SCALABLE FABRICATION AND CHARACTERIZATION OF MAGNETICALLY
ALIGNED AND DIAZOTIZED CNT-EPoxy COMPOSITES FOR INTERLAMINAR
REINFORCEMENT OF AEROSPACE COMPOSITES

A Thesis in
Aerospace Engineering
by
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ABSTRACT

Interlaminar integration of carbon nanotubes (CNTs) of high aspect ratio and high specific properties is a promising option to improve through-thickness mechanical properties, such as fracture toughness and fatigue life, of fiber-reinforced plastics (FRPs) without the adverse effects of degrading in-plane properties which results from stitching, z-pinning, and 3D weaving. The current challenges of CNT integration into FRPs include CNT dispersion and organization within matrices, and scalable process to infiltrate CNTs and carbon preforms. In this work, these challenges were addressed with the following two objectives, focusing on nanocomposites consisting of an aero-grade epoxy and CNTs for simplicity. The first objective was to develop a process to disperse CNTs and align CNTs in an epoxy matrix in a scalable manner, and the second objective was to evaluate the effectiveness of the above process and resulting composites on toughness reinforcement. To achieve these objectives, two research tasks were set. First, corresponding to the first objective, the process to functionalize and magnetically assemble CNTs in an epoxy matrix was scaled up. CNTs were grown using the chemical vapor deposition (CVD) process with increased hydrogen flow to produce multi-walled CNTs of higher quality with a faster growth rate. The grown CNTs were magnetized by coating them with a thin nickel layer, and then surface functionalized via diazotization. These magnetized and functionalized CNTs were processed up to 37 mg per process. The CNTs were mixed with an epoxy matrix (Epon 862 and Epikure W hardener) to form polymer nanocomposites of varying CNT volume fraction (0.1 vol.% and 0.5 vol.%) and organization (randomly oriented, magnetically aligned with 180 G and 300 G). Second, corresponding to the second objective, the fabricated CNT-epoxy composites were characterized for their fracture toughness using three-point bending test. Fracture toughness did not increase linearly with increasing CNT volume fraction for all aligned CNT-epoxy PNCs. When
aligned with 180 G, the fracture toughness was observed to increase 37.08% with 0.1 vol.% and to 71.66% with 0.5 vol.%. However, this trend of increasing toughness with higher CNT fraction was not seen with the CNT-epoxy PNCs aligned with 300 G: 47.15% improvement with 0.1 vol.%, and 20.49% with 0.5 vol.%. The higher magnetic field strength of 300 G could have caused agglomeration of CNTs with high volume fraction. Fracture toughness values did not show many differences when integrated CNTs (0.1 vol%) are randomly oriented or aligned (180 and 300 G); the highest improvement of 60.30% was observed with the randomly oriented CNT-epoxy sample. On the other hand, with 0.5 vol% of CNTs, the sample prepared with 180 G exhibited increased toughness, while the sample prepared with 300 G exhibited decreased toughness. This trend can again be attributed to CNT agglomeration with higher magnetic field of 300 G. Highest fracture toughness improvement of 71.66% was achieved with the sample of 0.5 vol.% CNTs aligned with 180 G, which is higher than that those achieved in the past (12.50% with 3 vol.%). When the fracture surfaces were inspected, CNT bridging and breakage were observed as major toughening mechanisms through SEM inspection of PNC fracture surface. Meanwhile, more detailed inspection about CNT morphology change with varying CNT fraction and magnetic field strength is necessary to further study the relationship between the process, CNT agglomeration and alignment, and toughening effectiveness. The fabrication technology to produce CNT-epoxy composites with magnetically aligned CNTs and resulting toughened CNT-epoxy will be useful when in the next step to integrate CNTs into FRPs.
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Chapter 1

Introduction

1.1. Nanocomposites in the aerospace field

Advanced composites have been used in multiple industries such as aerospace, automotive, and maritime. Polymer materials are reinforced with elements such as fibers and particles, leading to multifunctional properties. When carbon fibers are used as reinforcement, because of their high strength, high stiffness, and conductivity, carbon fiber reinforced plastics (CFRPs) achieve high specific stiffness (~100 GPa/(Mg/m^3)), high specific strength (~1000 MPa/(Mg/m^3)), low electrical resistivity (~1 Ω.cm), and moderate thermal conductivity (~1 W/m.K) in the in-plane direction [1]. Meanwhile, the through-thickness properties of the CFRPs are not as advanced, resulting in low electrical and thermal conductivities [2]. Due to the elastic property mismatch between the fibers and the matrix, stress concentrations may occur in the interlaminar boundary resulting in delamination and decreased fatigue life [3], which is disadvantageous in the aerospace industry. While weight is saved by using CFRPs, additional aluminum mesh layers need to be integrated as protection against lightning strike and electromagnetic interference [4].

Various methods to reinforce the through-thickness of composites using carbon fibers have been developed in the past years. These methods include, but are not limited to, stitching, z-pinning, and 3D weaving [3,5,6]. Those micro-fiber reinforcements improved through-thickness mechanical properties such as toughness (15-fold by stitching [7]) and compression strength (50% by stitching [8]), but reduced in-plane mechanical properties, such as strength and modulus [5,9]. During
integration of such micro-fiber reinforcement in the through-thickness direction, the integrated micro-fibers have damaged and/or broken fibers within CFRPs, and created resin-rich areas and residual stresses [5]. Unlike micro-fiber reinforcement, nano-sized CNT integration results in the improvement of mechanical properties of FRPs without compromising the in-plane properties.

In the past few decades, CNTs have been implemented into CFRPs to reinforce their mechanical and multi-functional properties. CNTs have advanced properties, such as stiffness (75 - 350 GPa/(g/cm³)) [10], strength (1036 - 2300 MPa/(g/cm³)) [10], thermal conductivity (6,600 W/(m.K)) [11], and electrical conductivity (1000 Ω.m) [11]. In past studies, with small CNT introduction, fracture toughness increased (22-32% [2] with 0.1 wt.%, up to 46.77% with 0.1 wt.%, and 41% with 2.5 wt.% [12]), fatigue life increased (115% with 1 vol.% [5]), and hardness also increased (225% with 0.5% wt.% [13]), when compared with the baseline CFRP composites without CNTs. As opposed to micro-fiber reinforcement, CNT reinforcement causes less damage to micro-structures, possesses higher crystallinity, and has larger surface-to-volume ratio, thus providing larger surface area for the same filler content. CNT reinforcement of through-thickness does not affect the in-plane properties of FRPs, unlike micro-fiber reinforcement. Electrical conductivity was also shown to increase by up to 300% in the in-plane direction for a CFRP made with CNT-grown CF preforms [5]. Methods of integrating CNTs into CFRPs have been researched in the past, including infiltration of CF preforms with CNT-mixed epoxy, epoxy infiltration of CNT-grown CF preforms, and epoxy infiltration of CF preforms and CNT preforms prepared separately. These methods will be discussed in more detail in Chapter 2.

1.2. Challenges

Current challenges in integrating CNTs to polymer matrices include effective CNT dispersion, process scalability, and controlling CNT assembly and orientation within the matrix.
First, CNT dispersion is a topic of high research importance since CNTs tend to agglomerate, which hinders reinforcement capabilities [14–18]. Functionalizing CNTs to achieve better bonding between the nanotubes and the polymer matrix is crucial to ensure maximum reinforcement and better dispersion [19]. Second, the process from CNT synthesis to nanocomposite fabrication needs to be scalable to be financially viable for companies or individuals to integrate this type of composite reinforcement into their products and projects. Third, control of CNT alignment and assembly characteristics within a polymer matrix is still a challenge. Aligning CNTs within the matrix can provide better reinforcement and more control of dispersion degree, as will be discussed later.

1.3. Objectives

In this work, the objectives are 1) to establish a scaled-up process of synthesizing and functionalizing CNTs, and fabricating CNT-epoxy composites with dispersed and controlled CNT organization using magnetic fields, and 2) to evaluate the effectiveness of CNT integration, with varying CNT fraction and organization, on fracture toughness reinforcement. The results and knowledge obtained from this work will be helpful to integrate CNTs into CFRPs for through-thickness mechanical property improvement, as will be discussed in Section 2.3.
Chapter 2

Background: CNT Reinforcement of CFRPs

In this chapter, first, the three main methods of CNT integration to CFRPs are discussed. The corresponding mechanical property reinforcements achieved by various authors per each method are discussed. Second, the effects of CNT organization on the fracture toughness reinforcement of CNT-epoxy PNCs are discussed. Third, the challenges of effective CNT integration will be discussed: CNT dispersion and precise organization. As solutions to these challenges, surface functionalization methods and CNT assembly methods in polymer matrices will be reviewed.

2.1. CNT integration to CFRPs

The methods to integrate CNTs have been observed to largely affect the dispersion and distribution of CNTs within the composites and the resulting mechanical property improvements. In this section, three methods are discussed: 1) infiltration of CF preforms with CNT-mixed epoxy, 2) epoxy infiltration of CNT-grown CF preforms, and 3) epoxy infiltration of CF preforms and CNT preforms prepared separately.
2.1.1. Infiltration of CF preforms with CNT-mixed epoxy

This method consists of mixing the CNTs with the resin, which is followed by infiltration into the fibers. One of the limitations of this method is a lower CNT concentration (< 1 wt.%); with increasing CNT fraction, the viscosity of the CNT-resin mixture increases and makes it more challenging to infiltrate the fibers. Another limitation of this method is that CNTs will be randomly oriented in the composite because no mechanisms exist to control CNT alignment degree. Epoxy mixed with CNTs has the higher viscosity than the pristine epoxy, and its infiltration between short inter-fiber distance (~ 1.6 μm at 60% fiber vol.) [20] can be a challenge. Song [20] has shown that due to these limitations, the mechanical properties increase were small (1.92% in flexural modulus, 1.38% in flexural strength, and 8.26% in impact strength).

2.1.2. Epoxy infiltration of CNT-grown CF preforms

Introduction of CNTs into FRPs can be done by epoxy infiltration of CNT-grown CF preforms, which is also called the “fuzzy fibers” method. With this method, CNTs are placed on the fibers through electrophoretic deposition (EPD) [21], chemical grafting, CVD [22], or graphitic structures by design (GSD) [2]: resin infiltration of such CNT-grown CF preforms achieve larger CNT vol.%. Using electrophoretic deposition, CNTs can be homogeneously coated onto CF preforms as charged CNTs migrate in a solution under the influence of an electric field [21]. When CNTs are integrated into a CF preform using EPD, mechanical property improvement was observed: 46.5% improvement of tensile strength, 57.5% improvement of modulus, and 53.8% improvement of through-thickness electrical conductivity [23].
Using the CVD process, CNTs (~100 μm length) were grown on alumina fiber woven cloth [22]. The FRP with in situ grown CNTs exhibited a 31% improvement in fracture toughness compared to the non-reinforced baseline sample [22], while their results are preliminary. The drawback of this CVD process is the required high temperature (700-1100 °C [2]), potentially damaging carbon fibers without property coatings and resulting in the in-plane property degradation (~46% for T650 CF tensile strength at 800 °C) [24].

Using the GSD process, CNTs were grown in various shapes and morphologies using pre-deposited catalyst templates [2]. Unlike the CVD process, GSD utilizes relatively lower temperatures (450-550 °C) and is performed inside a quartz tube containing the carbon fiber with the pre-deposited catalyst. CNTs integrated by GSD increased both in-plane and out-of-plane mechanical properties of CFRPs [2]. On top of carbon fiber fabrics, the authors [2] grew multi-walled carbon nanotubes (MWCNTs) using the GSD process in a uniform and checkered pattern. Integration of the CNTs grown in a checked pattern provided 32% enhancement in fracture toughness, while the CNTs that were uniformly grown demonstrated a 22% enhancement in fracture toughness when compared with a pristine CFRP sample [2]. The crack propagation distance was observed as larger when CNTs are grown in the checkered pattern due to mechanical interlocking of the matrix and the fibers. When CNTs are grown uniformly, the crack propagation more likely occurred at locations close to the CNT-matrix boundaries, where fewer obstacles exist to deflect the crack.

2.1.3. Epoxy infiltration of CF preforms and CNT preforms prepared separately

Integrating CNTs into FRPs can be done by preparing CF preforms and CNT preforms separately, and then infiltrating both at the same time with epoxy to form the composite. With this method, CNT distribution and alignment within the composite can be controlled.
An example of this method is “nanostitching” [22,25]; vertically aligned CNT forests grown using the CVD technique were transferred to carbon fiber prepreg in between the middle location of a 24-ply composite, where the CNTs had approximately 1% volume fraction and their heights were approximately 20 μm [25]. Mode I DCB tests resulted in a minimum 10% increase in the interlaminar fracture toughness [25]. In another work, horizontally aligned CNTs have been prepared as sheets (~50 mm wide) and transferred to glass fiber prepregs to align CNTs with the glass fibers [6]. To test fracture toughness reinforcement, a total of five 24-ply symmetric laminates were created: baseline (no CNTs); 2-layer parallel; 2-layer perpendicular; 4-layer perpendicular; 8-layer perpendicular; where the number corresponds to the layers of CNT sheets placed at the midplane interface between the 12th and 13th plies, either parallel or perpendicular to the fiber “warp” direction [6]. Mode I fracture toughness was measured about these five laminates using the double cantilever beam (DCB) test. The 2-layer parallel sample showed a 46.77% increase in fracture toughness when compared with the baseline sample. The 2-layer perpendicular sample showed a 20.97% increase in fracture toughness [6]. The samples with 4 and 8 layers of CNTs performed worse than the baseline sample in the Mode I test. The authors concluded that those thicker layers of CNT reinforcement allowed the crack to propagate easily through the midplane due to excess CNT content and resin-rich areas without the apparent presence of glass fibers.

Table 2-1: Improvement of mechanical properties of CFRPs by CNT integration.

<table>
<thead>
<tr>
<th>Authors/Ref</th>
<th>Method/CNT organization/location</th>
<th>CNT wt.%</th>
<th>Fracture toughness improvement (%)</th>
<th>Modulus improvement (%)</th>
<th>Strength improvement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Infiltration of CF preforms with CNT-mixed epoxy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Song [20]</td>
<td>CNT-mixed epoxy / Randomly oriented</td>
<td>3.0</td>
<td>-</td>
<td>1.92</td>
<td>1.38</td>
</tr>
<tr>
<td><strong>Epoxy infiltration of CNT-grown CF preforms</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wu et al. [23]</td>
<td>EPD / Randomly oriented</td>
<td>0.3</td>
<td>-</td>
<td>57.5</td>
<td>46.5</td>
</tr>
<tr>
<td>Hart et al. [22]</td>
<td>CVD / Randomly oriented</td>
<td>1.0 (vol.%)</td>
<td>31.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Boroujeni et al. [2]</td>
<td>GSD CNT patches / Randomly oriented</td>
<td>unknown</td>
<td>32.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Epoxy infiltration of CF preforms and CNT preforms prepared separately</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bhanushali and Bradford [6]</td>
<td>CNT sheet / Horizontally aligned</td>
<td>0.1 (two-layer cases)</td>
<td>46.77 (two-layer parallel)</td>
<td>3 (two-layer perpendicular)</td>
<td>0.7 (two-layer perpendicular)</td>
</tr>
<tr>
<td>Wardle et al. [25]</td>
<td>“Nanostitching” / Vertically aligned</td>
<td>1.0 (vol.%)</td>
<td>10.00</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
As described in this section, integrating CNTs into CFRPs can be done using three methods; each method has its advantages and disadvantages, and leads to varying improvements of mechanical and multifunctional properties. However, studying FRPs reinforced with CNTs is a complex task, therefore analyzing a simpler system of CNT-epoxy nanocomposite and corresponding reinforcement degree is preferred. The effects of the CNT dispersion and distribution on mechanical reinforcement of PNCs have been intensively studied in the past. In a theoretical model by De Villoria and Miravete [26], good CNT dispersion within an epoxy matrix, was observed to highly contribute to mechanical property reinforcement of PNCs. The volume fraction of carbon nanotubes in the matrix influences the property reinforcement significantly, however, property reinforcement has been experimentally observed to plateau and decrease at higher CNT concentrations [14–18]. The effects of CNT organization, in terms of agglomeration and assembly, and comparisons with previous work, are discussed in detail in Chapter 5 (see Table 5-2). Methods to improve CNT dispersion and organization within a polymer matrix, which are responsible for mechanical property reinforcement, including functionalization types and different assembly methods, will be addressed in the next section.

2.2. Improvement of CNT dispersion and organization

2.2.1. Functionalization

The mechanical reinforcement of epoxy matrices by CNTs is currently limited by increasing CNT agglomeration with increasing CNT fraction, and recent studies have tackled these challenges through CNT surface functionalization. The main objective of the functionalization process is to mitigate the hydrophobic nature of the CNTs, and to improve the interfacial bonding
between the CNTs and the polymer matrix, by attaching functional groups to the CNT surfaces. Two types of functionalization procedures exist: non-covalent and covalent [19,27].

The non-covalent functionalization process is done by polymer wrapping or surfactants. In the case of polymer wrapping, CNTs’ wettability is increased by wrapping water-soluble polymers on CNTs [19]; with the surfactants process, the hydrophilic portion of the functional groups interact with the polymer matrix, while the hydrophobic portion attaches to the carbon nanotubes through van der Waals forces and others [19]. Covalent functionalization, on the other hand, is done by surface-initiated polymerization, or grafting [27]. Types of covalent functionalization include oxidation, carboxyl functionalization, fluorination, amine functionalization, and diazotization [19]. Covalent functionalization was selected in this work because its interfacial bonding strength between the CNTs, functional groups, and the polymer matrix was observed to be stronger than that of non-covalent functionalization [19,28]. For example, a MWCNT-reinforced composite using non-covalent functionalization with poly(vinylcarbazole) resulted in a 6.3% increase in tensile strength, whereas a covalently functionalized MWCNT-reinforced composite with hyperbranched poly (trimellitic anhydride-diethylene glycol) led to an 18.9% increase in tensile strength [29].

This work used diazotization based on the previous work by Wang et al. [28], where diazotization increased bonding between single-walled carbon nanotubes (SWCNTs) and the curing agent EPI-W combined with EPON 862 resin, the same system that was used in this work. The authors reported a 24.6% improvement in elastic modulus of the functionalized CNT-epoxy composite via diazotization when compared with the baseline pristine CNT-epoxy sample [28].
2.2.2. CNT organization

The mechanical reinforcement of epoxy matrices by CNTs is also currently limited by poor control of CNT assembly, and recent studies have tackled these challenges through CNT organization by mechanical shearing and external field application. With shear mixing, CNTs were observed to reduce agglomeration, leading to better dispersion within the polymer matrix, but controlling the alignment degree with this method is not possible since CNTs are randomly aligned after mixing [30]. CNTs were also aligned within the polymer matrix using an electric field, gas flow, or magnetic field. Alignment using an electric field can lead to different types of CNT assembly; CNTs migrate towards an electrode when applied with a DC field, while CNTs align with the electric field lines when applied with an AC field [19]. CNTs, in a solution, can be aligned using gas flow, as the solution dries [19]. CNTs can be also aligned using a magnetic field. Assembling CNTs with a magnetic field allows for three-dimensional control of the alignment, is contactless, and is a fast and scalable method to assemble CNTs in a polymer matrix [19], and thus was used in this work. CNTs still needed to be magnetized by nickel coating; however, magnetic assembly does not have disadvantages presented by the other methods: electric fields can lead to migration, requires high field strength, and high frequency [19], and gas flow does not work in polymer matrices to align the CNTs due to their high viscosity [19].

In summary, current methods of CNT integration to CFRPs are infiltration of CF preforms with CNT-mixed epoxy, epoxy infiltration of CNT-grown CF preforms, and epoxy infiltration of CF preforms and CNT preforms prepared separately. Despite the ongoing efforts, dispersing and precisely aligning CNTs in a scalable manner within a polymer matrix remain a challenge. The work in this thesis was motivated by these challenges, therefore it was focused on process scalability and magnetic alignment of CNTs within the epoxy matrix to fabricate and assess fracture toughness reinforcement of samples at varying conditions.
Chapter 3

Approach

The goal of this thesis work is to develop a scalable process to fabricate CNT-epoxy composites, including CNT synthesis, dispersion, and magnetic alignment within an epoxy matrix. While CNTs have been integrated into a polymer matrix by multiple researchers (see Chapters 1 and 2), the current methods of integrating CNTs in a polymer matrix are limited mainly due to the difficulty of organizing the CNTs in the matrix. By controlling CNT orientation and distribution inside the matrix, improved mechanical property reinforcement is expected.

To achieve the objectives stated in Chapter 1, two research tasks were set: 1) to scale up the process to functionalize and magnetically assemble CNTs in an aero-grade epoxy, and 2) to characterize the fracture toughness of the fabricated CNT-epoxy composites and correlate the data with the CNT structures. The first research task directly corresponds with the first objective, and the second research task directly corresponds with the second objective.

By conducting research task 1, the goal is to increase the amount of CNTs to be prepared and integrated into polymer composites by up to 37 mg per functionalization process. CNTs will be synthesized by chemical vapor deposition, magnetized by nickel coating (~80 nm), surface-treated by diazotization for their strong covalent bonding with the selected epoxy matrix system (Epon 862 resin and Epikure W hardener), as explained in Chapter 2, and magnetically assembled within the epoxy for non-contact and controlled organization. Constant magnetic fields were applied through a Helmholtz coil based on the previous work [19,31]. Finally, the CNTs are characterized using various techniques including inspection using optical microscope, SEM, Raman spectroscopy, and TEM. In this work, a parametric study about CVD growth and scaling up the functionalization process is presented in the following chapters. Sizable, aligned CNT-epoxy
nanocomposites (30.8 mm length, 7 mm width, and 3.5 mm thickness) were fabricated and characterized about their fracture toughness using the three-point bend test; the toughening effect of CNTs with varying fractions (0.1 vol.% and 0.5 vol.%) and alignment degree (no field, and application of 180 G and 300 G) were evaluated.

By conducting research task 2, the goal is to understand the effects of CNT volume fraction and organization within the epoxy matrix on the fracture toughness of CNT-epoxy composites. The fracture toughness was measured using a macro-scale 3-point bend test following the ASTM 5045 standard. Raman spectroscopy was conducted to evaluate the CNT alignment degree on the PNC samples, SEM used to assess the fracture surface, and optical microscope to assess crack propagation on the surfaces. The fracture toughness data and the CNT alignment degree will be compared for the structure-property relationship study. The PNC samples produced have different volume fractions of CNTs, including a baseline sample with no CNTs, 0.1%, 0.5%, and 1%. In addition to fabricating samples with different volume fractions of CNTs, they were also made using different magnetic field magnitudes, including no field for randomly oriented CNTs, 180 G, and 300 G. The reason why those magnetic field values were chosen is based on the capabilities of the Helmholtz Coil (HHC) system utilized to magnetically align the CNTs during part of the curing process. The coil is limited to 300 G on the +X-axis, which was used for the fabrication of all samples presented in this thesis. Since the future work is related to producing vertically aligned CNTs, and the maximum magnetic field on the Z-axis for the HHC system is 180 G, that was also chosen to see if there is an actual difference in the resulting mechanical properties when using the lower 180 G field and the higher 300 G field.

This thesis work provides knowledge and technology to enhance an epoxy matrix reinforced with aligned, high-quality CNTs, with controlled alignment and less agglomeration. Such knowledge and technology will serve as a resource to achieve CNT-integrated CFRPs in the future with improved interlaminar through-thickness mechanical and multi-functional
reinforcement, in the form of a partially cured CNT-epoxy layer, a *nano-prepreg*. Nano-prepregs share characteristics with conventional prepregs, but are thinner, which is essential to be consistent with the CNT reinforcement length between fibers (20 - 50 μm). After fabricating the nano-prepregs, they would be integrated between dry CF layers, forming *semi-prepregs* [32,33], which would then be infiltrated with the B-staged epoxy present in the nano-prepregs during a vacuum bag only (VBO) process (see Figure 3-1, created by lab member Arya Roessler). Throughout the nano-prepreg fabrication and composite curing process, a magnetic field would be applied to ensure proper CNT alignment, thus providing the maximum reinforcement capability possible.

![Figure 3-1: Tentative OOA setup with nano-prepregs. Created by Arya Roessler.](image-url)
Chapter 4

Scalable Fabrication of Epoxy Composites with Aligned and Dispersed CNTs

In this chapter, four steps of fabricating a CNT-epoxy composite in a scalable manner are presented. The first step is consistent and scalable growth of CNTs to the desired length using chemical vapor deposition. The second step is magnetization of the CNTs with Nickel coating. The third process is surface functionalization of CNTs through diazotization, as discussed in Chapter 3. The fourth process is magnetic alignment of the functionalized, Ni-coated CNTs in the polymer matrix to form the CNT-thermoset composites.

4.1. Chemical Vapor Deposition of CNTs

CNTs in this work were synthesized by CVD. In the CVD process, a substrate, often deposited with a catalyst, was placed inside a chamber, and carbon source, reduction, and inert carrier gases were introduced and decomposed at a high temperature to deposit on the substrate and grow CNTs.

In this work, the CVD system was updated to improve the process scalability and repeatability by increasing the hydrogen gas flow. The CVD system and growth parameters were established by former members of our laboratory, but its capability to grow vertically aligned CNTs was limited in terms of the small areal density (up to ~0.5 mg/cm²), short CNT height (up to 200
µm), slow growth rate (15 min for 200 µm), and repeatability [19,31,34]. This CNT growth limitation was attributed to the small flow of hydrogen set by the mass flow controller (MKS GM50A007101R5M020, max 10 sccm). A different mass flow controller (MKS GM50A013502RLM020, max 500 sccm) was purchased to resolve those issues. In CNT synthesis by CVD, hydrogen is usually introduced to serve as the reduction agent on the catalyst layer [35]. In addition, hydrogen promotes dissociation of physisorbed hydrocarbons, and thus contributes to synthesizing CNTs with lower content of amorphous carbon [35,36], increased length, and tailored diameter [35]. On the other hand, excessive hydrogen in the system can introduce more defects to CNTs by promoting catalytic hydrogenation of carbon and wall surface modification [35]. Below, the effects of hydrogen flow rate on growth and qualities of CNTs is evaluated about our system.

4.1.1. Chemical Vapor Deposition Set-up and Process to Grow CNTs

The CVD growth set-up and process will be described in this section. The substrate was prepared by depositing an alumina diffusion barrier layer (30 nm thickness, 1 Å/s rate) and an iron (Fe) catalyst layer (1 nm thickness, 0.1 Å/s rate) on a silicon (Si) wafer (P-boron <100>, 4-inch diameter, test grade, University Wafer) using an electron beam deposition machine (Kurt J. Lesker AXXIS Multipurpose Physical Vapor Deposition System, base pressure of < 10⁻⁷ torr) [19,31,34]. When the Kurt J. Lesker AXXIS Multipurpose Physical Vapor Deposition System was down, the Temescal FC 2000 system was used as the backup to deposit these diffusion barrier layer and catalyst layer; the target thickness of the catalyst layer needed to be adjusted to 2 nm due to the machine’s calibration error. This substrate with the alumina and Fe layers was cut and placed in the middle of a quartz tube (99 cm length, 3.2 cm diameter) on a quartz boat, placed inside a furnace (Lindberg Blue M HTF55347C Single-zone Tube Furnace) as shown in Figure 4-1; the quartz tube used in this work is larger than the one previously used (107 cm length, 3.5 cm diameter) [19,31,34].
Ethylene (C$_2$H$_4$), hydrogen (H$_2$), and argon (Ar) were introduced to this quartz tube chamber as the carbon source, reduction, and inert carrier gases in this work, respectively. At high temperatures (~750 °C), the ethylene gas breaks down to carbon atoms to interact with the substrate, and the hydrogen gas reduces the Fe catalyst layer to nano-particle forms; the carbon atoms are deposited on the Fe catalyst nanoparticles to vertically grow carbon nanotubes [36]. An exemplary process recipe used in this work for CNT synthesis is shown in Figure 4-2 and in Table 4-1. The first step is to purge all the three gas lines for two minutes by flowing the three gases simultaneously. The second step is to purge the quartz tube by flowing argon for seven minutes. The third and fourth steps consist of ramping up the furnace temperature to 750 °C and stabilizing the temperature for 10 minutes with the hydrogen and argon gas flows; the Fe catalyst layer is reduced to nanoparticles in these steps. The fifth step is growing CNT for 50 seconds by introducing the ethylene gas flow, with the other two gases flowing simultaneously. The last three steps are about terminating the CNT growth and cooling down; the ethylene and hydrogen gasses are shut, while the argon flow was kept but at a reduced rate of 350 sccm. Once the furnace temperature was cooled below 400 °C, the furnace lid is opened for faster cooling rate; the CNT-grown substrate was taken out after the furnace temperature is cooled below 150 °C.
Figure 4-1: CVD set-up: a) schematic of quartz tube and b) digital image.
4.1.2. Parametric Study about CVD Growth of CNTs

A parametric study was conducted to evaluate the effect of growth parameters on CNT growth behaviors. To repeat, the goal is to homogeneously grow CNTs on a substrate with the large area with high areal density, controlled length, and high quality. The as-grown CNT height was aimed as 200 μm to be integrated between the CF prepregs, as previously chosen by [19]; after
functionalization and dispersion, the CNT length is expected to shorten to approximately 20-50 μm, which is comparable with the inter-ply distance [37]. If the CNT length is longer than the inter-ply distance, CNTs can potentially be bent, minimizing reinforcement, or even working as defects [38]. This moderate CNT length also helps dispersion in the epoxy matrix. The flow rates of all the gases and growth time were varied, and the mass, height, areal and volume densities of the grown CNTs are recorded as in Table 4-2. In Table 4-2, the resulted CNTs (sample #) are sorted by increasing hydrogen flow rate, and then by increasing growth time. When CNTs were grown with the recipe previously established by the lab member as a reference point (10 sccm hydrogen, see growth #1 in Table 4-2) [19], no CNT growth was observed; this unsuccessful growth can be attributed to some system change, including the quartz tube size. The CNT mass was calculated as the difference between the mass of the substrate before the CVD process and that of the CNT-grown substrate after the CVD process; measurement was done by microbalance (Precisa EP-225SM-DR, 0.02 mg repeatability), and was repeated three times per sample and averaged. The CNT heights were measured either using optical microscopy (Olympus BX51WI, 5x) or scanning electron microscopy (Thermo Fisher FESEM Verios, ~200,000x immersion mode); measurement was taken at 6 positions and averaged. The CNT diameters were measured using transmission electron microscopy, as will be discussed in Section 4.1.3. The areal and volume densities of CNT bundles, not of the CNTs, were calculated by dividing the measured CNT mass by the substrate area and by the CNT bundle volume (the substrate area × the CNT height); the density of CNTs by themselves will be discussed in Section 4.1.3. The CNT growth rate was calculated by dividing the CNT height with the growth time. Three observations were made based on this parametric study as discussed below.
Table 4-2: The measured and estimated characteristics of grown CNTs per varying CVD growth conditions. The CNT heights were measured either using optical microscope(*) or by SEM (**).

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Ar flow rate (sccm)</th>
<th>C₂H₄ flow rate (sccm)</th>
<th>H₂ flow rate (sccm)</th>
<th>Growth time (min)</th>
<th>Substrate area (cm²)</th>
<th>CNT mass (mg)</th>
<th>CNT height (µm)</th>
<th>CNT diameter (nm)</th>
<th>CNT growth rate (µm/min)</th>
<th>CNT bundle areal density (mg/cm²)</th>
<th>CNT bundle volume density (mg/cm³)</th>
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<tbody>
<tr>
<td>1</td>
<td>650</td>
<td>400</td>
<td>10</td>
<td>15</td>
<td>2.70</td>
<td>0.000</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>325</td>
<td>200</td>
<td>32.5</td>
<td>1</td>
<td>1.20</td>
<td>0.887</td>
<td>215*</td>
<td>8 to 13</td>
<td>198</td>
<td>0.74</td>
<td>37.43</td>
</tr>
<tr>
<td>3</td>
<td>325</td>
<td>200</td>
<td>32.5</td>
<td>3</td>
<td>1.19</td>
<td>1.246</td>
<td>400*</td>
<td>16 to 21</td>
<td>133</td>
<td>1.05</td>
<td>26.18</td>
</tr>
<tr>
<td>4</td>
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<td>32.5</td>
<td>5</td>
<td>2.09</td>
<td>2.117</td>
<td>350*</td>
<td>14 to 22</td>
<td>50</td>
<td>1.01</td>
<td>40.52</td>
</tr>
<tr>
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<td>48.75</td>
<td>1</td>
<td>1.57</td>
<td>1.234</td>
<td>190**</td>
<td>7 to 14</td>
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<td>0.78</td>
<td>41.29</td>
</tr>
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<td>300</td>
<td>65</td>
<td>1</td>
<td>1.80</td>
<td>1.060</td>
<td>180*</td>
<td>-</td>
<td>180</td>
<td>0.59</td>
<td>32.72</td>
</tr>
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<td>7</td>
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<td>400</td>
<td>65</td>
<td>1</td>
<td>0.55</td>
<td>0.420</td>
<td>220*</td>
<td>11 to 16</td>
<td>218</td>
<td>0.76</td>
<td>35.11</td>
</tr>
<tr>
<td>8</td>
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<td>400</td>
<td>65</td>
<td>1</td>
<td>1.58</td>
<td>1.513</td>
<td>230*</td>
<td>-</td>
<td>230</td>
<td>0.96</td>
<td>41.77</td>
</tr>
<tr>
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<td>650</td>
<td>400</td>
<td>65</td>
<td>1</td>
<td>12.81</td>
<td>6.384</td>
<td>185*</td>
<td>-</td>
<td>185</td>
<td>0.50</td>
<td>26.94</td>
</tr>
<tr>
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<td>400</td>
<td>65</td>
<td>1</td>
<td>1.28</td>
<td>0.893</td>
<td>190*</td>
<td>-</td>
<td>190</td>
<td>0.70</td>
<td>36.72</td>
</tr>
<tr>
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<td>400</td>
<td>65</td>
<td>2</td>
<td>0.95</td>
<td>0.274</td>
<td>420*</td>
<td>-</td>
<td>210</td>
<td>0.29</td>
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</tr>
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<td>400</td>
<td>65</td>
<td>5</td>
<td>0.66</td>
<td>0.727</td>
<td>790*</td>
<td>9 to 12</td>
<td>157</td>
<td>1.10</td>
<td>14.03</td>
</tr>
<tr>
<td>13</td>
<td>650</td>
<td>100</td>
<td>65</td>
<td>5</td>
<td>1.28</td>
<td>0.523</td>
<td>700*</td>
<td>-</td>
<td>140</td>
<td>0.41</td>
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<td>650</td>
<td>200</td>
<td>65</td>
<td>5</td>
<td>0.67</td>
<td>0.710</td>
<td>690**</td>
<td>9 to 14</td>
<td>138</td>
<td>1.07</td>
<td>15.47</td>
</tr>
<tr>
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<td>400</td>
<td>65</td>
<td>5</td>
<td>16.28</td>
<td>19.843</td>
<td>785*</td>
<td>-</td>
<td>157</td>
<td>1.22</td>
<td>15.53</td>
</tr>
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<td>16</td>
<td>650</td>
<td>400</td>
<td>65</td>
<td>10</td>
<td>0.95</td>
<td>1.001</td>
<td>720*</td>
<td>-</td>
<td>72</td>
<td>1.06</td>
<td>14.71</td>
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<td>17</td>
<td>650</td>
<td>400</td>
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<td>15</td>
<td>3.00</td>
<td>6.693</td>
<td>670*</td>
<td>-</td>
<td>45</td>
<td>2.23</td>
<td>33.30</td>
</tr>
<tr>
<td>18</td>
<td>650</td>
<td>400</td>
<td>97.5</td>
<td>1</td>
<td>1.29</td>
<td>1.023</td>
<td>280*</td>
<td>-</td>
<td>280</td>
<td>0.79</td>
<td>28.26</td>
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<tr>
<td>19</td>
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<td>400</td>
<td>97.5</td>
<td>0.83</td>
<td>2.16</td>
<td>1.313</td>
<td>215*</td>
<td>-</td>
<td>258</td>
<td>0.61</td>
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<tr>
<td>20</td>
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<td>97.5</td>
<td>0.83</td>
<td>5.67</td>
<td>2.974</td>
<td>145-220**</td>
<td>10 to 23</td>
<td>219</td>
<td>0.52</td>
<td>26.56</td>
</tr>
<tr>
<td>21</td>
<td>650</td>
<td>400</td>
<td>97.5</td>
<td>0.83</td>
<td>12.77</td>
<td>5.760</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>650</td>
<td>400</td>
<td>97.5</td>
<td>0.83</td>
<td>16.69</td>
<td>8.413</td>
<td>-</td>
<td>-</td>
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<tr>
<td>23</td>
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<td>0.83</td>
<td>18.87</td>
<td>7.417</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.39</td>
<td></td>
</tr>
</tbody>
</table>
First, the effects of hydrogen flow rate on the CNT growth rate and the CNT bundle volume density were studied. When the samples were prepared with 650 sccm of Ar, 400 sccm of C\textsubscript{2}H\textsubscript{4}, and 50 seconds or 1 minute of growth time, the CNT growth rate increased with increasing hydrogen flow rate (see Figure 4-3a); this trend was generally observed with the rest of the samples (see Table 4-2). The growth rate is seen to increase in a quartz tube CVD set-up with increasing hydrogen flow rate up to ~100 sccm (11.36% of Ar flow rate); the growth rate decreased when the hydrogen flow is above that value of ~100 sccm [35]. Meanwhile, the CNT bundle volume density decreased with the increasing flow rate (see Figure 4-3b); this trend was also generally observed with the rest of the samples (see Table 4-2). This decreasing volume density can be attributed to deposition of less amorphous carbon and more deposition of crystalline CNTs as will be discussed in Section 4.1.3.

![Figure 4-3](image)

Figure 4-3: The effects of hydrogen flow rate on a) CNT growth rate and b) CNT bundle volume density, when grown with 650 sccm of Ar, 400 sccm of C\textsubscript{2}H\textsubscript{4} and 50 sec or 1 min of growth time.
Second, the capability to control the CNT height by the growth time was confirmed. As shown in Figure 4-4a, the CNT height increases with the increasing growth time, up to 5 min, and increases with the hydrogen flow rate. Beyond 5 mins of growth time, the CNT height plateaued, indicating the CNT height limit. This plateauing of CNT height has been observed in the past and explained by catalyst or growth front’s poisoning and/or by limited diffusion of carbon precursor gas by growing CNT bundles to reach the catalyst layer [36]. Yet, the CNT height range in this work (<1000 µm) is not long enough to hinder CNT growth [39]. When observed with SEM, before the growth reaches a plateau, the CNT bundles lose their alignment over a micrometers thick region near the catalyst on the substrate, suggesting that amorphous carbon poisoning of the catalyst layer is the likely cause of the non-linearity of the growth with time [36]. This effect was confirmed by a decreasing G/D ratio in the Raman spectra during the growth, which indicates an increase in amorphous carbon content [36]. In contrast with the CNT height, the CNT bundle areal density exhibits the linear increase with the growth time, even beyond growth time of 5 minutes and after CNT height plateaues, as shown in Figure 4-4b. This trend can be explained that ethylene interaction with the catalyst can form amorphous carbon or adhere to an already existing amorphous carbon region [36], which adds to the mass but not to the height of CNT bundles.
Third, CNT growth on the substrate as large as up to ~19 cm$^2$ was confirmed. Based on the first and the second observations, the growth condition of 97.5 sccm hydrogen flow rate for a short growth time of 50 seconds was chosen; higher hydrogen flow rate resulted higher growth rate and higher CNT quality (to be confirmed in Section 4.1.3), when the growth time is shorter than 5 min.

Based on the observed CNT growth rate (240 $\mu$m/min) using this growth condition, 50 seconds was calculated to grow the desired 200 $\mu$m. Using this growth condition, the substrate area was gradually increased. As compared in Figure 4-5a, the grown CNT mass almost linearly increased with the increasing substrate area. Meanwhile, the CNT bundle areal density showed slight decrease with the increasing substrate size (see Figure 4-5b), which can be attributed to the CNT height decrease (see Figure 4-5c). This CNT height decrease with increasing substrate size can again be attributed to diffusion kinetics; the carbon sources need to diffuse not just vertically but also horizontally to reach the center sections of the substrate for the growth.

Figure 4-4: Changes of a) CNT height and b) CNT bundle areal density with varying growth time.
From this parametric study, the CVD growth process for the new set-up with the larger hydrogen gas flow of 97.5 sccm was successfully established, where grown CNTs have high quality (to be confirmed in the next section), controlled length of ~200 μm, CNT bundle volume density of ~26-28 mg/cm³, over large substrate surface of ~19 cm². In the previous set-up with 10 sccm hydrogen gas flow, the longer growth time (15 mins) was necessary to achieve ~200 μm height, the maximum substrate size was ~6 cm², and the CNT qualities were lower (to be confirmed in the next section). The fact that the CNT growth presented better bundle areal density at 97.5 sccm (15% of Ar flow rate) when compared to lower flow rates is in accordance with other works in literature [35,40]; the CNT height and G/D ratio increased, respectively, from 17.8 μm and 0.81 at 50 sccm H₂ to 33.4 μm and 0.91 at 100 sccm H₂ [35]. When the hydrogen flow was increased to 200 sccm, however, the CNT height decreased (29.1 μm) and the G/D ratio decreased (0.70) [35]. While CNT growth was not tested with the hydrogen flow larger than 97.5 sccm due to the mass flow controller capability, the larger hydrogen flow does not necessarily provide the positive effects. In the next section, CNT geometry and qualities will be characterized.

Figure 4-5: The effects of the substrate size on a) CNT mass, b) CNT areal density, and c) CNT height, when grown with 650 sccm of Ar, 400 sccm of C₂H₄, 97.5 sccm H₂, and 50 sec of growth time.
4.1.3. Characterization of CNTs grown with the updated CVD set-up and process

CNTs grown using the updated CVD set-up with the larger hydrogen flow (97.5 sccm) were inspected using various methods, and compared with the growth conducted with smaller hydrogen flow (10 sccm) using the old CVD set-up; scanning electron microscopy (SEM, Thermo Fisher FESEM Verios) was used for visual observation of amorphous carbons, transmission electron microscopy (TEM, FEI Titan) was used for evaluation of their wall structures and diameters, and Raman spectroscopy (Raman, Horiba Vlabinir) was used for their graphitic structures. The growth with the larger hydrogen flow (97.5 sccm) was conducted with 650 sccm of Ar, 400 sccm of C$_2$H$_4$ and 50 seconds. The growth with the smaller hydrogen flow (10 sccm) was conducted with 650 sccm of Ar, 400 sccm of C$_2$H$_3$ and 15 min of growth time, using the old CVD set-up. Both growths resulted in the CNT height of ~200 μm.

The CNTs grown with the larger hydrogen flow rate (97.5 sccm) vs. smaller hydrogen flow rate(10 sccm) are visually compared using SEM images in Figure 4-6. Both samples indicated directional growth, but the CNT bundles grown with 10 sccm hydrogen flow exhibited amorphous carbon at the top, while the CNTs grown with 65 sccm hydrogen flow were free of amorphous carbon.
Figure 4-6: SEM image comparison between CNTs grown a) with the smaller hydrogen flow (650 sccm Ar, 400 sccm C_{2}H_{4}, and 10 sccm H_{2}, 15 min growth time) [19] and b) with the larger hydrogen flow (650 sccm Ar, 400 sccm C_{2}H_{4}, and 97.5 sccm H_{2}, 50 s growth time).
The CNT wall structures and diameters were inspected from the TEM images, and their density was estimated; this density is the density of CNTs themselves, and different from the ones of CNT bundles mentioned in Section 4.1.2. The wall numbers of the CNTs grown with the larger hydrogen flow are smaller (three) than that of the CNTs previously grown with the smaller hydrogen flow (22), as compared in Figure 4-7. The inner diameter and outer diameter of the CNTs grown with the larger hydrogen flow were measured as 6.75±0.91 nm and 9.50±1.68 nm, respectively, when measured at 5 locations and averaged (see Figure 4-8). The density of individual CNTs was calculated based on these measurement values, using the following equation (1). Each concentric wall was assumed to evenly space between the inner and outer diameter and to have the same specific surface area as a graphene sheet (1315 m²/g) [41]. The total mass of the CNT walls was calculated by adding the mass of all the concentric walls. The CNT density was calculated by dividing this total mass by the tube volume determined by the outer diameter.

\[
\frac{d_{MW}}{d_{out}} = \frac{4000}{1315} \left[ \frac{n}{d_{out}} - \left( 2d_{s-s} \sum_{i=0}^{n-1} i \right) / d_{out}^2 \right] \cdots (1)
\]

\(d_{out}\) is the CNT outer diameter (in nm), \(d_{in}\) is the CNT inner diameter (in nm), \(n\) is the number of walls (set as three in this work), and \(d_{s-s}\) is the inter-wall distance defined as \(d_{s-s} = \frac{d_{out} - d_{in}}{2(n-1)}\). The density of the new CNTs was calculated as 0.822 g/cm³. This CNT density value is smaller than the value 1.55 g/cm³ [19] calculated for the CNTs grown with the smaller hydrogen flow (10 sccm). Hence, since the CNT bundle areal density obtained with the current set-up with the larger hydrogen flow (0.39-0.61 mg/cm², see Table 4-2) is similar than that obtained with the previous CVD set-up with the smaller hydrogen flow (~0.5 mg/cm²) for the same height, the CNT counts per unit substrate area is expected to be larger with the larger hydrogen flow.
Figure 4-7: TEM image comparison between the CNTs grown a) with the smaller hydrogen flow (650 sccm Ar, 400 sccm C_2H_4, and 10 sccm H_2, 15 min growth time) and b) with the large hydrogen flow (650 sccm Ar, 400 sccm C_2H_4, and 97.5 sccm H_2, 50 s growth time) [31].
Figure 4-8: Measurement of the number of walls and inner and outer diameters of the CNTs grown with the large hydrogen flow (650 sccm Ar, 400 sccm C$_2$H$_4$, and 97.5 sccm H$_2$, 50 s growth time) by TEM.
The crystallinity of the CNTs was evaluated using Raman spectroscopy by the D/G ratio and G peak full width half maximum (FWHM). The effect of the hydrogen flow was studied as shown in Figure 4-9. When grown with 10 sccm hydrogen flow using the old CNT set-up, the D/G ratio (0.940) and the FWHM of the G-peak (85 cm\(^{-1}\)) are largest, indicating high defect percentage and more existence of amorphous carbon [42]. As the hydrogen flow increases to 65 sccm and 97.5 sccm, the D/G ratio (to 0.591 and 0.414) and the FWHM of the G-peak decreases (55 cm\(^{-1}\) and 35 cm\(^{-1}\)) decreases, indicating that the increased hydrogen flow enhances graphitic structures of CNTs and decreases defects and amorphous carbon. This quantitative evaluation is compatible with the observation made with SEM above (see Figure 4-6) and explains that CNT bundle volume density decreased with increasing hydrogen flow rate (see Figure 4-3b) due to less deposition of amorphous carbon.
The CNTs grown using the new CVD set-up with larger hydrogen flow have highly graphitic structures, and do not require air/oxygen plasma treatment. Previously, when grown using the old set-up with 10 sccm of hydrogen flow, air plasma treatment (Harrick Plasma PDC-32G...
Basic Plasma Cleaner, 6.8W for 4 mins) was applied to eliminate the excessive amorphous carbons on the CNTs [19,31,34]; the D/G ratio changed insignificantly from 0.856 to 0.855, and the FWHM decreased from 91 cm\(^{-1}\) to 89 cm\(^{-1}\) (4 mins and 6.8 W) as shown in Figure 4-10. Even though the FWHM and D/G virtually did not change, the effect of amorphous carbon removal was confirmed by SEM imaging of the CNT surface before and after plasma cleaning [19]. In contrast, the air/oxygen plasma process decreased the crystallinity of the CNTs grown using the new CVD set-up and larger hydrogen flow as shown in Figure 4-11. With the air and oxygen plasma, the D peak became higher than the G peak, indicating that air/oxygen plasma attacks graphitic structures of CNTs, as amorphous carbon is not existent. With the clean surfaces (see Figure 4-6b), these CNTs grown using the new CVD set-up and larger hydrogen flow will be used as grown, without air/oxygen plasma treatment, for the next process.
Figure 4-10: Raman spectra to compare CNTs’ crystallinity with increasing air plasma treatment time (6.8 W). The CNTs were grown using the old CVD set-up (650 sccm Ar, 400 sccm C\textsubscript{2}H\textsubscript{4}, and 10 sccm H\textsubscript{2}, 15 min growth time) [43].
Figure 4-11: Raman spectra to compare CNTs’ crystallinity with increasing air/oxygen plasma treatment time (6.8 W). The CNTs were grown using the new CVD set-up (650 sccm Ar, 400 sccm C\textsubscript{2}H\textsubscript{4}, and 97.5 sccm H\textsubscript{2}, 50 s growth time).
4.2. Magnetization of CNTs

To successfully achieve magnetic assembly of CNTs within the polymer matrix, CNTs must have high magnetic anisotropy and susceptibility. Multiwalled carbon nanotubes (MWCNTs) have low magnetic anisotropy and susceptibility in their pristine form [10]. Thus, the surface of the CNT bundles was coated with a thin layer of approximately 80 nm of Nickel to magnetize the CNTs using an electron beam deposition machine (Kurt J. Lesker AXXIS Multipurpose Physical Vapor Deposition System, and Temescal FC 2000). The anisotropic magnetic responsiveness was measured and compared between the as-grown CNTs and the Ni-coated CNTs in Figure 4-12. The field strength (H) - magnetization (M) plot exhibit the diamagnetic behaviors for as-grown CNTs, while the Ni-coated CNTs exhibit ferromagnetic behaviors [19].

![Figure 4-12: H-M plot of pristine and Ni-coated CNTs [19.](image)](image)
4.3. Scalable Diazotization of Ni-coated CNTs

The Ni-coated CNTs were surface-treated using diazonium salt (diazotization), to improve their dispersion and suspension within the epoxy matrix during the mixing and assembly process. Diazotization was selected as it offers strong covalent bonding between the CNTs and the epoxy of our selection [19] while being a relatively simple process, as discussed in detail in Chapter 2.

In this thesis work, this functionalization process was scaled up to provide up to 37 mg of functionalized CNTs in one process (vs. 5 mg using the previous diazotization set-up [34]), by introducing a larger impeller and an improved filtering process. In the diazotization process, first, diazonium salts are generated by nitrosation of nitrous acid with aromatic amines. Second, nitrogen is lost due to instability. Third, aromatic rings bond to CNT sidewalls to form covalently bonded CNT walls and resin. The details about the diazotization chemical process are summarized in Figure 4-13.

The process steps of diazotization are summarized in Table 4-3. The first step was dissolving the carbon nanotubes in the Dimethylformamide (DMF) solvent. The CNTs, still attached on the Si substrate (~1mg, 1 mm × 2 mm area, for example), were placed facing down in a glass vial containing DMF (1 ml per 1 mg CNTs [19]), and the glass vial was placed in an ultrasonication machine (VWR Symphony 97043-976 Ultrasonic Cleaner) at ~60 °C for ~5-15 minutes until the CNTs were completely released from the substrate. The second step was to form the diazonium salt in the vial. For every 1 mg of CNTs in DMF, 1.1g of EPI-W curing agent and 43 μL of isoamyl nitrite were added [19] and mixed using a PTFE impeller (4 cm diameter) at 200 RPM while in an ultrasonication bath at ~60 °C for 3 hours (see Figure 4-14a). The third step was to filter out CNTs from the solution mixture using a syringe filter. As shown in Figure 4-14b and 4-14c, the syringe filter case (Advantec MFS Pp25 Syringe Filter Holder) allowed for the filter membrane (Foxx Life Sciences Hydrophobic PTFE EZFlow Membrane Disc Filter, 25 mm
diameter, 0.2 μm pore size) to be replaced to harvest the CNTs, while minimizing CNT loss by choosing a 0.2 μm filter pore size. The fourth step was to remove the remaining excess diazonium salt within the CNTs after filtration, using the centrifuge. The solution was diluted with DMF to dissolve the diazonium salt and centrifuged in centrifuging vials (Kimble 45600-15, 15 mL) at 3500 RPM for 10 minutes, and the supernatant was removed; the process was repeated until the supernatant became completely clear, indicating that the diazonium salt was removed. After removing the excessive diazotization salt, now to remove DMF, the CNTs were mixed with acetone in the same centrifuging vials and centrifuged twice at 3500 RPM for 10 minutes. The fifth and the final step was to dry the CNT-acetone mixture in an oven at 140 °C for 1 hour, and to air dry overnight inside the fume hood.

A challenge observed during the process was related to the CNT filtering process. Even though the time necessary to filter CNTs was significantly reduced, from days to hours, by using the syringe filter as opposed to just centrifuging, as the volume fraction increases, the time necessary to filter the CNTs increases significantly, from approximately 2 hours for 0.1 vol.% to 5 hours for 0.5 vol.% with the solution volume used. The time required is dependent on three aspects: the CNT amount in the solution, the filter pore size, and the filter membrane area. If the filter grid size is larger, the filtering speed would increase, but more CNTs will be lost.

The functionalized Ni-coated CNTs were analyzed using optical microscopy. As shown in Figure 4-15, the CNTs were relatively bundled together, due to the natural tendency of CNTs to agglomerate. The bundles of CNTs are longer than 200 μm, while precise assessment of the average length of individual CNTs and CNT bundles is difficult.
Table 4-3: Diazotization process steps.

<table>
<thead>
<tr>
<th>Step #</th>
<th>Procedure</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CNT dissolution in DMF by ultrasonicating at 60 °C.</td>
<td>5 – 15 mins each batch</td>
</tr>
<tr>
<td>2</td>
<td>Add EPI-W (1.1 g per 1 mg CNTs) and isoamyl nitrite (43 uL per 1 mg CNTs) to form diazonium salt and combine with harvested CNTs and DMF. Mix solution at 200 RPM with ultrasonication at ~60 °C.</td>
<td>3 hours</td>
</tr>
<tr>
<td>3</td>
<td>Use syringe filter to collect functionalized CNTs in a separate vial</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Centrifuge at 3500 RPM with DMF and remove supernatant until solution is clear.</td>
<td>10 min each batch</td>
</tr>
<tr>
<td></td>
<td>Centrifuge at 3500 RPM twice with acetone and remove supernatant.</td>
<td>10 min each batch</td>
</tr>
<tr>
<td>5</td>
<td>Dry acetone in oven at 140 °C for 1 hour. Leave overnight drying in the fume hood.</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4-13 Sketch showing diazotization steps of CNTs [19].
Figure 4-14: The updated diazotization set-up for scalability: a) functionalization setup with PTFE mixer and ultrasonic cleaner, b) modular filter casing with membrane, and c) assembled syringe filter setup.

Figure 4-15: Optical microscope images of functionalized Ni-coated CNTs in DMF (0.5 vol%): a) 5× magnification and b) 10× magnification.
4.4. CNT-epoxy composite fabrication with magnetic assembly for three-point bend test

A custom-made mold was used to fabricate CNT-epoxy samples with magnetically aligned CNTs to be tested by three-point bending based on ASTM 5045 standard. The mold was machined from an aluminum plate to hold three rectangular samples (30.8 mm length, 7.0 mm width, 3.5 mm thickness) and a notch (1.1 mm depth, 1 mm width) specified by this ASTM standard (see Figure 4-16). The fabrication steps are outlined in Table 4-4. The diazotized Ni-coated CNTs (density without Ni, 0.822 g/cm$^3$ or 822 kg/m$^3$, see section 4.1.3) were mixed with the resin (EPON 862, 1174 kg/m$^3$) and the hardener (EPIKURE W, 1019 kg/m$^3$, and resin: hardener ratio of 100:26.4) using an ultrasonication machine at 60 °C; the mass ratio between the CNTs and the resin/hardener was prepared to achieve the CNT fraction of 0.1 vol.% and 0.5 vol.% based on their densities. The CNT-resin-hardener mixture in a vial was placed under vacuum for 20 minutes (~ -28 inHg) to remove air voids. The mixture was poured on the mold, which was coated with release spray, and placed inside a Helmholtz coil system (see Figure 4-17) to apply the horizontal magnetic fields (180 G or 300 G) and to align CNTs along the direction to bridge the notch, as shown in Figure 4-16a. The mold was placed on top of the aluminum support plate underlined with a heating pad (Omega SRFG-201/10, 7 cm × 3 cm) and thermal paste was applied to the bottom of the mold plate (Techspray 1978-DP). The Helmholtz coil system can apply the uniform magnetic field to the volume of 38.1 mm length, 73.6 mm width, and 116.8 mm height; the mold fits within this volume. The mold was heated up to 70 °C for 30 minutes, to decrease the solution viscosity for effective magnetic alignment. After magnetic assembly of CNTs was complete, the temperature was increased to 121 °C for 1 hour to start the curing process with the magnetic field still on, and then placed in an oven (Shel Lab, 1330GM) for 2 hours at 171 °C for post cure, following the same process conducted by previous lab member [19]. In addition to the aligned CNT-epoxy composites,
epoxy-only baseline samples, and epoxy composites with randomly oriented CNTs were also prepared without magnetic field application as reference samples.

Figure 4-16: Samples for three-point bending testing: a) picture of the mold, and b) sketch showing the sample dimensions.
**Table 4-4: Fabrication steps of CNT-epoxy composites.**

<table>
<thead>
<tr>
<th>Step #</th>
<th>Procedure</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Add resin EPON 862 in a vial containing functionalized CNTs and ultrasonicate the mixture at 60 °C.</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>Add curing agent EPI-W in the vial and ultrasonicate the mixture at 60 °C.</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Vacuum the Epoxy/EPI-W/CNT mixture in the vial at room temperature.</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Place the mixture in the mold and apply the magnetic field in HHC coil at 70 °C.</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>Cure the mixture, with the magnetic field on in HHC, at 121 °C.</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>Place the mixture, still in the mold, in furnace at 171 °C for post-curing with no magnetic field.</td>
<td>120</td>
</tr>
</tbody>
</table>

Figure 4-17: Helmholtz coil system: a) top view, b) front view, and c) mold support inside HHC.
Chapter 5

Three-Point Bending Test

5.1. Sample Preparation, Testing, and Post-Testing Inspection

Three-point bending tests were conducted on the fabricated PNC and baseline samples for their fracture toughness following the ASTM 5045 standard. Three single edge notched bending (SENB) samples were prepared per each PNC sample condition. A natural crack was introduced by carefully tapping the samples with a razor blade in the notch section as shown in Figure 5-1. The crack length (the original notch length plus the introduced natural crack length) was kept so that the ratio \( x \) between total crack length (\( a \)) and specimen width (\( W \)) stays as \( 0.45 < x = a/W < 0.55 \) (see Figure 5-2a). Some samples exhibited longer crack lengths after natural crack introduction due to matrix brittleness and were not used for this testing. The prepared SENB samples were tested using an MTS Criterion electro-mechanical universal test system (1 kN load cell, 100 Hz acquisition rate) under the loading rate of \( 1.67 \times 10^{-4} \text{ m/s} \) (10 mm/min) as shown in Figure 5-2b. The load versus crosshead displacement data were acquired until the samples broke.
The fracture toughness, $K_Q$ [MPa.m$^{1/2}$], was calculated from the measurement data using the following equation.

$$K_Q = \left( \frac{P_Q}{BW^2} \right) f(x) \cdots (5-1)$$

$B$ is the sample thickness of 3.5 mm; $W$ is the sample width of 7 mm (see Figure 5-2). $f(x)$ is a function of $x$, where $x=a/W$, and can be described as

$$f(x) = 6x^{1/2} \left[ \frac{1.99-x(1-x)(2.15-3.93x+2.7x^2)}{(1+2x)(1-x)^{3/2}} \right] (5-2)$$

$P_Q$ is the load value to be obtained from the load versus crosshead displacement plot (see Figure 5-3). First, a line was drawn manually as the best fit straight line of the loading portion of the plot, and its slope’s reciprocal was defined as the initial compliance, $C$. Then, another line was drawn with its compliance that is 5% greater than that of the first line. When the maximum load $P_{max}$ is situated between these two lines, $P_Q$ is set as the same as $P_{max}$, as shown in Figure 5-3a. When $P_{max}$ is not situated between the two lines, $P_Q$ is set as the load value at the intersection of the load
curve and the second line, as shown in Figure 5-3b. The values $P_{max}/P_Q$ should be smaller than 1.1 for the test to be valid. The load versus crosshead displacement plots of all the samples can be found in the Appendix. The calculated fracture toughness data are summarized in Table 5-1. The standard deviation among the three samples per each condition was smaller than ~22.6 %, and the standard deviations increased with CNT introduction. The measured fracture toughness of the pure epoxy was 0.4280 MPa.m$^{1/2}$, whose value is lower than the previously obtained data of 0.7219 – 0.9010 MPa.m$^{1/2}$ [44]. This discrepancy can be attributed to aging of the epoxy and the curing agent. These test results will be interpreted in relation with the inspected CNT morphology, to be discussed in Section 5.2 and Section 5.3.

Figure 5-2: Three-point bending test based on ASTM 5045: a) schematic [45] (W: 7 mm, B: 3.5 mm) and b) a digital image.
Figure 5-3: Exemplary plots of load versus crosshead displacement of PNC samples under three-point bending test: a) the case where $P_{\text{max}}$ is situated between these two lines ($P_Q = P_{\text{max}} = 22.2364\, N$, 0.1 vol.%, randomly oriented), and b) the case where $P_{\text{max}}$ is not situated between the two lines ($P_Q = 18.35\, N$, 0.1 vol.%, 300 G). The solid line represents the first line with the slope $1/C$, and the dotted line represents the second line with the slope $1/(1.05C)$. 
5.2. Assessment of CNT alignment by SEM inspection and Raman Spectroscopy

After testing, the fracture surface of some samples (0.5 vol% CNT) was inspected using SEM to characterize toughening mechanisms by CNT integration, as summarized in Figure 5-4. Regardless of the CNT morphology, CNT bridging and breakage was observed as major toughening mechanisms with these samples. When the samples are prepared without magnetic alignment, pulled out CNTs are directed in various directions, indicating random orientation of CNTs (see Figure 5-4a left). When inspected with lower magnification, epoxy-rich areas were observed (see Figure 5-4a right), even with functionalization. When aligned with the magnetic field of 180 G, CNTs were observed as more straight pull-put directions, and more dispersed (see Figure 5-4b). When aligned with the stronger magnetic field of 300 G, this time, aligned CNTs were observed to be more agglomerated than the case aligned with 180 G; the stronger field might have assembled and bundled aligned CNTs together. While further SEM inspection will be necessary to provide more conclusive inspection, schematics of potential CNT distributions are given in Figure 5-4.

<table>
<thead>
<tr>
<th>Sample CNT vol%</th>
<th>CNT alignment</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Mean</th>
<th>Standard deviation</th>
<th>Standard deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Randomly oriented</td>
<td>0.6476</td>
<td>0.6949</td>
<td>0.7159</td>
<td>0.6861</td>
<td>0.0349</td>
<td>5.10</td>
</tr>
<tr>
<td></td>
<td>Aligned with 180 G</td>
<td>0.6845</td>
<td>0.6322</td>
<td>0.4434</td>
<td>0.5867</td>
<td>0.1268</td>
<td>21.62</td>
</tr>
<tr>
<td></td>
<td>Aligned with 300 G</td>
<td>0.558</td>
<td>0.5378</td>
<td>0.7935</td>
<td>0.6298</td>
<td>0.1421</td>
<td>22.57</td>
</tr>
<tr>
<td>0.5</td>
<td>Randomly oriented</td>
<td>0.6772</td>
<td>0.6641</td>
<td>0.5513</td>
<td>0.6309</td>
<td>0.0692</td>
<td>10.97</td>
</tr>
<tr>
<td></td>
<td>Aligned with 180 G</td>
<td>0.6159</td>
<td>0.9177</td>
<td>0.6704</td>
<td>0.7347</td>
<td>0.1608</td>
<td>21.89</td>
</tr>
<tr>
<td></td>
<td>Aligned with 300 G</td>
<td>0.5653</td>
<td>0.4688</td>
<td>0.5129</td>
<td>0.5157</td>
<td>0.0483</td>
<td>9.37</td>
</tr>
</tbody>
</table>

Table 5-1: Measured fracture toughness data from three-point bending.
In addition to the local inspection of CNT morphology by SEM, averaged and quantitative assessment of CNTs was attempted using Raman Spectroscopy. In the past, CNT alignment direction was identified; the G peak intensity becomes high when the polarization direction of the laser is aligned with CNT alignment direction [46]. Before characterizing the samples using Raman,
our aligned CNT-thermoset composites (0.5 vol%, aligned with 180 G) were polished, and applied with the polarized laser of the 20 μm spot size in the two directions: aligned with and perpendicular to the CNT alignment. Yet, as shown in Figure 5-5, the G-peak and other peaks did not show distinctive differences. This result can be attributed to the spot size (20 μm) being too small to capture full CNT alignment, or that the carbon nanotubes in this study are MWCNTs, and not SWCNTs as was the case in the literature [46]. The Raman spectroscopy characterization in this work was inconclusive.

![Figure 5-5: Raman spectra of a CNT-epoxy samples (0.5 vol%, aligned with 180 G), when the polarized laser is applied in the directions that are aligned with and perpendicular to the CNT alignment direction.](image)
5.3. Effect of CNT Integration on Toughening

The effect of CNT integration with varying CNT volume fraction and applied magnetic fields will be discussed by comparing the measured fracture toughness and inspected CNT morphology.

First, increasing CNT volume fraction increased fracture toughness, but not in a linear manner. As shown in Figure 5-6a, the fracture toughness increased with increasing CNT volume fraction when prepared with 180 G (37.08% toughness improvement with 0.1 vol.% CNT, and 71.66% toughness improvement with 0.5 vol.% CNT). Meanwhile, as shown in Figure 5-6b, when prepared with 300 G, the fracture toughness increased more with 0.1 vol.% CNT (47.15% toughness improvement) than with 0.5 vol.% (20.49% toughness improvement). These results can be attributed to increased CNT agglomeration when applied with the stronger magnetic field, as shown in the SEM observations of Figure 5-4. The dispersion level of CNTs in the polymer matrix directly affects the fracture toughness reinforcement effect due to toughening mechanisms such as crack deflection and CNT rupture [26]. The correlation study between the CNT distribution and agglomeration and toughening will be discussed in Section 5.4.
Second, the effect of magnetic CNT assembly on toughening was studied to be more effective with higher CNT vol%. For nanocomposites of 0.1 vol% of CNTs, the magnetic field application to align CNTs did not increase toughening (see Figure 5-7a); with or without magnetic alignment, the fracture toughness improvement was similar, with the highest (60.30%) being for the randomly oriented sample. For nanocomposites with 0.5 vol% CNTs, the ones prepared with 180 G exhibited the largest toughness improvement (71.66%) among all there samples with CNTs (see Figure 5-7b). With the larger CNT fraction, CNTs are more agglomerated (see Figure 5-4a), as supported by the fact that the toughness enhancement of randomly distributed CNT-epoxy nanocomposites is smaller with 0.5 vol% CNTs (47.41%) than with 0.1 vol% CNTs (60.30%). With magnetic field application, CNT alignment helps to avoid agglomeration (see Figure 5-4b), resulting in the highest toughness improvement (71.66%) when 0.5 vol% CNTs are aligned with 180 G. Yet, when the magnetic field strength is increased to 300 G, the CNTs again re-agglomerate by stronger magnetic CNT interactions (see Figure 5-4c), resulting in the smaller fracture toughness improvement (20.49%). Hence, it was concluded from these observations that a moderate magnetic

Figure 5-6: The effect of CNT volume fraction on fracture toughness reinforcement of the baseline samples and CNT-epoxy samples: a) aligned with 180 G and b) aligned with 300 G.
field (180 G in this work) is effective to improve toughness improvement with higher CNT volume fraction, providing alignment organization within the matrix without re-agglomeration of CNTs. Another reason behind the smaller fracture toughness improvement of the sample prepared with 0.5 vol% CNT and 300 G application is voids, which was also observed by [47] at the same volume fraction, and by [48] at 0.5 wt.%. With larger CNT volume fraction, the CNT-epoxy mixture viscosity increases and thus air bubbles are more likely to be trapped. This hypothesis will be investigated by inspection of the whole cross-section of the samples in the future.

![Graph showing fracture toughness comparison](image)

Figure 5-7: The effect of the applied magnetic field strength on fracture toughness reinforcement: a) the CNT-epoxy samples (0.1 vol%) and b) the CNT-epoxy samples (0.5 vol%) compared with a baseline sample.

### 5.4. Comparison with previous work

In this work, more CNT agglomeration was observed by increasing volume fraction and by applying stronger magnetic fields, resulting in less effective toughening. Past studies also showed the non-linear correlation between the increasing particle fraction and fracture toughness due to agglomeration [14–18], as summarized in Table 5-2.
PNCs prepared with randomly oriented, functionalized CNTs by Hong (1-3 wt.% [14]), Ayatollahi (0.1-1 wt.% [49]), and Schulte (0.1-0.3 wt.% [48]) exhibit fracture toughness increase with increasing CNT fractions in a non-linear manner, but without apparent reinforcement degradation for higher CNT concentrations. The effectiveness of toughening with CNT integration in this work was evaluated by comparing it with similar experimental work on CNT-epoxy composites. Most of the published literature on CNT-reinforced PNCs discusses results from randomly oriented CNTs. The highest fracture toughness improvement seen in this work from randomly oriented samples (60.30%, at 0.1 vol.% or 0.08 wt.%), is higher than or comparable with those of randomly oriented samples of ~0.1 wt% from the past work (18.46% [47], 15.67% [49], 8.54% [17], 68% [18], 21.54% [48], 15.19% [16]), as shown in Table 5-2. Among the results, the work done by Lahiri et al. [18] exhibited the largest toughness improvement, regardless of the volume fraction. This effective CNT reinforcement in Lahiri’s work [18] can be attributed to shorter CNT length (1-3 μm) compared to other studies including this study (~10-30 μm [16,17], ~200 μm in this work before functionalization), leading to lower agglomeration [50], and good CNT dispersion achieved by ice bath sonication [18]. On the other hand, even the lowest fracture toughness improvement of aligned CNT-epoxy samples (37.08% for 0.1 vol.% aligned at 180 G) in this work is higher than that observed by Wardle et al. (12.50% for 3 vol.% [51]). Wardle et al. did not use functionalization and used a much higher volume fraction of CNTs, which, as mentioned before, could have led to CNT agglomeration.

PNCs prepared with pristine CNTs without functionalization exhibit fracture toughness degradation when the CNT fraction becomes larger than a certain value: > 0.6 wt.% (Ebrahimi [17]), > 0.5 wt.% (Lahiri [18]), > 0.5 wt.% (Shokrieh [16]), and > 3 vol.% (Wardle [51]). Such CNT fraction values of PNCs with randomly oriented CNTs were smaller (0.5 wt.% [16,18] and 0.6 wt.% [17]) than those of PNC with aligned CNTs (3 vol%) [51]. This difference can be attributed to the CNT organization difference (randomly oriented vs. aligned).
Similar toughness degradation with increasing CNT fraction, but when CNTs are randomly oriented or when CNTs were aligned with the higher magnetic field of 300 G, was observed. This degradation effect, as discussed previously, can again be attributed to CNT agglomeration with increasing CNT fraction. On the other hand, when CNTs are aligned with the lower magnetic field of 180 G, the toughness increased with the CNT fraction. Preparation and testing of CNT-epoxy samples with higher CNT fraction are essential in determining the limit of toughness improvement by CNT aligned with 180 G.
Table 5-2: Fracture toughness improvement in this work compared to other works.

<table>
<thead>
<tr>
<th>CNT morphology</th>
<th>CNT mass fraction (%)</th>
<th>CNT functionalization</th>
<th>Test method</th>
<th>Fracture toughness of baseline epoxy [MPa m^{1/2}]</th>
<th>Fracture toughness improvement over baseline (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Randomly oriented</td>
<td>0.08 (0.1 vol.%)</td>
<td>Covalent diazotization</td>
<td>Three-point bending</td>
<td>0.428</td>
<td>60.30</td>
</tr>
<tr>
<td>Aligned at 180 G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aligned at 300 G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Randomly oriented</td>
<td>0.4 (0.5 vol.%)</td>
<td></td>
<td>Three-point bending</td>
<td>0.476</td>
<td>47.15</td>
</tr>
<tr>
<td>Aligned at 180 G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aligned at 300 G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Schulte et al. [47]</td>
<td>Randomly oriented</td>
<td>0.1</td>
<td>Amino-functionalized</td>
<td>0.650</td>
<td>18.46</td>
</tr>
<tr>
<td>Eswara et al. [13]</td>
<td>Randomly oriented</td>
<td>0.5</td>
<td>Amino-functionalized</td>
<td>1.720</td>
<td>17.44</td>
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<tr>
<td>Forero et al. [52]</td>
<td>Randomly oriented</td>
<td>0.5</td>
<td>Elastomer covalently bonded</td>
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<td>45.00</td>
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<td>Hong et al. [14]</td>
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<td>Noncovalent</td>
<td>1.010</td>
<td>96</td>
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<tr>
<td>Ebrahim et al. [17]</td>
<td>Randomly oriented</td>
<td>0.1 (0.087 vol.%)</td>
<td>Functionalized (type not specified)</td>
<td>U-notched semicircular bend</td>
<td>1.340</td>
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<tr>
<td>Ayatollahi et al. [49]</td>
<td>Randomly oriented</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li et al. [53]</td>
<td>Randomly oriented</td>
<td>0.7</td>
<td>None</td>
<td>0.670</td>
<td>38.80</td>
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<tr>
<td>Lahiri et al. [18]</td>
<td>Randomly oriented</td>
<td>0.1</td>
<td>None</td>
<td>2.500</td>
<td>68.00</td>
</tr>
<tr>
<td>Wardle et al. [51]</td>
<td>Aligned</td>
<td>(3 vol.%)</td>
<td>None</td>
<td>Three-point bending</td>
<td>~ 0.800 (9 vol.%)</td>
</tr>
<tr>
<td>Coelho et al. [15]</td>
<td>Randomly oriented</td>
<td>0.15 (0.5 vol.%)</td>
<td>None</td>
<td>Compact tension</td>
<td>0.870 (1.5 vol.%)</td>
</tr>
<tr>
<td>Schulte et al. [48]</td>
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<td>0.1</td>
<td>Amino-functionalized</td>
<td>Compact tension</td>
<td>0.650</td>
</tr>
<tr>
<td>Shokrief et al. [16]</td>
<td>Randomly oriented</td>
<td>0.1</td>
<td>Not specified</td>
<td>Three-point bending</td>
<td>1.619</td>
</tr>
</tbody>
</table>
Chapter 6

Conclusion

In this chapter, the results and contributions from this thesis work are summarized. In addition, planned future work will be discussed about further improvement of process scalability and mechanical property reinforcement by CNT integration into epoxy matrices, and integration of aligned CNTs into CFRPs.

6.1. Summary of Results and Contributions

In this presented work, two main research tasks were performed to fabricate a sizable, aligned CNT-reinforced PNCs using functionalization and magnetic assembly, and to evaluate effectiveness of CNT integration on toughening through relationship study between the measured toughness and CNT organization within the epoxy composites. The contributions made through this work are listed below.

1. Established a method to synthesize, functionalize, and magnetically align CNTs in a consistent and scalable manner.
   - The CVD setup was upgraded by increasing the hydrogen flow rate to 97.5 sccm from 10 sccm. This increase in the H₂ flow rate increased CNT mass per growth (up to ~8 mg) and CNT growth rate (240 μm/min), achieved growth on a large substrate size (19 cm²), and increased the CNT quality (D/G ratio of 0.414 and G peak FWHM of 35 cm⁻¹).
   - The functionalization process was updated by adding a syringe filter to eliminate unutilized diazonium salt in a shorter time (a few hours), even with the higher CNT vol.%
(>0.5 vol.%). This updated set-up enabled processing of more CNTs (up to ~37 mg per process).

2. Evaluated the effectiveness of diazotized and magnetically aligned CNTs on toughening of an epoxy matrix.

- Fracture toughness improvement of up to 71.66% (with 0.5 vol.% CNTs aligned with 180 G) was achieved by integration of aligned CNTs, which is higher than those achieved in the past (12.50% with 3 vol.% [51]).

- Fracture toughness improvement up to 60.30% (with 0.1 vol.% CNTs) was achieved by integrating randomly oriented CNTs. This value is higher than or comparable with those studied in the past (see Table 5-2).

- CNT bridging and breakage were observed as major toughening mechanisms through SEM inspection of PNC fracture surface.

- Fracture toughness was not observed to increase linearly with increasing CNT volume fraction (0.1 and 0.5 vol%) for all aligned CNT-epoxy PNCs (see Figure 5-6). When aligned with 180 G, the fracture toughness was observed to increase 37.08% with 0.1 vol.% and to 71.66% with 0.5 vol.. However, this trend of increasing toughness with higher CNT fraction was not seen with the CNT-epoxy PNCs aligned with 300 G: 47.15% improvement with 0.1 vol.%, and 20.49% with 0.5 vol%. The higher magnetic field strength of 300 G could have caused agglomeration of CNTs with high volume fraction.

- Fracture toughness values did not show many differences when integrated CNTs (0.1 vol%) are randomly oriented or aligned (180 and 300 G) (see Figure 5-7a); the highest improvement of 60.30% was observed with the randomly oriented CNT-epoxy sample. On the other hand, with 0.5 vol% of CNTs, fracture toughness values showed differences with varying CNT organization (see Figure 5-7b).
When compared with the randomly-oriented CNT-epoxy samples, the sample with CNTs aligned with 180 G exhibited increased toughness, while the sample with CNTs aligned with 300 G exhibited decreased toughness. This trend can again be attributed to CNT agglomeration with higher magnetic field of 300 G.

- Raman characterization was inconclusive in determining the alignment degree of CNTs within the epoxy.

### 6.2. Future Work and Recommendations

Based on this thesis work, the following tasks are planned to be conducted to further improve the fabrication process and to better understand the relationship between CNT organization and fracture toughness of CNT-epoxy composites.

1. **Improvement of the CNT functionalization process**
   - Upgrading the filter to a larger diameter will decrease the time necessary to complete the filtering process and enable higher CNT vol.% composite fabrication.
   - Quantification of CNT loss with varying filter grid size will allow better assessment of the optimal filter grid size. Selecting the grid size that will lead to faster filtering speed while not allowing significant CNT loss will enable more efficient and scalable composite fabrication.
   - Fabrication and characterization of CNT-epoxy samples using unexpired batches of the same epoxy and hardener combination at conditions comparable to those presented in this work will provide relevant toughness values than the presented work on the CNT-epoxy samples prepared with the aged resin and hardener in this work.

2. **Further relationship studies about fracture toughness and CNT organization**
• The SEM image inspection in this work was limited to a few CNT-epoxy samples of 0.5 vol% CNTs, at a few magnifications. More thorough SEM imaging of more samples prepared with multiple CNT volume fractions and magnetic fields is necessary to prove the hypothesis about CNT organization variation and its effect on toughening shown in Figure 5-4.

• The CNT-epoxy sample with the higher CNT fraction (0.5 vol.%) has higher viscosity than the one with 0.1 vol.% of CNTs and is expected to be more susceptible to void formation. The percentages of air void will be assessed by inspecting the whole cross-section of CNT-epoxy samples and their correlation with fracture toughness will be assessed.

Once the method to scale the preparation of CNT-epoxy composites is established and the sample preparation conditions to achieve effective toughening is identified, such knowledge will be translated to prepare “nano-prepreg,” which is a B-staged epoxy layer integrated with CNTs, as described in Section 2.3.
Bibliography


