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FERROMAGNETIC COATING AND MAGNETIC ASSEMBLY OF CARBON NANOTUBES
AS NANO-ADDITIVES INTO POLYMER MATRICES

STEVEN CENEVIVA
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Reviewed and approved* by the following:

Namiko Yamamoto
Assistant Professor of Aerospace Engineering
Thesis Supervisor

Philip Morris
Boeing, A.D. Welliver Professor of Aerospace Engineering
Honors Adviser

*Signatures are on file in the Schreyer Honors College.
Abstract

Ferromagnetic CNTs were developed and implemented as a magnetically responsive nano-additive when dispersed within polymer matrices, to form multi-functional CNT-polymer nanocomposites. The CNT nano-additives are highly desirable because of their unique mechanical and multi-functional properties. CNT-integrated nanocomposites are highly desirable in the field of aerospace engineering for their lightweight and multi-functional properties. When implemented properly, the CNTs can improve interlayer mechanical strength, along with electrical and thermal conductivity. Currently, the aerospace industry relies on carbon fiber reinforced plastics (CFRPs) for commercial aircraft structure. Despite the high mechanical strength, CFRPs have weak interlaminar strength causing them to be prone to delamination. Additionally, the lack of conductivity often requires additional layers of metal mesh to protect the aircraft structure from electromagnetic interference or lightning strikes. Polymer nanocomposites with Ni-coated CNT additives provide the improved interlaminar strength and electrical conductivity to be a solution to these existing issues. However, their application has been limited due to poor property scaling and poor scalability. Thus, capability to organize and control nano-additives within polymer matrices in bulk is the essential step toward effective bulk application of these novel advanced polymer nanocomposites. More specifically, I developed and implemented a three-step process to achieve magnetically aligned CNTs, as shown in Figure 2.1: 1) chemical vapor deposition (CVD) growth of vertically aligned, multi-walled CNTs, 2) low-temperature air plasma treatment to clean, etch, and functionalize CNTs, and 3) electron beam evaporation of ferromagnetic nickel (Ni) on functionalized CNT surfaces. The CNT growth, mostly vertically aligned morphology, was optimized by pre-conditioning of iron (Fe) catalyst layers using hydrogen (H₂) gas. Low-temperature plasma treatment etched away the entangled section of CNTs, exposing CNT tips to be ready for Ni coating. The degree of functionalization and degradation by plasma treatment was characterized via x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The Ni-coating on CNTs was inspected using energy dispersive x-ray spectroscopy (EDS) about their morphology and vibrating sample magnetometer (VSM) about their magnetic properties. With the 80-nm-thick Ni coating, the CNTs were well dispersed and suspended within solutions (DI water and a polymer matrix), and CNT alignment along magnetic fields was successfully demonstrated using the small field (∼150 G) in a short time (15 mins). This preliminary result confirms the potential of Ni-coated CNTs as magnetically responsive additives that can be organized in bulk using an energy-efficient set-up.
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Chapter 1

Introduction

The aerospace industry is always looking for ways to improve the mechanical, and other multi-functional properties, and decrease the weight of aerospace structures. Carbon nanotubes (CNTs) are especially intriguing as a composite reinforcement because of their high aspect (length-to-diameter) ratio, mechanical strength, and thermal and electrical conductivity [1]. CNTs are often described as rolled-up graphene sheets with the tube diameter on the order of $\sim 10 - 100$ nm. Due to their high crystallinity and unique circular boundary conditions, the CNTs have exceptional mechanical, thermal, and electrical properties [1, 2, 3, 4, 5, 6]. The CNTs produced in our lab have an aspect ratio of approximately 1000 (200 um in length; 35 nm in diameter), a common value for synthesized multi-walled carbon nanotubes (MWCNTs). Such high aspect ratios are necessary to form mechanical and conductive networks within composites. Table 1.1 compares CNT properties and the properties of common aerospace materials. The Youngs modulus of MWCNTs, due to carbon-to-carbon bonding, was measured to be above 1.06 TPa, over 100 times greater than steel [2]. CNTs themselves are very strong thermal and electrical conductors. The thermal conductivity of carbon nanotubes at room temperature has been measured as 6,600 W/m K, nearly twice that of diamond [3]. CNTs have been shown to carry an electronic current of up to 1 A/cm in voltage
fields as low as 5 V/mm [4]. However the overall conductance of MWCNTs is heavily reliant on quality, with higher temperature synthesis yielding cleaner CNT growth [5, 6].

### 1.1 Necessary Improvements of Carbon Fiber Reinforced Plastics

Carbon Fiber Reinforced Plastics (CFRPs) have gained popularity in the aerospace industry over the last three decades for their high strength and stiffness, and light weight. CFRPs are a composite consisting of hierarchical structure with tailorable ply stack combinations (see Figure 1.1; each ply consists of aligned carbon fibers (∼10 um) embedded within a thermoset polymer. Despite these advantages, further improvement is desired for CFRPs; specifically, inter-laminar and intra-laminar mechanical reinforcement to prevent delamination, and improved conductivity to protect against lightening strikes and electromagnetic interference [7, 8, 9].

CFRPs have weakness in inter-laminar shear strength and impact damage tolerance. Compared to metals, composites tend have a differing response to impact loading and dissipation of the low velocity incident kinetic energy. Metals absorb the energy from impact through deformation, both elastic and plastic, the second causing permanent deformation [10]. In contrast, CFRPs tend to be affected by the low velocity impact between the layers, leading to delamination from these interlaminar stresses. Even worse, this low velocity impact can leave the surface intact, but cause undetected subsurface delamination, leading to poor mechanical properties, and ultimately failure of the composite structure [11]. In addition, as more aircraft switch to CFRPs and begin to travel at higher speeds, the forces and high temperature due to friction with the atmosphere will be ever more apparent. Cross-ply laminates exposed to tensile thermos-mechanical loadings showed transverse matrix cracking as an initial sign of damage. This first sign of damage often leads to more crack sites within the composite and potentially failure of the composite structure [12]. Thus, both inter-laminar and intra-laminar mechanical reinforcement of matrices are desired for safety and longer product life.

CFRPs also have low thermal and electrical conductivity due to the presence of the insulating
matrix. The addition of CNTs can improve the thermal and electrical conductivity properties of CFRPs. These desirable properties can reduce or remove the needs for the additional metal meshes currently included with CFRPs that make up for the lack of conductivity present in the CFRPs alone [13].

1.2 Composite Property Improvement Using Nano-Additives

Implementation of nano-additives into polymer matrices can potentially improve mechanical and multi-functional properties of CFRPs. Among various nano-additives (nano-silica, carbon black, etc.), CNTs are one of the preferred choice due to their high aspect ratio and exceptional multi-functional properties as noted in Section 1.1. See Figure 1.1 for a schematic of CNTs integrated into CFRPs.

In the past, mechanical properties (stiffness, tensile strength, and inter-laminar strength) of polymers were improved with small amounts of CNT nano-fillers [14, 15, 16, 17]. Tensile testing on these nanocomposites show that the addition of 1 wt% of CNT to a host matrix results in a 36-42% increase of the elastic modulus, and an approximate increase of 25% of the ultimate tensile strength [14]. In order for carbon fibers to achieve this same effect, 10 wt% must be added to the host matrix. Additionally, the small amount of CNT nano-fillers can improve other properties of polymers, such as optical clarity and high melt flow viscosity, leading to the development of stronger windows and windshields [15]. Besides polymer nanocomposites, mechanical reinforcement with CNT nano-additives was also confirmed with fiber-polymer nanocomposites. The multi-walled CNTs in CFRPs can greatly improve the interlaminar shear strength of the composite. These CNTs add an extra mechanism of shear strength that prevents the delamination of CFRP layers [16]. The inclusion of CNTs in both fiberglass and IM7 was proven to increase the interlaminar strengths by 29.4% and 36.2%, respectively [17]. These resulting hybrid materials will have a longer lifespan and larger fatigue strength.

Electrical and thermal conductivity improvement with CNT implementation was also experimentally confirmed [18, 19]. These CNTs in CFRPs form conductive pathways for current carrying
capacity for electrical application and thermal absorptivity for thermal applications [18]. A 1 vol% CNT composite can more than double the thermal conductivity of the polymer, while higher volume fraction CNT organizations can increase the conductivity by a factor of 18 [19].

1.3 Existing Challenges of Polymer Nanocomposites

Aligning CNTs magnetically in polymer matrices will enable their tailored organization, improving the mechanical properties, and creating the necessary pathways to improve the electrical and thermal conductivity. Implementation of CNT nano-additives is a promising and powerful reinforcement option for polymer nanocomposites, as reviewed above. Yet, development and application of these multi-functional nanocomposites in bulk have stagnated due to their poor scalability. Nano-particles, specifically carbon nanotubes, have a specific cost to manufacture high quality CNTs. Chemical vapor deposition (CVD) has emerged as a promising technique for low-cost, high-quality continuous CNT synthesis. However, more work is still being carried out to optimize a low-cost manufacturing method [20]. Additionally, issues with CNT nano-additives in polymer nanocomposites arise in the dispersion of nano-particles in solvent. CNTs are susceptible to clustering and agglomeration in organic solvents and polymer matrices [21]. This agglomerations and clusters can be reduced by ultrasonication, and the overall dispersion properties can be improved by the attachment of functional groups to the CNT surfaces through chemical functionalization [22].
Figure 1.1: Schematic showing CFRP and integration of carbon nanotubes.
Table 1.1: Values of stiffness, and electrical and thermal conductivities of CNTs and common aerospace materials. The Young’s Modulus was found by Treacy [2]. The electrical conductivity was measured from the ballistic conduction phenomenon [23]. The thermal conductivity of multi-walled carbon nanotubes is taken at 300 K [24]. The electrical conductivity of carbon fiber is in accordance with Hexcel’s IM7 fiber [25].

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Chapter 2

Background

The goal of this thesis is to provide ferromagnetic CNTs as multi-functional nano-additives for polymer nanocomposites that can be organized using external magnetic fields. In this chapter, I review previous work on topics that are relevant to provide magnetically-responsive CNT nano-additives. First, CNT synthesis methods will be reviewed in terms of fabricated CNTs quality and quantity. Second, assembly methods of CNTs within polymer nanocomposites will be summarized in terms of scalability, including magnetic assembly. Third, functionalization of CNTs will be reviewed, as this process is essential to disperse and suspend CNTs within polymer matrices for compositing. Finally, magnetization of CNTs will be discussed. Based on this information, I determined the fabrication steps to deliver magnetically-responsive CNTs as nano-additives for this thesis work.

2.1 Fabrication of Carbon Nanotubes

Various methods exist to synthesize CNTs, with each method having its own set of advantages and flaws. Carbon nanotubes were first produced by Arc Discharge in 1991 when carbon soot was present on graphite electrode as a discharge occurred, with the intent to create fullerenes [26].
Here, carbon present on a negative electrode sublimates due to the high discharge temperature (above 1700 °C) [27]. Both multi- and single-walled CNTs can be produced by this method. Laser ablation is another method that can produce both single- and multi-walled CNTs by vaporizing a graphite target using a laser beam under high temperature in an inert gas chamber [27]. Despite being able to produce MWCNTs, laser ablation is more commonly used to produce SWCNT with minimal defect (90% pure) [28].

Chemical vapor deposition (CVD) is a catalytic growth method of CNT where a hydrocarbon gas is decomposed, in a chamber, onto an Fe, Ni, or Co metal catalyst substrate. This method tends to be cheaper, yield consistent CNTs, and be able to mass produce CNTs. However, the presence of defects can reduce the effectiveness of their properties [29]. Additionally, CVD allows for control of the CNT growths: powder, films, aligned or entangled, straight or coiled, and the ability to be patterned [30]. Chemical vapor deposition was selected as the method for the production of MWCNTs for this thesis work, due to its ability to have large control over the growth parameters and the ability to produce large amounts of high purity CNTs.

2.2 Alignment of CNTs

Below, I review selected methods used to align CNTs in dispersed solutions. Each method is appropriate for different applications and comes with its own set of advantages and disadvantages.

2.2.1 Alignment via Gas Flow

Alignment of CNTs can be achieved using gas flow over a CNT solution while simultaneously drying the solution [31]. This is rather a simple method, but has limitations. First, the method will not be effective when the solutions viscosity is high. Also, this method applies only to the surface regions, thus the processing is limited to thin films and will not accommodate volume processing or 3-D assembly [32].
2.2.2 Langmuir-Blodgett Method

The Langmuir-Blodgett method uses the forces involved in pulling a solid substrate through a CNT solution. The forces resulting from this pulling motion allow layered deposition of aligned CNTs onto the substrate. Although this method is highly scalable, it can only be applied to assembly using solid substrates, so alignment in liquid matrices is not possible [33, 34].

2.2.3 Electrophoresis

Electrically conductive CNTs can be aligned along the electric field direction between two electron electrodes [23]. While DC fields can lead to the movement of CNTs toward an electrode, AC fields reorient individual CNTs along the electric field. This method is not scalable or energy efficient because it requires a high field strength on the order of $10^3 \text{ V/cm}$ and frequency in the kHz-MHz range [35].

2.2.4 Magnetic Field Application

Magnetic alignment is a method similar to electrophoresis, but it relies on magnetic fields instead of electric fields. Due to this difference, this method reorients CNTs without causing attraction toward an electrode, ensuring more uniformity of CNT dispersion in the polymer matrix. However, in order to make this process possible, CNTs need to be altered to improve their magnetic properties from their weak diamagnetic behavior. After magnetization, the CNTs can align in the directions that are both parallel and normal to the substrate by adjusting the magnetic field application direction [36, 37]. Magnetic assembly was selected as the method of CNT alignment for this work because of its scalability potential, fast assembly time, and requirement for low magnetic fields allowing for simple experimental set-ups.

2.3 Functionalization of CNTs

As-grown CNTs agglomerate in bundles making their implementation into homogenous composites difficult. Several different methods exist to alter the surface of carbon nanotubes in order
to improve the wettability of CNTs through the attachment of functional groups, thus enhancing homogenous dispersion and suspension of CNTs in solutions [21, 38].

2.3.1 Acid Treatment of CNTs

Acid treatment of CNTs mostly attach carboxylic groups to the CNT surfaces, greatly improving the solubility of the nanotubes [39]. As-grown CNTs were added to nitric acid and placed in an ultrasonic bath to undergo functionalization. The longer the CNTs were exposed to the oxidation treatment, the higher the solubility. Additionally, the acid treatment acted as a cleaner, removing any amorphous carbon present on the CNT surface. However, with an increase in oxidation exposure leads to a loss in CNT crystalline structures. At 48 hours of oxidation in 60% nitric acid the CNT solubility achieved 40 mg/ml, but lost over 90% of the CNT mass. Through this process the morphology of the CNTs remain unchanged, as a result any entanglement from the CNT synthesis is not removed [40]. Additionally, due to the use of harsh chemicals, acid treatment for functionalization is a toxic and hazardous process.

2.3.2 Polymer Wrapping of CNTs

In this process, CNTs are wrapped in water-soluble linear polymers, greatly improving their wettability [41]. The resulting wrapped CNTs are stable for months, and can be easily redissolved into pure water after drying. However, the attachment forces between noncovalent wrappings and the CNT surface are weak, resulting in the load transfer as nano-fillers in polymer nanocomposites to be low [42].

2.3.3 Oxygen Plasma Treatment of CNTs

Oxygen plasma treatment of CNTs attaches oxygen functional groups to CNT surfaces in a non-polluting manner. Using a high energy plasma, in the presence of various gasses, discharged onto the CNT samples, small defects are made on the CNT surface, while also cleaning up the amorphous carbon [43]. These small defects are attachment sites for function groups and enable better adhesion of the ferromagnetic layer, improved dispersion characteristics, and less aglomer-
ation. Additionally, this method is highly scalable [44, 45]. In this thesis work, I use an oxygen plasma treatment to functionalize the CNT surfaces because of easy access to a high energy plasma, coupled with the non-polluting and scalable nature of the treatment. Additionally, this method cleans any amorphous carbon on the surface of CVD-grown CNTs which would inhibit attachment of ferromagnetic metals.

2.4 Magnetic Property Enhancement of CNTs

As-grown CNTs have diamagnetic properties. These diamagnetic CNTs require strong magnetic fields, up to 25 T, to align [46]. Post-processing of as-grown CNTs is required to improve the magnetic responsiveness.

2.4.1 Filling CNTs with Ferromagnetic Material

Magnetic properties of CNTs can be enhanced by filling in the hollow inner sections with strongly magnetic materials. Carbon nanotubes filled with ferromagnetic metals exhibit enhanced magnetic coercivities, while the carbon walls provide an effective barrier to prevent oxidation, simultaneously ensuring long-term stability of the ferromagnetism [47]. The CNTs are processed via CVD at \( \sim 120 - 180 \, ^\circ\text{C} \) with the inclusion of metalloocene on a quartz boat in the CVD furnace. After sublimation of this metalloocene, the vapor was transferred by gas flow to a second furnace at \( \sim 900 - 1150 \, ^\circ\text{C} \), where the metalloocene gas decomposes and deposits to fill carbon nanotubes [48]. At room temperature groups of Fe-filled carbon nanotubes have coercivities of up to 1800 G [49].

2.4.2 Atomic Layer Deposition

Magnetic properties of CNTs can be also enhanced by externally coating CNTs with strongly magnetic materials. Atomic layer deposition (ALD) is a thin film coating technique used to create conformal coatings on high aspect ratio structures and particles. ALD utilizes two self-limiting reactions between a gas phase precursor molecules and a solid surface to deposit atomic-scalable thickness onto a surface [50]. However, limitations to proper thin film coating attachment is present
with ALD as the sites must be active. It was found that the inert characteristics of CNTs prevented the bonding of iron oxide ($\text{Fe}_2\text{O}_3$); CNTs need to be doped with nitrogen, to create active precursor sites, for appropriate bonding [51].

2.4.3 **Electron Beam Evaporation**

Electron beam (e-beam) evaporation is a thin film deposition technique used in various industries, notably in the aerospace industry to provide thermal and chemical barriers that protect surfaces from corrosion. E-beam deposition method can be used to deposit magnetic materials on CNT surfaces, although less conformally compared with the ALD method. In this process, a sample is housed a vacuum sealed chamber. The high energy of the electrons bouncing off of the source cause small amounts of the metal to evaporate and deposit onto the desired surface. Electron beam evaporation allows deposition at inclined angles to improve conformal coating on non-flat surfaces, and also allows co-deposition of multiple materials [52]. Due to the coating quality, scalability, and ease of use, e-beam evaporation was the method selected to coat the functionalized-CNT samples in this work.

2.5 **Research Objectives**

The objective of this thesis is to develop ferromagnetic CNTs that can serve as magnetically organized nano-additives dispersed within polymer matrices to form multi-functional CNT-polymer nanocomposites. These CNT nano-additives are highly desirable because of their unique mechanical and multi-functional properties, but their application has been limited due to poor property scaling and poor scalability. Thus, capability to organize and control nano-additives within polymer matrices in bulk is the essential step toward effective bulk application of these novel advanced polymer nanocomposites. More specifically, I develop and implement a three-step process to achieve magnetically responsive CNTs, as shown in Figure 2.1: 1) chemical vapor deposition (CVD) growth of vertically aligned, multi-walled CNTs, 2) low-temperature oxygen plasma treatment to clean and functionalize CNTs, and 3) electron beam evaporation of ferromagnetic
nickel (Ni) on functionalized CNT surfaces. The CNT growth, with vertically aligned morphology was optimized by pre-conditioning of iron (Fe) catalyst layers using hydrogen (H₂) gas. Low-temperature plasma treatment etched away the entangled top section of CNTs, exposing CNT tips to be ready for Ni coating. The degree of functionalization and degradation by plasma treatment was characterized via x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The Ni-coating on CNTs was inspected using energy dispersive x-ray spectroscopy (EDS) about their morphology and vibrating sample magnetometer (VSM) about their magnetic properties. With 80-nm-thick Ni-coating, the CNTs were well dispersed and suspended within the solutions (DI water and thermoset polymer matrix) to be ready for magnetic assembly. These fabricated magnetic CNTs were dispersed in a polymer resin, and were aligned magnetically using the small field to demonstrate preliminary scalable fabrication of polymer nanocomposite using magnetic assembly of nano-additives.
Figure 2.1: Schematic and SEM images of a three-step process to fabricate and assemble magnetically responsive CNTs. SEM images courtesy of Jatin Haibat.
Chapter 3

Experimental Approach

3.1 Chemical Vapor Deposition Synthesis of MWCNTs

As noted in Section 2.1, CVD was chosen for this thesis work as the synthesis method over other methods because of it produces a high volume of moderate-quality MWCNTs. Endo was the first to synthesize MWCNTs using CVD in 1993 [53]. This method relies on a carbon source, either in the gas or liquid phase, being introduced to an appropriate energy source, such as high temperature (750 °C) or plasma, inside a growth chamber. The hydrocarbons from the carbon source are transformed into pure carbon molecules by the energy source, and diffused onto the substrate, being deposited onto the catalyst nanoparticles on the substrate. There are two different growth types: tip growth where the carbon molecules are deposited on top of each other, and base growth where these carbon molecules reach the substrate and add onto the carbon formations by pushing existing carbon depositions upward. These carbon molecules are highly ordered, forming carbon nanotubes. Characterization of the fabricated CNT morphology and wall structure was carried out through scanning electron microscope (SEM) and transmission electron microscopy (TEM). Specific details of this process will be given in Chapter 4.
3.2 Plasma Functionalization of MWCNTs

As noted in Section 2.3, plasma treatment accomplishes two main tasks, cleaning the entangled layer on the top surface and amorphous carbon present on the side walls, and functionalizes the CNT surfaces. Removing the entangled layer and amorphous carbon to create space between individual CNTs is crucial for conformal nickel coating by directional e-beam evaporation. Functionalization using oxygen plasma treatment has been observed to improve the suspension of CNTs in organic solvents and polymers, while potentially improving the bonding of Ni coating to CNT surfaces [54, 55]. In this work, oxygen functional groups (hydroxyl, carbonyl, and carboxyl) were used to CNT surfaces. This process uses oxygen (atmospheric air) as the plasma source gas to attach oxygen-containing functional groups (ether, carbonyl, and carboxyl) to the CNTs. These functional groups improve the wettability of the CNTs, helping to improve the dispersion characteristics. CNTs containing oxygen functional groups exhibit better dispersion in an epoxy matrix and reduced agglomeration, two characteristics that improve the mechanical properties of CNT-epoxy nanocomposites. The treatment conditions were modulated by changing the power, gas, treatment time, and pressure used during treatment. In this work, the power and treatment time were studied using the Asher Plasma Cleaner in Dr. Terrones. The samples that underwent plasma treatment were characterized qualitatively by SEM imaging and quantitatively by x-ray photoelectron spectroscopy (XPS). Additionally, the treatment time can be controlled to avoid excessive tip-opening or damaging to the sidewalls. Specific details of this process will be examined in Chapter 5.

3.3 Coating of Ferromagnetic Material

After plasma treatment, the CNTs were coated with a thin ferromagnetic layer of nickel using electron beam evaporation in Dr. Suzanne Mohneys lab (Department of Materials Science and Engineering, Penn State). The thin layers ranged from 20 to 100 nm of Ni, and were visually inspected under SEM and energy dispersive spectroscopy (EDS). The quantitative magnetic
properties of the coated CNTs were measured using a vibrating sample magnetometer (VSM) in Dr. Paris von Lockettes lab (Department of Mechanical and Nuclear Engineering, Penn State). In terms of ferromagnetic metal selection, Ni was chosen because Ni does not form carbide unlike iron, leaving the sidewalls undamaged. Specific details of this process can be found in Chapter 6.

### 3.4 Magnetic Alignment of Ni-Coated CNTs

After conformal coating of ferromagnetic Ni onto the CNT surface, the coated CNTs were dispersed in a small amount of solution. For the case of aligning CNTs in a low viscous solution, the CNTs were dispersed in a small amount of DI water before the magnetic field application. The CNTs aligned in DI water were qualitatively inspected under optical microscopy to determine the level of CNT alignment. For alignment in polymer, the CNTs were first dispersed in a small amount of acetone. The acetone served as a secondary solvent, whose purpose was to remove the CNTs from their substrate. After the acetone-CNT solution was prepared with ultrasonication, the silicon substrate was removed from the solution and the primary solvent, EPON 862, was added to the mixture. EPON 862 was chosen as the polymer resin because of its aerospace-grade mechanical properties. The acetone-CNT-polymer mixture was added to a heated ultrasonication bath to adequately mix all three mediums together. The acetone was then removed via a vacuum pump and the CNT-polymer solution was then applied with the low magnetic field for alignment. The cured CNT-polymer composite was visually inspected under a transmitted-light microscope to determine the level of alignment of CNTs. More on this selection will be found in Chapter 7.
Chapter 4

Chemical Vapor Deposition Synthesis of MWCNTs

The multi-walled carbon nanotubes used for this study were synthesized through a process of Chemical Vapor Deposition (CVD), using an apparatus designed and built by Jatin Haibat (graduate student, Penn State). In Figure 4.1 and Figure 4.2, the apparatus consists of gas cylinders (argon-Ar, ethylene-C$_2$H$_4$, hydrogen-H$_2$), mass flow controllers (MKS GM50A), quartz tube (107 cm length, 3.5 cm diameter), furnace (Lindberg Blue M HTF55347C Single-zone Tube Furnace), furnace controller (Thermo Scientific CC58434PC Furnace Controller), and vacuum trap (Sigma Aldrich Z549444-1EA) filled with silicon oil. The CVD system is located in Dr. Namiko Yamamoto’s lab. The CVD synthesis is done by flowing carbon source gas, ethylene, through the quartz tube at 750 °C. The hydrocarbons from the ethylene gas are transformed into carbon molecules by the heating and reduction gas (H$_2$), diffused onto the substrate, and deposit carbon nanotubes on the catalyst nanoparticles on the substrate. The growth method prevalent here is the base growth model, where pure carbon molecules deposit on the base of the substrate and push already deposited molecules upward, creating highly order carbon compounds that are CNTs (Figure 4.3).
4.1 Optimization of CVD Growth Process

The recipe to grow vertically aligned CNTs through parametric studies. Mychal Spencer (Ph.D. candidate, Penn State) prepared substrates by depositing a thin aluminum oxide (Al₂O₃) diffusion barrier (10-30 nm) and an iron (Fe) catalyst layer (1-30 nm) on a silicon wafer (Si, <100>, p-type, with boron dopant, 0.5 mm thick) using electron-beam evaporation (Kurt J Lesker Lab-18 E-gun and Thermal Evaporator). For CNT synthesis, a 1 inch² piece was cut from the catalyst substrate and cleaned with compressed air to remove any debris. The cleaned substrate was placed centrally in the quartz tube. The growth chamber was sealed with O-rings, purged with argon gas (Ar, 650 sccm, 99.999% pure), and heated to the growth temperature (750 °C) with argon and hydrogen gas (H₂, 10 sccm) flowing. The hydrogen gas is a reducing agent, and preconditions the Fe catalyst into nanoparticles. After the growth temperature was achieved and stabilized, the carbon source gas, ethylene (C₂H₄, 400 sccm), was flown for 15 minutes to grow CNTs. After the growth, the ethylene and hydrogen gasses were stopped; the quartz tube and the grown CNTs were cooled while the argon gas continued to flow to purge.

For the original recipe, gas flow rates were converted from other existing recipes to fit our set-up based on volume and cross sectional areas of the quartz tube, gas lines, and gas travel lengths within the heated section of the growth chamber [56]. The first growth recipe served as a preliminary test to examine the base conditions of the growth set-up. The first growth (505 sccm C₂H₄, no H₂) left large depositions of sooty carbon on the inner walls of the quartz tube, and the catalyst substrate. The ethylene flow rate was reduced (400 sccm), the resulting deposition on the catalyst substrate was confirmed to be multiwalled carbon nanotubes using TEM (FEI Tecnai G2 20 XTWIN), see Figure 4.7. However, with lower ethylene flow rates the overall deposition of CNTs was not satisfactory because of the insufficient carbon supply. Extensive parametric studies were done to optimize the CNT growth, yielding consistent, directional MWCNTs, as described below.
4.1.1 Effect of Temperature

The temperature used to synthesize carbon nanotubes controls the rate at which carbon molecules interact with the catalytic nanoparticles on the surface of the substrate in order to form carbon nanotubes [57]. Part of this study involved varying the growth temperature and observing the effect on respective CNT growths. SEM images of CNTs grown at different temperatures are shown in Figure 4.4.

The first temperature used was the baseline temperature of 750 °C, deduced from other existing synthesis of CNTs [30, 57]. This temperature yielded the most consistent CNT growths, producing vertically aligned and uniform CNTs of roughly 60 µm in length. The second growth temperature observed was 800 °C; the higher temperature growth was expected to result in a high quality of CNTs due to a change in the reaction rate of nanoparticles and gas conditioning [57]. At this temperature, no growth was observed, rather the result was sooty deposition on the substrate. At high temperatures the carbonizing gas has self-pyrolyzed leading to a lack of CNT growth [57]. Another growth temperature observed was 700 °C. At this temperature, the result was aligned CNT growth with poor uniformity due to poor catalyst preconditioning.

4.1.2 Effect of Catalyst Layer Thickness

The iron catalyst layer thickness is crucial for growing directional CNTs on the substrate, instead of a general deposition of nontubular carbon compounds. Throughout the optimization process, three different substrates were examined.

The first substrate (1 nm Fe, 10 nm Al₂O₃) was prepared based on previous growth studies [56]. Upon inspection using SEM, CNT growth on both sides of the catalyst layer thickness was observed (Figure 4.5A); possibly due to delamination of the iron catalyst layer. The cause of this delamination can be attributed to poor adhesion of the e-beam deposited catalyst layers on the silicon substrate. The second substrate (30 nm Fe, 30 nm Al₂O₃) was developed to provide more structural integrity to the e-beam deposited layers by increasing both of the catalyst and diffusion barrier thicknesses. Even though this substrate prevented delamination of layers, the
resulting growths were not CNTs, as shown in Figure 4.5B. The increased catalyst layer thickness limited the reduction of the nanoparticles that are required for CNT growth. Instead the resulting depositions were non-organized carbon compounds. Finally, the third substrate (1 nm Fe, 30 nm Al₂O₃) was prepared. This substrate successfully yielded uniform growths of vertically aligned CNTs, as shown in Figure 4.5C.

4.1.3 Effect of Ethylene Flow Rate

The effect of ethylene flow rate was observed on CNT synthesis by comparing the flow rate of 200 sccm for 30 minutes and 400 sccm for 15 minutes. The outcomes of these growths are shown in Figure 4.6.

The 200 sccm flow rate resulted in more entangled CNT growth with wider spacing between the bundles when compared to the sample grown with 400 sccm of ethylene. This more entangled growth is attributed to not enough carbonizing gas being supplied to the iron catalyst, resulting in shorter, more entangled CNTs. In contrast, the dense, uniform, and vertically aligned CNTs were grown with a flow rate of 400 sccm ethylene.

4.2 Characterization of MWCNTs

Based on the above parametric growth study, the substrate recipe used to grow MWCNTs is 1 nm Fe, 30 nm Al₂O₃. Meanwhile, the temperature and flow rate recipe used in this work can be found in Table 4.1. The as-grown samples were characterized qualitatively via visual inspection under SEM (FEI Nova NanoSEM 630 FESEM) and TEM (FEI Tecnai G2 20 XTWIN TEM). From TEM inspection the presence of multiwalled structure, with a diameter of 35 nm ± 15 nm and 20 to 30 walls (Figure 4.7). SEM characterization was used to gain information about the morphology of the CNT surface and tips, length (~200 μm), clustering of CNTs, and the presence of impurities and amorphous carbon. The top surface of as-grown CNTs showed an entangled layer of CNT tips, as shown in Figure 4.8. This entanglement may result of dispersed catalyst particles in the growth chamber, or delamination of the catalyst layer. In order to ensure conformal metal coating on
CNTs, this entangled layer and any amorphous carbon present needed to be removed, as discussed in Chapter 5.
Figure 4.1: Digital image of the CVD set-up. Adapted from Jatin Haibat [58].

Figure 4.2: Schematic of the CVD set-up. Adapted from Jatin Haibat [58].
Figure 4.3: Schematic of the base growth method for carbon nanotube synthesis.

Figure 4.4: SEM images of CNTs grown at (A) 800 °C, (B) 750 °C, and (C) 700 °C on substrates with 15 nm Fe and 30 nm Al₂O₃ layers.
Figure 4.5: SEM images of CNTs grown on substrates with (A) 1 nm Fe and 10 nm Al$_{2}$O$_{3}$, (B) 30 nm Fe and 30 nm Al$_{2}$O$_{3}$, and (C) 1 nm Fe and 30 nm Al$_{2}$O$_{3}$ layers.

Figure 4.6: SEM images of CNTs grown with an ethylene flow rate of (A) 200 sccm, and (B) 400 sccm on substrates with 1 nm Fe and 10 nm Al$_{2}$O$_{3}$ layers.
Figure 4.7: TEM image of MWCNT. Image adapted from Jatin Haibat [58].

Figure 4.8: As-grown CNTs showing an entangled top layer.
<table>
<thead>
<tr>
<th>Process Steps</th>
<th>Ar (sccm)</th>
<th>C$_2$H$_4$ (sccm)</th>
<th>H$_2$ (sccm)</th>
<th>Temperature (°C)</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purge Gas Lines</td>
<td>650</td>
<td>400</td>
<td>10</td>
<td>25</td>
<td>3</td>
</tr>
<tr>
<td>Purge Quartz Tube</td>
<td>650</td>
<td>0</td>
<td>0</td>
<td>25</td>
<td>7</td>
</tr>
<tr>
<td>Temperature Ramp</td>
<td>650</td>
<td>0</td>
<td>10</td>
<td>Transient</td>
<td>15</td>
</tr>
<tr>
<td>Temperature Stabilization</td>
<td>650</td>
<td>0</td>
<td>10</td>
<td>750</td>
<td>10</td>
</tr>
<tr>
<td>CNT Growth</td>
<td>650</td>
<td>400</td>
<td>10</td>
<td>750</td>
<td>15</td>
</tr>
<tr>
<td>Furnace Cooling and Purge</td>
<td>650</td>
<td>0</td>
<td>0</td>
<td>Transient</td>
<td>-</td>
</tr>
<tr>
<td>Stop Gas Flow and Extract Substrate</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>25</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.1: Table of the standard recipe of CNT synthesis.
Chapter 5

Plasma Functionalization of CNTs

The grown CNTs were treated with oxygen plasma for two reasons: cleaning of the amorphous carbon and entangled layer of CNT tips, and functionalization of the CNT surface. This section serves as an extension to Jatin Haibats thesis [58].

Three main steps exist that lead to the surface activation resulting from plasma treatment, 1) oxidation of atoms to break bonds on the CNT surface, 2) addition and connection of more reactive functional groups, and 3) substitution reaction to create the desired functional groups [59]. The attached functional groups modify the surface to reduce CNT agglomeration in organic solvents such as isopropyl alcohol (IPA) and improve the bonding of applied coatings. For this study, an oxygen plasma treatment is used to attach oxygen-containing groups (ether, carbonyl, carboxyl) to the CNT surface.

5.1 Asher Plasma Cleaner with Oxygen

As-grown MWCNTs underwent plasma treatment using a Harrick PDC-32G Basic Plasma Cleaner in Dr. Mauricio Terrones lab (Department of Physics, PSU). The cylindrical process chamber (3 inch diameter, 7 in depth) uses atmospheric air as the process gas with an RF range of 8-12
MHz. Vertically grown CNTs, still on the substrate, were placed inside the process chamber, which was then pumped down to create a vacuum. A current was applied and the RF coil was energized to the chosen power setting, while a small amount of air is allowed into the chamber, breaking the vacuum seal. This small amount of air is added to the near-vacuum chamber to provide an outlet for ionization and igniting a plasma discharge. Due to the cylindrical nature of the RF coil, the plasma acts on all sides of the sample, as shown in Figure 5.1. Two parameters, treatment time (4, 6, 8, and 10 minutes) and the RF power (6.8 W low, 10.5 W medium, and 18 W high), were varied.

5.2 Characterization of Functionalized CNTs

In order to evaluate the level of functionalization and cleanliness of the plasma treated CNTs qualitative and quantitative characterization methods were used in the form of digital images, SEM images, Raman Spectroscopy and XPS.

5.2.1 Dispersion Studies of Plasma-Treated CNTs

Effectiveness of the plasma treatment was evaluated through a series of dispersion studies involving treated CNTs suspended in IPA. In order to effectively assemble magnetic CNTs in polymer nanocomposites a longer suspension time and uniform particle size are desired. Suspension is the ability of particles to stay floating within the solvent. The experimental process involved placing a small substrate sample (~0.25 cm²) with CNTs still attached to the substrate, in a glass vial filled with 1500 µL of IPA. The CNTs were detached from the substrate by placing the CNT-IPA glass vial in a VWR Symphony 97043-976 Ultrasonic Cleaner for 1 minute. The resulting dispersion and suspension was observed over a span of three days, taking digital images immediately after the ultrasonication process and at the end of three days.

The CNT suspension that lasted longest corresponded to 4 minutes of treatment time with a low power setting (6.8 W). Upon visual inspection, CNT suspension showed a direct relationship with treatment time, as treatment time increased so did the quality of suspension. However, this trend is only applicable up to 6 minutes of treatment time. As the power setting was increased, both
medium (10.5 W) and high (18 W) power, more CNTs settled to the bottom of the glass vial and less remained suspended. Based on these results from a series of dispersion studies, the optimized suspensions were found at low power (6.8 W) for 4 minutes, among the conditions tested in this work. These are the functionalization conditions used to prepare Ni-coated CNTs.

5.2.2 SEM Imaging of Dispersed CNTs

Plasma-treated CNTs were inspected using scanning electron microscopy (Zeiss Merlin FE-SEM). In order to gain an accurate assessment of how the plasma treatment affects the CNTs, the first images taken were of CNTs still attached to the substrate. Cross section views of the attached CNTs show the entangled top layer of CNTs was eliminated. In addition, the dispersed CNTs were examined under the same SEM parameters. These samples were prepared by taking a drop of the dispersed CNT-IPA solution and placing it on a clean silicon substrate. The IPA quickly evaporated, leaving behind agglomerations of dispersed CNTs. From these images it was clear that as the treatment time went above 4 minutes, the cluster size and CNT length decreased, showing signs of damage to the CNTs. Meanwhile, as shown in Figure 5.2, CNTs treated at 4 minutes with low power were arranged in loose clusters, signaling agreement with the results from the suspension study.

5.2.3 Raman Spectroscopy of Treated CNTs

Raman spectroscopy was conducted by Maxwell Wetherington (Materials Characterization Lab; Penn State) using a Horiba LabRam HR Evolution UV optimized. Raman spectroscopy works by exposing a sample to a beam of monochromatic light, resulting in the light scattering. The majority of the light scattered has the same energy and wavelength as the incident photons. However, a small fraction of the scattered light is of different energy, and usually a lower frequency than the incident photons. The resulting fraction of low-frequency scattering is measured in bands, with each band corresponding to a different bond structure [60, 61]. For this work the exciting laser wavelength used was 488 nm, with an exposure time of 45 seconds.
In order to gain a more complete understanding of the effect of plasma treatment exposure on the CNTs’ graphitic structure, Raman spectroscopy was carried out. More specifically, the D- and G- peaks were examined to determine the effect of plasma treatment time on the degradation of graphitic structure. Using Horiba Scientific’s LabSpec 6 software, the areas under the D- and G-peaks were calculated. Three different samples were examined, with several sites being examined on each sample. Pristine CNTs (as-grown, no functionalization), CNTs functionalized with low power for 4 minutes, and CNTs functionalized with low power for 8 minutes were investigated (Figure 5.3). Compared to the pristine sample, the functionalized samples showed decreases in areas with the D-peaks (1355 cm\(^{-1}\)): a slight decrease of 11.00% was noticed after 4 minutes of low Asher treatment, while a more significant decrease of 16.02% for 8 minutes of Asher treatment. On the other hand, the G-peak (1580 cm\(^{-1}\)) area for 4 minutes low Asher treatment showed an increase of 1.15% compared to the pristine sample, while the 8 minutes low Asher treatment showed a decrease of 26.86% compared to the pristine sample (Table 5.1). The decrease in areas of the D-Peak are expected after plasma treatment due to alteration of the CNT surface. The decrease in G-Peak area from the 8 minutes Asher treatment indicates significant alteration to the graphitic structure with the attachment of functional groups. The slight increase in G-Peak area for 4 minutes Asher treatment is desirable, because it means the graphitic structure remains relatively unchanged compared to the pristine sample. The large change in peak area for 8 minutes Asher functionalization demonstrates excessive treatment that compromises the graphitic structure of the CNTs. On the other hand, 4 minutes Asher functionalization is an appropriate amount of functionalization because there is only a slight decrease in the D-peak, while the G-peak is similar, when compared to the pristine sample.

5.2.4 X-Ray Photoelectron Spectroscopy of Treated CNTs

X-Ray Photoelectron Spectroscopy with a PHI VersaProbe II Scanning XPS Microprobe at the Materials Research Institute was used to evaluate the elements attached the functionalized CNTs. XPS is a surface characterization technique that uses the photoemission of a sample to analyze
the chemical and electronic state of elements on a sample. When the X-rays are focussed on the sample, loosely-bound electrons from the sample are released. The number of the electrons along with the release of kinetic energy is measured to calculate the binding energy, which can be used to find the shell and spin-orbit peaks. These peaks are unique to the chemical and electronic structure of materials, making XPS an effective method for characterizing the functional groups attached to samples [62, 63]. The peak fitting done in this work was done using CASA XPS (ver. 2.3.17) by Jatin Haibat [58]. After the background noise from scattered electrons was removed, the C 1s peak measured from the pristine sample was used to find peak changes resulting from the plasma treatment. The peak fitting used symmetric peaks for each functional group: hydrocarbon (CHx), ether (C-O), carbonyl (C=O), and carboxyl (O-C=O), and positions and position constraints from the Scienta ESCA300 database [64]. XPS measurements were taken on samples at the same time, approximately four months after they underwent plasma treatment. For each sample, the plasma-treatment power remained constant at the low (6.8 W) setting. The first observations made are with respect to the percentage of hydrocarbon present on the CNT surface. The highest percentage was found at 4 minutes, and the samples treated for 6 and 8 minutes showed a percentage close to 0%. The sample treated for 10 minutes showed an increase of about 5.6% in hydrocarbon percentage compared to the 6 and 8 minute-treated samples. The XPS plot of a pristine CNT compared to a CNT sample treated with 4 minutes of low Asher treatment is shown in Figure 5.4. This hydrocarbon (CHx) peak corresponds to non-organized formations of carbon or defects in the crystalline structure of the CNTs. As part of the elimination of the amorphous carbon from plasma-treatment, too much treatment can result in the damaging of the crystalline structure allowing for the functional groups to attach. As the treatment increases, carbonyl (C=O) and carboxyl (O-C=O) functional group percentages show an increase. However, the ether (C-O) functional group did not show a similar linear trend. At 10 minutes, the ether group shows a high percentage, stemming from a higher number of defect sites being present. The small variation in ether group percentages between 4, 6, and 8 minutes can be attributed to measurement error or standard deviations.
Figure 5.1: Schematic of Asher plasma treatment demonstrating the plasma discharge acting on all sides of the CNTs.

Figure 5.2: SEM images of low powered (6.8 W) functionalized, dispered CNTs. As shown in (C), 4 minutes low power Asher treatment provided loosely organized cluster. Image courtesy of Jatin Haibat [58].
Figure 5.3: Raman plot of functionalized CNT samples.
Figure 5.4: XPS plots of a pristine CNT sample and a CNT sample exposed to 4 minutes of low power Asher treatment. Image courtesy of Jatin Haibat.
Table 5.1: Areas under the D- and G-peaks from the Raman plot. Both areas for 4 minutes low Asher functionalization are significantly lower compared to the pristine samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D Peak Area (counts)</th>
<th>G-Peak (counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>97956</td>
<td>35558.5</td>
</tr>
<tr>
<td>4 minutes low Asher</td>
<td>87177.4</td>
<td>35968.5</td>
</tr>
<tr>
<td>8 minutes low Asher</td>
<td>82267.2</td>
<td>26006</td>
</tr>
</tbody>
</table>
Chapter 6

Coating of Nickel on Functionalized CNTs

Functionalized MWCNTs were coated with thin layers of nickel (Ni) using electron beam evaporation to enhance the magnetic responsiveness of the CNTs. These magnetically responsive CNTs can be aligned using magnetic fields to create organized CNT structures in CNT-polymer nanocomposites [65, 66].

In this chapter, I evaluate the nickel coatings deposition morphology, adhesion to the CNT sidewalls, and the resulting magnetic properties. Nickel was selected as the coating film because it does not react with CNTs to form carbides, unlike Fe or Co [67]. Coating of Ni was done via electron beam evaporation by Miss Frances Kwok and Dr. Suzanne Mohney (Department of Materials Science and Engineering, Penn State) using a Kurt J. Lesker AXXIS Multipurpose Physical Vapor Deposition System. Visual inspection of the Ni-coating deposition, as deposited and after dispersion, was done via SEM and energy dispersive x-ray spectroscopy (EDS). Meanwhile, the magnetic properties of the Ni-coated CNTs were characterized via vibrating sample magnetometry (VSM) in Dr. Paris von Lockettes lab (Department of Mechanical and Nuclear Engineering, Penn State).
6.1 Electron Beam Evaporation of Nickel onto Functionalized CNTs

The AXXIS deposition system is illustrated in Figure 6.1. The plasma-treated CNTs on the Si substrate were loaded into the system in an inverted position. A charged filament releases an electron beam onto the crucible, causing the crucible to heat up and evaporate small amounts of metal. The evaporated metal is then deposited on the inverted sample [68].

Before deposition, the chamber pressure was reduced to a value less than 80 mTorr, and Ti vapor was introduced into the chamber to remove any oxygen and water vapor in the chamber (gettering process). During the gettering process, a shield was covering the CNT samples to avoid Ti deposition. After this gettering process, the CNTs are uncovered and Ni was deposited at a rate of 1 Å/sec until the Ni coating thickness reached 20 nm, 40 nm, 60 nm, 80 nm and 100 nm. The low deposition rate was chosen to provide a more uniform and complete coating on the CNT surface [65].

6.2 Characterization of Ni Coating

6.2.1 Inspection Using SEM and EDS

The morphology of the Ni coating on CNTs are shown as a function of the Ni coating thickness in Figures 6.2 and 6.3. As the thickness of Ni coating increases, the Ni coatings increase their coverage resulting in more clustered CNT bundles. As shown in Figures 6.2 and 6.3 with 20 nm-thick Ni coating the CNT tips are not evenly coated. While the 100 nm-thick Ni coating results in cluster formations and bundling of CNTs. The formations of these clusters has an adverse effect on the CNT dispersion and suspension. In order to break up these clusters, longer ultrasonication exposure time is required to create a uniform dispersion, thus promoting Ni layer delamination from the CNT surfaces.

Related to the above, adhesion of Ni coating to the CNT after dispersion is crucial so that CNTs remain magnetically responsive. Energy Dispersive X-ray Spectroscopy (EDS) was used to
visually inspect the Ni layer distribution on the CNTs. EDS works by using a high-energy incident beam of charged particles that excites electrons on the inner shell of an atom, creating an electron hole. An outer layer electron loses energy to fill that hole, and the lost energy is released from the molecule in the form of x-rays. The energy difference between the inner and outer shells is unique to each element, and thus the element can be identified [69]. In this work, samples were scanned for 5 minutes using a FEI Quanta 200 Environmental SEM EDS probe (Materials Research Institute, Penn State).

Ni-coated CNTs were dispersed in 1500 uL of isopropyl alcohol (IPA) by 6 minutes of ultrasonication (VWR Symphony 97043-976 Ultrasonic Cleaner). A drop of the resulting solution was taken from the middle of the suspension and placed on a clean Si substrate. The IPA was evaporated, leaving a sample of dispersed Ni-coated CNT bundles. When inspected under EDS (see Figure 6.4), the CNT with Ni layers of 20 nm and 40 nm thickness did not exhibit ample amount of Ni signals on the CNT surfaces. For the CNTs with Ni coating of 60 nm, 80 nm, and 100 nm thickness, more amount of Ni signals were observed on distributed areas of the CNTs. Meanwhile, the CNTs with larger thickness of Ni coating show larger bundles and, thus, poor dispersion. These bundles have a negative effect on the suspension properties of the CNTs.

6.2.2 Magnetic Property Characterization with VSM

In the VSM set-up, a sample is loaded between two solenoids that apply a uniform magnetic field. When the sample is vibrated, the sample causes a change in the magnetic current, which is measured by two pick-up coils, between the solenoid which is proportional to the magnetic moment of the sample (Figure 6.5). From the plot of the applied magnetic fields and measured magnetic moment (H-M plot), the magnetic properties such as magnetic saturation, remanence, coercivity, and squareness can be extracted [70]. The Ni-coated CNT samples, still attached to the Si substrates, were used for this testing; magnetic fields were applied in directions parallel (axial) and perpendicular (transverse) to the CNT alignment direction in order to evaluate the anisotropy of their magnetic property. The magnetic contribution from the silicon substrate and catalyst layer
(1 nm Fe, 30 nm Al$_2$O$_3$) needs to be subtracted from any measurement to eliminate effect from the catalyst Fe layer. The magnetic contribution from CNTs themselves were also evaluated (Figure 6.6). The CNTs exhibit either diamagnetic or very small ferromagnetic behaviors as expected [71]. The H-M plots of Ni-coated CNTs with varying thickness are summarized in Figure 6.7. From these data, the following properties were extracted: magnetic saturation, remanence, squareness, and coercivity. The magnetic saturation is the highest magnetic moment the sample can achieve, while the remanence is the amount of magnetic moment remaining when the external magnetic field is removed [70]. The squareness is the ratio of the magnetic saturation against the remanence. The coercivity is defined as the amount of magnetic field required to zero the magnetic moment of the sample [70]. For both squareness and coercivity, the values are higher in the transverse direction compared to the axial direction. This trend can be attributed to how Ni layers are formed on the CNT tips. With the small thickness, the Ni coating is deposited on the CNT tip surfaces, resulting in a morphology direction alignment in the direction perpendicular to the CNT alignment. As the Ni coating thickness increases, the Ni coating starts to cover along the CNT length direction, resulting in the larger values of squareness in the axial direction for the 100 nm-thick Ni coating (Figure 6.8). The selected coating for magnetic assembly is 80 nm because of these VSM results and the observations from the SEM imaging and EDS, in order to take advantage of a strong enough magnetization and moderate CNT dispersion.
Figure 6.1: Schematic of the electron beam evaporation set-up used to coat the CNT samples. In this case, the crucible used is Ni, in order to gain ferromagnetic properties on the CNTs.
Figure 6.2: SEM images of cross-sectional views of an (A) as-grown CNT sample, (B) CNT sample coated with 20 nm-thick Ni layer, and (C) CNT sample coated with 100 nm-thick Ni layer.

Figure 6.3: SEM images of top views of an (A) as-grown CNT sample, (B) CNT sample coated with 20 nm-thick Ni layer, and (C) CNT sample coated with 100 nm-thick Ni layer.
Figure 6.4: (Top) SEM and (Bottom) EDS images of dispersed Ni-coated CNT. From left to right, the Ni-coating thickness increases from (A, E) 20, (B, F) 40, (C, G) 60, and (D, H) 80nm.
Figure 6.5: Schematic of the VSM set-up.
Figure 6.6: VSM plot showing the magnetic behavior of as-grown CNTs. The magnetic contribution from the Si substrate, along with the Fe catalyst, have been removed to demonstrate only the magnetic contribution from the CNTs.
Figure 6.7: VSM plot demonstrating the ferromagnetic behavior of Ni-coated CNTs.
Figure 6.8: Plot of the squareness and coercivity for Ni-coated CNT samples.
Chapter 7

Magnetic Alignment of Ni-Coated CNTs

Magnetic fields were applied to CNTs with the 80 nm-thick Ni coating to evaluate the magnetic responsiveness of Ni-coated CNTs and for future implementation to CFRPs. The Ni-coated CNTs were aligned in two different matrices: DI water and EPON 862, an aerospace grade polymer resin. Both alignments were done with Mychal Spencer (Ph.D. Candidate, Department of Aerospace Engineering, PSU) using a custom designed alignment apparatus in Dr. Yamamoto’s lab. The magnetic alignment apparatus, as shown in Figure 7.1, consists of a voltage generator and a function generator connected to two solenoids, with soft iron cores, placed next to each other. This set-up can create induced, uniform magnetic fields between the two solenoids, where the CNT solution was placed. The magnetic fields assembled the Ni-coated CNTs after a short period of time, indicating that magnetic assembly can be an energy efficient and effective method to organize magnetically responsive nanoparticles [37, 72].

7.1 Alignment of Ni-Coated CNTs in DI Water

A small amount of Ni-coated CNTs (0.00208 g) were aligned in DI water to determine the minimum magnetic field required to align magnetically susceptible CNTs in a low viscous solvent.
Ni-coated CNTs, still attached to their substrate, were added to a vial of 1500 uL DI water. The vial was placed in an ultrasonication bath (VWR Symphony 97043-976 Ultrasonic Cleaner) for 6 minutes to detach the Ni-coated CNTs from their substrate and break up the CNT bundles that result from the Ni coating. The Si substrate was removed from the vial, leaving a Ni-coated CNT-DI water solution of CNT volume fraction of 0.09%. A small drop was taken from the middle of the dispersed Ni-coated CNT-DI water solution and was dropped on a KOVA Glasics slide (0.1 mm height and 6.6 µL volume). The slide containing the CNT-DI water solution was placed in a uniform magnetic field of 125 G for 15 minutes. After 15 minutes, alignment of the Ni-coated CNTs was confirmed in the direction parallel to the magnetic field direction, as shown in Figure 7.2. The alignment of Ni-coated CNTs in head-to-tail fashion demonstrates the anisotropic property of the Ni-coated CNTs that results from the dipolar interaction of the Ni-coated CNTs [37].

7.2 Alignment of Ni-Coated CNTs in a Polymer

A small amount of the Ni-coated CNTs were aligned within a thermoset resin under the magnetic field to create a CNT-polymer nanocomposite. The Ni-coated CNTs (0.0048 g) were dispersed in 1500 uL of Acetone by ultrasonicating (VWR Symphony 97043-976 Ultrasonic Cleaner) for 6 minutes to detach the Ni-coated CNTs from the Si substrate and break up the CNT bundles that result from Ni coating. The acetone solvent served as a dispersing agent that improves the CNT dispersion [73, 74]. After ultrasonication, the Si substrate was removed from the Ni-coated CNT-Acetone solution, and 2.8 g of EPON 862 was added to the solution. The CNT-Acetone-Resin mixture was placed in a Branson Ultrasonic Cleaner Model: CPX-952-117R heated ultrasonication bath (∼65°C) for 5 minutes to decrease the viscosity of the resin [75]. The Ni-coated CNT-Acetone-resin mixture was placed in a vacuum chamber, that reached a pressure of 711.2 mm Hg; acetone was evaporated from the mixture after leaving the sample for 10 minutes. Finally, the curing agent, Curing Agent W, was added (0.7 g) to the CNT-resin mixture. The ratio by weight of EPON 862 and Curing Agent W used for the process is 100:26.4. The CNT mixture was placed in the heated ultrasonication bath (∼65°C) for 10 minutes for mixing and to lower the
viscosity. The thermoset resin and Ni-coated CNT mixture was poured into a square mold (3.175 cm x 3.175 cm). A magnetic field of \(~400\) G was applied across the mold for 110 minutes. For the first 50 minutes the mold temperature was held at the working temperature of the thermoset resin (70°C), during the last 60 minutes the temperature was increased to 121°C to initiate the curing process. After the magnetic assembly and procuring process was over, the mold was removed from the magnetic field and placed in a heated furnace (171°C) for 120 minutes to postcure the resin.

Unlike the assembly in DI water, large CNT agglomerations were observed in the direction of the magnetic field in this polymer matrix resin. This assembly difference can be attributed to the higher viscosity of the thermoset resin, preventing individual movement of Ni-coated CNTs along their axis that allows them to align with the magnetic field. This trend held true for both a volume fraction of 0.01% and 0.02% CNTs (Figure 7.3). The samples were also inspected using transmitting light microscopy (Carl Zeiss Optical Microscope). With the the 0.01 vol% of Ni-coated CNTs, CNT bundles showed alignment in the direction of the applied magnetic field within their agglomerations and outside the agglomerations (Figure 7.4). When the volume fraction was increased to 0.02%, less alignment was observed (Figure 7.5) possibly due to a smaller magnetic material (Ni) ratio for the CNTs.
Figure 7.1: (A) Schematic and (B) digital image of the magnetic alignment apparatus designed by Mychal Spencer and housed in 113M Research West, PSU [76]

Figure 7.2: Optical microscope image of Ni-coated CNTs assembled in head-to-tail fashion in DI water.
Figure 7.3: Digital images of CNTs aligned from a magnetic field running right to left in EPON 862 after post-cure. The CNT volume fractions are (A) 0.01% and (B) 0.02%.

Figure 7.4: Microscopic image of 0.01 vol% CNT-Polymer nanocomposite demonstrating alignment parallel to the right-to-left magnetic field in (A) the Ni-coated CNT agglomeration, and (B) smaller CNT bundles. Image credit: Shreya Trivedi.
Figure 7.5: Microscopic image of 0.02 vol% CNT-Polymer nanocomposite created using a right-to-left magnetic field. No magnetic response was observed in either (A) the Ni-coated CNT agglomeration, or (B) smaller CNT bundles. Image credit: Shreya Trivedi.
Chapter 8

Conclusions and Future Work

This chapter presents a summary of contributions in this thesis, along with suggestions for future work required to fabricate magnetically responsive CNTs as nano-additives for use in polymer nanocomposites.

8.1 Contributions to Polymer Nanocomposites

CVD Synthesis of MWCNTs:
- Uniform, vertically aligned CNT forests were synthesized using an optimized CVD process resulting in MWCNTs in length 200 μm and diameter 35 ± 10 nm with 20 to 30 walls.

Plasma Treatment of As-Grown MWCNTs:
- Air plasma treatment via an Asher plasma treatment eliminated the top, entangled layer of CNT growth, exposing the CNT tips for uniform ferromagnetic coating.
- Parametric studies of Asher plasma treatment were conducted to determine an appropriate treatment (time and power) using Raman Spectroscopy examination of the D- and G-peaks. The CNTs treated with low power (6.8 W) for 4 minutes yielded minimum graphitic structure degradation and satisfactory functionalization.
- Functional group attachment resulting from Asher plasma treatment was observed using XPS. XPS analysis on the plasma treated CNTs confirmed attachment of oxygen functional groups; functionalization of CNTs improved the CNT dispersion and Ni-coating attachment quality.
Ferromagnetic Coating Using E-Beam Evaporation:

- Thin layers of Ni-coating thickness ranging from 20 nm to 100 nm were deposited to plasma treated CNT surfaces.
- SEM and EDS were used to inspect the morphology of Ni-coated samples attached to the substrate and dispersed in IPA. Ni coating stayed attached to the CNT surface after dispersion. As Ni coating thickness increased, the size of CNT bundles increased, however Ni remained mostly on CNT tips without penetrating through the CNT forest.
- VSM was used to determine the anisotropic magnetic behavior of as-grown CNT samples and Ni-coated CNT samples. As-grown CNTs were measured to be diamagnetic, and with the Ni coating, CNTs were measured to be ferromagnetic with large enough magnetic moments for magnetic assembly.
- By balancing magnetic strength and anisotropic properties a Ni-coating thickness of 80 nm was selected for alignment in magnetic fields.

Alignment of Ni-Coated CNTs Using Magnetic Fields:

- Head-to-Tail assembly of CNTs with 80-nm-thick Ni coating was achieved in DI water using a low magnetic field (~125 G) over a short period of time (~15 minutes).
- Preliminary samples of CNT-polymer nanocomposites were fabricated using aerospace grade EPON 862 in a uniform magnetic field (~400 G).

8.2 Recommendations for Future Work

Further investigation into the following areas is recommended to reach scalable fabrication of CNT nano-additives for polymer nanocomposites. For the CVD synthesis of MWCNTs, more studies should be conducted to improve the scalability of CNT growth while maintaining or improving the uniformity and cleanliness of as-grown MWCNTs. For Asher plasma treatment of CNTs, more investigation into the functional groups should be conducted to determine the effect time has on degradation of functional group attachment. For ferromagnetic coating on CNTs, further investigation of the properties of different ferromagnetic materials attached to the CNT surface is necessary. Other coating techniques such as atomic layer deposition (ALD) or Layer-by-Layer (LbL) assembly should be attempted. For magnetic assembly, the dispersion of Ni-coated CNTs in polymer resin needs to be improved to achieve uniform dispersion. Finally, characterization
of fabricated CNT-polymer nanocomposites about the electrical, thermal, and strength properties should be conducted, in relation to CNT assembly structures.
Bibliography


Academic Vita

Steven Ceneviva  
sic5556@psu.edu

EDUCATION

The Pennsylvania State University  
Schreyer Honors College
Bachelor of Science in Aerospace Engineering  
Dean’s List: 6 of 7 semesters

The Pennsylvania State University  
University Park, PA  
Schreyer Honors College
Class of May 2017  
Bachelor of Science in Aerospace Engineering

THESIS INFORMATION

Ferromagnetic Coating and Magnetic Assembly of Carbon Nanotubes as Nano-Additives into Polymer Matrices
Research Advisor: Dr. Namiko Yamamoto
Honors Advisor: Dr. Philip Morris

WORK EXPERIENCE

Department of Aerospace Engineering  
University Park, PA  
Undergraduate Research Fellow  
June 2015 – Present
Undergraduate Teaching Intern  
University Park, PA  
AERSP 204H/404H & AERSP 306  
August 2016 – Present

LEADERSHIP

Sigma Gamma Tau  
University Park, PA  
Aerospace Engineering Honor Society – Member  
April 2016 - Present
Flight Vehicle Design and Fabrication Course  
University Park, PA  
Team Lead  
August 2013 – May 2016
PNC Leadership Assessment Center  
University Park, PA  
Participant  
October 2015

ACTIVITIES

Schreyer Consulting Group  
August 2015 – Present
Penn State Dance Marathon  
September 2013 – Present
Alliance Christian Fellowship  
September 2013 – Present

AWARDS

Henrietta M. Fisher Memorial Honor Scholarship  
August 2015
President’s Freshman Award  
Spring 2014

Presentations

Penn State Undergraduate Exhibition  
April 2017
Penn State Material’s Day as part of the PPG Undergraduate Research Fellowship  
September 2015
PPG Industries as part of the PPG Undergraduate Research Fellowship  
July 2015