In Situ Curing of Polymeric Composites via Resistive Heaters Comprised of Aligned Carbon Nanotube Networks

by

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B.S., Mechanical Engineering
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Abstract

The widespread application of polymer matrix composites (PMCs) has encouraged the use of nanofibers, especially carbon nanotubes (CNTs), to concurrently enhance the physical properties of such composites while adding multifunctionality. However, current-generation manufacturing routes of PMCs have drawbacks including geometrical limitations and high energy utilization. Improvements to manufacturing processes are needed, and in this thesis the in situ curing of a PMC using a resistive heating film comprised of an aligned CNT network is developed, and the underlying physics that govern the electron transport properties of the aligned CNT network as a function of temperature and orientation are explored. Aligned CNT film heaters have anisotropic electrical properties and show negative coefficient of resistance with temperature. A carbon fiber reinforced plastic (CFRP) system is effectively cured by a single (top layer) CNT network heater. Evaluation of the curing efficacy (via degree of cure) shows that the in-plane spatial variation of the degree of cure directly correlates to maximum temperature during cure as evaluated with a thermal camera. Through-thickness spatial variation in degree of cure is found to be < 8% for the one-sided curing heater. Future work will include characterization and modeling of the underlying physics that govern the performance of aligned CNT networks as resistive heaters, exploration of possible methods to scale-up the in situ curing process to laminates with sizes on the order of meters, and evaluation of the structure and properties of composites manufactured using the method reported here to elucidate any difference in composite performance when compared to materials synthesized using current-generation techniques.

Thesis Supervisor: Brian L. Wardle
Title: Associate Professor of Aeronautics and Astronautics
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<tr>
<td>CFRP</td>
<td>Carbon-fiber-reinforced plastic</td>
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<td>CNT</td>
<td>Carbon nanotube</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>FITC</td>
<td>Fluctuation induced tunneling conduction</td>
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<tr>
<td>GNPT</td>
<td>Guaranteed nonporous Teflon</td>
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<tr>
<td>IPS</td>
<td>Ice protection system</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>OOA</td>
<td>Out-of-autoclave</td>
</tr>
<tr>
<td>Prepreg</td>
<td>Pre-impregnated fiber reinforced plastic</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TCR</td>
<td>Temperature coefficient of resistance</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>VDP</td>
<td>Van der Pauw</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Average inter-CNT spacing</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of the sinusoid</td>
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<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>$\rho_{array}$</td>
<td>Apparent density of the as-grown A-CNTs</td>
</tr>
<tr>
<td>$\rho_{cnt}$</td>
<td>CNT intrinsic density</td>
</tr>
<tr>
<td>$\rho_{film}$</td>
<td>Apparent density of the aligned CNT film</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>Theoretical density of a single graphene sheet</td>
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<td>$\theta$</td>
<td>Orientation angle of CNT alignment</td>
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<td>$A$</td>
<td>In-plane area of the as-grown A-CNTs</td>
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<tr>
<td>$a$</td>
<td>Amplitude of the sinusoid</td>
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<td>$D_i$</td>
<td>Inner diameter of a carbon nanotube</td>
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<td>$D_o$</td>
<td>Outer diameter of a carbon nanotube</td>
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<tr>
<td>$E_a$</td>
<td>Tunneling activation energy</td>
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<td>$H$</td>
<td>Height of an as-grown A-CNT array</td>
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<td>$I_{AB}$</td>
<td>Current through A and B</td>
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<tr>
<td>$I_{AD}$</td>
<td>Current through A and D</td>
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<td>$k$</td>
<td>Modulus factor in VDP measurements</td>
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<td>$L_{cnt}$</td>
<td>Length of the wavy CNTs($-H$)</td>
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<tr>
<td>$N$</td>
<td>Two dimensional coordination number</td>
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<td>$R_{</td>
<td></td>
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<td>$R_{\perp}$</td>
<td>Sheet resistance $R$ in the transverse direction</td>
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<td>$R_{xx}$</td>
<td>Sheet resistances in the x-axis</td>
</tr>
<tr>
<td>$R_{yy}$</td>
<td>Sheet resistances in the y-axis</td>
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<tr>
<td>$t$</td>
<td>Thickness of an aligned CNT film</td>
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<td>Symbol</td>
<td>Description</td>
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<tr>
<td>$V_f$</td>
<td>CNT volume fraction</td>
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<tr>
<td>$V_{BC}$</td>
<td>Voltage drop across B and C</td>
</tr>
<tr>
<td>$V_{DC}$</td>
<td>Voltage drop across D and C</td>
</tr>
<tr>
<td>$w$</td>
<td>Waviness ratio of A-CNTs</td>
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Chapter 1

Introduction

1.1 Motivation

Carbon-fiber-reinforced plastic (CFRP) composites have been widely used in various applications, especially in the fabrication of aerospace and automotive structures. Due to their low density and outstanding mechanical properties, such as high specific strength and an excellent resistance to impact and corrosion, CFRPs have had the limelight with the expectation that they can be used in various important structural components. By replacing metal bodies of vehicles with CFRP structures, it is possible to reduce the fuel consumption while preserving the performance of the structural components. In the manufacturing process of these CFRPs for aerospace structural components, autoclave curing has been often used to obtain the desired properties, but is accompanied by high costs, which comes from the introduction and operating process of the autoclave. In this respect, the interest in out-of-autoclave (OOA) curing has come to the forefront in aircraft structure manufacturers for the purpose of reducing the autoclave’s intrinsic costs. Also, a lot of prepreg producing companies and polymer companies have been trying to develop new prepregs which can be cured without an autoclave. However, with respect to composite manufacturing from prepreg, OOA manufacturing does not effectively overcome the autoclave’s shortcomings due to the usage of a heat chamber in which the required heat for curing is transferred via convection. Therefore, in order to achieve real meaning of out-of-autoclave (a composite manufacturing method without using a heat chamber), development of a new composite
manufacturing process is needed.

The motivation of this thesis work starts from the multi-functionality of carbon nanotubes (CNTs) embedded in composites. Since CNTs have exceptional specific properties, such as strength and stiffness as well as high electrical and thermal conductivities,\(^6\) the introduction of CNTs into a composite (called nano-engineered composites) has taken the first position among composite enhancement research. For example, aligned CNTs have been implemented into composites, and previous studies report that interlaminar shear strength and toughness is improved by implementation of CNTs.\(^7,8\) Moreover, CNTs have been shown to be used as additional composite reinforcement such as a shield for lightning strikes,\(^9\) a resistive heater for deicing and ani-icing on aerosurface,\(^1\) and a self-health monitoring system that functions by detecting changes in electro-thermal properties.\(^10\)

As one more additional function of CNTs related with composites, this thesis develops a new composite manufacturing process that utilizes the function of resistive heating originally applied to deicing and ani-icing on aerosurface, potentially eliminating the need for an oven altogether.\(^11\) Finally, it is expected that the CNT film on manufactured composites works as previously listed composite enhancements after it is used for manufacturing. As the first phase, this thesis work focuses on the characterization of the aligned CNT film as a heating element and the first trial tests of composite curing via resistive heating of the CNT film.

1.2 Thesis Outline

In this thesis, electrical properties of the aligned CNT film as a heating element were explored, and an experimental attempt to cure carbon-fiber-reinforced polymers with the aligned CNT film was conducted. The primary goal of this thesis is to demonstrate a novel composite-manufacturing method without using a heating chamber, and to evaluate the behaviors of the aligned CNT film as the heating element. Also, findings in this thesis may be the starting point of the replacement of current composite-manufacturing process.

In Chapter 2, an overview of the aligned CNT network and its application to composite enhancement is presented, followed by a discussion of the shortcomings of a conventional
autoclave and oven composite-manufacturing.

In Chapter 3, the objectives of this thesis are presented, and the general approach for understanding behavior of the aligned CNT film and curing the laminate via resistive heating is described.

In Chapter 4, synthesis of multi-walled carbon nanotube (MWCNT) arrays and fabrication of the aligned CNT film are described. Further, the morphology of synthesized MWCNT arrays such as their inner and outer diameters, intrinsic density, and volume fraction is characterized.

In Chapter 5, the electrical properties of the aligned CNT film as a heating element are measured and analyzed. The impact of the CNT length on the electrical properties of the film, the electrical anisotropy of the aligned CNT network, and the dependence of the electrical properties of the film as a function of temperature are discussed.

In Chapter 6, composite curing via resistive heating of the aligned CNT film is presented. The vacuum bag scheme for resistive heating on the surface of the laminate is introduced, followed by a degree of cure analysis of the cured composite for evaluating the applicability of this newly developed manufacturing method on composite manufacturing.

In Chapter 7, important findings from this work are summarized and perspectives on these findings are discussed. Also, recommendations for future studies are presented.
Chapter 2

Background

2.1 Electrical Transport Behavior of an Individual CNT and CNT Network

Since carbon nanotubes were highlighted by Iijima,[12] they have been extensively studied and implemented in many areas due to their extraordinary multi-functional properties. Especially, single-walled carbon nanotubes have been widely explored as a new electrical conductor because of their ballistic electron transport and insensitivity to electromigration.[13–16] The multi-walled carbon nanotubes are composed of several layers of the single-walled carbon nanotubes in a coaxial geometry, and electrical properties of MWCNTs show variability due to defects such as discontinuous shells throughout the tube.[17,18] Resistance of MWCNT varies from a few kΩ to a few MΩ depending on transport behaviors such as ballistic and diffusive transport.[19,20] Previous studies reported that electrical conductivity of individual CNTs is on the order of $10^4 - 10^7$ S/m.[21,22] The most important feature of individual CNT's electrical property is high specific electrical conductivity. That is, CNTs are expected to be used as a replacement of conductive metal such as aluminum and copper with comparable electrical conductivity as well as lower mass addition to components. Mostly, CNTs are implemented in ceramics and polymers in order to improve electrical conductivity. In this case, CNTs form a conductive network as pathways for electronic transport. It was reported that the overall conductivity is dominated by electronic
transport (tunneling) at junctions between CNTs, and varies depending on the diameter of the interconnecting bundle.\textsuperscript{[23-26]} Also, previous studies reported that electrical and thermal conductivity along the tube axis is an order of magnitude higher than that of in-plane direction in case of the CNT array.\textsuperscript{[27,28]} These findings indicate the potential of anisotropy in properties depending on alignment of CNT network.

2.2 CNT Film and its Application Toward Composite Enhancement

With the landmark properties of individual CNTs, CNT films can find many uses including sensors and actuators,\textsuperscript{[29-33]} optoelectronics,\textsuperscript{[31-37]} and energy storage architectures,\textsuperscript{[33,38-40]} since they are in macroscopic and utilizable film form. CNT film, called Buckypaper, is commonly prepared by filtration. In this process, MWCNTs synthesized via chemical vapor deposition (CVD) process are suspended in solvent by sonication, and then the suspensions are filtered with pressure.\textsuperscript{[41]} Since MWCNTs are randomly oriented, the properties of CNT film prepared by filtration is isotropic and degraded compared to that of individual CNTs. In addition, CNTs in the film could be highly curved or folded beyond waviness if CNT length becomes too long (curved or folded shape cause CNT length limitation and possibly general property degradation), and could not be well-described as of yet. In this case, the degradation of the conductivity and mechanical strength was reported.\textsuperscript{[42,43]} Therefore, in order to maximize the advantages from the inherent properties of individual CNTs, the film should be composed of aligned and straight CNTs, even though electrical properties of CNT film are strongly dependent on the junction between CNTs.

There have been many studies on the implementation of CNT networks. Among them, two studies are introduced in this chapter in that these studies utilized resistive heating of the CNT film to reinforce composites. Buschhorn et. al. utilized the CNT film as heater for ice protection systems (IPS) of an aerosurface in 2013.\textsuperscript{[1]} Since ice formation on aerosurfaces affects the operation of aircraft, IPS are critical in some applications, and the intended function of them is to prevent the formation of ice and to remove already
accumulated ice on aerosurfaces. They installed a CNT film on an aerosurface, and then validated anti-icing capabilities of it through a wind tunnel test. They demonstrated that the CNT-based IPS can be used as an effective method for ice protection, and claimed that other multi-functional applications can be integrated with their IPS. In addition, they suggested that CNT film heaters can provide equivalent performance compared to conventional metal heaters with significant power savings.

Figure 2.1: Optical images of IPS on aerosurface. Accumulated ice was removed by activation of the CNT film heater. Images were taken from the work published by Buschhorn et. al.\textsuperscript{[1]}

In addition, Brampton et. al. used this CNT film heater for actuation of bistable laminates.\textsuperscript{[2]} In their work, the CNT film was attached to the surface of the laminate for direct heating. The bistable laminates were composed of two layers of composite, and manufactured in curved shape by creating residual thermal stresses upon cooling. The difference in thermal expansion coefficient between two layers enables switching from one stable shape to another stable shape when heated. They claimed that the CNT film heater could generate enough thermal energy to make transformation of laminate shape.
2.3 Composite Manufacturing Process Challenges for Prepreg

Pre-impregnated fiber reinforced plastic (Prepreg) is a group of materials commonly used in composite manufacturing. Since prepreg is easy to handle and can be tailored into complex shaped molds, it is possible to reduce excessively complicate manufacturing process and waste of materials by using it very efficiently compared to other manufacturing techniques. Also, composite manufacturing from prepreg can guarantee uniformity and repeatability in composite quality; for instance, volume fraction of fiber in cured composite and void content are highly repeatable, and there is a low possibility of resin-rich or dry spots in the composite.

Even though there has been a lot of manufacturing processes for curing thermoset prepreg, especially in manufacturing process of CFRPs for aerospace and aircraft structural components, autoclave curing has been most commonly used to repeatedly obtain the desired properties. An autoclave is a closed vessel for controlling temperature and pressure in order to cure polymeric matrix composites. In the autoclave process, prepreg laminates are subjected to temperature of the cure cycle and pressure for removing entrapped air and volatiles, and then high fiber volume fraction and low void content in components can be acquired. However, for reaching the internal high pressure, liquid nitrogen is typically injected into the heated autoclave. Also, the whole manufacturing process by autoclave is accompanied by apparent high costs, which comes from installing and operating of the autoclave pressure vessels. That is, autoclave curing has challenges such as high capital investment, need for large factory, high cost of nitrogen, poor energy efficiency, and long turn-around times. In this respect, the interest in Out-of-autoclave (OOA) processes has
come to the fore in aircraft structure manufacture. As a result, the new technology which is called OOA process has gained in popularity and adoption in recent years.

OOA manufacturing process particularly for prepreg is vacuum bag-only curing of newly-designed prepreg in conventional oven, called oven curing. The most important aspects of composites are maximized mechanical properties such as tensile and compressive strength per specific weight. Therefore, it was controversial whether the quality of OOA cured composites are comparable to that of original autoclave cured composites, in that OOA process is an alternative of the conventional autoclave manufacturing process. Most articles on OOA prepreg curing compare the quality of prepreg developed for OOA manufacturing with that of original prepreg cured in autoclave, and previous literature reports that mechanical properties of composites from OOA prepreg are comparable to that from autoclave prepreg in case of certain mechanical testings such as short beam shear, tension, and compression.\textsuperscript{[44–46]} Interlaminar dominated properties are a concern and area for OOA improvement relative to autoclave-cured composites. For effective evacuation of air and volatiles (produced during prepreg lay-up process and curing) under vacuum bag pressure, prepregs designed for OOA have semi-impregnated resin system; that is, resin is impregnated in the outer surface of the prepreg with dry regions inside of prepreg for creating passages of gas evacuation.\textsuperscript{[47]} Also, with resin which is curable in lower temperature, tooling costs and the problematic points on matching thermal expansion of tool and composite can be resolved. Hence, OOA manufacturing provides a number of benefits in terms of economic and environmental potential\textsuperscript{[48]} while potentially satisfying requirements for aerospace structural component.

However, when it comes to prepreg curing process, both autoclave and OOA process cannot sufficiently increase manufacturing flexibility and efficiency because there are still size, shape constraints and ineffective energy consumption associated by using heating chamber to match temperature of cure cycle. In detail, heating chamber for controlling temperature causes limitations on designing the structural components because component should be restricted by the capacity and shape of the heating chamber. Also, both methods transfer heat necessary for curing composite by convection from resistively heated coil to the tooling surface with a blower. Thus, the amount of energy for curing composite is
determined not by the size of composite but by the capacity of heating chamber because of controlling fixed volume of air inside of chamber. Therefore, in spite of comparatively small size of component, a heating chamber consumes a fixed amount of energy. Moreover, the temperature distribution inside the composite during curing should be uniform in order to obtain uniformity of degree of cure and residual stresses. However, temperature distribution cannot be uniform as heat flow changes due to the shape of the component, the number and displacement of components loaded into a chamber. These challenges aim to be addressed with the direct conductive curing approach developed herein.
Chapter 3

Objectives and Approach

As discussed in Chapter 2, there is a need for a new composite manufacturing technique which can overcome the shortcomings of the conventional manufacturing methods such as an autoclave and oven. The basic idea of a new manufacturing technique is to remove the heating chamber by only using conduction to transfer energy to cure a composite. In this thesis, the CNT film initially functions as the heating element, but once cured, the CNT film can be used for enhancement of the mechanical and multifunctional properties of the composite.

The objectives of this thesis are to:
- explore the electrical properties of the aligned CNT film considering its application as a heating element and the anisotropy of the aligned CNT film that is expected from its morphology.
- verify whether resistive heating of the aligned CNT film is enough to enable curing of typical prepregs.
- attempt composite manufacturing via resistive heating of the aligned CNT film
- suggest future enhancements of this new composite manufacturing technique.

In detail, the aligned CNT film is introduced to obtain higher electrical and thermal conductivity as well as its ease of handling compared to the as-grown MWCNT arrays. Characterization of MWCNT arrays and the aligned CNT films is conducted, and then electrical properties of the aligned CNT film are measured in order to evaluate which parameters affect the electrical properties, and to check the anisotropy of the aligned CNT film. Also,
changes in electrical properties depending on the temperature are explored for automated
temperature control in the future. After characterization, an aligned CNT film is attached to
the surface of an uncured laminate as the heating element. After curing via resistive heating
of the aligned CNT film, a degree of cure analysis is conducted with differential scanning
calorimetry (DSC) in order to evaluate whether the composite is successfully cured.
Chapter 4

Fabrication and Morphology of Aligned CNT Film

In this chapter, synthesis and characteristics of vertically aligned MWCNT forests and aligned CNT films are described.

4.1 Synthesis of Aligned MWCNT Arrays

In this work, vertically aligned MWCNT forests are grown in a 44 mm inner diameter quartz tube furnace at atmospheric pressure by a modified thermal chemical vapor deposition (CVD) process. See Figure 4.1 for schematics of the CVD process of vertically aligned MWCNT array. 30 mm x 40 mm Si substrates with catalytic layer of 10nm/1nm of Al$_2$O$_3$/Fe deposited by electron-beam evaporation are used for the standard substrate size of CNT growth. The 30 mm x 40 mm Si substrates are placed in the middle of the quartz tube furnace. The quartz tube is first flushed with 2070 sccm of He for 5 minutes in order to remove unnecessary gases from the tube, and then the substrates are annealed at 680 °C with 1040 sccm of hydrogen gas to form nano-particle catalyst from the Fe film. Once the temperature of the quartz tube is stabilized, 400 sccm of ethylene gas is injected into the furnace as the carbon source in order to grow CNTs under the same temperature of 680 °C. In the CNT growth process as currently understood, dissolved carbon forms a thin graphitic cap at the nucleation site of the catalyst, and then the cap is lifted off in vertical direction.
while further dissolved carbon forms a tube shape structure connected to the cap.\textsuperscript{[3]} The length of CNTs can be changed by controlling the time of ethylene gas insertion. After CNT growth, helium gas is introduced for 4 minutes with hydrogen gas to weaken bonding between CNT forests and the Si substrate. The grown CNT arrays with this delamination process can be easily removed from the substrate.\textsuperscript{[51]} After this process, the whole growth process is terminated, and the furnace is cooled down to room temperature.

![Figure 4.1: Illustration of the vertically aligned CNT array synthesis via CVD process. This illustration is taken from Hart, A.J.'s PhD thesis.\textsuperscript{[3]}

4.1.1 Inner and Outer Diameters

As Figure 4.2 shows, A-CNT arrays are composed of multi-walled CNTs. The inner ($D_i$) and outer ($D_o$) diameters of the CNTs were measured from TEM micrographs (JEOL 2100, 120 kV accelerating voltage). To accurately estimate the average values of $D_i$ and $D_o$, Gaussian functions were fit to the obtained discrete distributions (see Fig. 4.3 for histograms and fits) and the following values were obtained: $\simeq 5.12 \pm 0.76$ nm (coefficient of determination = 0.9715) for $D_i$, and $\simeq 7.78 \pm 0.85$ nm (coefficient of determination = 0.9462) for $D_o$. These values are very similar to those found in previous studies ($D_i \sim 5$ nm
and $D_o \sim 8$ nm).\textsuperscript{52-55} Using the average values of $D_i$ and $D_o$, an average number of walls of 4.9 can be evaluated. Grown MWCNTs in this work have an average outer diameter of $\sim 7.8$ nm (3 – 7 walls\textsuperscript{52} with an average inner diameter of $\sim 5.1$ nm), evaluated intrinsic CNT density of $\sim 1.6$ g/cm\textsuperscript{3},\textsuperscript{54} inter-CNT spacing of $\sim 59$ nm, and corresponding $V_f$ of $\sim 1.6\%$ CNTs.\textsuperscript{53}

![HRTEM micrograph of as-grown vertically aligned MWCNT array. HRTEM courtesy of Dr. Noa Lachman (taken at Harvard CNS).](image)

**4.1.2 Intrinsic Density**

While most theoretical studies utilize the CNT volume fraction ($V_f$) as the primary measure, the majority of experimental studies only report the CNT film density, and a measure that enables the proper conversion from one to the other is necessary, and is defined as the CNT intrinsic density ($\rho_{cnt}$). As discussed in a previous study,\textsuperscript{54} $\rho_{cnt}$ is a strong function of their inner diameter and number of walls, and in order to achieve an accurate estimate of the average $\rho_{cnt}$ for an array of CNTs, the population of CNTs with respect to their number of walls needs to be properly accounted for. The previous study suggested using a discrete summation form (see Equation 4.1a) to represent the probability density function of CNTs with respect to their number of walls, but a continuous integral form is more convenient,
Figure 4.3: (a) Histogram and fit for the CNT inner diameter ($D_i$) showing that $D_i \approx 5.12 \pm 0.76$ nm. (b) Histogram and fit for the CNT inner diameter ($D_i$) showing that $D_0 \approx 7.78 \pm 0.85$ nm.

and is included below (see Equation 4.1b):

$$
\rho_{\text{cnt}} = 4\rho_g \ell_\pm \left( \sum_{k=3}^{7} \frac{p_k}{(D_i + 2\ell_\pm(k-1))^2} \left( \sum_{j=1}^{k} (D_i + 2\ell_\pm(j-1)) \right) \right) \quad (4.1a)
$$

$$
\rho_{\text{cnt}} = 4\rho_g \ell_\pm \left( \sum_{k=3}^{7} \frac{p_k}{(D_i + 2\ell_\pm(k-1))^2} \left( \int_{0}^{k} (D_i + 2\ell_\pm(j-0.5)) \, dj \right) \right) \quad (4.1b)
$$

where $\rho_g$ is the theoretical density of a single graphene sheet ($\approx 2.25$ g/cm$^3$), $\ell_\pm$ is the inter-layer spacing value for MWCNTs ($\approx 3.41$ Å), $D_i$ is the inner diameter ($\approx 5.12$ nm from Section 4.1.1), and the summation/integration limit variables $j$ and $k$ represent the 3 to 7 wall nature of the CNT population. To further simplify Equation 4.1b, the probability distribution can be approximated with a Gaussian centered at $\mu$ with a standard deviation $\sigma$ (see Figure 4.4a for exemplary fits of discrete distributions centered at $\mu = 5$), enabling the first summation term to be replaced with a scaling factor $\alpha(\mu, \sigma)$ as follows:

$$
\rho_{\text{cnt}} \approx 4\rho_g \ell_\pm \alpha(\mu, \sigma) \frac{\mu(D_i - \ell_\pm(1-\mu))}{(D_i + 2\ell_\pm(\mu-1))^2} \quad (4.2)
$$

Where $\alpha(\mu, \sigma) \lesssim 1$ and $\alpha(\mu, \sigma) = 1$ corresponds to the ideal $\sigma = 0$ Delta function.

To evaluate the scaling of $\alpha(\mu, \sigma)$, Equation 4.1b was studied with discrete distributions that correspond to Gaussians centered at integer values of $\mu$ ($3 \leq \mu \leq 7$) with
0.4 \leq \sigma \leq 2.0. The resulting values of \( \rho_{\text{cnt}} \) were then compared to the ideal Delta function centered at the respective \( \mu \) value (Equation 4.2 with \( \alpha(\mu, \sigma) = 1 \)), leading to the value of the scaling factor \( \alpha(\mu, \sigma) \). See Fig. 4.4b for a plot of \( \alpha(\mu, \sigma) \) as a function of \( \sigma \) and \( \mu \). As Fig. 4.4b demonstrates, \( \alpha(\mu, \sigma) \geq 0.98 \), and since \( \rho_{\text{cnt}}(\mu = 4.9) = 1.602 \, \text{g/cm}^3 \) for \( \alpha(\mu, \sigma) = 1 \) (ideal Delta function), \( \rho_{\text{cnt}} \approx 1.6 \, \text{g/cm}^3 \) for the CNTs used in this study regardless of the distribution of the CNTs with respect to their number of walls (assuming the form remains Gaussian in nature).

### 4.1.3 Packing Morphology and Volume Fraction

A previous study[53] included a detailed discussion of the scaling relationship between the average inter-CNT spacing (\( \Gamma \)), the CNT volume fraction (\( V_f \)), the CNT outer diameter (\( D_o \)), and the notional two dimensional coordination number (\( N \)) of an idealized aligned CNT system. The functional forms of this scaling relationship are included in Equation 4.3 below:[53]

\[
\Gamma = D_o \left( (11.77(N)^{-3.042} + 0.9496) \sqrt{\frac{3\pi}{6V_f}} - 1 \right) \quad (4.3a)
\]

\[
N = 2.511(V_f) + 3.932 \quad (4.3b)
\]

Using the isosceles angle (\( \theta \)) of the constitutive triangles at each \( N \), the minimum (\( \Gamma_{\text{min}} \)) and maximum (\( \Gamma_{\text{max}} \)) inter-CNT spacings were previously separated from \( \Gamma \) (Equation 4.3a), yielding the following:[55]

\[
\theta = \pi \left( \frac{1}{2} - \frac{1}{N} \right) \quad (4.4a)
\]

\[
\Gamma_{\text{max}} = 4\cos(\theta) \left( \frac{\Gamma}{1 + 2\cos(\theta)} \right) \quad (4.4b)
\]

\[
\Gamma_{\text{min}} = 2 \left( \frac{\Gamma}{1 + 2\cos(\theta)} \right) \quad (4.4c)
\]

To evaluate the \( V_f \) of the CNTs in the as-grown arrays, the average inter-CNT spacing must first be evaluated experimentally, and is defined as \( \Gamma_{\text{exp}} \). \( \Gamma_{\text{exp}} \) was evaluated from
SEM micrographs (JEOL 6700, 6.0 mm working distance) by first adjusting their contrast to have 0.5% saturated pixels, and then reducing noise by applying a median filter. All processing was done in ImageJ. \( \Gamma^{\text{exp}} \) was estimated from these images by counting the number of in-focus (bright) CNTs, and dividing the width of the picture by that number. The counting had been done by taking a line plot across two places on the image, where peaks with a brightness greater than 150 (on a 0–255 scale) were counted as a single CNT. A histogram of \( \Gamma^{\text{exp}} \), along with a Gaussian fit (coefficient of determination = 0.9913), can be found in Figure 4.5a. The Gaussian fit indicates that \( \Gamma^{\text{exp}} \simeq 58.6 \pm 10.6 \) nm.

Using Equation 4.3, Equation 4.4, \( \Gamma^{\text{exp}} \) can be used to approximate \( V_f \) for \( D_o \simeq 7.78 \) nm (from Section 4.1.1), where the mean of \( \Gamma^{\text{exp}} \) is approximately equal to \( \Gamma \) (\( \rightarrow \Gamma \simeq 58.6 \) nm), and the standard deviations of \( \Gamma^{\text{exp}} \) are used to define \( \Gamma_{\min} \) (\( \rightarrow \Gamma_{\min} \simeq 48.0 \) nm) and \( \Gamma_{\max} \) (\( \rightarrow \Gamma_{\min} \simeq 69.2 \) nm). The resulting estimates indicate that 1.567 vol. \% \( \leq V_f \leq 1.604 \) vol. \%, meaning that \( V_f \sim 1.6 \) vol. \% for the as-grown CNT arrays used in this study. See Figure 4.5b for a comparison of the \( V_f \) estimate, \( \Gamma \), \( \Gamma_{\min} \) and \( \Gamma_{\max} \).
Figure 4.4: (a) Exemplary Gaussian fits of discrete distributions centered at 5 ($\mu = 5$) with standard deviations ($\sigma$) of $\sim 0.5$, 1, and 2. (b) Plot of scaling factor, $\alpha(\mu, \sigma)$, of the average CNT intrinsic density as a function of $\mu$ and $\sigma$. According to the empirical scaling relationship, $\alpha(\mu, \sigma) \gtrsim 0.98$ for the CNTs used in this study ($\mu \simeq 4.9$ and $\sigma \sim 1$), meaning that the average CNT intrinsic density $\sim 1.6$ g/cm³.

Figure 4.5: (a) Histogram and fit for the experimentally determined inter-CNT spacing ($\Gamma$) showing that $\Gamma^{\exp} \sim 58.6 \pm 10.6$ nm. (b) Comparison of $\Gamma^{\exp}$ to $\Gamma$ (Equation 4.3a), $\Gamma_{\min}$ (Equation 4.4b), $\Gamma_{\max}$ (Equation 4.4c) illustrating that $V_f \simeq 1.6$ vol. $\%$ CNTs in the as-grown CNT arrays used to synthesize the aligned CNT films.
4.2 Aligned CNT Film Fabrication

The aligned CNT film is produced with a 'knocking down' technique. The basic idea of this technique is to knock as-grown vertically aligned CNTs down on the horizontal plane by pushing CNTs with a small radius rod. The as-grown CNT arrays on the Si substrate are first covered with a guaranteed nonporous Teflon (GNPT) film, and then pushed down by rolling a small radius rod (3mm radius, steel) with constant pressure in the desired alignment direction. These compressed CNTs then form one piece of film-shaped material with CNTs sticking to each other. Since the post-growth \( H_2 \) anneal step weakens the attachment of the CNTs to the catalyst layer of substrate, such knocked-down CNT films on GNPT can be easily and repeatedly removed from the Si substrate. See Figure 4.6 for an illustration of the knocking-down technique.

![Illustration of the knock-down process of aligned CNT film](image)

Figure 4.6: Illustration of the knock-down process of aligned CNT film, and a cross sectional morphology of the knocked-down (and densified) aligned CNT film.

Figure 4.7 shows a high resolution scanning electron microscopy (JEOL 6700, 3.0 mm working distance) micrograph of the cross sectional morphology of an aligned CNT film produced via densification of an A-CNT array. This cross sectional morphology should
Figure 4.7: Pulled-out CNTs after tearing an inner part of aligned CNT film. CNTs in the cracked area are aligned, while CNTs around that area are randomly oriented.

be taken from the edge of intact aligned CNT film. If the inner part of aligned CNT film is torn to create the cross section, CNTs are pulled out or wrinkled, ruining the true film morphology. See Figure 4.7 for a micrograph of a cross sectional morphology of a torn aligned CNT film. Since the attachment of the CNTs to the substrate is weaker than that to the GNPT film, the part of CNT film close to the Si substrate shows aligned morphology with a small angle to the horizontal plane, whereas that close to the GNPT film still has a morphology perpendicular to the GNPT film. From the morphology of an manufactured CNT film, it is concluded that CNTs are aligned along the knocking-down direction and alignment may cause anisotropy of electrical and thermal properties of the CNT film.
Chapter 5

Electrical Properties of Aligned CNT Film as Heating Element

In order to utilize aligned CNT films as heating element, the electrical properties of films are measured and analyzed. The experimental details, manufacturing of specimen, and results are presented in this chapter.

5.1 Definition of Orientation Angle

Since the intrinsic properties of CNTs are highly anisotropic, the importance of morphology of aligned CNT film was evaluated as a function of the orientation angle $\theta$. As illustrated in Figure 5.1, the aligned direction is defined as $\theta = 0^\circ$, and the transverse direction is defined as $\theta = 90^\circ$. With this definition of orientation angle $\theta$, any properties of aligned CNT film are expressible. Additionally, properties in $\theta = 0^\circ$ and $\theta = 90^\circ$ are expressed as $\parallel$ and $\perp$, respectively; for example, sheet resistance $R$ in the longitudinal direction ($\theta = 0^\circ$) is expressed as $R_\parallel$, and transverse direction $R$ ($\theta = 90^\circ$) is expressed as $R_\perp$. 
5.2 Characterization of CNT Length, Thickness, and Density of CNT Film

An optical microscope (Carl Zeiss Axiotech 30 HD) is used to measure the height of as-grown A-CNT arrays and the thickness of aligned CNT film, defined as $H$ and $t$, respectively. It is assumed that the focal length of the bottom surface of the CNT forests is the same as that of the Si substrate. The height of the as-grown CNT array is then evaluated by measuring the stage displacement necessary for an optical microscope to transition from focusing on the bottom of the CNT forest to the top of the CNT array. In a similar way, the thickness of aligned CNT film can be measured.

Additionally, the length of the CNTs ($L_{\text{cnt}}$) can be corrected with the $H$ values of the CNT waviness (waviness ratio $\leq 0.3$),\cite{56} and the $<1 \, \mu m$ thick growth initiation region.\cite{57} Since the growth initiation region is small relative to $H$, error originating from the CNT waviness is the focus of this calculation. The error induced by waviness can be estimated by first assuming a simple sinusoidal shape for the wavy CNTs (see Figure 5.2a), and varying the waviness ratio ($w$), which is the ratio of the wavelength ($\lambda$) and amplitude ($a$) of the sinusoid. The length of CNTs accounting for waviness ($L_{\text{cnt}}$) can then be compared to that of the height of the aligned CNT forest ($H$) as follows (see Figure 5.2b for the error as a function of $w$):
\[
\frac{L_{\text{cnt}}}{H} = 2 \int_0^\frac{1}{2} \sqrt{\left(1 + (2\pi w \cos(2\pi x))^2\right)} \, dx
\]  
(5.1)

Therefore, an approximation of \( L_{\text{cnt}} \sim 1.3 - 1.5H \) is obtained for these CNTs.

The density of the aligned CNT film is evaluated with the height of as-grown A-CNTs (defined as \( H \)), the thickness of the aligned CNT film (defined as \( t \)), and the density of the as-grown A-CNTs (defined as \( \rho_{\text{array}} \)).

\[
\rho_{\text{array}} A H = \rho_{\text{film}} A t
\]  
(5.2)

in which the in-plane area of the as-grown A-CNTs is defined as \( A \), and the density of the aligned CNT film is defined as \( \rho_{\text{film}} \). There is no change in the in-plane area \( A \) before and after the densification process.

Then, the equation for the density of the aligned CNT film can be obtained as follows:

\[
\rho_{\text{film}} = \rho_{\text{array}} \frac{H}{t}
\]  
(5.3)
Figure 5.2: Length correction for A-CNT waviness. (a) Functional form of waviness approximation where the amplitude of the sinusoid is simply defined using the waviness ratio \( w \) and the wavelength \( \lambda \). (b) Plot of the ratio of the true CNT length \( L_{\text{cnt}} \) and the height of the CNT forest \( H \) as a function of \( w \) evaluated using Equation 5.1. Neglecting the waviness of the CNTs can lead to errors of \( \geq 100\% \) when using \( H \) as an approximation of \( L_{\text{cnt}} \).
5.3 The Van der Pauw Method for Electrical Conductivity of Anisotropic Layers

The four-point probe method is mostly used to measure electrical properties of conducting layers to eliminate contact resistances between electrodes and sample.\cite{58} Recently, work conducted by Kazani et. al. theoretically and experimentally demonstrated that anisotropy cannot be obtained with the collinear four-point probe method.\cite{59} Alternatively, the Van der Pauw (VDP) method which is also a four-point probe method can be used for investigating anisotropic conductive layers.\cite{60,61} Kazani et. al. demonstrated how to obtain anisotropic sheet resistances with a rectangular conductive layer, and this method was adopted in this work with a square-shaped specimen for simplicity.\cite{62} With the VDP method, four contacts are used in measurement and labeled A, B, C, and D. (See Figure 5.3.)

First, the voltage drop across D and C ($V_{DC}$) is measured while supplying a current through A and B ($I_{AB}$). Second, the voltage drop across B and C ($V_{BC}$) is measured while supplying a current through A and D ($I_{AD}$). With these measurements, the modulus factor $k$ is obtained by Equation 5.4.

\[
\frac{V_{DC}}{I_{AB}} = \frac{\ln \frac{4/k}{(1/k+1)^2}}{\ln \frac{1}{(1/k-1)^2}} \label{5.4}
\]

Then, the resistive anisotropy ratio $\frac{R_{yx}}{R_{xx}}$ is calculated by

\[
\frac{a/2}{b\sqrt{R_{yy}/R_{xx}}} = \frac{K(k)}{K(\sqrt{1-k^2})} \label{5.5}
\]

where $R_{xx}$ and $R_{yy}$ are sheet resistances in the x- and y-axes, and $K(k) = \int_0^{\pi/2} \frac{d\phi}{\sqrt{1-k^2\sin^2\phi}}$.

The geometric mean of the sheet resistance $\sqrt{R_{yy}R_{xx}}$ is measured by the VDP method.\cite{61} Therefore, with $\sqrt{R_{yy}R_{xx}}$ and $\frac{R_{yx}}{R_{xx}}$, $R_{xx}$ and $R_{yy}$ can be achieved. See an article published by Kazani et. al. for details.\cite{62}
Figure 5.3: Illustration of locations A, B, C, and D on specimen for VDP measurements.

5.4 Sample Preparation and Measurements of Electrical Properties of CNT Film

Electrical conductivity is usually representative of electrical properties of the CNT network no matter how the CNT network is aligned. If the CNT network is produced by dispersion in a solvent and filtration of CNT suspensions, the network is isotropic through the thickness and considered as a bulk material if the CNTs are well-distributed. Also, there is no morphological parameter which is representative of one layer of network. However, the aligned CNT film in this work has clear definition of one layer because the two ends of each CNT contact the top and bottom surfaces of the film, respectively. Therefore, sheet resistance is more representative to indicate electrical properties of the aligned CNT film than the electrical conductivity.

To evaluate the electrical properties of the aligned CNT film, electrical test specimens were prepared by cutting aligned CNT films composed of different CNT lengths into 14.5mm x 14.5mm square-shaped films. The orientation of alignment is parallel to the edge of square (x-direction in Figure 5.3). To quantify electrical properties with parameters, $H$ and $t$ were recorded in the process of preparation with methods described in the previous section. The sheet resistance of each 14.5mm x 14.5mm specimen was measured by modified Van der Paw method to obtain $R_{\parallel}$ and $R_{\perp}$ as described in Section 5.3. Be-
cause contact resistance could play a role on the sheet resistance of the A-CNT networks, the sheet resistance was evaluated using the VDP four-point probe method with a Keithley SCS-4200, where adequate electrode-CNT connections were established using silver paint. Then, each 14.5mm × 14.5mm specimen was cut into a 10mm × 10mm square-shaped specimen with the CNT alignment oriented along the square diagonal. With this 10mm × 10mm specimen, $R(45^\circ)$ was evaluated. See Figure 5.4 for an illustration of specimen.

![Figure 5.4: Illustration of specimen and four contact points for each measurement.](image)

5.5 Results and Discussion

5.5.1 Impact of CNT Length on Electrical Property of Film

The effect of A-CNT height on the sheet resistance of the CNT network is presented as a function of $H$ in Figure 5.5. Both $R_\perp$ and $R_\parallel$ values show a very strong dependence on $H$, starting at $\sim 75 \, \Omega/\square$ for $H \sim 60 \, \mu$m, and decreasing to $\sim 10 \, \Omega/\square$ for $H \sim 310 \, \mu$m. Additionally, the sheet resistance of the aligned CNT network shows anisotropic behavior ($R_\perp/R_\parallel \approx 1.44 \pm 0.19$ in case of $H > 100 \, \mu$m). Details of the anisotropy of the sheet resistance is presented in the next section.

Since defects present in the CNTs can lead to vastly altered electronic properties, the defect concentration of the CNTs that comprise the networks was quantified via Raman spectroscopy. Raman spectra were collected using a Raman microscope (LabRam
Figure 5.5: Sheet resistance ($R$) as a function of the as-grown CNT array height ($H$) indicating that the electron transport in the A-CNT networks strongly depends on the length of the CNTs that comprise it.

HR800, Horiba Jobin Yvon) with 532 nm (2.33 eV) laser excitation through a 50× objective (N.A. 0.75), and defect concentrations were evaluated using the integrated intensities (area ratios) of the G ($\sim 1350$ cm$^{-1}$) and D ($\sim 1580$ cm$^{-1}$) peaks,\(^{[67]}\) known as the $I_G/I_D$ ratio.\(^{[55]}\) As illustrated by Figure 5.6, the Raman spectra of the CNTs does not vary significantly as a function of $H$. ($I_G/I_D \approx 0.7$) That is, the wall defect concentrations are of similar magnitude, and the intrinsic properties of the CNTs can be approximated as constants. Since the intrinsic CNT properties are likely invariant with $H$, the large changes in $R$ can be attributed to the impact of the A-CNT network morphology on the number of electron pathways available for electron transport. Previous work on percolated CNT networks showed that $R \propto cH^{-n}$, where $c$ and $n$ are constants. A study on single-walled CNTs
Figure 5.6: Raman spectra illustrating that the bond character does not vary significantly as a function of the CNT length.

with $L_{\text{cnt}} \lesssim 4 \ \mu\text{m}$ showed that $n \approx 1.46$, and that the power law relationship holds until $L_{\text{cnt}}$ becomes comparable to the CNT-CNT junction resistance ($L_{\text{cnt}} \gtrsim 25 \ \mu\text{m}$ in the previous work). Application of this model yields a $R \propto cH^{-1}$ dependence (see Figure 5.5), meaning that CNT-CNT coupling is what limits the electron transport properties in the A-CNT networks, and not the intrinsic CNT resistance. These results indicate that the previously proposed scaling relationship is appropriate for A-CNT networks with CNTs that are more than an order of magnitude longer than those of Hecht et. al. 168, and that the CNT intrinsic resistance is much lower than that of the CNT-CNT junction resistance.

5.5.2 Impact of Alignment Direction on Electrical Property of Film

As presented in the previous section, it is concluded that the aligned CNT film has an anisotropic sheet resistance. Here, the sheet resistance of an aligned CNT film as a function of the orientation angle can be modeled with tensor rotation and anisotropic theory.
The values of the components of the resistivity tensor change depending on the orientation of the CNTs. Assuming that the longitudinal, transverse, and through-thickness directions of the aligned CNT film correspond to eigenvectors (See Section 5.1), the resistivity tensor $\rho$ can be described by its eigenvalues: $\rho_1$, $\rho_2$, and $\rho_3$; and the rotation matrix $A$ with corresponding Euler angles in each axis. If the aligned CNT film is rotated normal to the film thickness with an angle $\theta$, the new resistivity tensor can be defined as:

$$\rho = A^T \hat{\rho} A$$  
(5.6a)

$$\hat{\rho} = \begin{bmatrix} \hat{\rho}_1 & 0 & 0 \\ 0 & \hat{\rho}_2 & 0 \\ 0 & 0 & \hat{\rho}_3 \end{bmatrix}$$  
(5.6b)

$$A = \begin{bmatrix} \cos(\theta) & \sin(\theta) & 0 \\ -\sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$  
(5.6c)

The resistivity of the CNT film as a function of angle $\theta$, $\rho(\theta)$, can then be described using $\rho(1,1)$ (the first term of $\rho$ in $\rho(m,n)$ notation, where $m$ designates the row and $n$ the column), and $\hat{\rho}_1$ (defined as $\rho_\parallel$ in the main text) and $\hat{\rho}_2$ (defined as $\rho_\perp$ in the main text):

$$\rho(\theta) = \rho(1,1) = \hat{\rho}_1 \cos^2\theta + \hat{\rho}_2 \sin^2\theta$$

$$= \rho_\parallel \cos^2\theta + \rho_\perp \sin^2\theta$$  
(5.7)

Since sheet resistance ($R$) can be calculated by dividing $\rho(\theta)$ by the film thickness, $R$ as a function of angle $\theta$ can be modeled as follows:

$$R(\theta) = R_\parallel \cos^2\theta + R_\perp \sin^2\theta$$  
(5.8)

Figure 5.7 presents measured values of sheet resistance $R(\theta)$ with $\theta = 0^\circ$, $45^\circ$, and $90^\circ$. Since $R$ for $H < 100 \ \mu m$ exhibited much lower anisotropy ($R_\perp/R_\parallel \approx 1.19 \pm 0.13$) due to potential squashing during the knockdown process, $R$ for $H > 100 \ \mu m$ is presented. $R$ for
H > 100 μm showed anisotropy on the order of ~40% ($R_\perp/R_\parallel \simeq 1.44 \pm 0.19$), and the experimentally determined $R(\theta = 45^\circ)$ values are placed in the middle of $R_\perp$ and $R_\parallel$. That is, results showed good agreement with the predictions of Equation 5.8 (using $R_\perp/R_\parallel \sim 1.44$). The predictions of Equation 5.8 (using $R_\perp/R_\parallel \sim 1.19$) also showed very good agreement with the experimentally determined $R(\theta = 45^\circ)$ values. Further work is necessary to determine the degree of squashing (i.e. excess waviness that leads to additional potential CNT-CNT junctions in the in-plane directions) that occurs during the densification of A-CNT arrays with $H < 100$ via a rigid roller, and future studies should utilize simulation to better quantify the impact of the waviness on the electrical properties of A-CNT networks. Since the CNT-CNT junction potentials are a strong function of temperature and because resistive heating for curing is one application, the physics that underly electron transport in A-CNT networks were further studied by evaluating the temperature response of $R$.

![Graph](image)

Figure 5.7: Sheet resistance $R$ as a function of orientation $\theta$. In case of $H > 100$ μm, a ratio of $R_\perp/R_\parallel \sim 1.44$ was observed.
5.5.3 Thermal Coefficient of Resistance of Aligned CNT Film

Since the electrical conductivity of CNT networks is limited by the CNT-CNT junction resistance,\cite{24} their temperature coefficient of resistance (TCR) is expected to have a negative value (i.e. nonmetallic behavior).\cite{69} The measurements of $R_\perp$ and $R_\parallel$ were conducted while increasing the temperature, and is presented in Figure 5.8 (b). The TCR for the A-CNT networks used in this study is $\simeq -1.2 \times 10^{-3} \, \text{K}^{-1}$, which is consistent with those reported in previous studies ($-0.4 \text{ to } -1.4 \times 10^{-3} \, \text{K}^{-1}$).\cite{70-72} Since the activation energy ($E_a$) for electron transport via tunneling in the CNT-CNT junction decreases with the number of walls of the CNTs in the network,\cite{71} the order of magnitude span of the TCR in the previous studies can be attributed to the differences in CNTs that comprised the networks. Such uncertainty demonstrates that accurate and complete documentation of the CNTs comprising the networks is necessary for a fair comparison of their transport properties. To evaluate the $E_a$ for the tunneling mediated electron transport in the A-CNT network, the following expression from the fluctuation inducted tunneling conduction (FITC) model can be applied:\cite{73-75}

$$\frac{R(T)}{R(298 \, \text{K})} = \beta \exp \left( \frac{T_b}{T + T_s} \right)$$  \hspace{1cm} (5.9)

where $T_b$ corresponds to the tunneling activation energy, $T_s$ defines the point at which thermal activation occurs, and $\beta$ is a scaling parameter. Fitting the experimental data (See Figure 5.8 (b)) yields the following parameters for Equation 5.9 (coefficient of determination = 0.9976): $\beta = 0.581$, $T_b = 165 \, \text{K}$, $T_s = 6.10 \, \text{K}$. The value of $T_b/T_s \sim 27$ indicates that the fitting parameters are consistent with previous investigations utilizing the FITC model.\cite{73-75} $E_a$ can now be evaluated using $kT_b$, where $k$ is the Boltzmann constant, yielding $E_a \simeq 14.2 \, \text{meV}$. This value is consistent with previous work on electron transport in CNT networks.\cite{69,71} Since the fitting parameters for Equation 5.9 can be applied to data from both $R_\parallel$ and $R_\perp$ with the same coefficient of determination (= 0.9976), these results indicate that $E_a$ is independent of both $H$ and orientation in the A-CNT networks. That is, TCR of aligned CNT network is isotropic contrary to anisotropy of sheet resistance. As described in the FITC model, even though properties of junctions between disordered
material varies through network, the properties of the network can be expressible in terms of the single junction behavior.\textsuperscript{[73,74]} Therefore, isotropy of TCR occurs because the activation energy of each junction does not change depending on direction, and then effective activation energy should be isotropic as is that of each junction.

![Diagram of CNT Network and Equivalent Circuit](image)

**Figure 5.8:** A-CNT film TCR. (a) Illustration of the fluctuation induced tunneling conduction (FITC) mechanism which dominates the thermal response of the electron transport properties in the A-CNT networks. (b) Sheet resistance as a function of the operating temperatures. Evaluation of the parameters of Equation 5.9 indicates that the activation energy for tunneling is $\sim 14.2$ meV independent of orientation and CNT length.
Chapter 6

Composite Curing via Resistive Heating of Aligned CNT Film

6.1 Degree of Cure Analysis

In this work, degree of cure analysis was used to check the quality of the cured composites because degree of cure of composite is one of the parameters that determines the properties of the composite.\textsuperscript{[76]} Differential scanning calorimetry (DSC) analysis is one of the thermal analysis techniques used to obtain the degree of cure of thermosetting materials by measuring the difference in the heat flow to a specimen and a reference.\textsuperscript{[77]} A thermosetting resin in a composite material exists in a partially reacted form, and is irreversibly cross-linked during curing.

Figure 6.1 presents an example of DSC data of an exemplary thermoset resin. The sharp fluctuation at 40°C is start-up transient response. The cure starts at the temperature that heat flow deviates from a linear line, and then heat flow creates an exothermic peak. After curing is completed, heat flow returns to a linear line as presented. In the case of a fully cured thermosetting resin, heat flow draws almost linear line without an exothermic peak. Therefore, the integrated area of the exothermic peak is the heat of cure. After undergoing the curing process with usual cure cycle, a laminate is not fully cured. Therefore, the heat of cure needed for uncured residuals ($H_{\text{sample}}$) is obtained from DSC analysis. Also, the heat of cure needed for a fully uncured laminate ($H_{\text{uncured}}$) is evaluated with a pristine laminate.
Degree of cure $\alpha$ is then calculated as follows:

$$\alpha = \frac{H_{\text{uncured}} - H_{\text{sample}}}{H_{\text{uncured}}}$$

(6.1)

As described in Equation 6.1, if there is no heat of cure, degree of cure has the value of 1.

Figure 6.1: DSC analysis of (a) uncured laminate and (b) fully cured laminate.
6.2 Fabrication of Specimen

6.2.1 Materials

6.2.1.1 Prepreg

Cycom® 5320-1 from Cytec Engineered Material Inc. was used to fabricate composite laminates in this study. Cycom® 5320-1 is a commercial toughened epoxy resin system for out-of-autoclave process, and is designed for primary structural applications can be obtained with this prepreg.[4] OOA prepregs are designed to be cured in vacuum bags and are therefore suitable for experiments of composite curing via resistive heating of CNT film. See Table 6.1 for resin characteristics of Cycom® 5320-1.

6.2.1.2 Bagging Materials

One of the key features of prepregs designed for OOA curing is the usage of the same bagging materials that are used for standard autoclave-cured prepregs. In addition, the function of bagging materials used in this work is identical to that of bagging materials for autoclave curing. Table 6.2 describes the bagging materials used in this study and their function in the manufacturing process.

6.2.2 Laminate Preparation

For laminate preparation, recommended handling instructions for prepreg were followed. The prepreg stored frozen in a sealed bag was removed from the freezer and allowed to warm until the prepreg reached room temperature in order to avoid moisture condensation on the prepreg. After removal from the bag, the prepreg was cut into 40mm x 50mm

<table>
<thead>
<tr>
<th>Shelf Life</th>
<th>1 year at &lt; -12°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tack Life</td>
<td>20 days at room temperature</td>
</tr>
<tr>
<td>Shop Life</td>
<td>30 days minimum at room temperature</td>
</tr>
<tr>
<td>Cured Resin Density</td>
<td>1.31 g/cc</td>
</tr>
<tr>
<td>Wet Glass Transition Temperature</td>
<td>163°C</td>
</tr>
</tbody>
</table>

Table 6.1: Resin characteristics of Cycom® 5320-1[4].
<table>
<thead>
<tr>
<th>Cure Material</th>
<th>Model Name</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom cure plate</td>
<td>CFRP laminate 2mm thick</td>
<td>Protect the laminate from wrinkles, guide the composite shape, and assure uniform pressure</td>
</tr>
<tr>
<td>Vacuum bagging film</td>
<td>WL8400</td>
<td>Provide the laminate with vacuum and hold vacuum during curing</td>
</tr>
<tr>
<td>Release film</td>
<td>GNPT film</td>
<td>Keep excessive epoxy off the tooling surface</td>
</tr>
<tr>
<td>Vacuum tape</td>
<td>AT200Y sealant tape</td>
<td>Seal the vacuum bag down to the cure plate</td>
</tr>
<tr>
<td>Air breather</td>
<td>Airtech Breathers</td>
<td>Allow air pathway during curing</td>
</tr>
</tbody>
</table>

Table 6.2: Details of vacuum bagging materials.

rectangles (50mm in fiber direction). For simplifying the complex effect of heat transfer through carbon fiber in prepreg, a 16-ply unidirectional lay-up was chosen in this study. The plies were stacked by hand lay-up technique, and 5mm of release film was introduced into both the left and right ends of the laminate in between each layer for easy delamination after curing. The release film prevents resin flow between layers, and such separated region works as pre-cracks in delaminating process for through-thickness spatial analysis of degree of cure. Considering the area with release film, the total consolidated area was 40mm × 40mm. See Figure 6.2 for 16-ply unidirectional laminate with release film at both ends.

6.2.3 Installation of Aligned CNT Film as Heating Element

In order to evaluate how many heating elements are required for curing 16-ply laminate, aligned CNT Film was only attached to the top surface of composite. One-sided heating element is the "worst case" in that the composite is cured only by one heat source. Also, since a temperature gradient is expected to exist through the laminate thickness during curing, the effect of heat distribution on composite during curing can be evaluated with this case.

As presented in Chapter 4, aligned CNT films were manufactured by 'knocking down' technique from as-grown MWCNT array. The 40mm × 50mm of CNT film transferred on
Figure 6.2: Cycom® 5320-1 16-ply unidirectional laminate with release film at both ends.

GNPT film was produced so that the prepared laminate was fully covered by CNT film. See Figure 6.3 for as-grown MWCNT array and aligned CNT film on GNPT film.

(a)  

Figure 6.3: CNTs used in this work (a) As-grown MWCNT array, and (b) aligned CNT film on GNPT film.

In this work, TC235-1SF composite surfacing film from Tencate advanced composites was used as the adhesive material for installation of aligned CNT film on the surface of the laminate. The general function of surfacing film is to provide the composite with a smooth surface for painting. In addition, surfacing film offers virtual elimination of porosity and imperfections on the composite surface. This surfacing film is designed to be applied to vacuum-bag-only curing so that low porosity and smooth surface can be obtained under low
cure pressures and temperature environments. The most important feature of this surfacing film is electrical isolation. CNT film cannot be installed directly on the surface of the laminate because it loses the function of the heating element with direct installation. If current flows through the conductive carbon fiber composite as well as the aligned CNT film, the spots on the CNT film where high current density flows through can break down, and then appropriate heat distribution is not achievable. Therefore, with electrically isolated surfacing film, the aligned CNT film works as the only medium of electron transport and Joule heating.

As electrodes, copper mesh used for lightning strike protection of composite structure were installed parallel at both edges of 44mm × 54mm rectangular-shaped surfacing film. The dimension of surfacing film was determined to be larger than the size of CNT film in order to achieve perfect electrical isolation at four edges of the CNT film. The length between two electrodes was 40mm to match the area of real consolidation. Because surfacing film is more robust than CNT film, electrodes were first introduced onto surfacing film and then covered with CNT film. Lastly, the manufactured CNT film heater component was attached onto the top surface of the prepared laminate. See Figure 6.4 for a scheme of CNT film heater and manufactured aligned CNT film heater on laminate.
6.2.4 Vacuum Bag Scheme and Cure Cycle

As a baseline, a 40mm × 50mm 16-ply unidirectional laminate was cured in oven following the given vacuum bag scheme in the Cycom®5320-1 technical data sheet. See Figure 6.5 for the given vacuum bag scheme. Cycom®5320-1 offers two recommendations for cure cycle, and Cure Cycle B described in Table 6.3 was selected for baseline in order to save total curing time.

In case of a specimen cured by CNT film heater, thermography of aligned CNT film during curing is required to analyze the degree of cure and to track the status of the heater. Since bagging materials can alter the thermography at the surface of the CNT
Figure 6.5: Cycom®5320-1 vacuum bag scheme for oven curing\cite{4}.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cure Cycle A</th>
<th>Cure Cycle B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramp Rate</td>
<td>0.6 – 1.7°C/minute</td>
<td>0.6 – 2.8°C/minute</td>
</tr>
<tr>
<td>Cure Temperature</td>
<td>93 ± 6°C</td>
<td>121 ± 6°C</td>
</tr>
<tr>
<td>Cure Time</td>
<td>12 hours</td>
<td>3 hours</td>
</tr>
<tr>
<td>Post Cure</td>
<td>2 hours at 177°C</td>
<td>2 hours at 177°C</td>
</tr>
</tbody>
</table>

Table 6.3: Recommended cure cycle of Cycom®5320-1\cite{4}

heater through thermal insulation, air breather was removed from the original vacuum bag arrangement so that the CNT film under the GNPT film could directly contact the vacuum bagging film. Figure 6.6 shows modified vacuum bag scheme for curing via aligned CNT film heater and picture of prepared vacuum bag. Electrodes were extended through vacuum tape to connect to the power supply.

6.2.5 System Setup and Data Acquisition during Curing

Prepared vacuum bag was placed on a glass plate under ambient environment. That is, the laminate was cured without any thermal insulations, and affected by natural convection on the surface of vacuum bag. In case of autoclave and oven curing, the inside of heating chamber is thermally isolated from the outside world. Therefore, this vacuum bag setting can be called 'worst case scenario' of curing via CNT film heater. If the condition without thermal isolation considerably affects thermal distribution of CNT film heater and laminate, addition of insulation can be a simple resolution later. Also, such experimental conditions could provide the information where most heat losses occur in the vacuum bag.
Cure Cycle B in Table 6.3 is identical to the cure cycle of the baseline that was chosen for this specimen. Since aligned CNT film heater on the laminate was heated by Joule heating, DC power supply (~30V) was directly connected to two electrodes of CNT film heater. By manually adjusting the input voltage, the average temperature of CNT film heater followed the selected cure cycle.

In order to acquire thermal distributions and changes in electrical properties of CNT film heater during curing, a measurement scheme was devised. As illustrated in Figure 6.7, input voltage and current were recorded using a digital multimeter (Hewlett Packard 34401A) with alligator clips every 300ms. Thermography was taken using a thermal camera (PCE-
TC 3 from PCE Group, 160 × 120 pixels with temperature range or -10 to 250°C and 0.15°C resolution) every 6 seconds, and then the average temperature of the CNT film heater was calculated from the temperature data in the area between the two parallel electrodes.

![Figure 6.7: Schematic of data acquisition during curing.](image)

### 6.2.6 Differential Scanning Calorimetry Measurements

To conduct DSC analysis for obtaining degree of cure, each layer of the cured composite was delaminated. In order to analyze spatial degree of cure, three layers among 16 layers were selected as the first study. Because the top ply (ply 1) is fully integrated with the CNT network heater and surfacing film after laminate manufacture, DSC measurements were conducted on the 2nd, 7th, and 15th ply of the laminate. In addition, three regions defined as left, center and right area were used to analyze the in-plane degree of cure as shown in Figure 6.8. Therefore, degree of cure of 9 different spatial regions was evaluated.

The DSC analysis was conducted with a TA Instruments DISCOVERY DSC. The amount of cured composite (4 – 8mg) was cut and put into a Tzero Aluminum pan for each region, and then analyzed. The measurements were performed under a constant flow of nitrogen of 50mL/min as purge gas. The temperature of the DSC cell was ramped up from 40°C to 300°C at 4°C/min. For calculation of degree of cure, uncured prepreg was also included in the measurements, and the DSC data were analyzed via a provided software of TA instruments.
Figure 6.8: Degree of cure spatial analysis (a) Manufactured composite and (b) Illustration of selected three layers and location of left, center, and right region for analysis. Dashed square is directly heated area.
6.3 Results and Discussion

Thermal distribution and electrical properties were measured and recorded during the whole process of curing. This section presents analysis of these data.

6.3.1 Thermal History and Change in Electrical Property during Curing

As presented in Figure 6.9, temperature of CNT film heater was manually controlled to follow the required cure cycle, and the aligned CNT film showed stable Joule heating during curing cycle. Since it was reported that the MWCNT network breakdown occurred over 500°C under ambient conditions, Joule heating of the aligned CNT film for this application is expected to be enough as long as other bagging materials endure the cure temperature.

![Temperature vs. Time Graph](image)

Figure 6.9: Temperature of CNT film heater during curing. CNT film heater well followed desired cure cycle.

Figure 6.10 presents thermography of the aligned CNT film heater at the average temperature of 121°C. Since electrical current flowed in the area between the two electrodes,
Figure 6.10: Thermography of aligned CNT film heater at the average temperature of 121°C.

Joule heating occurred in that area. Since CNT film heater was not thermally insulated, there were temperature gradients at four edges of CNT heater. Also, because the average temperature of the sample was obtained from the area of the dashed box in Figure 6.8, temperature at the center of the heater was higher than the average temperature.

Electrical properties during curing are presented in Figure 6.11. These changes are evaluated by dividing into five stages as follows:

**Stage 1:** Temperature ramp up from room temperature to 121°C in this stage. Resistance first decreased from ~13Ω to ~8.9Ω, and then increased to ~9.7Ω. Power increased from 0W to ~15.8W. Resistance of CNT film decreased because of negative thermal coefficient of resistance of aligned CNT network. (See Section 5.5.3 for details of negative thermal coefficient of resistance.) However, resistance started to increase around 100°C even though temperature still ramped up. At this temperature, polymer from the surfacing film is expected to flow into the aligned CNT network by capillarity-driven wetting.\(^{79}\) In addition, such liquid polymer infiltration causes separation of bundle-bundle junctions.\(^{80}\) Therefore, it is hypothesized that the resistance increases because junction resistance, which is dominant for aligned CNT networks, is increased through separation...
of the junction.

**Stage 2**: Temperature was maintained at 121°C in this stage. Resistance increased from \(\sim 9.7\Omega\) to \(\sim 13.8\Omega\). The infiltration of surfacing film polymer into the aligned CNT network caused a continuous increase in resistance. Power decreased from \(\sim 15.8\text{W}\) to \(\sim 14.7\text{W}\). Increase of resistance resulted in decrease of power, and jagged shape in power value resulted from input voltage increase for compensating this temperature decrease.

**Stage 3**: Temperature ramps from 121°C to 177°C in this stage. Resistance decreased from \(\sim 13.8\Omega\) to \(\sim 13.2\Omega\). Power increased from \(\sim 14.7\text{W}\) to \(\sim 27.5\text{W}\). The behavior of resistance change is similar to that of Stage 1. Perhaps, polymer infiltration into the CNT network reduced the decreasing rate of resistance.

**Stage 4**: Temperature was maintained at 177°C in this stage. Resistance increased from \(\sim 13.2\Omega\) to \(\sim 15.4\Omega\). Power decreased from \(\sim 27.5\text{W}\) to \(\sim 24.4\text{W}\). The explanation of the behavior of resistance and power could be similar to that of Stage 2.

**Stage 5**: This stage is ramp down of temperature after curing. Resistance increased

---

Figure 6.11: Change in resistance and power of CNT film heater during curing.
from \( \sim 15.4\Omega \) to \( \sim 17.8\Omega \) because of the aligned CNT network’s negative thermal coefficient of resistance.

The maximum power consumption was 27.5W to cure 40mm × 50mm 16-ply unidirectional laminate. With resistive heating on the surface of laminate, energy consumption is directly related with the dimension of components. By using direct heating (conduction), unnecessary energy consumption such as energy for heating up the fixed volume of the whole chamber of autoclave or oven is removed.

### 6.3.2 Spatial Analysis of Degree of Cure

To evaluate whether a laminate can be cured via resistive heating of the CNT film heater, degree of cure analysis was conducted (See Appendix A for all DSC graphs). As presented in Figure 6.12, degree of cure decreases through composite thickness. That is, the region closest to CNT heater shows higher degree of cure. Since heat generated in the CNT film is transferred through conduction from the 1st layer to the 16th layer, a temperature gradient is formed, where the 16th layer is expected to have the lowest temperature. The final extent of degree of cure \( \alpha_{\text{max}} \) is limited by the cure temperature as follows:

\[
\alpha_{\text{max}} = \frac{1}{\alpha} \left( \frac{1}{T_0} - \frac{1}{T_{\text{cure}}} \right) 
\]

where \( \alpha \) is a fitting parameter, \( T_0 \) is the theoretical temperature where the cure reaction does not proceed \( (\alpha_{\text{max}} = 0) \), and \( T_{\text{cure}} \) is the cure temperature.\(^{[81]}\) See Figure 6.12 for experimental data indicating that the final extent of degree of cure is limited by cure temperature.

As presented in Equation 6.2 and Figure 6.12, the final extent of degree of cure increases as cure temperature increases. Therefore, the degree of cure for this specimen follows thermal distribution through thickness in that it increases as the analyzed region becomes closer to the CNT film heater. In addition, the degree of cure follows in-plane thermal distribution. The values along the x-axis in Figure 6.13 show the temperature of the CNT film heater at each region, and the temperature of the 2nd layer is expected to be similar to that of the CNT film heater. (See Figure 6.14 for details of left, center, and right region.) Then, the right region of the 2nd layer \( (T_{\text{cure}} = 176.8^\circ \text{C}) \) has 0.925 of degree of cure. The
baseline specimen ($T_{\text{cure}} = 177^\circ \text{C}$) which was cured in oven has 0.928 degree of cure. Also, the left region of the 2\textsuperscript{nd} layer ($T_{\text{cure}} = 189.5^\circ \text{C}$) and the right region of the 2\textsuperscript{nd} layer ($T_{\text{cure}} = 203.5^\circ \text{C}$) shows 0.98 and 0.987 of degree of cure, respectively. Therefore, it is concluded that degree of cure of composite from CNT film heater shows good agreement with the spatial thermal profiles. Overall, even though this specimen was cured in the worst case scenario (one-sided heater and no insulation), enough degree of cure was obtained as presented in Figure 6.13.

If aligned CNT film heater is manufactured to have a uniform thermal distribution, uniform extent of degree of cure throughout the whole composite can be obtained. Here, ununiformity of thermal distribution of CNT film heater is expected, and can be attributed primarily to non-insulated boundary conditions. Therefore, in order to confirm whether a laminate can be uniformly cured or not, curing experiments with thermal insulation on all boundaries is suggested in future work. Curing a thicker laminate has similar considerations in autoclave or oven curing in that thermal energy for curing transfers through the outer surface of laminate. An additional CNT film heater can be installed on the opposite surface of the laminate to create a symmetric thermal profile, while adjusting the ramp rate may help to reach enough cure temperature inside of the laminate.
Figure 6.13: Histogram of degree of cure on the 2\textsuperscript{nd}, 7\textsuperscript{th}, and 15\textsuperscript{th} layer. Dashed line 0.928 indicates degree of cure of oven-cured specimen. The value 1 of degree of cure indicates fully-cured. The values in box present the average.

Figure 6.14: Thermography of the aligned CNT heater at post cure temperature, and analyzed regions for degree of cure.
Chapter 7

Conclusions and Recommendations

7.1 Contributions of This Work

In this thesis, the possibility of a new composite manufacturing process via resistive heating of the aligned CNT film was studied.

First, the electrical properties and thermal behavior of the aligned CNT film were explored as the heating element. While the intrinsic electrical properties of isolated CNTs were extensively studied both experimentally and theoretically,\cite{31,82,83} previous studies on the electrical properties of networks with and without CNT alignment were very limited, leading our understanding of the impact of morphology on electron transport in such CNT architectures to remain incomplete. Recent work on A-CNT networks made via roller densification of vertically aligned CNT arrays showed that the sheet resistance is directly proportional to the density of the network,\cite{84} and mildly anisotropic in nature.\cite{70,72} However, an important factor that was largely absent from these studies was CNT length. Previous studies indicated that A-CNT arrays comprised of longer CNTs have significantly higher resistances,\cite{72} but these reports do not fully describe the underlying physics. In this thesis, the scaling of the sheet resistance of A-CNT networks as a function of the CNT length was quantified, and sheet resistance was observed to be inversely proportional to the CNT length. Also, the sheet resistance was shown to vary as a function of orientation by up to $\sim 50\%$, and the value of the sheet resistance as a function of the angle with respect to the primary CNT alignment direction can be predicted using a simple equation (see
Eq. 5.8). Since Raman spectroscopy indicated that the defect concentration in the CNTs is not a function of their length, and the thermal dependence of the sheet resistance indicated that the activation energy for electron transport via tunneling in the CNT-CNT junctions (≈ 14.2 meV) is independent of both CNT length and orientation, the scaling relationship of the sheet resistance with CNT length is attributed primarily to the CNT junctions in the network morphology.

Second, a new composite manufacturing which is expected to remove the shortcomings of conventional manufacturing methods was attempted. A 40mm × 50mm 16-ply Cycom®5320-1 unidirectional CFRP laminate was cured by installing a characterized aligned CNT film on the top surface of it. In this work, a vacuum bag was set in "the worst case scenario" (one-sided heater and no insulation) in order to evaluate the effect of thermal distribution of the aligned CNT film heater throughout the laminate. After curing the laminate by controlling the electrical current flow in the film, the DSC results were used to determine the degree of cure of the composite. Then, it is concluded that degree of cure is determined by the thermal distribution inside a composite. Also, this composite manufacturing method via resistive heating of the aligned CNT film is expected to be an industrial alternative to using an autoclave or an oven in the future in that enough degree of cure was obtained in spite of testing in the worst case scenario.

7.2 Recommendations for Future Work

This thesis work is the starting point of the research which explore curing CFRPs via resistive heating of an aligned CNT film, and further research is needed to develop this manufacturing technique as an alternative to conventional composite manufacturing methods. Based on the findings in this work, recommendations for future work are presented into four categories as follows:

- **Characterization of the aligned CNT film**
  
The morphology of the aligned CNT film in this work is different from other CNT films manufactured by filtration of suspension. Therefore, with respect to intrinsic
properties of the aligned CNT film, computational simulation of length-dominance will be interesting, and provide the effect of morphology on electrical properties of CNT network. In addition, in order to cure a bigger laminate, a corresponding size of the aligned CNT film is required. However, the size of MWCNT arrays is limited by the inner diameter of quartz tube under the lab synthesis conditions. Even if it is possible to obtain a larger area CNT film, the need for a connection between two CNT films is inevitable in the future to install it on the complex shape of the laminate. Therefore, the connecting method which minimizes the change of thermal distribution of the CNT film heater should be developed.

- **Composite curing with the aligned CNT film**

  First, composite curing with thermal insulation on the surface of vacuum bagging will be conducted, and then the effect of thermal insulation should be established. Since thermal insulation on the outer surfaces obstructs one’s ability to obtain the thermal distribution of the aligned CNT film heater and laminate during curing, alternatives to a thermal camera should be introduced. In addition, it is expected that resistance change of the CNT film heater can be exploited as an indicator of the curing situation. The establishment of the relationship between electrical properties of the aligned CNT film and the extent of the degree of cure will be useful.

- **Characterization of the aligned CNT network after curing**

  The usage of the aligned CNT film as the heating element can impart additional functionality such as a conductive layer for lightning strikes, a de-icing component on aerosurface, and electro-thermal self-health monitoring system once curing is complete. Since the aligned CNT film absorbs the resin of the surfacing film during curing, the aligned CNT film may form a different morphology with resin. Considering it as a composite enhancer, electrical properties and thermal behavior of the aligned CNT film should be re-evaluated.

- **Quality of manufactured composites**

  The ultimate goal of this manufacturing process is to obtain composites which show
comparable mechanical properties to that of composites manufactured by conventional methods. Void content of manufactured composite should be first evaluated in that a void is one of the most important factors in determining mechanical properties of a composite. In addition, actual mechanical tests such as tensile, compression, and in-plane shear, among others, should be carried-out in order to confirm the quality of manufactured composites.
Appendix A

Supplementary Information for Differential Scanning Calorimetry Analysis

DSC graphs of the analyzed regions for obtaining degree of cure are given here. The Tzero Aluminum pan was used for a specimen container. The measurements were performed under a constant flow of nitrogen of 50mL/min as purge gas. The temperature of the DSC cell was ramped up from 40°C to 300°C at 4°C/min.
Figure A.1: DSC graph of the left region in the 2nd layer.

Figure A.2: DSC graph of the center region in the 2nd layer.
Figure A.3: DSC graph of the right region in the 2\textsuperscript{nd} layer.

Figure A.4: DSC graph of the left region in the 7\textsuperscript{th} layer.
Figure A.5: DSC graph of the center region in the 7th layer.

Figure A.6: DSC graph of the right region in the 7th layer.
Figure A.7: DSC graph of the left region in the 15th layer.

Figure A.8: DSC graph of the center region in the 15th layer.
Figure A.9: DSC graph of the right region in the 15th layer.
References


