onset and evolution of damage in advanced fibrous composites [95, 97]. They showed CNTs that form a conductive percolating network throughout the polymer matrix are remarkably sensitive to initial stages of matrix-dominated failure. More recently, the electrical resistance change method was utilized by Todoroki to examine the cracking behavior of carbon fiber composites for use in cryogenic tanks [101].

2.2.2 Raman spectroscopy

Raman is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with molecular vibrations phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system.

As shown in Figure 2.15, when photons are scattered from an atom or molecule, most photons are elastically scattered (Rayleigh scattering), such that the scattered photons have the same kinetic energy (frequency) and wavelength as the incident photons. However, a small fraction of the scattered photons are scattered by an excitation, with the scattered photons having a frequency different from, and usually lower than, that of the incident photons.

The Raman scattering corresponds, in perturbation theory, to the absorption and subsequent emission of a photon via an intermediate quantum state of a material. The intermediate state can be either a “real”, i.e., stationary state or a virtual state. The Raman interaction leads to two possible outcomes:

- 1) The material absorbs energy and the emitted photon has a lower energy than the absorbed photon. This outcome is labeled Stokes Raman scattering.
- 2) The material loses energy and the emitted photon has a higher energy than the absorbed photon. This outcome is labeled anti-Stokes Raman scattering.

The energy difference between the absorbed and emitted photon corresponds to the energy difference between two resonant states of the materials and is independent of the absolute energy of the photon.

Figure 2.15 Energy level diagram showing the states involved in Raman signal. (Reference [106])

In the case of CNT fibers and CNT arrays, there are three typical peaks located at 1350 cm^{-1} , 1580 cm^{-1} , and 2640 cm^{-1} . The stretching of the C-C bond in CNTs gives rise to the so-called G band Raman feature which is common to all sp^2 carbon systems. The G band is highly sensitive to strain effects in sp^2 nanocarbons and can be used to probe any modification to the geometric structure of nanotubes, such as the strain induced by external forces. The presence of disorder in sp^2 -hybridized carbon systems leads to rich and intriguing phenomena in their resonance Raman spectra, thus making Raman spectroscopy one of the most sensitive and informative techniques to characterize disorder in sp^2 carbon materials, giving rise to the so-called disorder induced D band. Quantifying disorder in a nanotube is usually made by analyzing the I_D/I_G intensity ratio between the disorder-induced D band and the Raman allowed G band. All kinds of sp^2 carbon materials exhibit a strong Raman

feature which appears in the range 2500 to 2800 cm^{-1} , as shown in Figure 2.16. Together with the G band, this spectrum is a Raman signature of graphitic sp^2 materials and is called the G' band to emphasize that it is a Raman-allowed mode for sp^2 carbon. Interestingly, the G' band is a second-order two-phonon process and, intriguingly, it exhibits a strong frequency dependence on the excitation laser energy. It has been demonstrated that G' band is more sensitive to strain than G band [22, 107]. A typical Raman spectrum is shown in Figure 2.16.

Figure 2.16 A typical Raman spectrum

Raman spectroscopy was extensively employed to characterize the structural properties of CNTs and CNT-based composites both ex-situ and in-situ in mechanical tests [19, 21, 22, 24, 75, 77, 78, 106, 108-118]. As a nondestructive and readily available measurement, Raman scattering has been widely used to identify CNT's diameters or alignment degree [77, 78, 106, 110, 115]. Moreover, since Raman

scattering is sensitive to the inter-atomic distance, when CNTs are mechanically strained, there is a linear relationship between the Raman peaks' shift and local strain [107, 119-121].

By investigating the variation of the G' band under strain, Ma inferred the structural deformation process of micrometer-scale SWNT networks, and further gave prediction of the macrostructures' moduli [22]. Together with systematic tensile tests, they elucidate the influence of CNT fibers' geometries on their mechanical performance. Li studied the deformation mechanisms of CNT fibers under tensile loading by using in-situ Raman spectroscopy to detect the CNT deformation and stress distributions in the fibers [19]. It is deduced that in their fibers the individual CNTs only deform elastically without obvious damage or bond breaking. The yield and fracture of fibers can be due to the slippage among the CNTs. Vilatela *et al.* also utilize the in-situ Raman measurements during tensile deformation and the results indicate that the transfer of stress between bundles in the fiber is not uniform, with the Raman peak downshift rates for the D, G and G' bands varying by as much as a factor of 2 in different areas of the fiber [21]. Lachman *et al.* studied the strain-induced shift of G' Raman band of SWNTs in polyvinyl alcohol-nanotube composite fibers [113]. They found that due to improved interfacial adhesion, stronger shifts of the G' Raman band are observed when carboxylic functional groups are present at the nanotube surface. However, they also observed that the improvements of interfacial adhesion do not lead to substantially better mechanical properties of the fibers. They attribute the reason to possible degradation of nanotubes during surface functionalization. Raman

spectroscopy was also used to measure the interfacial shear strength by monitoring band shift [111]. Roy *et al.* found that when a composite structure is formed with the collagen, an improved load transfer from matrix to the nanotube lead to improvement of interfacial shear strength.

The polarization of the Raman scattered light also contains useful information. This property can be measured using polarized laser excitation and a polarization analyzer. Spectra acquired with the analyzer set at both perpendicular and parallel to the excitation plane can be used to calculate the depolarization ratio. Study of the technique is useful in teaching the connections between group theory, symmetry, Raman activity, and peaks in the corresponding Raman spectra.

Polarized Raman spectroscopy was used to investigate structure and anisotropy properties of isolated CNT, and the alignment of CNTs in CNT fibers, films, or composites. Gommans *et al.* measured polarization-dependent Raman spectra on the oriented fibers [115]. They found that contrary to what is expected from their theoretically assigned vibration-mode symmetries, all the Raman line intensities are observed to decrease in nearly equal amounts for the 647.1 nm laser excitation polarized perpendicular to the fiber axis versus that polarized parallel to the fiber axis [112]. The effect is explained as a loss of resonance Raman scattering for the perpendicular polarization case. They also utilized polarized resonant Raman and optical spectroscopy to characterize aligned SWNTs showing that the optical transitions are strongly polarized along the nanotube axis. This behavior is consistent with the electronic structure calculations. Duesberg also performed polarized

micro-Raman spectroscopy on spatially separated SWNTs in the form of individual nanotubes or thin ropes of only a few SWNTs [122]. The Raman spectra are composed of well-resolved peaks which allow a direct comparison of experimental data with theoretical calculations. Orientation-dependent measurements revealed that maximum intensity of all Raman modes appear when the nanotubes are aligned parallel to the polarization of the incident laser light. The angular dependences clearly deviate from the selection rules predicted by theoretical studies. These differences were attributed to depolarization effects caused by the strong anisotropic geometry of the nanotubes and to electronic resonance effects for excitation at 633 nm. Zhang used polarized Raman spectroscopy to give quantitative measurement of alignment of CNT arrays [18]. They found that the intensity ratio of the G band for polarizations parallel and perpendicular to the orientation of CNTs in the arrays decreases monotonically from well aligned array to wavy ones, indicating that a much higher degree of alignment occurs in well straight arrays. Zheng *et al.* also employed polarized Raman spectroscopy to evaluate the alignment of CNTs in their fibers. The fiber in Figure 2.17a was spun from a wavy array, while the fiber in Figure 2.17b was spun from a well aligned array. For both samples, the intensities of G band and D band for polarization parallel ($I_{//}$) to fiber axis are much stronger than those for polarization normal ($I_{\perp}$) to fiber axis, but the ratio $I_{//}/I_{\perp}$ in Figure 2.17b, which is 6.4, is much large than that in Figure 2.17a, which is about 2.5, suggesting fiber in Figure 2.17b has much better alignment.

Figure 2.17 Raman spectra of G band and D band of CNT fibers for incident light polarization parallel and perpendicular to the CNT fibers. (a) Fibers spun from wavy array, and (b) Fibers spun from a well-aligned array. (Reference [24])

The spectral information arising from this analysis gives insight into molecular orientation and structural change due to external stress/strain. In essence, it allows us to obtain valuable information relating to mechanical behaviors, for instant stress transfer under tension, and deformation mechanisms.

2.3 Statistical analysis of fibers' mechanical strength

Beside experimental approach, people always want to build up a mathematical model to predict the distribution of fibers' mechanical strength and their failure mechanisms. For brittle materials, the majority of mathematical descriptions of fracture statistics are based on weakest-link theory. Examples of the weakest-link theories are the Weibull distribution, the three extreme-value distributions, and flaw density distributions. Among them, the Weibull distribution has become most popular due to its mathematical simplicity and relatively good success in its applications. Weibull distribution function is statistically applicable to a wide field of problems. It could be modified to accommodate different influence parameters as variants and has been utilized to characterize brittle ceramic fibers and some high modulus polymer fibers for their strength distribution, strength dependence on diameter and gauge length, as well as CNT or CNT-based composite fibers. For examples, Zhu and Sembach have employed Weibull distribution to statistically analyze the effects of diameter, twisting angle, strain rate and gauge length on the failure of CNT fibers and ultra-high strength polyethylene fibers [89, 123, 124].

Its principles can be generally described as follows:

If a variable X is attributed to the individuals of a population, the distribution function (df) of X , denoted as $F(x)$, may be defined as the number of all individuals having an $X \leq x$, divided by the total number of individuals. This function also gives the probability P of choosing at random an individual having a value of X equal to or

less than x , and thus we have [86, 123, 125-127]

$$P(X \leq x) = F(x) \quad (2-1)$$

Any distribution function may be written in the form

$$F(x) = 1 - \exp[-\phi(x)] \quad (2-2)$$

This seems to be a complication, but the advantage of this formal transformation depends on the relationship

$$(1-P)^n = \exp[-n\phi(x)] \quad (2-3)$$

Assume that we have a chain consisting of several links. If we have found, by testing, the probability of failure P at any load x applied to a “single” link, and if we want to find the probability of failure P_n of a chain consisting of n links, we have to base our deductions upon the proposition that the chain as a whole has failed, if any one of its parts has failed. Accordingly, the probability of nonfailure of the chain $(1-P_n)$, is equal to the probability of the simultaneous nonfailure of all the links. Thus we have $(1-P_n) = (1-P)^n$. If then the df of a single link takes the form Eq. (2-2), we obtain

$$P_n = 1 - \exp[-n\phi(x)] \quad (2-4)$$

This equation gives the appropriate mathematical expression for the principle of the weakest link in the chain, or, more generally, for the size effect on failures in solids.

2.4 Summary

CNT fibers, as a macro-scale assembly of CNTs, are promising candidates for practical applications as they inherit excellent properties of individual CNTs, such as high mechanical strength, and excellent electrical and thermal conductivity. Among the several different synthesis methods that have been developed to assemble CNTs into fibers, the most attractive approach is to spin CNT fibers from vertically aligned arrays.

Various efforts have been paid to improve the mechanical strength of CNT fibers spun from vertically aligned arrays. One critical concern is the characterization and improvement of load stress transfer between CNTs in the fibers, which is serious structure dependent, and great progress has been achieved. However, regarding to the test condition dependent mechanical properties, specially strain rate dependent mechanical properties, and the relationship between mechanical behaviors and fibers' microstructures, more detailed studies are still needed. To give a further understanding of fiber's mechanical behavior under different strain rates and to build the relationship between fiber's physical performance and their microstructures will be the subject of research in this thesis.

Chapter 3 Experimental Details

Based on the understanding from literature review and the scope of this study, the research will be carried out as following: fiber fabrication and testing, strain-rate study, and statistical analysis. Accordingly, the experimental chapter has been categorized into three sections: 1) materials preparations (including synthesis of CNT arrays, fiber spinning, and sample preparation for mechanical tests), 2) characterization methods introduction (including ex-situ characterizations such as morphological, mechanical, electrical characterizations, Raman spectroscopy and in-situ measurements), and 3) statistical analysis (Mathematical model derivation and fiber selections).

3.1 Materials preparation

This section will present the experimental work of synthesizing vertically aligned CNT arrays by using a thermal CVD method, the fiber spinning process from such spinnable CNT arrays through traditional cotton spinning approach, and the preparation of fiber samples for tensile tests.

3.1.1 Synthesis of spinnable CNT Arrays

Vertically aligned CNT arrays were synthesized in a 1-inch horizontal quartz tube furnace at atmospheric pressure. The thermal catalytic CVD method was employed. Typically, a layer of 0.8 nm Fe film was first deposited as catalyst on silicon substrate coated with 30 nm Al_2O_3 by sputtering technique. The thicknesses

were controlled by deposition times. The sample was placed in a CVD reactor for annealing in Ar and H₂ environment where Ar was serving as the carrier gas, H₂ as reductant. The growth was initiated by introducing carbon source C₂H₄. Figure 3.1a shows the schematic diagram for CNT growth process.

During the growth process, temperature is an important parameter, which needs to be carefully controlled. In this study, the temperatures for both catalyst annealing and CNT array growth were optimized and fixed at 750 °C. The whole process can be separated into four steps (as shown in Figure 3.1b):

Figure 3.1 (a) Procedure of CNT growth. (b) Scheme of CNT growth process

1. Temperature ramp (heat-up to required temperature of 700 to 800 °C for catalyst annealing): Before the start of experiment, the tube was flushed with the forming gas for a few minutes in order to eliminate the residue air. The sample was put in the middle of the quartz tube, and then the furnace was heated up continuously at a constant rate to the required growth temperature of (700 to 800 °C).

2. Catalyst pre-treatment (anneal): As the temperature reached to the set-point, the sample was annealed under hydrogen environment for a range of time (5 to 60 min). During this period of time, the catalyst nanoparticles, which will catalytically decompose the carbon source and initiate the CNT growth, will be formed by sintering the Fe thin-film at high temperature and be reduced by hydrogen.

3. CNT growth: After the annealing, the carbon source was introduced into the furnace starting the CNT growth.

4. Cooling: cooled down to room temperature to take out the sample.

Different growth parameters, such as the thickness of catalyst films, the growth temperatures, the growth duration, the value of reactant gas flow were systematically investigated.

When the total gas flow was fixed at 200 sccm, the dependence of CNT growth rate on flow ratio of reactive gas C_2H_4 was firstly studied. The result is shown in Figure 3.2a, where the growth duration was kept constant at 20 min. It is found for the first time that when increasing the concentration of C_2H_4 , the height of CNT arrays

varies non-monotonically, with two maximum growth rates at 25% and 45%, respectively. The time evolution of forests' heights at a fixed growth condition (total gas flow 200 sccm and the concentration of C_2H_4 is 25%) showed that the growth rate was highest at the onset of growth, gradually decreased over the subsequent 20 min, and finally terminated with a height of 600 μm . The results have been shown in Figure 3.2b. In the following studies, we fixed the growth duration at 15 min.

Figure 3.2 (a) The influence of C_2H_4 concentration on array height, and (b) The variation of array height versus growth duration

The structures of CNTs were characterized by TEM, including diameters and wall numbers of nanotubes. By counting under TEM, the average diameter and wall numbers were found, as shown in Figure 3.3a and b, to be 11 nm and 6 walls, respectively.

Figure 3.3 (a) The distribution of nanotube's diameter, and (b) The distribution of nanotube's wall number

By pulling and/or twisting CNT films/fibers from as-grown vertically aligned arrays, the spinnability of each array was evaluated in a comparative way. Criteria of

spinnability has been generated and listed in Table 3.1.

Rank of Spinnability	Description
10	Fibers can be spun continuously and uniformly
9	Fiber length >1meter, and spinning success rate is high
8	Fiber length >1 meter, but spinning success rate is low
7	Fiber length: 50 cm – 100 cm
6	Fiber length: 20 cm – 50 cm
5	Fiber length: 10cm – 20 cm
4	Fiber length: 5 cm – 10 cm
3	Can spin fibers, but fiber length < 5 cm
2	Cannot spin fibers, but can initial small ribbons
1	Cannot spin fibers, soft arrays
0	Cannot spin fibers, hard arrays

Table 3.1 Description of fiber spinnability for CNT arrays

Table 3.1 is utilized to rank the array spinnability from 0 to 10, with a higher number representing better spinnability, based upon the relative ease, uniformity, and repeatability of the spinning. For a CNT array with spinnability larger than 8, continuous fibers over a meter long could normally be spun out. Once the growth parameters are fixed, then the as-grown CNT arrays are ready for fiber spinning.

3.1.2 CNT Fibers spinning process

CNT fibers were produced by directly drawing a film from CNT arrays by a solid-state spinning process (Figure 3.4a). The film was started by pulling CNTs from one side of CNT array using a sharp tip tweezers, producing a highly oriented, free standing CNT sheets. Figure 3.4b shows a typical side-view SEM image that the CNT sheet was pulling out from side of a CNT array. The thickness of the CNT array used

in this study is around 250~500 μm . Twisting was introduced to enhance the strength of CNT fibers, and a volatile solvent (ethanol) was utilized to shrink CNT yarns at the same time to increase the packing density. The morphologies of CNT fibers were characterized by SEM and TEM as shown in Figure 3.4c. It is found that the morphology of a CNT fiber is similar to a cylinder with circular periphery. There are plenty of wrinkles on the surface of CNT fibers, and CNTs in the fiber are well orientated in the same direction. The top-right inset of Figure 3.4c shows a HRTEM image, indicating that the diameter of individual CNTs is about 12 nm.

Figure 3.4 (a) Schematic of CNT fiber spinning process. (b) Side-view of CNT yarn pulled out from CNT array. (c) As-spun CNT fibers (the inset shows high resolution TEM image of individual CNT)

3.1.3 Sample preparations

Usually, a long fiber of around 15 to 20 cm was spun and placed on a piece of clean white paper for easy visual observation. The CNT fibers were then cut into shorter pieces and placed on to a sample holder. The sample holder is a piece of white paper with a 6 mm in diameter hole created in the centre. At the two ends, double sided tape is placed to transfer the fiber firmly from paper to the frame holder. The individual fiber was placed horizontally across as seen in Figure 3.5. In order to firmly stick fiber on to the frame holder, superglue and conductive silver epoxy were used for mechanical tensile tests and electrical conductive tests, respectively.

Figure 3.5 A photographic image of as-prepared fiber sample for tensile & electrical measurement

3.2 Characterization Methods

Several characterization methods/tools were used to characterize the structure and morphology, mechanical and electrical properties of produced CNT fibers.

3.2.1 Structure/Morphology Characterization

1. Scanning Electron Microscopy

The SEM (Hitachi S-3500N and Carl Zeiss, LEO 1550 VP) was used to characterize the thickness of as-prepared CNT arrays and the diameter of fibers and the morphologies of CNT arrays and fibers, including alignment of CNTs and twisting effect of fibers, as well as the fracture surface of broken fibers.

2. Transmittance Electron Microscopy

TEM imaging of CNTs was performed in a JEOL 2010 TEM. The structural information, including tube diameter, wall number and their distribution, can be statistically obtained. TEM samples were prepared by drop-casting nanotube/ethanol solutions onto copper grids in the open air.

3.2.2 Mechanical test

The measurement of tensile strength of CNT fibers was performed. The dependence of mechanical properties on surface twisting angle, fiber diameter and test condition (strain rates) have been extensively studied. The as-prepared CNT fibers were first stabilized on a paper frame using superglue as shown in Figure 3.6. Then the tensile test was performed on a puller after cutting the edges of the paper frames.

From the experimental tests, results received are the force in terms of gram force and its respective displacement value. Then, the corresponding stress and strain could

be calculated by the following equations

$$\text{Tensile strength, } \sigma = \frac{\text{force}}{\text{cross-section area}} \quad (3-1)$$

$$\text{Strain, } \varepsilon = \frac{\text{displacement}}{\text{original length of fiber}} \quad (3-2)$$

In order to study the details of the load transfer process, several techniques, including static and cyclic tensile test were utilized to monitor the stress relaxation and permanent strain generation process of CNT fibers.

As shown below, different numbers represent different elements in the mechanical equipment setup which are listed as: 1. as-prepared CNT fiber and paper frame assembly, 2. double-side tape for holding paper frame, 3. load sensor, 4. metal wire for pulling the CNT fiber, 5. motor, 6. microscope, 7. controller of the motor, 8. monitor of the motor controller, 9. monitor of the sensor, 10. monitor of microscope, 11. computer.

Figure 3.6 Scheme of the puller for (a) tensile test (1. as-prepared CNT fiber and paper frame assembly, 2. double-side tape for holding paper frame, 3. load sensor, 4. metal wire for pulling the CNT fiber, 5. motor, 6. microscope, 7. controller of the motor, 8. monitor of the motor controller, 9. monitor of the sensor, 10. monitor of microscope, 11. computer.)

3.2.3 Electrical test

Electrical measurements were conducted using a two-probe method at room temperature. The current-voltage (I - V) characteristics were obtained by sweeping the bias voltage, typically between 50 mV and -50 mV. Ag conductive epoxy was employed to connect a CNT fiber to the probe station. The schemes are shown below in Figure 3.7a.

Constant voltage measurement was performed at 50 mV and the current flowing through CNT fiber was monitored.

Figure 3.7 (a) Schemes of electrical measurement on CNT fibers, and (b) A typical I - V curve of CNT fiber

Normally, the I - V curves of measured CNT fibers are linear with asymmetry shape as shown in Figure 3.7b, thus the conductivity could be calculated from Ohm's law.

$$R = \rho \frac{l}{A} \quad (3-3)$$

where, R is resistance, ρ is the resistivity, l is length and A is the cross-sectional area or the of the specimens. In our case, the length of CNT fibers is fixed to be 6 mm, the diameter of the sample holders' hole. Readings are always taken from the two ends of the fibers. Thus, the conductivity is the reciprocal of resistivity.

$$\sigma = \frac{1}{\rho} = \frac{l}{R \times A} \quad (3-4)$$

As long as we obtain R and A , the conductivity of CNT fibers could be calculated out. However, one concern is the contact resistance exists between CNT fibers and

conductive epoxy when use two-probe method instead of more accurate four-probe method. The resistance between two terminals is actually given by:

$$R = R_c + R_{\text{fiber}} \quad (3-5)$$

where, R_c is the contact resistance between fiber and silver epoxy, while R_{fiber} is the resistance of fiber measured. Resistance values for individual electrode separations were calculated from the slop of I - V plots. From the straight line fits, similar to that shown in Figure 3.8, typical contact resistance is around $131.3 \, \Omega$. Compared to the resistance of CNT fibers, the contact resistance could be neglected. The inset of Figure 3.8 shows the schematic devices used for contact resistivity measurement.

Figure 3.8 Plot of resistance *versus* pattern separation used to calculate R_c . (the inset shows the schematic of patterning procedure for contact resistivity measurement)

3.2.4 Polarized Raman spectroscopy

The polarized micro-Raman spectroscopy (Reinshaw, RM1000, 20 mW) was used for characterization of CNTs using a He-Ne laser with the exciting wavelength of 633 nm to distinguish ordered and disordered crystal structures of carbon. During the measurements, a microscope with 50 $\times$ objective lens was used for focusing the laser beam and collecting the scattered light. All Raman spectra were taken in backscattering configuration, with the polarization direction of the laser along the x -axis of the measuring windows. The polarization behaviors of CNT fibers were obtained by changing the angle between the fiber axis and x -axis of measuring windows. Typically, there are three main modes: the G-band which related to the tangential mode vibration of the C atoms, D-band which is a second-order Raman scattering mode induced by the disorder part in CNTs, and G' mode which can be regarded as the overtone of the D mode and is ideally suited for a quantitative assessment of the defect density in graphite and graphite-based materials. The ratio between integrated intensity of G band and D band is usually used for analyzing the quality of the as-grown CNT arrays, while the G' band shift is used to evaluate the structural deformation of CNTs. The setup is shown schematically in Figure 3.9.

Figure 3.9 Schemes of Raman measurement on CNT fibers

It has been reported that the Raman intensity of an oriented CNTs is proportional to $\cos^4 \theta$ in a parallel polarization geometry, where θ is the angle between the CNT axis (in the plane perpendicular to the pointing vector of the incident excitation) and the incident excitation polarization. For a fiber comprised of CNTs distributed over a range of angles the total Raman intensity can be integrated to sum the contribution from nanotubes at each angle. Thus, the intensity of a Raman peak may be written as

$$I(\psi) = \int_{\psi - \pi/2}^{\psi + \pi/2} c F(\theta - \psi, \Delta) \cos^4 \theta d\theta \quad (3-6)$$

where ψ is the fiber angle with respect to the incident polarization, $F(\theta - \psi, \Delta)$ is a distribution function of angular width characterized by the parameter Δ , and c is a parameter that gives the maximum intensity when $\theta = 0$. The degree of CNT alignment is determined by measuring $I(\psi)$ for a convenient Raman peak at several fiber angles and performing a least squares fit to Eq. (3-6) (adjusting c and Δ to minimize the variance). The choice of distribution function is left to that which fits the data best [112].

3.2.5 In-situ tests during tension

In order to monitor the structural changes, the stress transfer in the fiber and the failure evolution, the in-situ characterization approaches were developed: 1) in-situ electrical test; and 2) in-situ Raman scattering.

Carbon black and CNTs as additives in polymer or glass fibers functioning as health monitoring have been developed in recent years. By tracking direct current resistance during mechanical deformation, which is remarkably sensitive to the initial stage of matrix microcracking, the damage initiation and evolution could be in-situ monitored [95, 96, 128]. The same methods could be borrowed in in-situ characterizing failure mechanisms of CNT fibers under tension.

As depicted in section 2.2.2 and 3.2.4, the structural information and deformation evolution could be characterized by polarized Raman spectroscopy and it has been successfully employed in in-situ measuring the structural deformation process of SWNT networks and fibers. By investigating the variation of the G' band under strain, together with tensile tests, the influence of fibers' geometries on their mechanical performance could be elucidated. So, in this study, the in-situ methods will be extensively utilized in characterizing the mechanical behaviors of CNT fibers spun from vertically aligned arrays and their relationship to fibers' microstructures.

Figure 3.10 Schematic of in-situ electrical and Raman measurements under tension

Figure 3.10 shows the schematic of experimental setup. And within this setup, several techniques could be assembled together. For example, a CNT fiber was mounted between a sample holder, with a micrometer-loading device for displacement control and a force sensor for stress monitoring. Incremental static mechanical test, where the strain was increased step by step, was utilized to directly examine the stress relaxation of the CNT fiber. The electrical current was measured by using a probe station. By monitoring the current flowing through the fiber during an incremental cyclic loading, reversible or permanent deformation could be identified. Raman spectra were collected to give evidences of load bearing condition and load transfer efficiency.

3.3 Statistical tests for Weibull analysis

As described in section 2.3 that Weibull model could be used to predict the

distribution of mechanical strength and further failure mechanisms, in this study, derived from single-modal Weibull function, modified Weibull models by adopting strain rate and scale effects were proposed in order to analyze the failure mechanisms observed in experiments. In our case, the simplest model to characterize the strength variation of CNT fibers is the standard Weibull distribution (single-modal Weibull distribution). If σ is the failure strength, the probability of failure of CNT fibers, $P_f(\sigma)$, is given by [123]:

$$P_f(\sigma) = 1 - \exp \left[- \left[\frac{\sigma}{\sigma_0} \right]^m \right] \quad (3-7)$$

where σ_0 is the scale parameter, and m is the shape parameter which indicates the variation in strength distribution. Eq. (3-6) is widely used to fit experimental data for a set of identical single fibers (same gauge length and diameter).

In this study, in order to utilize Weibull distribution to analyze the failure mechanisms of CNT fibers tested under different strain rates, both strain rate and diameter were adopted in the equation.

$$P_f(\sigma) = 1 - \exp \left[- \dot{\epsilon}^k \left[\frac{\sigma}{\sigma_{\dot{\epsilon}}} \right]^m \right] \quad (3-8)$$

$\sigma_{\dot{\epsilon}}$ is the scale parameter after taking strain rates into account, $\dot{\epsilon}$ is the strain rate, k is the strain rate dependent parameter, and m is the Weibull shape parameter.

$$P_f(\sigma) = 1 - \exp \left[- d^h \left[\frac{\sigma}{\sigma_d} \right]^m \right] \quad (3-9)$$

σ_d is the scale parameter after taking fiber diameter into account, d is the fiber diameter, and h is the diameter dependent parameter.

For Eq. (3-8), the strain rates in this study were chosen in the range of 1×10^{-5} to 0.1 s^{-1} . While for Eq. (3-9), the diameters of CNT fibers were controlled between 3 to $10 \text{ }\mu\text{m}$.

Chapter 4 General Properties of CNT fibers

4.1 Background

This chapter will discuss several fundamental behaviors and properties of CNT fibers, such as fiber tensile behavior, ultimate strength, electrical conductivity, the uniformity in mechanical strength and conductivity, characteristics of Raman spectra and influence of twisting on fiber ultimate mechanical strength and structures.

4.2 Uniformity of CNT fibers

As shown in Figure 4.1a, continuous CNT fiber was pulled out from the side of a vertically aligned array. Normally, the pulling speed is 5 cm s^{-1} and the rotating speed is 170 rpm. In Figure 4.1b, the magnified SEM image shows that the CNT fibers are loosely packed with a twist angle of about 10° on the surface of the fiber. After being densified by ethanol and fixed on paper frame, these fibers are ready for mechanical, electrical and Raman measurements.

Figure 4.1 (a) SEM image of CNT fiber being pulled from a vertically aligned CNT array. (b) Enlarged SEM image of the CNT fiber

It has been widely accepted that during spinning process, twisting combined with solvent wetting will give an enhanced tube-tube interactions, leading to a higher mechanical strength. The mechanical properties of CNT fibers were measured by tensile test under tensile loading speed of $1 \mu\text{m s}^{-1}$ with a gauge length of 6 mm (i.e. a strain rate of $1.67 \times 10^{-4} \text{ s}^{-1}$). The fiber diameters were measured by SEM, and the fiber strength was calculated according to the force and cross-section area. Typical stress-strain curves have been shown in Figure 4.2a. The relationship between stress and strain is non-linear at large strain, indicating inelastic deformations. And the fibers show ultimate mechanical strength of about 0.5 and 0.65 GPa, respectively. The Young's modulus calculated according to initial linear part is around 40 GPa which is smaller than previous results [4]. The uniformity of the fibers was also checked by statistically testing four segments of one long CNT fiber. It could be seen in Figure 4.2b, with fixed spinning parameters, the ultimate mechanical strengths are in the range between 0.5 and 0.7 GPa, with an average strength of about 0.6 GPa.

Figure 4.2 (a) Typical stress-strain curve tested at a strain rate of $1.67 \times 10^{-4} \text{ s}^{-1}$. (b) The uniformity of fibers mechanical strength

Besides mechanical strength, another excellent property is its high electrical conductivity. In order to characterize the conductivity of CNT fibers and their uniformity, conductive silver epoxy was used to electrically connect CNT fibers and electrodes, at the same time offering strong mechanical bonding for tensile tests. Figure 4.3a shows a typical current-voltage (I - V) characteristic, which was obtained by using a two-probe method. The bias voltage was swept from -50 mV to 50 mV. A linear and symmetric dependence of current on voltage was observed, confirming an Ohmic contact between the CNT fiber and silver paste. The conductivity was calculated based on conductance and diameter of CNT fibers. The uniformity of the fibers conductivity was evaluated by measuring a batch of fibers originating from the same long CNT fiber as shown in Figure 4.3b. Normally, the conductivity of CNT fibers has a slight variation ranging from 380 to 480 S cm^{-1} with an average conductivity of around 400 S cm^{-1} .

Figure 4.3 (a) Electrical measurement of CNT fiber by sweeping bias voltage from -50 mV to 50 mV. (b) The uniformity of the fibers conductivity

The variation of electrical property of CNT fibers against the tensile strain has also been examined for reliability. The current flowing through CNT fiber, which is under tension, has been monitored according to time. The CNT fiber was tensioned by displacement step controlled process with an elongation of 10 μm per step and at each step, the fiber was held for 30 s. As can be seen in Figure 4.4, the current decreases

accordingly till breakage. Moreover, during the holding time, the current almost keeps a constant value.

Figure 4.4 Current variation as CNT fiber tensioned step by step

4.3 Effect of twist angle on fibers' tensile strength

The effect of twisting on fiber's mechanical strength has been examined and a generic equation could be employed to provide useful insights for spinning CNT fibers [14]. Specially, the ratio of fiber tensile strength (σ_f) to the tensile strength of the component tubes (σ_{CNT}) is approximately

$$\sigma_f / \sigma_{CNT} \approx \cos^2 \theta [1 - (k \operatorname{cosec} \theta)] \quad (4-1)$$

where $k = (dQ / \mu)^{1/2} / 3L$, θ is the helix angle that CNTs make with the fiber axis, d is the tube diameter, μ is the friction coefficient between CNTs, L is the tube length, and

Q is the tube migration length (i.e., the distance along the fiber over which a nanotube shifts from the fiber surface to the deep interior and back again). The $\cos^2 \theta$ term in Eq. (4-1) describes the strength decrease of a twisted assembly of continuous fibers, which occurs because the CNTs in the twisted fiber are inclined at the angle θ with respect to the tensile axis. For short tubes, however, in the absence of twist there is little strength because there are no significant transverse forces to bind the tube assembly together. The $[1-(k \operatorname{cosec} \theta)]$ term describes the generation of transverse forces by transfer of the tensile load to the fiber surface, which locks the CNTs together as a coherent structure. The components of k show that the strength obtainable for a given level of twist increases with increasing coefficient of friction and CNT length and with decreasing CNT diameter and CNT migration length.

During our fabrication process, different twisting could be easily realized by changing fiber spinning parameters, and different morphologies could be obtained. As shown in Figure 4.5, when we keep the linear pulling speed constant at 5 cm min^{-1} , twisting effect will be enhanced with increased rotating speed. Figure 4.5a shows a CNT fiber with a diameter of about $6 \text{ }\mu\text{m}$ and a surface twist angle of about 6° (the angle between CNT alignment direction and the fiber axis). By increasing the rotating speed the surface twist angle shown in Figure 4.5b is estimated to be about 10° .

Figure 4.5 SEM images of CNT fibers with different surface twist angle a) 6 ° and b) 10 °

In order to examine the twisting effect on the mechanical strength of CNT fibers, tensile tests have been performed on CNT fibers with different surface twist angles. The tensile test results have been plotted in Figure 4.6. It is obvious that the average mechanical strength increases with surface twist angle in the range from 0 to 16°, which is similar to the results reported by others [23]. So, in the following studies, the spinning process is fixed and the parameters are: 340 rpm for the rotating motor and 5 cm min⁻¹ for linear motor.

Figure 4.6 The twist angle dependent distribution of fiber strength

4.4 Structural characterization by polarized Raman spectroscopy

Raman spectroscopy, which is a non-destructive measurement, was employed to characterize the structural properties of CNTs. As shown in Figure 4.7, the peak located at 1329 cm^{-1} corresponds to the D band (structural defects) of CNTs, while the band near 1600 cm^{-1} could be resolved into two modes at 1580 and 1612 cm^{-1} using Lorentzian fitting, respectively. 1580 cm^{-1} is typically named as G band (graphitization) whereas 1612 cm^{-1} mode is normally originated from the compression of CNTs inside the fibers named as D' band. The G' peak, which is very sensitive to the deformation of CNTs, is located at 2648 cm^{-1} . So, from the band shift and intensity ratio between D and G bands, it is easy to evaluate the structural deformation of CNT fibers.

Figure 4.7 Typical Raman spectra of pristine CNT fiber. The smooth thin lines were obtained by using Lorentzian fitting. a) D peak, b) G & D' peaks and c) G' peak. (Solid lines are experimental data, the dash lines are fitting curves)

Similar to individual CNTs, CNT fibers also show an orientation dependence in Raman measurements: the maximum intensities of all Raman modes appear when the CNTs are parallel to the polarization of the incident laser light ($\alpha_i = 0^\circ$ and $\alpha_i = 180^\circ$), and very weak signals could be detected when the CNTs are perpendicular to that of the incident laser light ($\alpha_i = 90^\circ$). Further analysis indicates that the intensities of all Raman modes show the same angular dependence which can be described as $I(\alpha_i) \propto$

$\cos^4(\alpha_i)$ for parallel polarization. However, different from the small CNT bundles or thin ropes, a twisted CNT fiber has a surface twisting angle, and this twisting angle is not a constant in the fiber but changes in the radial direction because of the finite diameter of the fiber, resulting in non-uniform distribution of CNT alignment. The non-uniformity could be even worse if the twisting is not effectively transferred during twisting process. In order to study the influence of such a non-uniform distribution on the fibers' properties, it is necessary to open a generic methodology to analyze and evaluate the real alignment distribution.

Figure 4.8 compares the dependence of the intensities of G band of the pristine and twisted fibers as a function of rotation angles between the fiber axis and x -axis of measuring window. The intensities used here and thereafter are integrated area intensities. It can be found that Raman spectra of the fibers show a polarization behavior with a period of 180° . For the untwisted fiber, from 0° to 90° , the intensity of G band decreases monotonously; from 90° to 180° , the intensity increases monotonously. The maximum intensity appears at 0° (180°), and the minimum intensity appears at 90° . This observation is consistent with previous results. For the twisted fibers, the maximum and minimum intensities do not appear at 0° and 90° . There exists a polarization angle offset of about 20° between the untwisted and twisted fibers.

Figure 4.8 Intensities of G peak of the untwisted and twisted fibers as a function of rotation angles between the fiber axis and x-axis of measuring window ($-40^{\circ} - 200^{\circ}$)

Such a variation in polarization angle reflects the microscopic alignment change in the twisted CNT fiber. In order to investigate the effect of surface twisting angle on the polarization behavior of CNT fibers, Figure 4.9 compares the dependence of intensities of G peak of CNT fibers with different twisting as a function of rotation angles. For the sample with twisting angle of 6° , it can be seen that the maximum intensity of G peak appears at -5° (175°) and minimum intensity appears at 85° . For samples with twisting angles of 10° , 19° and 24° , the maximum intensities of G peaks appear at -10° (170°), -20° (160°) and -25° (155°), respectively; the minimum intensities appear at 80° , 70° and 65° , respectively. Compared with the untwisted fiber, there exists a polarization angle offset of 5° , 10° , 20° and 25° for these four samples, respectively. Those results indicate that the twisting angles can greatly affect the

polarization behaviors of the CNT fibers.

Figure 4.9 Dependences of intensities of G peak of fiber samples with twisting angle of 6°, 10°, 19° and 24° as a function of rotation angles

When comparing the surface twisting angles obtained from SEM images and polarization angle offsets from Raman measurements (as shown in Figure 4.10a), it can be seen that both surface twisting angle and polarization angle offset change in the same manner with the twisting time, indicating the effect correspondence between each other. This also suggests that polarized Raman spectra can be well used to determine the surface twisting angle of CNT fiber.

Similar to an individual CNT, a CNT fiber also shows an anisotropic polarization. The ratio of G band intensities obtained with fiber axis parallel to *versus* perpendicular to the polarization direction of the laser (i.e. $I_{//}/I_{\perp}$) was usually used to

evaluate the alignment degree of CNTs in the fibers. Figure 4.10b shows the effect of twisting time on the alignment degree ($I_{//}/I_{\perp}$ ratio) of the CNTs in the fibers. Surprisingly, it is seen that the alignment degree of the CNTs decreases with twisting time, which seems to contradict the previous results. The observation can be explained by the non-uniform twisting in the CNT fibers and will be further discussed by Raman depth profile.

Figure 4.10 (a) Comparison between surface twisting angles obtained from SEM and polarization angle bias from Raman measurements as a function of twisting time and (b) Dependence of G

peak $I_{\parallel} / I_{\perp}$ ratio of fiber samples as a function of twisting time

In a normal CNT fiber spun from vertically aligned arrays, the twisting may not be fully transferred to all individual CNTs, then there should exist a so-called ‘surface twisting angle’ between the alignment directions of the core CNTs and surface CNTs. Here, depth-profiled Raman measurements were employed to evaluate the alignment distribution of CNTs in the fibers. Figure 4.11a shows the depth profile of Raman signals obtained from sample with a twisting angle of 19° . The focus depth of ‘0 μm ’ means that the laser spot is focused on the surface of the fiber, and the fiber shows a polarization angle offset of 20° . By increasing the focus depth (from 0 to -4 μm), the polarization angle value decreases monotonously and reaches its minimum value of 7.5° at the focus depth of -3.0 μm . Further increasing the focus depth, the polarization angle will increase and reach 10° at focus depth of -4.0 μm .

Figure 4.11 (a) Dependences of intensities of G peak of fiber with twisting angle of 19° as a function of rotation angle with different focus depth (0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0 μm) and (b) Dependences of polarization angle bias as a function of focus depths

The dependence of the polarization angle on the depth is shown in Figure 4.11b. These results indicate that twisting angle at the surface and a small twisting angle near the core of the fibers. As the focus depth increases, core part contributes more in Raman signal, resulting in the decrease of the polarization angle. However, when the depth is larger than the radial of the CNT fiber, the polarization angle will increase again because of the surface CNTs on the other side of the fiber start to produce Raman signals.

Referred to the fiber model by Vilatela et al. and results from Baughman's group [14, 20, 21], we simply consider that the twisted fibers consist of the surface CNTs (orientated as θ_s) and the core CNTs (oriented as the fiber axis). Figure 4.12a shows a simulation diagram of a twisted CNT fiber. We simply construct a two-layer film structure model (surface part and core part) to do the optical geometry calculation, as

shown in Figure 4.12b. The CNT fiber was put on x - y Raman measuring platform with a rotation angle (θ) between fiber axis and x -axis direction (stand for the polarization direction of the laser). The laser propagates along the z axis to the center of the fiber surface.

Figure 4.12 (a) Simulation diagram of a twisted CNT fiber, θ_s indicates the surface twisting angle; (b) Schematic description of relationships between the laser propagation direction (k), the laser polarization direction (e), the x axis of measuring window (x), and the tube axis direction in the measurements. θ (defined as rotation angle in this research) is the angle between x and the CNT fiber axis direction

As well known, the Raman intensity of oriented CNTs is proportional to $\cos^4\alpha$, α

is the angle between the polarization direction and fiber axis. For a common measurement, ignoring the energy absorption by CNT fiber and scattering energy loss during the propagation, one part of the laser will act on the surface of the fiber, marked with I_1 ; then, the other will act on the core of the fiber, marked with I_2 . Then, the total Raman intensity of the twisted fiber should be estimated as

$$I(\theta) = I_1 \cos^4(\theta + \theta_s) + I_2 \cos^4 \theta \quad (4-2)$$

Here, θ is the rotation angle between the fiber axis and x axis, θ_s is the surface twisting angle of the fiber.

According to $\cos^2 \alpha = \frac{1 + \cos 2\alpha}{2}$, Eq. (4-2) could be expanded as:

$$\begin{aligned} I(\theta) &= I_1 \left[\frac{1 + \cos 2(\theta + \theta_s)}{2} \right]^2 + I_2 \left[\frac{1 + \cos 2\theta}{2} \right]^2 \\ &= \frac{I_1}{4} [1 + \cos^2 2(\theta + \theta_s) + 2 \cos 2(\theta + \theta_s)] + \frac{I_2}{4} (1 + \cos^2 2\theta + 2 \cos 2\theta) \\ &= \frac{I_1}{4} \left[1 + \frac{1 + \cos 4(\theta + \theta_s)}{2} + 2 \cos 2(\theta + \theta_s) \right] + \frac{I_2}{4} \left(1 + \frac{1 + \cos 4\theta}{2} + 2 \cos 2\theta \right) \\ &= \frac{3I_1}{8} + \frac{1}{8} I_1 \cos 4(\theta + \theta_s) + \frac{1}{2} I_1 \cos 2(\theta + \theta_s) + \frac{3I_2}{8} + \frac{1}{8} I_2 \cos 4\theta + \frac{1}{2} I_2 \cos 2\theta \\ &= \frac{3I_0}{8} + \frac{1}{8} [I_1 \cos 4(\theta + \theta_s) + I_2 \cos 4\theta] + \frac{1}{2} [I_1 \cos 2(\theta + \theta_s) + I_2 \cos 2\theta]. \end{aligned} \quad (4-3)$$

Here, I_0 is the total intensity of the incident laser ($I_0 = I_1 + I_2$).

According to $\cos(\alpha + \beta) = \cos \alpha \cos \beta - \sin \alpha \sin \beta$, Eq. (4-3) then can be further expanded as:

$$\begin{aligned} I(\theta) &= \frac{3I_0}{8} + \frac{1}{8} [I_1 (\cos 4\theta \cos 4\theta_s - \sin 4\theta \sin 4\theta_s) + I_2 \cos 4\theta] \\ &\quad + \frac{1}{2} [I_1 (\cos 2\theta \cos 2\theta_s - \sin 2\theta \sin 2\theta_s) + I_2 \cos 2\theta] \end{aligned}$$

$$\begin{aligned}
&= \frac{3I_0}{8} + \frac{1}{8}[(I_1 \cos 4\theta_s + I_2) \cos 4\theta - I_1 \sin 4\theta_s \sin 4\theta] \\
&+ \frac{1}{2}[(I_1 \cos 2\theta_s + I_2) \cos 2\theta - I_1 \sin 2\theta_s \sin 2\theta]
\end{aligned} \quad (4-4)$$

For a given fiber, θ_s is a constant. According to

$a \cos \alpha \pm b \sin \alpha = \sqrt{a^2 + b^2} \cos(\alpha \mp \phi)$ ($\tan \phi = \frac{b}{a}$), Eq. (4-4) can be rewritten into

another form:

$$\begin{aligned}
I(\theta) &= \frac{3I_0}{8} + \frac{1}{8} \sqrt{(I_1 \cos 4\theta_s + I_2)^2 + (I_1 \sin 4\theta_s)^2} \cos(4\theta + \phi_1) + \\
&\frac{1}{2} \sqrt{(I_1 \cos 2\theta_s + I_2)^2 + (I_1 \sin 2\theta_s)^2} \cos(2\theta + \phi_2)
\end{aligned} \quad (4-5)$$

where, $\phi_1 = \arctan\left(\frac{\sin 4\theta_s}{\cos 4\theta_s + I_2/I_1}\right)$, $\phi_2 = \arctan\left(\frac{\sin 2\theta_s}{\cos 2\theta_s + I_2/I_1}\right)$.

To well illuminate our model in this research, we do some calculation using our deduced Eq. (4-5), which can be written in another form:

$$\begin{aligned}
I(\theta) &= \frac{3I_0}{8} + \frac{1}{2} \sqrt{I_1^2 + I_2^2 + 2I_1I_2 \cos 2\theta_s} \cos(2\theta + \phi_2) \\
&+ \frac{1}{8} \sqrt{I_1^2 + I_2^2 + 2I_1I_2 \cos 4\theta_s} \cos(4\theta + \phi_1)
\end{aligned} \quad (4-6)$$

a) For an untwisted CNT fiber, $\theta_s = 0$, then $\phi_1 = \arctan\left(\frac{\sin 4\theta_s}{\cos 4\theta_s + I_2/I_1}\right) = 0$,

$\phi_2 = \arctan\left(\frac{\sin 2\theta_s}{\cos 2\theta_s + I_2/I_1}\right) = 0$; thus Eq. (4-6) can be simplified as

$$\begin{aligned}
I(\theta) &= \frac{3I_0}{8} + \frac{1}{2} \sqrt{I_1^2 + I_2^2 + 2I_1I_2} \cos(2\theta) + \frac{1}{8} \sqrt{I_1^2 + I_2^2 + 2I_1I_2} \cos(4\theta) \\
&= \frac{3I_0}{8} + \frac{1}{2} (I_1 + I_2) \cos 2\theta + \frac{1}{8} (I_1 + I_2) \cos 4\theta \\
&= \frac{3I_0}{8} + \frac{I_0}{2} \cos 2\theta + \frac{I_0}{8} \cos 4\theta
\end{aligned}$$

$$= I_0 \cos^4 \theta . \quad (4-7)$$

Figure 4.13 Simulation curve of function of $I(\theta)=I_0\cos^4\theta$

The curve shown in Figure 4.13 could well describe the polarized Raman results from the untwisted fiber presented in Figure 4.8.

b) For a twisted CNT fiber, when the laser was focused on the surface of the sample,

i.e., $I_1=I_0$, $I_2\approx 0$, then $\phi_1 = \arctan\left(\frac{\sin 4\theta_s}{\cos 4\theta_s}\right) = 4\theta_s$, $\phi_2 = \arctan\left(\frac{\sin 2\theta_s}{\cos 2\theta_s}\right) = 2\theta_s$; thus Eq.

(4-6) can be simplified as

$$\begin{aligned} I(\theta) &= \frac{3I_0}{8} + \frac{1}{2}I_0 \cos(2\theta + 2\theta_s) + \frac{1}{8}I_0 \cos(4\theta + 4\theta_s) \\ &= I_0 \cos^4(\theta + \theta_s) . \end{aligned} \quad (4-8)$$

Figure 4.14 Simulation curve of function of $I(\theta)=I_0\cos^4(\theta+\theta_s)$.

c) For a twisted CNT fiber, θ_s is usually a small angle (e.g., samples with twisting angles of 20 °, and 24 °), then

$$\frac{1}{2}\sqrt{I_1^2 + I_2^2 + 2I_1I_2 \cos 2\theta_s} \gg \frac{1}{8}\sqrt{I_1^2 + I_2^2 + 2I_1I_2 \cos 4\theta_s}.$$

The period of Eq. (4-6) is dominated by the item of $\cos(2\theta + \phi)$, i.e., when the laser was focused into the sample, Eq. (4-6) can be simplified as

$$I(\theta) \propto \sqrt{I_1^2 + I_2^2 + 2I_1I_2 \cos 2\theta_s} \cos(2\theta + \phi), \quad (4-9)$$

where, $\phi = \arctan\left(\frac{\sin 2\theta_s}{\cos 2\theta_s + I_2/I_1}\right)$.

From the simulation diagram of a twisted CNT fiber shown in Figure 4.14, we consider that one twisted CNT fiber consist of a twisted surface CNT layer (oriented as θ_s) and a bound CNT core (oriented as the fiber axis), i.e., there might exist a

effective twisting layer in a twisted fiber. Then the depth profile of I_2/I_1 ratio has been summarized in Figure 4.15. When the laser illuminates at the fiber, the I_2/I_1 ratio will increase with depth towards the core of the fiber. Once the depth increases from the core further to reach the effective twisting layer, I_2/I_1 ratio will decrease with more movement.

Figure 4.15 Radial depth profile of I_2/I_1 ratio

Using depth profile of I_2/I_1 ratio shown in Figure 4.15, we can draw a plot of ϕ

as a function of I_2/I_1 ratio using $\phi = \arctan\left(\frac{\sin 2\theta_s}{\cos 2\theta_s + I_2/I_1}\right)$.

Figure 4.16 Radial depth profile of angle offset ϕ

It can be found that Figure 4.16 is well agreed with the result shown in Figure 4.11b.

Furthermore, as for our fiber, $\theta_s = 20^\circ$, the polarization angle offset of the fiber decreased to 10° when focusing the laser at the center of the fiber (about $-2 \mu\text{m}$). Then using equation $\phi = \arctan\left(\frac{\sin 2\theta_s}{\cos 2\theta_s + I_2/I_1}\right)$, $\phi = 10^\circ$, and $\theta_s = 20^\circ$, we can get the ratio of I_2/I_1 is about 2.87.

Thus in sum, Eq. (4-6) can be used to explain the polarization behaviors of our CNT fibers:

(i) For an untwisted CNT fiber, $\theta_s = 0$, then the expression can be simplified as

$$I(\theta) = \frac{3I_0}{8} + \frac{I_0}{8} \cos 4\theta + \frac{I_0}{2} \cos 2\theta = I_0 \cos^4 \theta. \text{ This equation could well describe the}$$

polarized Raman results from the untwisted fiber presented in Figure 4.8.

(ii) For a twisted CNT fiber, when the laser is focused on the surface layer, few light can enter the core CNTs, i.e. $I_1=I_0$, $I_2\approx 0$. Then, the contribution of the fiber core can be ignored, and the total Raman intensity is

$$I(\theta) = \frac{3I_0}{8} + \frac{I_0}{8} \cos 4(\theta + \theta_s) + \frac{I_0}{2} \cos 2(\theta + \theta_s) = I_0 \cos^4(\theta + \theta_s).$$

This equation can also well fit the polarized Raman results presented in Figure 4.9.

(iii) For a twisted CNT fiber and when the laser is focusing on the fiber core, i.e., both surface and core CNTs contribute to Raman signal, the angle offset $\phi_1 = \arctan\left(\frac{\sin 4\theta_s}{\cos 4\theta_s + I_2/I_1}\right)$ and $\phi_2 = \arctan\left(\frac{\sin 2\theta_s}{\cos 2\theta_s + I_2/I_1}\right)$ will decrease with the increase of the ratio of I_2/I_1 . This result indicates the distribution/non-uniformity of twisting angle in the twisted fiber. From Figure 4.10b, we can find that the polarization angle offset of the fiber decreased to 10° when focusing the laser at the center of fiber (about $-2 \mu\text{m}$). Thus, using the surface twisting angle $\theta_s=20^\circ$, the ratio of I_2/I_1 can be estimated as 2.87.

4.5 Summary

In this part, typical mechanical & electrical tests and Raman characterization have been performed to examine the performance and behavior of CNT fibers spun from vertically aligned CNT arrays. The uniformity of mechanical strength and electrical conductivity is good and the influence of fabrication factor, for instance surface twisting angle, on the mechanical strength and structural properties of CNT fibers has also been investigated. By fixing spinning parameters, the CNT fibers are

ready for the following characterizations.

Chapter 5 Investigation of strain rate dependent failure mechanisms of CNT fibers

5.1 Background

Observations on polymer synthetic fibers and a few studies on CNT fibers, show that the fiber performance is limited by weak point, alignment, and contact length/area. Since a CNT fiber composed of millions of short individual CNTs, it inevitably includes tube ends distributed in the CNT fiber. These tube ends, as well as other defects such as inclusions, voids and structural defects, will function as the weak points and will break first during the tensile loading. Although efforts have been paid to improve fibers' mechanical strength recently, these studies mainly focus on the performance improvement. A systematic study and a comprehensive understanding on the failure mechanism of CNT fibers are still lacking.

It is well known that strain rate has serious influence on mechanical behavior of tested materials, in this part, the mechanical behaviors of CNT fibers have been studied in a wide range of strain rates. The failure mechanism was then discussed from the strain-rate dependences, together with the results from fiber fracture. By utilizing static/dynamic mechanical tests, and in-situ electrical & Raman measurement, the relation between mechanical behavior and microstructures of CNT fibers was also investigated.

5.2 Strain rate dependent failure mechanism of CNT fibers

5.2.1 Tensile test at different strain rates

As illustrated in section 4.2 that the uniformity of CNT fibers is good, the length dependence of fiber strength was then first studied by measuring the fiber strength using a gauge length of 1, 2, 5, 10, and 20 mm, respectively. As shown in Figure 5.1, it is found with some surprise that our CNT fibers show very weak dependence on the gauge length. This result is different from CNT fibers directly spun from CVD, but similar to that in high-strength polyethylene fibers [44, 89], and could be explained by the factors that the CNT ends are uniformly distributed in the fiber, the average length (~ 0.03 mm according to $L_x = L^{1/3} d^{2/3}$) between these discontinuities is much shorter than the gauge length (>1 mm), and there are no other serious weak points in our fibers. The strength uniformity and the weak dependence on gauge length not only imply fiber's practical potentials, but also allow us to conduct comparable and systematic measurements to study their failure mechanism.

Figure 5.1 Gauge-length dependence of the fiber strength

Using fibers from the same batch and the same gauge length, tensile testing is conducted and the results are compared under different strain rates (2×10^{-5} , 2×10^{-4} , 2×10^{-3} , 2×10^{-2} and 0.2 s^{-1} , respectively). Here the same batch samples were spun from the same array with the same fabrication process, and supposed to have similar original properties. Figure 5.2 shows the stress-strain curves of these samples under different strain rates. All the curves show three stages: a typical linear stage at the beginning, a non-linear stage with a lower slope in the middle, and a final failure stage. A higher strain rate results in a high strength and a small fracture strain, while a lower strain rate produces a much larger fracture strain but a lower strength. The slope of stress-strain curve at the beginning of tension is also changed accordingly, indicating higher Young's modulus of CNT fibers under faster tensile conditions.

Figure 5.2 The tensile stress-strain curves of CNT fibers under different strain rates

To determine the exact mechanical dependence of CNT fibers on the strain rate, we have tested more than 20 CNT fibers and plotted their fracture strengths, Young's modulus, and also the fracture strains against the strain rate in Figure 5.3. It was found that, the tensile mechanical properties strongly depend on the strain rate. As the increase of strain rate, the tensile strength and Young's modulus increase significantly, indicating a strain-rate strengthening effect, while the fracture strain decreases according to the increase of the strain rate. Within the tested range of the strain rates, the strength can increase from 0.5 GPa to 1.2 GPa, the fracture strain decreases from 3.2% to 1%, and the Young's modulus changes from 40 GPa to 260 GPa. The highest strength of 1.2 GPa, the highest modulus of 260 GPa and the smallest fracture strain of 1% are obtained under the strain rate of $0.2 s^{-1}$, while the largest fracture strain of 3.2%, the smallest strength of 0.5 GPa and the smallest modulus of 40 GPa are

observed under $2 \times 10^{-5} \text{ s}^{-1}$ low strain rate. Another interesting finding from Figure 5.3 is that the change of strength, modulus and fracture strain according to the strain rate could be characterized into two regimes: at low strain rate, they change significantly with the strain rate; while at high strain rate, they reach relatively saturated values. If we plot the strain rate in logarithmic scale, as shown in the insets of Figure 5.3, it is found that they follow power laws of the strain rate in the form of $\sigma_f(E, \varepsilon_f) \propto v^\gamma$ (with γ of ~ 0.1 for σ_f , ~ 0.2 for E , and -0.1 for ε_f in this batch of fibers), where σ_f represents the strength, E represents the modulus, and ε_f represents the fracture strain, v is the strain rate, and γ represents the exponent.

Figure 5.3 The dependences of strength (a), Modulus (b), and fracture strain (c) of CNT fibers on the strain rates

5.2.2 Morphological characterizations

This strain-rate strengthening effect makes CNT fibers different from carbon fibers which are insensitive to the strain rate [90]. But such a strengthening effect were previously observed in metals [84] and polymer fibers [84, 85]. In these materials, the strengthening usually associates with an increase of the fracture strain.

From theoretical calculation [129], individual CNTs also show a large fracture strain under a high strain rate due to the formation of unraveling chains. However, in our CNT fibers, the improvement of strength and modulus seems to happen at the expense of the fracture strain, indicating a different mechanism. The existence of two regimes in property/strain-rate responses also suggests that the governing factors are different at low strain rates and high strain rates. As a result, the fibers show plastic at low strain rates but more elasticity at higher strain rates. To understand it better, fiber fractures were studied by SEM. Figures 5.4a-c show fractures under 3 different strain rates, and Figures 5.4d-e show SEM images scanned at 100 μm away from the breaking end for fibers tested at high and low strain rates. From these SEM images, we have two interesting findings: 1) Fibers show a sharp break at high strain rates and a gradual attenuation & pull-out break at low strain rates. The pull-out length increases with the decrease of the strain rate; 3) After breaking, the CNTs 100 μm away from the breaking end show wavy & entangled morphology (similar to the un-tested fibers) under fast strain rates (Figure 5.4d) but a straight & well-aligned morphology under low strain rates (Figure 5.4e). From the SEM image of fiber's surface away from the fracture end (Figure 5.4f), it could be seen that the whole fiber has been stretched and the alignment is slightly improved also. Meanwhile, the shape of the fiber is not as uniform as original fibers anymore, giving further evidence that the CNTs have been aligned due to tension.

Figure 5.4 The SEM images of fiber fractures under different strain rates at (a) 0.2 s^{-1} , (b) $2 \times 10^{-3} \text{ s}^{-1}$, and (c) $2 \times 10^{-5} \text{ s}^{-1}$. Enlarged SEM images scanned at $100 \text{ }\mu\text{m}$ away from the breaking ends for fibers tested under (d) 0.2 s^{-1} , (e) $2 \times 10^{-5} \text{ s}^{-1}$ and (f) SEM image of fiber's surface away from the fracture end where strain rate is $2 \times 10^{-5} \text{ s}^{-1}$

From above tensile testing results and SEM observations, we proposed the following reasonable failure mechanisms for our CNT fibers: a sliding-to-break mechanism at low strain-rate regime, and a “cascade-like” breaking due to the CNT mis-alignment at high strain-rate regime. At low strain rates, individual CNTs or small CNT bundles have enough time to relax through tube sliding to redistribute the strain before they break, giving a much larger breaking strain and a pull-out fracture. At the same time of sliding, interconnections between CNTs could be partially destroyed to realize CNT's globe rearrangement, resulting in a low tensile strength and a low modulus. As strain rate increases, tube relaxation through sliding is becoming a slow process compared with the applied loading. The strain re-distribution becomes more and more difficult, and eventually the local strain breaks some CNTs and then the

whole CNT fiber. Accordingly, a relatively sharp breaking fracture, a small fracture strain, and high tensile strength & modulus are resulted. The key difference is that the tube can rearrange themselves at low strain rates but cannot at high strain rates. Direct evidence supporting such a statement is actually shown in Figure 5.4d-f, in which a stretch-to-straight effect was observed at low strain rates but no morphological change was seen in CNT fibers tested at high strain rates.

5.3 Effect of sliding on failure mechanism at low strain rate

In this part, different approaches have been employed to investigate the mechanical behaviors of CNT fibers under low strain rates and static tensile process. In situ electrical measurement and Raman spectroscopy have been utilized to study the deformation of CNT fibers, load transfer between individual CNTs and their deforming behavior inside the fibers. A correlation between nano-structure (e.g. morphologies and connections) of CNTs and mechanical behavior of CNT fibers has been established, and the low efficiency of load transfer between CNTs inside the fiber has been identified as the most significant factor for degrading fiber's reliability.

Improvement approach is proposed and studied by introducing 3-D cross-lined network polymer to improve the load transfer efficiency between CNTs inside the fibers. It is found that the composite fibers show better stress relaxation resistance than that of pure CNT fibers.

5.3.1 Stress relaxation of CNT fibers

Figure 5.5a shows a typical stress-strain curve measured at a strain rate of $1.67 \times 10^{-4} \text{ s}^{-1}$. The stress initially increases linearly versus strain, followed by an inelastic-like deforming process, which behaves similar to other types of CNT fibers [19, 21]. Three stages could be approximately identified as shown in Figure 5.5a: In stage 1, the stress of CNT fiber increases with strain linearly, indicating that within this strain range CNT fiber is elastic-like deformed; in stage 2, the relationship between mechanical stress and strain becomes nonlinear as the strain further increases, suggesting permanent elongation once the CNT fiber has been further tensioned; and finally in stage 3, the stress almost keeps constant till breakage. For most of CNT fibers, they break at a strain in the range between 2% and 3%, and exhibit good mechanical strength around 600 MPa. SEM image shown in Figure 5.5b gives direct observation that the fracture of a broken CNT fiber does not have a sharp edge, indicating a sliding-dominated breaking mechanism. It is well known, elastic deformation, which is reversible, corresponds to the linear part in stress-strain curve. Once the forces are no longer applied, the object returns to its original shape. While the non-linear part in stress-strain curve indicates that the deformation is irreversible, where serious sliding/breakages between CNTs inside the fiber probably exists. The stress-strain behavior and lower fiber's strength compared to individual CNTs indicate that the performance of the CNT fibers is dominated by load transfer efficiency between CNTs rather than the quality of individual CNT.

Figure 5.5 (a) typical stress-strain curve of CNT fiber at loading speed of $1 \mu\text{m s}^{-1}$ (e.g. a strain rate of $1.67 \times 10^{-4} \text{ s}^{-1}$) and (b) SEM image of breaking fracture of a CNT fiber

To verify the validity of our model proposed in Section 5.2, we further performed a new set of experiments. A direct observation of stress relaxation is shown in Figure 5.6a. In each step, the CNT fiber was elongated for a strain of 0.083%, and maintained for 3 min, repeating the cycle until breaking. It is found that the stress changes slightly during the 3 min holding time in several initial steps. As the strain increases (longer time in Figure 5.6a), the stress decreases faster and more significantly during holding time. The number (1) and (2) in the inset of Figure 5.6a

represent the stress decrement during holding time and stress increment between adjacent two steps. The ratio of these two values could reflect the relaxation degree of the fiber. Here, we define “Relaxation=decrement in stress (1)/increment in stress (2)”, and use this “Relaxation” to evaluate the decreasing rate of stress during the holding stages. The results are plotted in Figure 5.6b. The inset shows the magnified plot marked in red rectangular shape of Figure 5.6b. When the strain is (less than 0.67%), the relaxation of stress is around 55%. However, when the strain is higher than 0.67%, the stress relaxes faster with a value of 70% to 90%. Obviously, the relaxation of CNT fibers becomes more significant as the strain increases. If we consider that the CNT fiber is composed of large number of linear molecular chains (individual CNTs or small bundles), such a relaxation behavior is reasonable, because individual CNTs have enough time to re-arrange themselves through stretching and sliding during the holding time.

Figure 5.6 (a) Stress relaxation of CNT fiber as a function of time (the CNT fiber was elongated 5 μm every 3 min) and (b) Relaxation of CNT fiber as a function of strain (the inset shows a magnified plot in red area)

5.3.2 Observation of failure evolution by in-situ electrical measurement

Although static mechanical test gives direct evidence that the local stress cannot transfer from tube to tube effectively, the failure evolution of the connections between CNTs is difficult to differentiate. Here, we use electrical technique, widely utilized in carbon fiber reinforced composites, to monitor the fiber damage [94]. During incremental cyclic tensile loading test (apply a fixed strain for 3 min and then fully release the strain to zero, and repeat with an increased strain in next cycle; the incremental of strain between adjacent two steps is 0.167%), the current flowing through the fiber was monitored in real-time to evaluate the damage evolution and failure mechanism within the fiber. As shown in Figure 5.7, the current varies accordingly when the CNT fiber is elongated and released. When the tensile strain is small, the current could be recovered with very slight decrement as the strain is

released to 0%. However, after exceeding certain total strain (around 0.67%), it can be seen that current cannot be recovered even though CNT fiber is released to its original position. This phenomenon shows good agreement with the tensile test shown in Figure 5.5a and 5.6a. When the tensile strain is small, CNT fiber shows elastic-like deformation. The properties as well as the structure of CNT fiber could be reversibly changed. As the strain increases, the permanent deformation of CNT fiber will be generated, because the slippage of CNTs or even breakage of the connection between CNTs happen inside the fiber, and as a result the current cannot be recovered any more. In words, there is a critical value of shear strength originated from the interfacial friction between CNTs, below which the stress could be transferred effectively, but the slippage occurs and finally leads to breakage of connections between CNTs when stress is above this critical value.

Figure 5.7 Current monitoring during the elongation of CNT fibers (the blue points correspond to current and the red points correspond to strain change, showing the incremental cyclic loading-unloading process)

5.3.3 Stress transfer monitoring by Raman scattering

The techniques used to understand the load transfer and the failure of nanotubes have been micro-Raman spectroscopy and Kelly-Tyson approach to measuring the interfacial shear stress. These studies have been given some evidence for good load transfer between the polymer and the nanotubes. The Kelly-Tyson approach requires fragmenting the nanotubes, but it is unclear if the failures observed in the MWNT and SWNT composites are failures of individual CNTs or local instabilities of the aggregates (MWNT or SWNT bundles). Comparatively, Raman spectroscopy, as a powerful and nondestructive technique, has been employed to quantitatively examine the efficiency of load transfer between CNTs and characterize the structural change of CNT fibers. Since the Raman peak position is sensitive to the local mechanical strain, it is extremely favorable to utilize Raman spectroscopy in-situ to monitor the load bearing and load transfer process in micro-scale in CNT-based materials [19, 21, 22, 119]. In Figure 5.8a, typical G' band of Raman spectra for unstrained (0%) and 2%-strained fibers are shown. Obviously, the peak position shows downshift from 2646 cm^{-1} for unstrained CNT fiber to 2636 cm^{-1} for 2% strained CNT fiber. Another characteristic is that the width of G' band shows slight broadening when the fiber is strained and almost all broadening of G' band comes from the low-wave number edge. Figure 5.8b shows the peak position changes according to strain. It is found that the G' peak downshifts with increasing strain almost linearly with a rate of 7.5 cm^{-1} per 1% strain which is smaller than band shift rate of 37.5 cm^{-1} per 1% stain measured for individual nanotubes but larger than the value reported in the literatures for other

types of CNT fibers [19, 22, 119]. When the strain is above a certain value (in our case is around 1.3%), the position of G' peak reaches a constant, which is similar to that reported by others [22]. The inset in Figure 5.8b is the variation trend of full width at half maximum (FWHM) of G' peak, also showing three-stage features: at low strain (less than 0.67%), FWHM almost keeps constant; as the tensile strain increases, FWHM increases linearly; finally, once the strain exceed a certain point (around 1.3%), FWHM plateaus at around 108 cm^{-1} till the breakage of the specimen.

The downshift of G' peak indicates load transfer between CNTs, while the downshift rate of G' band with respect to strain gives the efficiency of load transfer. The relative value of 7.5 cm^{-1} per 1% strain indicates a more efficient load transfer between CNTs inside the fiber. The differences of downshift rate of G' band between our result and the value reported by others are probably due to that the as fabricated CNT fibers have different structures. The shape broadening of G' peak suggests that the loading on the CNTs inside the fiber is non-uniform. The asymmetric broadening of the G' peak particularly gives the evidences that CNTs took load gradually instead of taking load at the same time. Such a non-uniform stress distribution inside the fiber accelerates the stress concentration, lowers the strength of CNT fibers and leads to the final breakage of specimen. Such variations of Raman spectra also suggest the microscopic deformation process of CNTs in strained fibers.

Figure 5.8 (a) Comparison of the G' band Raman spectra for unstrained and 2%-strained CNT fiber and (b) the Raman shift of the G' band as a function of applied strain (the inset shows the widths of G' band for a strained fiber where FWHM represents the full width at half-maximum)

5.3.4 Structure dependent analysis of failure mechanism

In order to get a good understanding on the relationship between structure/morphology of CNTs and deformation mechanism of the fibers, a direct observation of the microstructures of CNT fibers is conducted. As the CNT fibers

were fabricated from yarns which were drawn from vertically aligned CNT arrays, a top view of untwisted CNT yarn was observed by using TEM. As shown in Figure 5.9a, CNTs inside the film are roughly oriented in one direction as the arrow shows. However, the CNTs are not exactly parallel. There exist plenty of waviness and entanglements existing intra/inter CNTs. Small bundles and tube-tube joints could also be found in the TEM image. Since the connections of CNTs at the top and bottom parts of CNT array are critical for fiber spinning, they probably also determine the final mechanical performance of CNT fibers. The detailed morphologies of top and bottom parts are then examined. Figure 5.9b shows the formation of tube-tube connection at top part of CNT arrays, indicating that small bundles are formed among CNTs due to either entanglement or van der Waals force. Comparatively, the connections at bottom part of CNT arrays are formed through catalyst particles. As shown in Figure 5.9c, a few CNTs are connected by one big catalyst particle or several small particles. These morphological features have a direct reflection on fiber's performance: the waviness and poor orientation of CNTs will result in reorientation and sliding of CNTs during tension, and thus degrade load transfer efficiency; the existence of small bundles and entanglements will degrade load transfer efficiency as well, leading to stretching and sliding of CNTs inside the fiber; while the breakage of joints formed by catalyst particles and entanglements could result in permanent degradation of fiber's properties [17, 24, 65, 130].

Figure 5.9 TEM images obtained from CNT yarn drawn from vertically aligned CNT arrays: (a) well oriented CNTs (arrow direction) with waviness, (b) connection among CNTs at top part of CNT arrays and (c) connection among CNTs at bottom part of CNT arrays

Combined with experimental data obtained above, analysis of the failure mechanisms of CNT fibers spun from vertically aligned arrays requires an estimation of the strength of small CNT bundles. The model proposed by Windle's group was employed here to evaluate the strength of small bundles which could be given by [20]

$$\sigma_f = \left(\frac{\tau_f N A \pi R L / 4}{N \pi (R^2)} \right) = \left(\frac{\tau_f A L}{4 R} \right) \quad (5-1)$$

where L is the length of individual nanotubes. N is the number of tubes per cross section of the small bundles and R the radius of the tubes. The symbol A represents a fraction as the tubes are in contact over a fraction of their circumference. Thus the area of contact will be $NA2\pi RL/4$. There is also another factor which needs to be

taken into account, namely, that on average, only half of the tubes surrounding a given one will belong to the “other half” of the sample, and thus the contact area is reduced by another factor of 2, giving $NA\pi RL/4$. If the interfacial fracture strength in shear is τ_F , the fracture load is $\tau_F NA\pi RL/4$.

The shear strength of the interface could be calculated according to Kelly-Tyson mode. The governing equation modified for hollow tubes is [109]

$$\tau_F = \left(\frac{\sigma_{NT}(L_c)}{2\left(\frac{L_c}{D_{NT}}\right)} \right) \left(1 - \frac{d_{NT}^2}{D_{NT}^2} \right) \quad (5-2)$$

where τ_F is the interfacial shear stress, σ_{NT} is the failure stress of the nanotube, d_{NT} and D_{NT} are the inner and outer diameters of the CNTs.

The height of CNT array used in this study is around 400 μm , which is actually the value for L , and L_c could be determined as 100 μm by using effective length. The average diameters and wall numbers have been determined by TEM as 11 nm and 6 walls. If we take the experimental values measured by Yu [3] for the tensile strength of individual CNTs, where σ_{NT} ranges from 11 to 63 GPa, then the τ_F could be obtained in the range of 0.38 to 2.15 MPa [109].

The most forward factor affecting A is that of “polygonization” as shown in Figure 5.10, whereby neighboring tubes flatten themselves against each other and gain bonding area at the expense of an increase in curvature energy. In our case, we assume an A value of 0.5 [20], and then the minimum strength of a small bundle (the

largest bundle contains around 100 nanotubes [64]) in CNT fibers could be calculated by using Eq. (5-1) in the range of 3.45 to 19.5 GPa. If we take the lower limit, 3.45 GPa, as the estimated strength of CNT bundles, it could be seen that when the CNT fibers are tensioned at a low strain rate, it is still far easier to slide a nanotube or small bundles together with minor breakage of small CNT bundles which is in good accordance with our experimental observation and prediction.

Figure 5.10 Polygonized cross section of CNT bundle with $A = 0.5$

Based on the data analysis, the mechanical performances of macro-scale CNT fibers, serving under low strain rate or static loading conditions, are determined by the load transfer efficiency between CNTs. We propose a deformation behavior of CNTs undergoing inside fibers as schematic shown in Figure 5.11: Firstly, when the fiber is stressed with a small strain, CNT fiber exhibits an elastic-like deformation, only the straight CNTs carrying load, resulting in the downshift of G' peak. As the input stress is still small, the van der Waals force and the friction between CNTs constrain the

individual tubes, leading to a linear relationship between stress and strain; In second stage, the straight CNTs are further elongated, the wavy CNTs get straightened, resulting in more and more CNTs bearing load with different extent. During this process, Raman peak is broadening because of non-uniformly loading on CNTs, and permanent elongation occurs; Finally, once the tensile stress exceeds the critical value, local stress cannot be further transferred to neighboring CNTs, resulting in sliding-dominate deformation process and even breakage between CNTs' joints. At this point, Raman peak stop downshifting and broadening, and the stress loaded on CNT fiber increases very slowly versus strain. Because the strength of individual CNTs and small bundles is much higher than the shear force between CNTs (a covalent carbon bond is four orders stronger than the friction force between CNTs) [131], the overloaded junctions (the connection among CNTs, as well as some large bundles) will eventually fail, leading to final breakage of the fibers.

Figure 5.11 Schematic diagrams for explaining the mechanism

Since the relaxation (sliding) of CNTs inside the fiber will have significant influence on fiber's long term reliability and serving performance, it is worth emphasizing that future endeavor should be focusing on not only the morphology/structure control of CNTs but also the interlock between CNTs inside the

fiber to enhance the inter-tube connections, load transfer efficiency and constraint of individual CNTs.

5.3.5 Constraint sliding by infiltration of cross-linked polymer

As well known, twisting, densification, long CNT arrays and morphology control have been employed and introduced to enlarge the interfacial area, increase the load transfer efficiency and strengthen the interfacial interactions between CNTs [14, 17, 23, 24, 132]. Despite the effort that has been made, when taking stress relaxation into account, the constraint of individual CNTs or small CNT bundles is still an issue. This is because the atomically smooth surface and chemical inertness of pristine CNTs induce weak interfacial adhesion between each others, thus making load transfer very poor.

Inspired from natural plants, such as *Triticum aestivum* which utilize cross-links for structural rigidity, a 3-D cross-linked structure is more favorable as those “bridges” formed between individual CNTs will transfer local stress efficiently, leading to more relaxation resistive CNT fibers [133, 134]. Functionalization of CNTs has been proven to be an effective approach to engineering individual CNTs and, more importantly, enabling modification of nanotube surfaces at a molecular level for various applications [41, 135-138]. Of the available strategies, covalent attachment of functional groups on the oxidized nanotube surface is the most commonly used method [137]. However, this may damage the well-defined π -conjugated electronic systems of CNTs, degrading their mechanical, electrical and thermal properties [65,

139]. Moreover, it is difficult to realize in CNT fiber spinning process [140, 141]. On the other hand, non-covalent functionalization is preferred, as this approach preserves the intrinsic structural and electrical properties of CNTs [135, 136]. For instance, a π - π interaction, which is an electrostatic interaction, was originally proposed as an explanation for the attractive interaction that exists between molecules containing π orbitals in the absence of spectroscopic evidence for HOMO-LUMO interactions. Such interactions with CNTs can be surprisingly strong, depending on the opposing molecules, capable of withstanding temperatures of $> 400\text{ }^{\circ}\text{C}$ [142, 143]. In typical studies, polymers with phenyl rings were utilized to conjugate with CNTs by means of π - π stacking.

5.3.5.1 Structural characterizations of composite fibers

It has been well proven that the phenyl rings have strong π - π interactions with surface of CNTs [135]. Here in Figure 5.12, we show the design and fabrication of SU8 modified CNT fibers by using SU8 as a non-covalent cross-linking agent for CNTs to build bridges between adjacent CNTs insider the fiber. As depicted in Figure 5.12, the phenyl units make SU8 monomers strongly interact with the nanotubes surfaces through a non-covalent π - π stacking interaction. Once the freshly-spun composite fibers expose to high temperature or UV illumination, the epoxy functional groups existing in SU8 monomers are ready to crosslink together, forming a 3-D network, offering a good load transfer between adjacent CNTs.

Figure 5.12 Schematic of the interaction between SU8 and CNTs and the fabrication process for composite fibers

The morphologies of CNT fibers and SU8 modified CNT fibers have been compared by FE-SEM. From the SEM images shown in Figures 5.13a and b, it is found that the fibers are uniform along the axial direction. After filtration, the diameter of SU8 modified CNT fibers is slightly larger than that of pure CNT fibers. For pure CNT fibers, there are plenty of wrinkles and voids in the fibers, which were originated from the spinning and densification processes. Spinning results in twisting effect on the surface of CNT fibers, leading to good alignment of CNTs. While, during solvent-evaporation (herein we use ethanol), the CNTs collapse into small bundles induced by capillary effect, resulting in voids on the surface of the fibers. Comparably, for the SU8 modified CNT composite fibers, the voids have been infiltrated by SU8 polymers without changes of CNTs orientation.

Figure 5.13 SEM images of (a) CNT fiber and (b) SU8 modified CNT fiber

To examine possible structure change of CNTs insides the fibers after polymerization of SU8, Raman spectra were collected from the surface of spinnable CNT arrays, unstrained CNT fibers and SU8 modified CNT composite fibers, and are shown in Figure 5.14a. The Raman spectroscopic data were collected in back scattering configuration under a 633 nm He-Ne laser with polarization direction parallel to the fiber axis. The laser beam is focused on the surface of CNT fibers under objective 50 $\times$. It is found that Raman G' band have the same position for all three cases, indicating that the CNTs on the surface of pure CNT fibers and SU8 modified CNT composite fibers are in their intrinsic state without any residual stress/strain. Depth profiles of both pure CNT fibers and SU8 modified CNT fibers were also performed to identify the structure changes of the CNTs inside the fibers (as shown in Figure 5.14b and c). As expected, for pure CNT fiber, the G' band up-shift from its original state of 2646 cm^{-1} to 2652 cm^{-1} when the focus depth moves from the surface to the center of CNT fibers. The up-shift of Raman G' band is probably due to the compression induced by outer surface CNTs during the spinning process [4, 23].

While for SU8 modified CNT composite fiber, Raman G' band shows down-shift from 2646 cm^{-1} to 2639 cm^{-1} when incident laser focus from the surface to the center of SU8 modified CNT fibers [19, 22]. This phenomenon implies that after polymerization of SU8 monomers the carbon-carbon bonds in CNTs have been elongated leading to a downshift of G' band. It is reasonable to get these observations: as phenyl units have a strong stacking interaction with surface of CNTs, once the epoxy groups cross-linked to a 3-D network, at the same time a small molecules (H_2O) get away, leading to the stretching of CNTs. Normally, the elongation of CNTs give a downshift of Raman G' band. So, compared to up-shift of G' band in pure CNT fibers, the downshift of G' band in SU8 modified CNT composite fibers also gives evidence that SU8 cross-linked network has been formed and there is a strong interaction at the interface between SU8 network and individual CNTs.

Figure 5.14 (a) The G' band position of spinnable CNT arrays, pure CNT fibers and SU8 modified CNT fibers, and Depth profile of Raman G' band spectra as a function of focusing depth: (b) CNT fibers and (c) SU8 modified CNT fibers

Tensile tests of both pure CNT fibers and SU8-modified composite fibers have been performed and the results have been shown statically in Figure 5.15. The average strength of SU8-modified composite fiber is almost the same to pure CNT fibers with a larger scattering, but the strain is comparatively smaller (less than 1.5%). The smaller strain at fracture indicates that the interaction between SU8 network and

CNTs inside the fiber is stronger, leading to an efficient load transfer without serious sliding of CNTs. Consequently, sliding and relaxation of CNTs inside the fibers, found in our previous work, are well controlled by the help of SU8 3-D network. Meanwhile, the conductivities of composite fibers are slightly decreased due to the infiltration of SU 8 polymer network, which is reasonable as the polymer used is an insulator.

Figure 5.15 Comparison of strength (a), strain (b) and conductivity (c).

5.3.5.2 Mechanical behavior of composite fibers

Figure 5.16 compares typical stress-strain curves for both pure CNT fibers and SU8 modified composite fibers measured at a low strain rate of $1.67 \times 10^{-4} \text{ s}^{-1}$. Same as that we have shown in Figure 5.5, pure CNT fiber shows non-linear stress-strain curves because of slippages of CNTs. While composite fibers show straight line, suggesting a wholly elastic deformation process. The linear relationship between stress and strain also supports a more efficient load transfer between CNTs as a result of the addition of SU8 network.

Figure 5.16 Typical stress-strain curves of (a) CNT fiber and (b) SU8 modified CNT fibers

5.3.5.3 Stress transfer in composite fibers

Figure 5.17 shows Raman G' band positions of unstrained SU8 modified composite CNT fiber, 2% strained CNT fiber and 0.5% strained SU8 modified CNT fibers. Obviously, the G' band of 2% CNT fibers downshifts from 2646 cm^{-1} to 2636 cm^{-1} with a rate of 7.5 cm^{-1} per 1% strain, while the G' band of 0.5% strained SU8-based composite fiber downshifts from 2646 cm^{-1} to 2633 cm^{-1} with a rate of 26

cm^{-1} per 1% strain which is much closer to that for axially strained individual single-walled CNTs (rate of 37.5 cm^{-1} per 1% strain) [119]. The elevated efficiency of stress transfer between CNTs inside the fiber should be attributed to the existence of 3-D SU8 network. The macroscale strain mainly comes from the deformation of the network rather than axial slippage of CNTs [134].

Figure 5.17 Comparison of G' band Raman spectra between CNT fiber (2% strained) and SU8 modified CNT fiber (unstrained and 0.5% strained)

To further verify the influence of SU8 network on relaxation behavior of CNT fibers, static mechanical measurements and incremental cyclic tensile tests were performed. As shown in Figure 5.18a, fibers were tensioned step by step through a precisely controlled micro-loading device; meanwhile the stresses were in situ monitored. Due to the nature of this in situ testing, with strain applied incrementally rather than continuously, time-dependent behavior of these fibers could be observed in between strain steps. In the case of pure CNT fibers, the stress on fibers was found to

quickly jump as the strain was applied. However, its incremental rate keeps decreasing over the strain and finally the stress reaches to an almost constant value. On the other hand, in the case of SU8 modified CNT composite fibers, the stress increases linearly versus applied strain calculated according to each step, which could be found in the inset of Figure 5.18a. Incremental cyclic tensile test was also employed to examine the load transfer efficiency and relaxation of CNTs inside the fibers. As shown in Figure 5.18b, only around 0.1% permanent strain was generated until the breakage of SU8 modified CNT composite fibers, which is much lower than that reported by other groups [14, 19]. The relationship between stress and strain in each cycle maintains linear, indicating an efficient load transfer process. And this result gives further evidence that the stress could be effectively transferred between CNTs inside the fiber by the help of SU8 3-D network.

Figure 5.18 (a) Static mechanical test with strain increased step by step and (b) Incremental cyclic tensile test of SU8 modified CNT fibers

As the content of SU8 polymer is serious process dependent, right now it is still difficult to achieve composite fibers with precisely-controlled small concentration of polymer because of its high viscosity. Though the load transfer efficiency has been improved, the strength is actually determined by the content of polymer. So, in the future study, controllable process needs to be designed to obtain high performance and reliable CNT fibers serving for long term utilizations.

5.4 Morphology dependent mechanical strength at high strain rate

It has been widely studied that the orientation of nanotubes shows great effect on the mechanical performance of CNT-polymer composites. Based on the fact that at high strain rate CNT fibers break without any obvious morphology change shown in section 5.2, attention has been paid to the improvement of CNT alignment and their influence on mechanical performance on CNT fibers in this part. A liquid-based

pre-stress-relaxation approach is introduced and better CNT alignment is achieved. Moreover, the mechanical behavior of CNT fibers has been observed and the failure mechanism at high strain rate is further discussed.

5.4.1 Alignment characterization by Raman spectroscopy

We know that the sliding is not a problem at high strain rates from the strain-rate dependence of the fiber strength, and it can also be seen from SEM images in Figure 5.4 that almost all the individual CNTs in the fiber break at the same position. There must be some other limiting factors that determine the maximum strength of the CNT fibers at high strain rates. In our previous study [24], we have found that the CNT alignment within the fibers is critical for the fiber strength. Because of the wavy and entangled nature of individual CNTs within the fibers, individual CNTs cannot carry the load at the same time during the tensile testing, and they have no enough time to redistribute the strain through sliding at high strain rates. Therefore, some relatively straight CNTs will break first before those wavy CNTs can take the load, resulting in a “cascade-like” breaking mode (CNTs break one after another).

In order to demonstrate the influence of CNT's alignment on fiber's mechanical behavior and give further evidence to the failure mechanism proposed in Section 5.2, here we introduce a facile liquid-based approach based on our understanding on morphologies of CNTs/fibers. CNT fibers were first fixed on a plastic frame, which supplies a solid support to the fibers even in liquid environment. After impregnated in a dilute HCl solution for certain period of time, the re-wetted CNT fibers were then

pulled out from solution. Due to the capillary force generated at the interfaces between fibers and solution, the fibers will be stressed, resulting in a stress-relaxation of CNTs and thus give a better alignment. Figure 5.19 exhibits the experimental procedures.

Figure 5.19 Schematic diagram of liquid-based post-treatment of CNT fibers

The morphologies of CNTs before and after post-treatment were characterized by FE-SEM and typical SEM images are shown in Figure 5.20. As can be seen that the CNTs in Figure 5.20a are roughly oriented in one direction and on the surface of CNT fibers there are plenty of wrinkles and small bundles formed because of capillary forces induced by ethanol evaporation. Serious entanglement between CNTs could be seen on the surface of the fibers. After re-wetted, swollen and re-dried, the diameter of CNT fiber is slightly reduced with a smooth surface as shown in Figure 5.20b. Moreover, CNTs have a better alignment on the surface of the fiber, which may lead to a better mechanical performance.

Figure 5.20 Typical SEM images of CNT fibers before (a) and after (b) re-wetting treatments

Polarized Raman spectroscopy was extensively used to investigate structure and anisotropy properties of isolated CNTs, and the alignment of CNTs in the fiber or composites [18, 24, 122, 144]. In this work, we use Raman spectroscopy (excited wavelength at 633 nm, using a He-Ne laser) to evaluate the alignment of CNTs in our fibers. During the measurement, a microscope with 100 $\times$ objective lens was used for focusing the laser beam and cross polarization of incident and scattered light for study. Figure 5.21 displays the G-band and D-band Raman spectra of CNT fibers. The spectroscopy in Figure 5.21a is corresponding to the fiber before treatment whereas the spectroscopy in Figure 5.21b corresponds to the fiber after the treatment. For both samples, the intensities of G-band and D-band for polarization parallel ($//$) to fiber axis are much stronger than those for polarization perpendicular ($\perp$) to fiber axis, but the ration $I_{//}/I_{\perp}$ (around 5) of re-wetted fibers is much larger than that of un-treated fiber (around 2.3).

Figure 5.21 Raman spectra of G-band and D-band of CNT fibers for incident light polarization parallel and normal to the CNT fibers before (a) and after (b) post-treatment

5.4.2 Alignment dependent mechanical behavior of CNT fibers

Tensile tests were performed on fibers before and after post-treatments as shown in Figure 5.22. In agreement with the observation in SEM images that the alignment of CNTs has been improved after post-treatment, tensile stress measurements reveal a substantial improvement on the tensile strength with a value of 0.6 GPa for un-treated

fiber and 1 GPa for re-wetted fibers at a strain rate of 0.01 s^{-1} . It is also seen that after post-treatment, the CNT fibers have been elongated and lead to a calculated strain up to 8%, indicating there is a 5% strain without generating any stress indicating CNT fiber after post-treatment becomes 5% longer than the original one. This gives further evidence that the CNT fibers have been stressed and the alignment of CNTs has been improved during the post-treatment process.

Figure 5.22 CNT diameter and wall number distribution histograms of the as-grown CNT arrays

To verify the role of alignment and check whether it is a universal and process-independent structural factor that limits the maximum strength of our CNT fibers, we choose CNT fibers from different batches (different post-treatment and/or different fabrication processes). Polarized Raman spectroscopy was used to evaluate the alignment of CNTs in the fibers. As shown in Figure 5.23, we plotted the obtained strength of CNT fibers against their alignment represented by Raman intensity ratios of $I_{//}/I_{\perp}$ (polarization parallel to fiber axis/polarization perpendicular to fiber axis). It

is found that under the same fast testing condition, the tensile strength of CNT fibers is almost linearly proportional to the alignment of CNTs in the fibers: stronger CNT fibers possess better alignment, while the poor alignment leads to a low tensile strength. This result gives direct evidence that the maximum strength of a CNT fiber is limited by the CNT alignment, and suggests a “cascade-like” breaking mechanism at high strain rates.

Figure 5.23 The dependence of tensile strength of CNT fibers on the CNT alignment represented by polarized Raman ratio ($I_{\parallel}/I_{\perp}$) of G band along parallel (//) and perpendicular ($\perp$) directions

5.5 Summary

The strain-rate dependence of CNT fibers’ mechanical behaviors were studied in a wide range of tensile-strain rates and the failure mechanisms were proposed accordingly. CNT fibers show a strain-rate strengthening effect: the strength and Young’s modulus increase with the strain rate at the expense of the fracture strain. The mechanical response of CNT fibers to the strain rate falls into two regimes: at low

strain rates regime, CNT fibers show plastic, with the tensile strength, Young's modulus and fracture strain changing significantly with the strain rate; while at high strain rate, CNT fibers show more elasticity, and all the mechanical properties reach relatively saturated values.

By applying in-situ static mechanical tests, electrical measurements and Raman spectroscopy, the mechanical behavior of CNT fibers serving under very low strain rate or static loading conditions was monitored. Based on the analysis, the deformation of CNT fibers could be distinguished into three segments: elastic-like deformation, failure evolution and breakage of tube-tube connections, where CNTs inside the fiber exhibit different behaviors. When CNT fibers exhibit an elastic-like deformation, only the straight CNTs take load, and the local stress transfers effectively owing to the friction between CNTs. As the loading strain increases, permanent deformation emerges. Finally, when the stress loaded on the fiber is too large that the overloaded junctions begin to fail, resulting in breakage of CNT fibers. This finding gives us an indication that future efforts to enhance the creep resistive properties of CNT fibers may need to focus on both the morphology/alignment of CNTs and constrain of individual CNTs inside the fiber at the same time.

By introducing SU8 monomer into the fiber during spinning process, followed by a solar irradiation, a 3-D cross-linked network has been formed. As a result of polymerization of the epoxy groups in SU8, the status of CNTs inside the fibers has been changed from compression to stretching. Meanwhile, due to existence of the

phenyl units in SU8 monomers, strong π - π stacking interactions between polymer and CNT surfaces function as “bridges”, which play a critical role in freezing individual CNTs, and lead to a more efficient load transfer.

At high strain rates, studies on the improvement of CNT alignment and its influence on mechanical performance of CNT fibers have been performed. Mechanical behaviors of CNT fibers indicate that at high strain rate, tube relaxation through sliding is becoming difficult, and the fibers show a relatively sharp breaking fracture, and high tensile strength & modulus. It is further found that such strength is proportional to the alignment of CNTs in the fibers. The failure mechanism at high strain rates can be described as a “cascade-like” breaking: individually CNTs break serially one after another because they cannot take the load at the same time due to the imperfection in alignment.

It is worth emphasizing that in practice, the sliding mechanism will degrade the long-term reliability of the CNT fibers, while the “cascade-like” breaking mechanism will limit the short-term performance (strength & modulus) of the fibers. Improvement on one aspect doesn’t guarantee the same on the other. Future improvement must deal with both tube sliding and tube alignment at the same time to obtain reliable and high performance CNT fiber for practical applications.

Chapter 6 Statistical analysis of failure mechanisms

6.1 Background

There is now an increasing interest in developing practical solutions for fabricating carbon nanotube (CNT) fibers, spun from vertically aligned CNT arrays because of its excellent mechanical performance combined with good conductivity and simplicity in the spinning fabrication process [4, 5, 14, 15, 17, 24, 65, 145, 146]. Recent research attention attempts to enhance the mechanical strength of CNT fibers [14, 17, 23, 24, 36, 147], and some progress has been made. However, due to the complex nanostructure and defect sensitivity of individual CNTs, and the complex interaction of individual CNTs inside a spun fiber, the tensile strengths of CNT fibers are expected to exhibit wide variations. Hence a statistical analysis approach is needed. Furthermore, fabrication of CNT fiber specimens leads to a variation in fiber diameter and it is noted that as fiber diameter increases, there is a reduction in tensile strength. The dependence of the CNT fiber strength on strain rate also leads to a wide variation in tensile strength due to the complex scenarios in CNT fiber slippages and stress relaxation behavior. It has been demonstrated in our previous work that CNT fibers exhibit a strain rate strengthening effect, which makes CNT fibers different from commercialized carbon fibers [108, 145]. Hence, predicting CNT fiber tensile strength distributions needs to incorporate the effects of strain rate and fiber size in the design and development of future CNT fiber-based materials and structures. Unfortunately, to date, insufficient attention has been paid to elucidate these variation

trends.

Mathematical analysis of fracture statistics was investigated using Weibull cumulative failure distribution concepts and its applications [89, 123, 125-127, 148, 149]. In this study modified Weibull models is developed to characterize different influence parameters. This has been utilized to characterize brittle ceramic fibers and some high modulus polymer fibers for their strength distribution, strength dependence on diameter and gauge length, as well as CNT or CNT-based composite fibers. Wagner *et. al.* [127] tensioned MWNTs directly by using a combined atomic force microscope-scanning electron microscope method. In their work, they employed the standard Weibull distribution to model the nanotube tensile strength data, obtaining Weibull shape and scale parameters of 1.7 and 109 GPa without the consideration of the influence of CNT diameter. Later on, Chou performed a series of tensile tests on CNT fibers spun from vertically aligned array with diameters ranging from 20 μm to 50 μm [123]. A modified Weibull strength distribution model which takes the flaw density variation with fiber diameter into account has been adopted for the statistical strength analysis. Weibull shape and scale parameters are 4.1 and 1.61 GPa respectively, indicating smaller scattering than those of MWNTs but larger scattering than those of commercial glass fibers [127, 150]. The present explorative study is to examine the distribution of tensile strength of CNT fibers as a function of strain rates and fiber diameters. A modified Weibull distribution model was developed to characterize the strength distribution dependence of CNT fibers on strain rates and diameters.

In previous sections, it has been demonstrated the strengths of CNT fibers are sensitive to strain rate. When changing strain rate from 2×10^{-5} to 0.2 s^{-1} , the mechanical behaviors of CNT fibers exhibit gradual transition from plastic-like to elastic-brittle like behavior with an increased mechanical strength. The Weibull strength distribution model will be developed to correlate strain rate effect to the fiber strength and give mathematical evidence to the failure mechanisms proposed in Chapter 5.

6.1 Single-mode Weibull distribution

The stress-strain curves for CNT fibers tested at low to high strain rates are shown in Figure 6.1. The diameters of tested fibers are $4 \text{ }\mu\text{m}$. The CNT fibers show different behaviors when the strain rates are low ($1 \times 10^{-5} \text{ s}^{-1}$) and high (0.1 s^{-1}), respectively. The fibers exhibit transition from plasticity at low strain rate to elasticity at high strain rate, indicating that fibers are sensitive to the strain rate. Furthermore, the mechanical strength increases with the increase of strain rate.

Figure 6.1 Typical stress-strain curves obtained at low ($1 \times 10^{-5} \text{ s}^{-1}$) and high strain rate (0.1 s^{-1})

In order to statistically understand tensile strength distribution of CNT fibers, the standard Weibull distribution was firstly employed. If σ is the failure strength, the probability of failure of CNT fibers, $P_f(\sigma)$, is given by [127]:

$$P_f(\sigma) = 1 - \exp \left[- \left[\frac{\sigma}{\sigma_0} \right]^m \right] \quad (6-1)$$

where σ_0 is the scale parameter, and m is the shape parameter which indicates the variation in strength distribution. Eq. (6-1) is widely used to fit experimental data for a set of identical single fibers (same gauge length and diameter). The Weibull model plots $\ln[1/(1-P_f)]$ against $\ln\sigma$, where the slope gives the shape parameter, m . From the intercept $-\ln\sigma_0$ and the knowledge of m , one gets the scale parameter σ_0 . Figure 6.2a shows the variation of mechanical strength of CNT fibers with exactly the same diameters of 4 μm . These fibers were tested at two typical strain rates, where L represents low strain rate of $1 \times 10^{-5} \text{ s}^{-1}$, and H represents high strain rate of 0.1 s^{-1} . All the data points are arranged in ascending order. It is obvious that the fiber strength at high strain rate is much higher than that at low strain rate. To estimate the probability of failure P_f , we used the lowest mean-squared error estimator, given by $(i-0.5)/N$, where N is the total population size and i , denotes the failure rank (thus σ_1 is the lowest failure stress, σ_N is the highest). The calculation processes reported below are all the same. Weibull plots of the fracture strength of the CNT fibers tested under low and high strain rates are compared in Figure 6.2b. These fiber strength data Weibull plots are linear, indicating that the Weibull model is indeed appropriate in both cases.

Figure 6.2 (a) Strength distributions of CNT fibers with the same diameters (b) Weibull plot for the tensile strength of CNT fibers. (Tested under different strain rates: H represents 0.1 s⁻¹ and L represents 1 × 10⁻⁵ s⁻¹)

The calculated values of m and σ_0 are summarized in Table 6.2. The value of m is inversely proportional to the scattering in strength distribution, smaller m indicates larger scattering and vice versa. The comparatively low value of the shape parameter m for fibers tested under low strain rate indicates a wider variability in tensile strength than those fibers tested under high strain rate. The scale parameter σ_0 is an estimator

of the mean of tensile strength. Remarkably, CNT fibers tested at high strain rate show a two-fold increase in their scale parameter when compared with the fibers tested under low strain rate.

Strain rates (s ⁻¹)	Shape parameter m	Scale parameter σ_0 (GPa)	Strength distribution
1×10^{-5}	2.41	0.45	Wide
0.1	7.08	1.01	Narrow

Table 6.1 Parameters comparison between high and low strain rates

6.3 Modified Weibull distribution adopting strain rate effect

The distribution dependence of CNT fiber strength on strain rates has also been examined. The variation of tensile strength of CNT fibers versus strain rates is similar to our previous work as shown in Figure 6.3a [145]. It is found that, the tensile strength of CNT fibers strongly depends on the strain rates and fits a power law relation. In order to make a statistical description, by keeping the fiber diameter constant at 4 μm , a modified Weibull model with consideration of strain rate as a variant was developed.

$$P_f(\sigma) = 1 - \exp \left[-\dot{\epsilon}^k \left[\frac{\sigma}{\sigma_{\dot{\epsilon}}} \right]^m \right] \quad (6-2)$$

Here, $\sigma_{\dot{\epsilon}}$ is the scale parameter after taking strain rates into account, $\dot{\epsilon}$ is the strain rate, k is the strain rate dependent parameter, and m is the Weibull shape parameter. Eq. (6-2) predicts the average fiber strength as [123, 148]

$$\bar{\sigma} = D \dot{\epsilon}^{-\frac{k}{m}} \quad (6-3)$$

where $D = \sigma_{\dot{\epsilon}} \Gamma(1 + \frac{1}{m})$ is a constant, and $\Gamma(1 + \frac{1}{m})$ is a gamma function.

By fitting Eq. (6-2), as shown in Eq. (6-4), a linear relation between $\ln \ln[1/(1-P_f)] - k \ln \dot{\varepsilon}$ and $\ln \sigma$ could be derived. The shape parameter m and the scale parameter $\sigma_{\varepsilon 0}$ could be obtained from its slope and the intercept $-m \ln \sigma_{\varepsilon 0}$, respectively.

$$\ln \ln \left[\frac{1}{(1-P_f)} \right] - k \ln \dot{\varepsilon} = m \ln \sigma - m \ln \sigma_{\varepsilon 0} \quad (6-4)$$

By fitting experimental data with the power law function of Eq. (6-3), as shown in Figure 6.3a, we get $k/m = -0.0757$ with the consideration of strain rates. Given any an initial k value, a plot of $\ln \ln[1/(1-P_f)] - k \ln \dot{\varepsilon}$ versus $\ln \sigma$ can be obtained. Then by fitting the data with the linear function of Eq. (6-4), we obtain m . Next, a new k value can be calculated using the relationship k/m . After repeating the above process several times, m converges to 5.65. Furthermore, the plots in Figure 6.3b are linear, showing that the modified Weibull model is indeed suitable in describing the strain rate effects with a prediction of mean strength of 1.0 GPa and shape parameter of 5.65.

Figure 6.3 (a) The dependences of strength of CNT fibers on the strain rates and (b) Weibull plot of the tensile strength of CNT fibers including strain rate as variant.

6.4 Modified Weibull distribution adopting scale effect

The relationships between CNT fiber diameters and tensile strength of tested at low and high strain rates are shown in Figure 6.4a. The initial population included 192 tested specimens. As expected: 1) the strength of CNT fibers increases with decrease in diameter; 2) the fiber strength at high strain rate is much higher than that at low strain rate. Moreover, the incremental variation trend for the fibers tested at high strain rate is faster than that at low strain rate. When taking the flaw density variation with fiber diameter into account, the Weibull distribution model has to be modified to analyze the CNT fiber strength characteristics, which has been shown in Eq. (6-5) [123]. The cumulative probability of failure of a fiber with constant gauge length but a varying fiber diameter, loaded to stress level σ is given [123]

$$P_f(\sigma) = 1 - \exp \left[-d^h \left[\frac{\sigma}{\sigma_d} \right]^m \right] \quad (6-5)$$

Here, σ_d is the scale parameter after taking fiber diameter into account, d is the

fiber diameter, and h is the diameter dependent parameter. Similar to Eq. (6-2), Eq. (6-5) predicts the average fiber strength as

$$\bar{\sigma} = Dd^{-\frac{h}{m}} \quad (6-6)$$

By fitting Eq. (6-5), a linear relation between $\ln \ln[1/(1-P_f)] - h \ln d$ and $\ln \sigma$ could be derived as shown in Eq. (6-7). The shape parameter m and the scale parameter σ_d could be obtained from its slope and the intercept $-m \ln \sigma_d$, respectively.

$$\ln \ln \left[\frac{1}{1-P_f} \right] - h \ln d = m \ln \sigma - m \ln \sigma_d \quad (6-7)$$

Through fitting the experimental data with the power function of Eq. (6-6), as shown in Figure 6.4a, we obtain $h/m = 0.375$ and 0.792 for low and high strain rates respectively. By repeating the above calculation process, m converges to 4.32 and 6.77 for low and high strain rate, respectively. Furthermore, the plots in Figure 6.4b are linear, showing that the modified Weibull model is appropriate in both cases.

Figure 6.4 (a) Diameter dependent distribution of fiber strength tested at high and low strain rates, and (b) Weibull plots of the tensile strength of CNT fibers tested at low and high strain rates including diameter as variant

Table 6.2 summarized the shape parameters and scale parameters calculated from data in Figure 6.4a. The same conclusion as Table 6.1 could be obtained: fibers tested under low strain rate show a wider variability in tensile strength; tensile strength for the fiber tested at high strain rate is comparatively higher.

Strain rates (s^{-1})	Shape parameter m	Scale parameter σ_d (GPa)	Strength distribution
1×10^{-5}	4.3	0.665	Wide
0.1	6.8	2.745	Narrow

Table 6.2 Diameter dependent parameter comparison between high and low strain rates

The sources of CNT fiber strength scattering can be attributed to the variation of strengths of individual CNTs as well as the microstructure of CNTs in the fiber, including the connection between CNTs. These fibers were spun from the same array with the same spinning parameters, so the only factors, resulting in such a difference, are strain rates and fiber diameters. The variation in strength distribution could be

well explained by the failure mechanisms proposed in our previous finding: sliding-to-break mechanism at low strain-rate regime and “cascade-like” breaking due to the CNT mis-alignment at high strain rate regime [108, 145]. At low strain rate, individual CNTs have enough time to relax through tube sliding to redistribute the strain before they break. At the same time, interconnections between CNTs may partially be destroyed to realize the rearrangement, giving a larger variability in tensile strength [89, 108, 126, 145]. Comparably, at high strain rate, tube relaxation through sliding is becoming a slow process, thus strain re-distribution becomes more difficult, and eventually the local strain breaks some CNTs then the whole fiber, which is in accordance with weakest link theory. When taking diameter into account, almost the same strength distributions have been observed. Moreover, at low strain rate, the tensile strength is less sensitive to diameter, which probably because that it is approaching to the intrinsic property of the fiber, determined primarily by the friction and interaction forces between CNTs in a fiber. As the strain rate increases, strengthening effect could be seen and tensile strength decreases promptly with the increase of fiber diameter, due to the flaw density variation in the fiber.

6.5 Summary

CNT fibers exhibit strain rate effects that may be seen in the ultimate strength, the stress-strain behavior, and topography of the fracture surfaces. At low strain rates, the tension behavior of a CNT fiber is more-like inelastic deformation, while at high strain rates it becomes more-like elastic behavior. Fiber strength is influenced more

significantly by diameter at high strain rate than that at low strain rate. The reason is probably because that the stress needed to break a fiber at low strain rate is determined by interconnection between CNTs and the slippages lead to the final breakage. Furthermore, the strength variation decreases with increasing the strain rate, which may be due to the absence of relaxation at the higher strain rates. These findings give further evidence to support the conclusion and the failure mechanisms proposed for different strain rate tests in our previous study (Chapter 5) that at low strain rate slippage dominates the performance of CNT fibers while at high strain rate morphology/alignment dominates the performance of CNT fibers. When the diameter increases, the defect density will increase, leading to lower mechanical tensile strength. However, due to the different failure mechanisms at low and high strain rates, the strength variation of CNT fibers at low strain rates is not as sensitive to diameters as that at high strain rates.

Chapter 7 Conclusions

Mechanical and electrical tests have been performed to examine the performance and behavior of CNT fibers spun from vertically aligned CNT arrays. The uniformity of mechanical strength and electrical conductivity is good and the influence of surface twisting angles on fiber' mechanical strength and structural properties has also been investigated.

The strain-rate dependence of CNT fibers' mechanical behaviors were studied in a wide range of tensile-strain rates and the failure mechanisms were characterized accordingly. CNT fibers show a strain-rate strengthening effect: the strength and Young's modulus increase with the strain rate at the expense of the fracture strain. The mechanical response of CNT fibers to the strain rate falls into two regimes: at low strain rates, CNT fibers show plasticity-like behavior, with the tensile strength, Young's modulus and fracture strain changing significantly with the strain rate; while at high strain rate, CNT fibers show more elasticity-brittle like behavior, and all the mechanical properties reach relatively saturated values. In practice, the sliding mechanism at low strain rates will degrade the long-term reliability of the CNT fibers, while the "cascade-like" breaking mechanism at high strain rates will limit the short-term performance (strength and modulus) of the fibers.

The mechanical behavior and failure mechanism of CNT fibers serving under very low strain rates or static/monotonic loading conditions was further monitored by applying in-situ mechanical tests, electrical measurements and Raman spectroscopy.

Based on the analysis, the deformation of CNT fibers could be distinguished into three segments: elastic-like deformation, failure evolution and breakage of tube-tube connections, where CNTs inside the fibers exhibit different behavior. When CNT fibers exhibit an elastic-like deformation, only the straight CNTs take load, and the local stress transfers effectively owing to the friction between CNTs. As the loading strain increases, permanent deformation emerges. Finally, when the stress loaded on the fiber is too large such that the overloaded junctions begin to fail, resulting in breakage of CNT fibers. This finding gives us an indication that future efforts to enhance the stress relaxation resistive properties of CNT fibers may need to focus on both the morphology and alignment of CNTs and constrain of individual CNTs inside the fiber at the same time. A concept of introducing a second element in the spinning process to enhance the load transfer efficiency between CNTs inside the fibers has been demonstrated. By introducing SU8 monomer into the fiber during spinning process, followed by a solar irradiation, a 3-D cross-linked network has been formed. As a result of polymerization of the epoxy groups in SU8, the status of CNTs inside the fibers has been changed from compression to stretching. Meanwhile, due to existence of the phenyl units in SU8 monomers, strong π - π stacking interactions between polymer and CNT surfaces function as “bridges”, which play a critical role in freezing individual CNTs, and lead to a more efficient load transfer.

At high strain rates, studies on the improvement of CNT alignment and its effect on mechanical performance of CNT fibers were performed. Mechanical behavior of CNT fiber indicates that at high strain rates, tube relaxation through sliding becomes

difficult, and the fibers show a relatively sharp breaking fracture, with higher tensile strength and modulus. It is noted that such strength is proportional to the alignment of CNTs in the fibers. The failure mechanism at high strain rates can be described as a “cascade-like” breaking chain action: individually CNTs break serially one after another because they cannot take load at the same time due to the imperfection in alignment.

The failure mechanisms were further supported by Weibull failure analysis models for characterizing the cumulative failure distributions. It is found that the fibers tested under low strain rate have a wider variability in tensile strength than those fibers tested under high strain rate. The mean of the strength tested at high strain rates is much higher than that at low strain rates. This is seen when comparing CNT fibers tested under different strain rates. Furthermore, when the diameter increases, the defect density will increase leading to lower mechanical tensile strength. However, due to the different failure mechanisms at low and high strain rates, the strength variation of CNT fibers at low strain rates is not as sensitive to diameters as that at high strain rates.

Chapter 8 Recommendation for future work

Recommendation for future work can be directed towards several aspects for further improvement of the physical performances of CNT fibers, including CNT fiber fabrication quality on enhancing mechanical strength, electrical conductivity and potential applications. The future work may aim at the following aspects:

1. To improve the uniformity of twisting in CNT fibers.
2. To improve the alignment of CNTs and interfacial friction forces between individual CNTs at the same time. Try to control the morphology of CNT arrays, including the site density, wall numbers, alignment, and length of CNTs.
3. To develop post-treatment approaches by introducing polymers which have affinity to CNTs (including electrostatic interaction: like π - π stacking, van der Waals force: line wrapping) in a controlled manner to enhance the mechanical performance of CNT fibers.
4. To increase the electrical conductivity of CNT fibers.
5. To utilize the excellent electron transport properties of CNT fibers coupled with good mechanical performance. Perform surface functionalization or modification of CNT fibers and study their potential applications.

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Publications

Book Chapter

1. *Yani Zhang, Gengzhi Sun, Lianxi Zheng*, “CNT Mechanical Applications” for the book “Applications of Carbon Nanotube”, *Pan Stanford*, ISBN: 9789814303187, 2011.

Selected Relevance Papers

1. *Gengzhi Sun, Lianxi Zheng, Jinyuan Zhou, Yani Zhang, Zhaoyao Zhan, John H. L. Pang*, “Load-transfer efficiency and mechanical reliability of carbon nanotube fibers under low strain rates”, *International Journal of Plasticity*, 40, 56, 2013.
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3. *Gengzhi Sun, Yani Zhang, Lianxi Zheng*, “Fabrication of micro-scale CNT fibers”, *J Nano Materials*, DOI: 10.1155/2012/506209.
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5. Jinyuan Zhou, **Gengzhi Sun**, Zhaoyao Zhan, Jianing An, Yongzhe Zhang, Yani Zhang, and Lianxi Zheng, “Polarization behaviours of twisted carbon nanotube fibers”, *J. Raman Spectroscopy*, 43, 7, 2012. (**Co-first author**)
6. Lianxi Zheng, **Gengzhi Sun**, Zhaoyao Zhan, “Tuning Array Morphology for High-Strength Nanotube Fibers”, *SMALL*, 6, 132, 2010.

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