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Development of scalable methods for the utilization of multi-walled carbon nanotubes in polymer and metal matrix composites

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Development of scalable methods for the utilization of multi-walled carbon nanotubes in polymer and metal matrix composites

by

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A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

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I want to thank my family for their unwavering support throughout my academic career. My accomplishments are only possible because of the love and encouragement of my parents, for whom I am truly grateful. Finally, I want to thank my fiancé, Kelsey, for her patience and support throughout my graduate studies.
Multi-walled carbon nanotubes (MWCNTs) have received considerable attention as reinforcement for composites due to their high tensile strength, stiffness, electrical conductivity and thermal conductivity as well as their low coefficient of thermal expansion. However, despite the availability of huge quantities of low-cost, commercially synthesized nanotubes, the utilization of MWCNTs in engineering composites is extremely limited due to difficulties in achieving uniform dispersion and strong interfacial bonding with the matrix. A proven method of enhancing the nanotube-polymer interface and degree of MWCNT dispersion involves functionalizing the MWCNTs through oxidation with strong acids. While effective at laboratory scales, this technique is not well-suited for large-scale operations due to long processing times, poor yield, safety hazards, and environmental concerns.

This work aims to find scalable solutions to several of the challenges associated with the fabrication of MWCNT-reinforced composites. For polymer matrix composite applications, a rapid, dry, and cost-effective method of oxidizing MWCNTs with O\textsubscript{3} in a fluidized bed was developed as an alternative to acid oxidation. Oxidized MWCNTs were further functionalized with silane coupling agents using water and supercritical carbon dioxide as solvents in order to endow the MWCNTs with matrix-specific functionalities. The effect of silanization on the cure kinetics, rheological behavior, and thermo-mechanical properties of model epoxy nanocomposites were investigated. Small additions of functionalized MWCNTs were found to increase the glass transition temperature, strength, and toughness of the epoxy.

In order to achieve composite properties approaching those of individual nanotubes, new approaches are needed to allow for high loadings of MWCNTs. One strategy involves
making macroscopic mats of nanotubes called buckypaper (BP) and subsequently infiltrating the mats with resin in processes familiar to traditional fiber-reinforced composites. The latter part of this thesis work explores a new method of producing BP comprised of oriented nanotubes through the use of a modified Taylor-Couette setup capable of simultaneously shearing and filtering an aqueous MWCNT dispersion. BP produced with this setup exhibited anisotropic electrical and mechanical properties as a result of the nanotube alignment.

Finally, a new technique for producing MWCNT metal matrix composites was developed using the nanotubes as the heating element and carbon source in a microwave-assisted carbothermic reduction of copper oxide. The extremely rapid heating of MWCNTs upon microwave irradiation allowed Cu-MWCNT composites to be produced in times on the order of a minute. Because this approach requires none of the specialized equipment generally used in metal matrix composite processing, it has promise as a scalable fabrication technique.
CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

The discovery of carbon nanotubes (CNTs) and their extraordinary mechanical, thermal, and electrical properties has sparked significant effort to develop lightweight composites using CNTs as reinforcement. While individual nanotubes have properties at the extreme of known materials, composites filled with CNTs often fall short of expected improvements due to poor dispersion and interfacial bonding. Over the last two decades, a significant amount of research has been devoted to modifying the surface of multi-walled carbon nanotubes (MWCNTs) for use in polymer matrix composites, and several promising approaches have been discovered. Among these, covalent functionalization of the outer walls of MWCNTs has proven effective at improving nanotube dispersion in and interfacial bonding with polymer matrices. Unfortunately, the vast majority of functionalization reactions are not amenable to industrial use because of long processing times, poor yield, safety hazards, and environmental concerns. Recent commercial expansion in the synthesis of MWCNTs has enabled the production of high quality nanotubes in huge quantities at low cost and opened the door for widespread application of MWCNT-reinforced composites. However, in order for the industrial production of these composites to become viable, alternative functionalization strategies are needed to address the unique challenges of nanotube modification on a large scale.

This thesis encompasses my efforts to develop scalable strategies for covalently functionalizing MWCNTs and subsequently using them to fabricate polymer matrix composites. A two-step reaction is adopted to functionalize the MWCNTs, which consists of first oxidizing the nanotubes and subsequently using the oxygen-bearing moieties as a
platform for further functionalization with silane coupling agents. This approach deliberately allows for a great deal of flexibility in the final functionality of the nanotube, as silane coupling agents with a wide variety of terminal functional groups are commercially available at low cost. While the functionalized MWCNTs can be made compatible with many resin systems, the scope of this work is limited to the incorporation of nanotubes in a model epoxy. The effects of both pristine and functionalized MWCNT additions on the thermo-mechanical, rheological, and curing behaviors of the epoxy are evaluated. Economic, environmental, and regulatory constraints associated with large-scale nanocomposite production are considered at each stage of composite fabrication and silanization and composite processing are performed without the use of any organic solvents.

While CNT composite research has been dominated by polymer matrices, metal matrix composites reinforced with CNTs also have great potential because the same advantages CNTs afford polymer matrix composites apply to metal matrix composites as well. In particular, CNTs exhibit higher strength, stiffness, thermal conductivity, and electrical conductivity than the matrix phase while having lower density. A major reason that CNT-metal matrix composites are not as well established as PMCs is due to the fact that metals are more difficult to process than polymers, because high temperatures and/or large forces are usually needed to introduce reinforcement into the metal matrix. In addition to work on polymer nanocomposites, this dissertation also presents a novel method of producing carbon nanotube metal matrix composites. Using a microwave-assisted carbothermic route, copper-MWCNT composites are prepared in very short times (on the order of a minute) starting from copper oxide and pristine MWCNTs. This new approach for fabricating carbon nanotube-reinforced metal matrix composites eliminates many of the
challenges associated with traditional methods while requiring a fraction of the time and energy.

1.2 Dissertation Organization

This dissertation is organized into eight chapters with the middle six consisting of manuscripts that have either been published in or prepared for submission to peer-reviewed journals. Chapter 1 serves as an introduction to CNTs and previous efforts to fabricate CNT-reinforced composites. An emphasis is given to the functionalization and dispersion of CNTs in polymer resins, as the bulk of this work focuses on strategies for producing polymer nanocomposites. Chapter 2 discusses a method for the uniform oxidation of MWCNTs with O$_3$ through the use of a fluidized bed and examines the role of nanotube defect structures on their oxidation.

Chapters 3 and 4 encompass efforts to silanize MWCNTs that had been previously oxidized by O$_3$ in the fluidized bed described in Chapter 2. Chapter 3 focuses on aqueous silanization of the MWCNTs using both di-functional and tri-functional amino-silanes. The presence of water in this reaction allowed for the self-condensation of the silane molecules, which resulted in the grafting of two different oligomeric structures on the surface of the nanotube. Chapter 4 focuses on silanization of the MWCNTs using an epoxy-terminated silane with supercritical carbon dioxide as the solvent for the reaction. In contrast to the aqueous route, the absence of water produces a nearly monolayer deposition of silane on the nanotube surface. Both chapters also provide detailed results of the characterization of the thermo-mechanical properties of composites made with the functionalized MWCNTs. An emphasis is placed on understanding the role of surface structure in developing the observed properties.
Chapter 5 details the development of a novel method to orient MWCNTs in solution and deposit them as a macroscopic sheet termed buckypaper. This approach lends itself to the fabrication of composites with much higher loadings of nanotubes than the types of composites explored in Chapters 3 and 4. Alignment of the nanotubes within the buckypaper sheet produces anisotropic properties, which are useful for composite fabrication and other potential applications such as in sensors or filters.

Chapter 6 describes a completely new method of making metal matrix composites starting from metal oxides using a microwave-assisted carbothermic reaction. The technique is applied to copper oxide to form copper-MWCNT composites with excellent hardness and offers several benefits over traditional metal matrix composite fabrication technologies in terms of safety and ease of processing.

Chapter 7 summarizes the conclusions drawn from the entire body of work. Ideas for future areas of inquiry and extensions of the presented findings are also given. As a supplement to Chapters 3 and 4, appendices A and B review the effects of pristine, oxidized, and silanized MWCNTs on the epoxy curing and rheological behavior, respectively.

1.3 Literature Review

1.3.1 Carbon nanotube structure

CNTs consist of carbon atoms bonded trigonally in a curved, hollow cylinder resembling a sheet of graphene rolled into a tube. These tubes are generally 1-50 nanometers in diameter and microns to millimeters in length, although lengths up to 18.5 cm have been observed.[1] CNT structures are often categorized by the number of concentric graphitic layers making up the tube. Single-walled carbon nanotubes (SWCNTs) consist of only one nanotube, double-walled carbon nanotubes (DWCNTS) are made up of two nested
nanotubes, and multi-walled carbon nanotubes (MWCNTs) contain several concentric nanotubes. Examples of each type of CNT are shown in Figure 1-1.

![Figure 1-1. SWCNT, DWCNT, and MWCNT structures (from left to right)[2]](image)

In addition to the number of nested nanotubes, the CNT structure is also defined by the chirality of each nanotube. The hexagonal rings making up the sidewall of a nanotube have a discrete number of configurations relative to the longitudinal axis of the CNT, which gives rise to a finite set of structural possibilities. The chirality is most easily described by a pair of indices \((n,m)\) defined by a vector called the chiral vector \(\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2\), in which \(n\) and \(m\) are integers and \(\mathbf{a}_1\) and \(\mathbf{a}_2\) are unit vectors shown in Figure 1-2. Creation of a nanotube from a graphene plane such as that shown in Figure 1-2 can be visualized by rolling the sheet in the direction of the chiral vector \(n\) atoms in the \(\mathbf{a}_1\) direction and \(m\) atoms in the \(\mathbf{a}_2\) direction. The resulting nanotube axis will then be orthogonal to the chiral vector. Using this convention, any SWCNT can be fully defined by simply specifying \(n\) and \(m\). If \(m = 0\), the SWCNT is called *zig-zag*. If \(n = m\), the nanotube is termed *armchair*. All other configurations are called *chiral*. The chirality of a nanotube has a profound effect on its electrical properties. If \(n-m\) is divisible by 3, the nanotube will be a metallic conductor. Otherwise, it will behave as a semiconductor with a bandgap of \(\sim 0.5\) eV.[3] The concentric
nanotubes within a MWCNT have a random chirality distribution under most growth conditions, although it is possible to produce monochiral MWCNTs.[4]

Figure 1-2. Schematic showing how a graphene sheet (a) can be “rolled” up into zig-zag (b), armchair (c), and chiral (d) nanotubes[5]

The history of the discovery of CNTs is an interesting and often misrepresented tale. Sumio Iijima is widely credited as the first researcher to produce a CNT after his transmission electron micrographs were published in *Nature* in 1991.[6] However, CNTs have been synthesized by humans as far back as 1889 from thermal decomposition of methane during attempts by Thomas Edison to produce carbon filaments for light bulbs,[7] although the direct observation of CNTs was not possible until the advent of transmission electron
microscopy in the 1930s. The first known image of a MWCNT was published in 1952 by Russian scientists,[8] and several other reports of nanotube structures were reported up until 1991.[9] Nevertheless, the report by Ijima was widely read and was published at a time when researchers across many disciplines were eager to explore nano-scale materials. Subsequent work yielded a variety of methods to grow CNTs using summarized in the following section.

1.3.2 Synthesis of CNTs

The three major methods of CNT synthesis today can be classified as arc discharge, visible light vaporization, and chemical vapor deposition (CVD). A catalyst is required to produce SWCNTs with all three routes and for CVD of MWCNTs. At present, CVD is the most economical method of CNT production, and all MWCNTs used in this work were produced by this technique.

Arc discharge represents a relatively simple technique for producing CNTs. The setup usually consists of two moveable graphite rods contained in an air-tight chamber. After evacuation of the chamber, helium or argon gas is flowed continuously until a pressure of ~ 500 Torr is reached. A bias of ~20 V is placed across the graphite rods, which are subsequently brought closer together until current arcs between them. The temperature at the anode rod reaches several thousand degrees Celsius, which causes the carbon to sublimate and eventually condense on the surface of the cathode in the form of MWCNTs and other products such as graphite and amorphous carbon. [10] Metal catalyst can also be introduced into the center of the anode to produce SWCNTs or to control the growth of MWCNTs. The exact mechanism of MWCNT formation by arc discharge is debatable, but SWCNT formation with a catalyst is believed to follow a vapor-liquid-solid (VLS) model regardless of the synthesis route. Arc discharge has the advantage of being relatively easy and
inexpensive to set up, especially on a lab-scale, and an arc welder can be used to supply current across the electrodes. However, the method has poor yield (generally producing less than 10% nanotube material) and is not easily scaled, as increasing the diameter of the electrodes reduces the fraction of nanotubes produced.

Visible light vaporization involves illuminating a piece of graphite with a high energy light source while under a controlled atmosphere of helium or argon. The graphite becomes hot enough to vaporize and small clusters of gaseous carbon recombine into CNTs given a proper temperature gradient, which is supplied by a cold finger and continuous flow of gas.[11] Several variants of the technique exist that can be defined by their light source: a pulsed laser is used in “laser ablation synthesis”, a continuous laser for “laser vaporization”, or multiple continuous wavelengths from a solar furnace may be used for “solar vaporization”. Visible light vaporization apparatuses are generally more expensive and complicated to set up than arc discharge growth chambers, although they produce better yields of CNTs (up to 50%) and the nanotubes have fewer defects.[11]

CVD represents the third, and most widely used technique for synthesizing CNTs. CVD requires a carbon-bearing gas feedstock and a catalyst.[12] The catalyst, usually a transition metal, lowers the temperature required to thermally decompose a feed gas, which can be a variety of hydrocarbons or CO. The catalyst can be suspended in a gas (floating) or placed on an inert support material such as silica or alumina. In either case, during the synthesis reaction, feed gas is heated until it decomposes (generally 600-1200 °C) into carbon and another byproduct. The carbon dissolves in the catalyst and precipitates out as a CNT according to the VLS model. The key to obtaining high quality CNTs at high yields lies in the design of catalyst particles and in optimizing the furnace atmosphere and temperature.
Metal catalysts must be small, have a high solubility for carbon, and be stable at high temperatures to prevent coalescence. Ni, Fe, and Co are common constituents in a catalyst formulation and refractory metals are often added to increase the melting temperature; however, the specifics of modern catalyst design are the closely guarded property of CNT manufacturers. The reaction temperature is another critical parameter that must be high enough to decompose the feed gas but low enough to prevent coalescence of the catalyst particles. Thus, different feed gases such as CO, methane, acetylene, and benzene require different reaction conditions and allow for flexibility in developing different catalysts. CVD is the most economically favorable and scalable CNT synthesis technique known.

One of the exciting aspects of CVD for industrial production of CNTs is the fact that the feedstock is very inexpensive (and almost negligible in the case of CO). This situation is the opposite case of polymers, in which monomers dictate the price of the final product. If catalyst efficiency can be improved, CNTs could be produced at very low costs approaching that of the energy needed to heat the reactor. As an illustration, catalyst costs for CNT production are comparable to that of high density polyethylene (HDPE). HDPE yields from ethylene are about 10,000:1 in terms of polymer weight:catalyst weight, and HDPE sells for about $1/lb. Current yields for MWCNTs and SWCNTs are around 10:1 and 0.1:1 and cost ~$100/lb and $10,000/lb, respectively. Thus, yield is the determining factor in the price of CNTs from CVD today, and better catalysts could allow the production of CNTs near or below the price of commodity plastics.

1.3.3 Properties of individual nanotubes

Measuring the properties of an individual CNT is a difficult task not only because nanotubes are so small in dimensions, but also because the properties are affected by the
types and quantities of defects present, the chirality of the nanotube, and the number of nested layers (in the case of MWCNTs). Nevertheless, serious effort has been expended to determine the mechanical, electrical, and thermal properties of both SWCNTs and MWCNTs and a survey of the findings is given below.

The mechanical properties of CNTs originate from the strong, in-plane sigma bonds formed between sp²-hybridized carbon atoms in the hexagonal sidewall, which have bond energies of ~ 346 kJ/mol, and the weak pi bonding between shells (in MWCNTs) with energies of ~ 3.4 kJ/mol.[13] The modulus of a material is defined by the following equation

\[ E = \frac{1}{V} \left( \frac{\partial^2 G}{\partial \varepsilon^2} \right) = \left( \frac{\partial \sigma}{\partial \varepsilon} \right) \]

in which E is tensile modulus, V is volume, G is Gibbs free energy, \( \varepsilon \) is strain, and \( \sigma \) is stress. One problem with the determination of the modulus (and tensile strength) of nanotubes arises from the definition of the area (A) upon which a force (F) is applied in the \( \sigma = F/A \) term. One popular convention has been to consider the nanotube 0.34nm thick (the intershell spacing in a MWCNT) and to calculate the area based on the nanotube radius. Using this approach the theoretical modulus of CNTs has been found to be ~ 1 TPa.[14, 15] Experimental characterization of MWCNTs and SWCNTs has yielded moduli on the same order of magnitude.[16-20] The most direct of these measurements involved fixing individual nanotubes between two AFM tips and straining to failure while monitoring with SEM, as shown in Figure 1-3. MWCNTs tested using this setup were found to have moduli values between 0.27–0.95 TPa, failure strains up to 12%, and ultimate tensile strengths from 11-63 GPa.[17] A similar set of measurements on SWCNT bundles yielded modulus values in the
range of 0.32-1.47 GPa, failure strains on the order of 5.3%, and ultimate tensile strengths from 13-52 GPa.[16]

![Image of experimental setup](image)

**Figure 1-3. Experimental setup used by Ruoff to perform tensile tests on individual CNTs[17]**

CNTs also have extraordinary and complicated electrical properties. Electron flow is confined to the long axis of the nanotube resulting in one-dimensional electronic conduction. As previously mentioned, the chirality of a CNT dictates its electrical behavior. Nanotubes having structures satisfying the condition of \((n-m)/3 = \text{integer}\) are metallic and the remainder are semiconductors. Thus, 1/3 of all CNTs have no band gap and the remaining 2/3 are semiconductors with band gaps that are inversely proportional to the tube diameter.[21] This size-dependent behavior arises because curvature in the sidewall slightly misaligns neighboring \(\pi\) orbitals (and may induce partial \(\sigma-\pi\) hybridization in small diameter tubes), which increases the band gap.[22, 23] For all metallic nanotubes besides armchair structures,
curvature effects also cause a tiny band gap to form; however, thermal fluctuations at temperatures close to room temperature render these nanotubes metallic. Armchair CNTs are ballistic conductors, meaning that the mean free path of electronic scattering is much larger than the nanotube dimensions. As a result, resistance does not depend on the nanotube length, and no resistance heating is observed because no electron scattering occurs (which normally dissipates heat in the form of phonons via inelastic interactions). Measurements performed on a single 4 mm long, 1.7 nm diameter metallic SWCNT yielded a conductivity of about $5 \times 10^7$ S/m.[24] Measurements of MWCNT conductivity are more challenging as a result of multiple shells with varied chirality, and a range of conductivities from $2 \times 10^7$ – $8 \times 10^5$ have been reported.[25, 26]

Thermal conductivity represents another remarkable property of CNTs. Values of 1400 W/(mK),[27] 2000 W/(mK),[28] and 3000 W/(mK)[29] have been determined from measurements performed on single MWCNTs. The thermal conductivity was found to depend heavily on temperature, reaching a maximum value around 47 °C and decreasing sharply at higher temperatures.[29] Other measurements of individual MWCNTs have yielded lower conductivity values around 300-800 W/(mK).[30, 31] Bundled MWCNTs and buckypaper sheets were found to have even lower thermal conductivities of 150 W/(mK) and 50 W/(mK),[32] respectively, due to thermal resistances caused by inter-tube junctions. The large range in measured values may be due to the fact that the thermal conductivity is theoretically predicted to depend on nanotube length,[33] diameter,[34] and structural defect density[32] (which is relatively high in CVD-synthesized nanotubes) as well as interactions with substrates. The studies performed to date have not explicitly taken account of all of these factors, and, as a result cannot be readily compared.
1.3.4 Dispersion of CNTs in a matrix

A significant body of work has been devoted to producing CNT-reinforced polymer nanocomposites for structural and functional applications.[35-42] However, despite over two decades of research, CNT composites have still underperformed their potential because of the challenges associated with dispersion of CNTs in the resin during processing and the poor interfacial bonding between nanotubes and matrix. The extremely high aspect ratio and surface area of CNTs makes them more difficult to disperse than traditional fillers or spherical nano-scale particles. Furthermore, commercially available CNTs consist of intertwined bundles that are especially difficult to disentangle. This section will briefly review the most popular techniques that have been adopted to disperse CNTs in polymers.

The most common dispersion method is ultrasonication, which involves disentanglement through the use of ultrasound energy. When CNTs mixed in a resin or solvent are subjected to a high frequency, oscillating pressure wave, shockwaves are produced in the dispersing medium which causes nanotubes on the outer extremities of an agglomerate to separate from the bundle.[43] Ultrasonication requires that the CNTs be dispersed in a low-viscosity liquid in order to limit attenuation. As a result, CNT/resin mixtures are often diluted with an organic solvent during sonication processing; however, sonication produces a substantial amount of heat, and volatile solvents must be actively cooled to prevent loss via evaporation. Two types of sonication equipment are commonly employed: bath and horn sonicators. Bath sonicators generate 15-400 kHz waves through a medium of water at powers less than 100 W. With this technique, CNT mixtures in a container such a glass vial are placed in the water bath and subjected to uniform pressure waves. The relatively mild pressure waves generated by bath sonicators are effective at
dispersing CNTs in very low viscosity liquids (especially with the aid of surfactants) without severely damaging nanotubes. Horn (or probe) sonicators produce a high powered (100-1500 W), directional pressure waves. While effective at dispersing CNTs, long exposure times can lead to structural damage of the nanotube sidewalls, which degrades electrical and mechanical properties.[44, 45]

Another common method of dispersion is calendaring. With this technique, very viscous resin containing CNTs is fed through a three-roll mill consisting of closely spaced, adjacent rollers that are spinning in alternating directions and varying speeds. As the nanotube-filled resin passes through the small gaps between rollers, it experiences high shear stresses, which break up agglomerations. By controlling the angular velocity of the rollers and the gap size, the magnitude of the shear can be adjusted, and dispersions are often calendered several times using consecutively smaller gap widths. While this method is simple and convenient for homogenizing CNTs, it has limitations. The CNT/resin mixture must be paste-like in viscosity for the rollers to pull the dispersion through the gaps, which restricts its use with most thermosetting resins and some thermoplastics. Furthermore, most three-roll mills have minimum gap sizes of 5 μm, which is insufficient to fully disentangle CNT bundles.[46] Instead, calendaring often distributes microscopic agglomerates of CNTs very evenly in a resin.[46-50]

A third popular dispersion technique involves shear mixing with high-speed mixers or extruders. Laboratory-scale overhead mixers capable of reaching speeds of several thousand rpm have been used to produce fine levels of dispersion in thermosetting resins.[51] However, overhead mixing is restricted to use with low and medium viscosity resins, and reagglomeration of CNTs post-mixing is common. CNTs can be compounded with high
viscosity resins using extruders. Extrusion is the most popular method of fabricating thermoplastic nanocomposites and the widespread use of industrial extrusion makes this technique readily scalable for engineering applications. Typical processing involves feeding solid plastic pellets mixed with CNTs into an extruder and subjecting them to large shear forces provided by rotating screws, which disperse the CNTs and generate heat to melt the polymer. Melt mixing via extrusion is generally less effective at dispersing the CNTs on a nano-scale level than solvent-assisted sonication due to the lower shear rates involved and the absence of small molecules to infiltrate the interstices between nanotubes in a bundle.[37] Interestingly, while MWCNTs can be adequately dispersed with twin-screw extrusion, the technique has proven less effective for SWCNT/resin mixtures.[11] Nevertheless, extrusion has several advantages over other dispersion methods including simplicity, availability, and the fact that reagglomeration of CNTs is limited by the long relaxation times of viscous polymers.

1.3.5 Functionalization of CNTs

All of the dispersion techniques outlined above can be aided by the introduction of functional groups on the CNT sidewalls that are compatible with the matrix resin. Furthermore, for nanocomposites to attain excellent mechanical properties requires more than simply achieving a homogeneous physical distribution; it requires strong adhesion between the MWCNTs and matrix. Functionalization of the MWCNT surface is a widely acknowledged strategy for improving dispersion and strengthening the interface simultaneously, and previous approaches can generally be divided into two categories: covalent and noncovalent functionalization. A few examples from each category are briefly described below.
Noncovalent functionalization involves covering the MWCNT surface with polymers [52] or surfactants [53], which are held to the nanotube surface by Van der Waals forces, as shown in Figure 1-4. An advantage of this approach is that the sidewalls of the MWCNT remain intact, so the electrical conductivity of the nanotubes remains very high, and composites with excellent electrical properties have been fabricated.[42] However, because the polymers or surfactants are only weakly attached to the MWCNTs, they easily slip off the nanotube surface under applied stress. Furthermore, many techniques use polymers that are cost-prohibitive for industrial processing.[54, 55]

**Figure 1-4. Schematic depiction of noncovalent functionalization via polymer wrapping[42]**

Covalent functionalization involves chemical attachment of a moiety to the outer sidewalls or ends of the MWCNTs. Myriad techniques have been explored to functionalize the MWCNT sidewall. Several popular routes have been broadly categorized below as addition reactions, acid oxidation, and physical oxidation.

Like all fullerenes, the MWCNT walls have an associated strain energy which renders them more reactive than planar aromatic molecules. As a result, a variety of chemical addition reactions are possible including fluorination, hydrogenation, and cycloaddition of groups such as carbenes, nitrenes, and azomethines.[42, 56, 57] While this approach allows a
high degree of control over the nature of functional groups added to the MWCNT, the rigorous reaction conditions and long treatment times required are impractical for industrial-scale processing.

Exposure of MWCNTs to strong acids is a popular method to generate defect sites on the MWCNT surface containing a mixture of functionalities including carboxylic, carbonyl, and hydroxyl groups.[56, 57] Sulfuric acid, sulfuric and nitric acid mixtures, and piranha solution (sulfuric acid and hydrogen peroxide mixture) are commonly used to oxidize MWCNTs,[58] and ultrasonication is often employed to disperse MWCNTs in the acids and improve their oxidation efficiency.[59] This method is simple and effective at introducing oxygen functional groups on the MWCNT surface, but it has several disadvantages. Acid oxidation often has poor yield, and the MWCNT structure is often severely damaged after functionalization, which dramatically decreases the mechanical properties of the nanotubes and reduces their aspect ratios. In addition, the use of strong acids is unattractive for large-scale processing due to safety and environmental concerns.[60]

Physical oxidation involves oxidation of preexisting defects on the outer walls of MWCNTs using sources such as plasmas [61] or UV light.[62, 63] Felten et al. effectively used O₂ plasma to oxidize the MWCNT surface and control the nature of functional groups (hydroxyl, carboxylic acid, and carbonyl) by tuning the reaction atmosphere. Asano et al. introduced 3 wt% COOH groups onto MWCNT surfaces after only 1 min of exposure to intense UV light. Physical oxidation methods such as these are industrially attractive because they are nonpolluting, require no harsh chemicals, and can be performed rapidly. However, dry processing in the absence of solvents introduces challenges in attaining uniform MWCNT functionalization.


1.4 Research Objectives

While many functionalization routes developed in the past have proven effective, very few are amenable to industrial-scale processing, and those that are promising for large-scale production have not been optimized. Furthermore, few studies have addressed the practical challenges of functionalizing huge quantities of CNTs. For instance, any functionalization methods involving the use of solvents generates liquid waste containing CNTs. Proper disposal of such waste provides a costly challenge and may be subject to regulatory scrutiny for environmental and health reasons. Nonetheless, almost all reported functionalization methods employ copious amounts of solvents. This work aims to address the major issues limiting MWCNT utilization on a large scale by developing functionalization routes that use inexpensive and commercially available reagents, do not require organic solvents, and proceed quickly. The great diversity of resin-MWCNT combinations precludes the study of even a fraction of all possible composite systems. The bulk of this work focuses on a model epoxy to test the efficacy of MWCNT functionalization in improving composite properties. However, the techniques reported here have been made intentionally versatile to broaden their utility for any composite application.

The specific goals of this research are to:

(i) Develop dry MWCNT oxidation strategies for rapid, cost effective production of oxidized MWCNTs (o-MWCNTs).

(ii) Functionalize the o-MWCNTs with a variety of silane coupling agents to attach epoxy or amine end groups and facilitate chemical reactions of these
functionalized MWCNTS (f-MWCNTs) with either the epoxy matrix or the amine hardener.

(iii) Validate the efficacy of the hybrid MWCNT functionalization strategies by preparing epoxy nanocomposites with various loadings of f-MWCNTs

(iv) Characterize the effect of f-MWCNT type and loading on the cure, rheological, thermal, and mechanical properties of the model epoxy matrix to demonstrate the ability of f-MWCNT end groups to react with the epoxy matrix or the hardener.

(v) Advance new processing methods that allow MWCNT composites to be fabricated with much higher nanotube loading levels than traditional melt/resin mixing.

(vi) Explore alternative uses for inexpensive, commercially synthesized MWCNTs such as heating media and carbon sources in carbothermic reactions.

1.5 References


2.1 Abstract

Multi-walled carbon nanotubes (MWCNTs) were simultaneously fluidized and oxidized with gaseous ozone in a vertical reactor. Two different varieties of MWCNTs were compared to determine the versatility of the treatment and to elucidate the effect of defects on the oxidation behavior of MWCNTs. The extent of oxidation and nature of functional groups introduced on the nanotube surfaces were determined using Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Boehm titration, and structural changes were monitored with Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). After only a few minutes of treatment, non-graphitic impurities were removed from the MWCNTs and significant levels of oxidation (~8 at% O) were achieved with very little damage to the nanotube sidewalls. Short \( \text{O}_3 \) exposure resulted in primarily hydroxyl functionalities while longer exposure led to the
formation of mainly carboxylic acid groups. Aliphatic defects present in the commercially-produced MWCNTs were found to play an important role in the oxidation mechanism. Because of its ability to remove impurities and evenly oxidize the sidewalls of nanotubes without the use of any solvents, the fluidized O$_3$ reaction developed in this study was found to be an attractive option for industrial-scale MWCNT functionalization.

2.2 Introduction

Carbon nanotubes (CNTs) possess extraordinary mechanical, thermal, and electrical properties, making them ideal candidates for a wide range of applications in areas as diverse as energy storage,[1, 2] electronics,[3] and biosensors.[4, 5] CNTs are expected to be particularly suitable as reinforcement for composites due to their high aspect ratio. However, the addition of CNTs to polymers does not always engender outstanding mechanical properties and, in fact, has been reported to have deleterious effects in some instances.[6, 7] This under-performance stems from several possible sources. The graphene walls of as-grown CNTs are hydrophobic and have low surface energy, making CNTs incompatible with polar solvents and most polymer matrix materials. Furthermore, strong inter-tube van der Waals attractions cause CNTs to agglomerate into bundles, which have poor mechanical properties. Surface modification is an established approach to overcome poor dispersion and weak interfacial bonding in CNT-reinforced composites. Oxidation of CNTs by exposure to concentrated acids is a popular functionalization method at the laboratory-scale that has proven to be effective in improving composite properties.[8-12] However, acid exposure causes significant damage to the nanotube structure and leaves behind weakly adsorbed debris, which interferes with interfacial bonding in a composite if not removed.[13] Acid oxidation is also unattractive for industrial-scale functionalization because of safety hazards
associated with flammable and corrosive acids as well as the need to repeatedly wash and dry the CNTs post-reaction. Furthermore, any functionalization methods involving the use of solvents generates liquid waste containing CNTs. Proper disposal of such waste provides a costly challenge and may be subject to regulatory scrutiny for environmental and health reasons.

Alternative, gas-phase oxidation reactions eliminate waste and drying steps, making them appealing for mass production of functionalized CNTs. Oxidation by gaseous O$_3$ is particularly well-suited for industrial use as O$_3$ is currently generated inexpensively in large quantities and readily decomposes to O$_2$ in water or upon reaction with unsaturated molecules.[14] Several reports of successful functionalization of single-walled carbon nanotubes (SWCNTs) using O$_3$ have been reported in the literature beginning with Smalley et al.[15-19] As with other fullerenes, the curvature strain of small diameter SWCNTs makes them reactive towards O$_3$, and a variety of oxygen bearing functional groups can be generated including alcohols, ketones, esters, and carboxylic acids. These moieties permit the SWCNTs to disperse much more easily in solvents. For instance, SWCNTs simultaneously exposed to UV light and O$_3$ were functionalized with hydroxyl and carbonyl groups, which increased their solubility in ethanol by more than 500%.[16] Multi-walled carbon nanotubes (MWCNTs) are also reactive towards O$_3$, though less so than SWCNTs due to their larger diameters. A few reports have shown that by sonicating MWCNTs in water and bubbling O$_3$ through the dispersion, oxidation levels on the order of 3-7% can be achieved.[20-22] Functionalization of MWCNTs by gaseous O$_3$ has not been as well studied as SWCNTs, but a few reports indicate that significant oxidation is possible.[23-25] Kim et al. used a single UV-O$_3$ source to endow MWCNTs with approximately 5 at% oxygen after 1 hr of
exposure.[23] Zhang et al. used an O$_3$/water vapor mixture to generate oxygenated functional groups, though substantial damage to the tube walls was observed upon prolonged exposure.[25]

While gas-phase O$_3$ reactions have been shown to successfully oxidize both SWCNTs and MWCNTs, achieving even oxidation is a challenge.[19] especially as the reaction size scales up. Thus, previously reported methods are not suitable for large-scale functionalization. High quality MWCNTs are currently available in huge quantities at low cost, and market forecasts predict further increases in production to 12,800 metric tons by 2016 with concomitant price declines.[26] With a scalable, inexpensive functionalization method, widespread use of MWCNT-reinforced composites is a realistic possibility in the near future.

This work is part of a program to develop industrially scalable functionalization methods for MWCNTs that do not require solvents or acids and which do not significantly damage the nanotube structure. Here we discuss our efforts to rapidly and evenly purify and functionalize MWCNTs using an O$_3$/O$_2$ mixture as the bubbling gas in a fluidized bed reactor. In contrast to previous reports on the oxidation of MWCNTs with gaseous O$_3$, the fluidized bed employed in this method allows for uniform treatment of large quantities of CNTs. A corona discharge O$_3$ source, the most cost effective method of producing O$_3$ on large scales, is used instead of the UV-O$_3$ type generators popular in past work. Two types of commercially available MWCNTs with similar size but different defect densities were treated in order to elucidate differences in oxidation behavior and to determine the versatility of the method. Structural changes in the nanotubes were monitored by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Raman spectroscopy, and oxidation was
characterized with Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Boehm titration.

### 2.3 Experimental Details

#### 2.3.1 Materials

Kumho multi-walled carbon nanotubes (\(k\)-MWCNTs) with an average diameter of 10 nm and purity greater than 90% were supplied by Kumho Petrochemical Co. (South Korea). NC7000 multi-walled carbon nanotubes (\(n\)-MWCNTs) with an average diameter of 10 nm and purity of 90% were supplied by Nanocyl, S.A. (Belgium). O\(_3\) was produced with a corona discharge O\(_3\) generator (L-50, Ozonology Inc.) using O\(_2\) as the feed gas.

#### 2.3.2 Fluidized ozone treatment

Pristine MWCNTs (1 g) were placed into an empty gas purifier flask that was adapted for use as a fluidized bed, as shown schematically in Figure 2-1. An O\(_3\)/O\(_2\) mixture containing 6% (wt/wt) O\(_3\) was then flushed through the glassware from the lower insertion at a flow rate of 1.4 L/min through a stainless steel distributor plate, causing the MWCNTs to fluidize. A porous membrane affixed to the top of the reactor allowed venting of excess gas, which was scrubbed into a 2% potassium iodide solution to remove any remaining O\(_3\) before discharging to atmosphere in a fume hood. The MWCNTs were treated for 5-90 min at a relative humidity of about 50%.
2.3.3 Characterization

The structures of pristine and oxidized MWCNTs were probed with TEM (JEOL 1200EX), SEM (FEI Quanta 200) and Raman spectroscopy. Raman spectra were collected with a Renishaw inVia spectrometer using backscattered light from a 488 nm laser focused through a 50x objective lens. Changes in surface chemistry were monitored with XPS, Boehm titration, and FTIR. FTIR spectra were collected in a Bruker IFS66V spectrometer. The nanotubes were thoroughly mixed with potassium bromide and pressed into a pellet before data acquisition. XPS measurements were carried out in a Physical Electronics 5500 Multitechnique system with a monochromatic Al Kα radiation source, and CasaXPS software was employed for data processing. Analysis of the elemental surface composition of each sample was performed using MWCNTs taken from at least 5 different regions of the fluidized bed. An optimized acid-base (Boehm) titration technique was used to determine the concentration of protic functional groups on the surface of MWCNTs.[27] Briefly, MWCNTs were stirred overnight in three different 0.05 M basic solutions of NaOH, Na₂CO₃, and NaHCO₃. The samples were then filtered to remove the MWCNTs, and 10 mL aliquots
of the filtrate were saved for analysis. 20 mL of 0.05 M HCl was then added to the NaOH and the NaHCO$_3$ filtrate aliquots, and 30 mL of 0.05 M HCl was added to the Na$_2$CO$_3$ filtrate aliquot. Once the aliquots had been acidified, they were back-titrated with 0.05 M NaOH and the endpoint was determined with a digital pH meter. Triplicate titrations were performed for each sample.

2.4 Results and Discussion

2.4.1 Material assessment

As-produced MWCNTs may contain a variety of structural defects and impurities that critically affect their reactivity and ultimate performance. Amorphous carbon adsorbed to the surface of a MWCNT is chemically less stable than the nanotube sidewall, and, therefore, will react preferentially with reagents intended to modify the MWCNT. Removal of amorphous carbon is necessary in order for covalent bonds to be formed directly with the MWCNT sidewall.[13] This study compares the oxidation behavior of two types of commercially available MWCNTs that are both produced by chemical vapor deposition (CVD) and have the same nominal dimensions and carbon purity levels. However, while SEM (Figures 2-2a and 2-3a) imaging shows no significant differences in the bundling morphology of the $k$-MWCNTs and $n$-MWCNTs, structurally, the two types of nanotubes are dissimilar. Figure 2-2b reveals the presence of amorphous carbon on the surface of pristine $n$-MWCNTs that is absent from the pristine $k$-MWCNTs, as shown in Figure 2-3b.
Figure 2-2. Representative SEM and TEM images of pristine $n$-MWCNTs (a-b) as-received, (c-d) fluidized for 10 min, and (e-f) fluidized for 90 min. Scale bars represent 1 µm and 5 nm for SEM and TEM images, respectively. Red arrows demarcate sidewall functionalization and dashed yellow arrows highlight amorphous carbon.
Raman spectroscopy, a sensitive probe of CNT structure, also confirmed structural differences as seen in the representative spectra of $k$-MWCNTs and $n$-MWNCTs given in Figure 2-4. Two prominent spectral features at 1354 and 1575 cm$^{-1}$ correspond to a defect-induced disorder (D) peak and graphite (G) peak, respectively. The ratio of these peak areas, $R = D/G$, reflects the defect density present in the MWCNTs. Pristine $k$-MWCNTs had $R = 0.66$ while $n$-MWCNTs had $R = 0.95$, indicating that the $n$-MWCNTs contained many more $sp^3$ hybridized carbon atoms, which correspond to defect sites and amorphous carbon.
2.4.2 Effect of oxidation on MWCNT structure

The effects of ozone treatment on MWCNT structure were monitored with SEM. Representative images of $n$-MWCNT and $k$-MWCNT are given in Figures 2-2 and 2-3, respectively. No obvious shortening of the nanotubes was observed for either type of MWCNT. However, the average MWCNT bundle size decreased with increasing exposure, and this change in bundle morphology was manifested on the macroscopic scale by a transition from tightly packed spherical particles to low density, fluffy foams. MWCNT debundling is thought to occur from (i) physical separation by gas flow through the bundles during fluidization, as well as (ii) chemical changes on the surface of the MWCNTs including removal of amorphous carbon between nanotubes and the introduction of functional groups on the nanotube sidewalls.
Structural changes were probed further with TEM. Comparison of Figures 2-2b, 2-2d, and 2-2f reveal that amorphous carbon originally present on pristine \( n \)-MWCNTs is removed after 10 min of \( O_3 \) exposure and does not reappear upon further treatment up to 90 min. In addition, small breaks in the outer sidewalls of \( n \)-MWCNT exposed to \( O_3 \) are visible while the inner walls remain intact. These features are indicative of oxidation originating at the MWCNT surface. Figures 2-3b, 2-3d, and 2-3f also illustrate changes in \( k \)-MWCNT structure with increasing \( O_3 \) exposure. No amorphous carbon was visible in any \( k \)-MWCNTs, including the pristine samples. However, as with \( n \)-MWCNTs, imperfections in the outer walls of the nanotubes were observed after \( O_3 \) treatment. Notably, even after oxidation for 90 min, the overall structure of both types of tubes was largely intact, which is important for retention of mechanical properties.

2.4.3 FTIR spectroscopy

The surface chemistry of pristine and treated MWCNTs was studied with the complimentary techniques of FTIR spectroscopy, XPS, and Boehm titration. Figure 2-5 presents typical FTIR spectra of \( n \)-MWCNTs and \( k \)-MWCNTs normalized to the peak observed near 1580 cm\(^{-1}\) in all samples, which is attributed to infrared active vibration modes of the curved graphene lattices comprising the MWCNTs.\(^{[28]}\) The broad peak centered at about 3445 cm\(^{-1}\) originates from –OH stretching of hydroxyl groups and ambient moisture adsorbed on the MWCNT surface. The weak bands at 2849 and 2918 cm\(^{-1}\) (C-H stretching) are ascribed to the presence of CH\(_2\) moieties, which implies that the structures of both types of MWCNTs are more complex than simple sheets of rolled graphene. Similar observations have been reported previously for MWCNTs synthesized by CVD, with potentially significant implications for the oxidation mechanism when hydroxyl radicals are
Interestingly, treatment of both types of MWCNTs causes the relative intensities of these peaks to increase significantly after 10 min of fluidization and subsequently decrease with further O₃ exposure. Comments on this behavior will be expanded upon later in this article when discussing XPS results. The sharp band observed at 1384 cm⁻¹ is attributed to bending of –OH groups. The low intensity of this peak in the case of pristine n-MWCNTs indicates that few hydroxyl groups are present in the as-received state. However, the relative intensity increases dramatically upon O₃ exposure for 10 min before decreasing with increased treatment time, meaning that significant numbers of hydroxyl groups are added to n-MWCNTs early in the reaction before they are subsequently depleted. Despite the lack of oxygenated defects found by XPS (vide infra), a peak at 1384 cm⁻¹ is present in the spectrum of pristine k-MWCNTs. The intensity of this band increases upon O₃ treatment and remains a prevailing feature in the spectra of all functionalized samples. A band at about 1635 cm⁻¹ corresponds to C=O stretching of quinone groups and another at 1735 cm⁻¹ derives from COOH groups. Quinone groups are present in all MWCNTs. While carboxylic acid moieties are present in pristine n-MWCNTs, after 10 min of exposure, the band at 1735 cm⁻¹ nearly disappears, which could be due to complete oxidation of carboxylic acid-bearing amorphous carbon present on the nanotube surface. Pristine k-MWCNTs do not have a discernible peak at 1735 cm⁻¹, though O₃ exposure causes one to appear. The intensity of this peak is greatest for both types of MWCNTs after a long treatment time of 60 min. The concomitant increase in intensity of the carboxylic acid band and decrease in intensity of the hydroxyl peak with prolonged O₃ treatment could be the result of oxidation of the -OH groups to form COOH moieties.
2.4.4 XPS and Raman analyses

While FTIR can help to elucidate the nature of functional groups grafted to the MWCNT, the technique is not amenable to quantitative analysis. To better understand the nature of changes in surface composition before and after oxidation, XPS was employed. Figure 2-6 shows representative survey spectra taken of \( n \)-MWCNTs and \( k \)-MWCNTs as a function of
O₃ treatment time. The peaks centered at 532.0 eV, which correspond to O1s photoelectrons, have been normalized to their respective C1s peaks at 284.6 eV to allow direct comparison of their intensities across samples treated for different times. Clearly, the amount of oxygen increases with exposure time for both MWCNT varieties, though n-MWCNTs oxidize more gradually than k-MWCNTs with time. Quantitative analyses of the XPS spectra are summarized in Figure 2-7. As-received n-MWCNTs contain 2.3 at% oxygen while pristine k-MWCNTs have a negligible 0.5 at%. 10 min of O₃ exposure increased the surface oxygen level to 4.2 at% for n-MWCNT and 7.5 at% for k-MWCNT. After 90 min of fluidization, the amount of surface oxygen began to plateau around 6.3 at% and 8.1 at% for n-MWCNTs and k-MWCNTs, respectively. Because of the small MWCNT diameters, even the surface specific XPS signal probes several nanotube walls, and it is possible that an atomic oxygen content of approximately 10% translates to a fully functionalized outer wall.[31]

Figure 2-6. XPS survey spectra of (a) n-MWCNTs and (b) k-MWCNTs as a function of O₃ exposure time. All spectra are normalized to the C1s peak.
The oxidation levels found in this study together with TEM observations indicate that oxidation occurs predominantly on the outer sidewalls of the MWCNTs. Though the oxidation behavior of the two varieties of MWCNTs is not identical, similar trends in R were observed with Raman spectroscopy, as seen in Figure 2-7. As both types of MWCNTs are oxidized, R initially increases, then it decreases, and finally levels off with prolonged treatment times. Possible reasons for the evolution of defects in this manner are discussed below in terms of three stages. In the first stage, oxidation is rapid as defect sites are oxidized to form predominantly –OH groups, which can be further oxidized to carboxylic acids. R increases due to the formation of large numbers of sp\(^3\) hybridized functional groups, which are symmetry-breaking defects that significantly increase the Raman D-band intensity. In the second stage, many –OH groups are oxidized to form carboxylic acids, while carboxylic acid groups formed previously on reactive amorphous carbon or adsorbed carbonaceous debris are further oxidized to CO\(_2\). The loss of some oxidized species causes the apparent rate of oxidation to slow, though it still increases due to the introduction of large amounts of oxygen in the form of carboxylic acid groups. R decreases slightly at this stage as defects are completely oxidized away. At a certain point, the reactive carbon defects present initially are completely oxidized and the majority of –OH groups on the nanotube surfaces have oxidized to form carboxylic acids. At this final stage, the number of carboxylic acid groups formed and completely oxidized stabilizes and both R and the surface oxygen concentrations do not vary appreciably with additional exposure time.
Figure 2-7. R-values obtained from Raman spectra and surface oxygen concentration of (a) n-MWCNTs and (b) k-MWCNTs.

Figure 2-7 illustrates that while the overall trends involving changes in R and O at% with exposure time are similar for both types of MWCNTs, they differ in time scales and magnitude. This is likely due to differences in the initial defect structures of the two MWCNT varieties. n-MWCNTs contain a significant number of defects in the as-received state (R = 0.95) while pristine k-MWCNTs possess relatively low defect densities (R = 0.66).
Initial oxidation causes little change in the R value of \( n \)-MWCNTs, as the complete oxidation of amorphous carbon may balance out the contributions of nanotube sidewall oxidation on the Raman D-band intensity. In contrast, R increases rapidly to 0.88 after 10 min of \( O_3 \) exposure for \( k \)-MWCNTs, as large numbers of symmetry-breaking functional groups are introduced on the nanotube surfaces without amorphous carbon removal. The differences in the apparent oxidation rate of \( n \)-MWCNTs and \( k \)-MWCNTs observed by XPS are believed to be directly linked to their dissimilarities in initial defect densities. However, despite initial differences in defect structure, \( k \)-MWCNTs and \( n \)-MWCNTs treated for at least 30 min with \( O_3 \) have similar R values at similar levels of oxidation. This trend indicates that after removal of amorphous carbon, the Raman D band stems primarily from sidewall functionalization and that defects initially present in \( n \)-MWCNTs are completely removed during the early stages of oxidation. It should be noted that defects can also arise from mechanical ablation of the MWCNTs. To ensure that fluidization has no effect on the nanotube structure, a control experiment was performed using compressed air in place of \( O_3 \) as the bubbling gas. No changes in R were observed for pristine \( n \)-MWCNTs or \( k \)-MWCNTs after 90 min of treatment, indicating that the fluidization forces are not sufficient to mechanically damage the nanotubes.
XPS is very sensitive to the bonding environment of carbon atoms, and high resolution scans of the C1s envelope can be used to identify and compare the number of functional groups present on the surface of a MWCNT. Figure 2-8 shows representative high resolution C1s spectra of the pristine and treated MWCNTs, which have been fitted with six peaks. The peaks correspond to graphitic sp² hybridized carbon (284.6 eV), sp³ hybridized defects including hydrocarbons (285.5 eV), hydroxyl or ether groups (286.4 eV), carbonyl groups (287.3 eV), carboxylic or ester groups (288.9 eV), and π-π* “shakeup” transitions (291.0 eV).[32]

The relative distribution of oxygen-bearing functional groups present on the surface of n-MWCNTs as a function of treatment time is summarized in Figure 2-9a. The fraction of C-O
groups increased rapidly during the first 10 min of exposure and then decreased slightly upon further treatment. In contrast, the fractions of C=O and O-C=O moieties did not increase until exposure times greater than 30 min, suggesting that C-O groups are oxidized to become C=O and O-C=O groups. The large fraction of sp\(^3\) hybridized carbon initially present in \(n\)-MWCNTs reflects the structural disorder in as-received nanotubes. After 30 min of oxidation, the relative number of C-C bonds decreases slightly before increasing upon further oxidation. Figure 2-9b summarizes the functional group evolution with treatment time for \(k\)-MWCNTs. The fraction of C-C and O-C=O groups increase more quickly for \(k\)-MWCNTs than for \(n\)-MWCNTs, while the rate of C-O generation is similar. As with \(n\)-MWCNTs, the number of C=O moieties increases slightly throughout the reaction. Unlike \(n\)-MWCNTs, which contain some amorphous carbon on the surface, pristine \(k\)-MWCNTs possess relatively few C-C bonds. However, upon exposure to O\(_3\), \(k\)-MWCNTs quickly develop a large fraction of sp\(^3\) hybridized carbon bonds up to about 8%. This C-C fraction is similar to that of \(n\)-MWCNTs oxidized to the same degree and suggests that in the case of \(n\)-MWCNTs, the relatively steady percentage of C-C bonds observed with oxidation time is due to a balance between the complete oxidation of sp\(^3\) defects initially present in the form of amorphous carbon and the formation of sp\(^3\) defects in the nanotube sidewall through covalent functionalization. This idea is further supported by the evolution of the \(\pi-\pi^*\) peak, which is sensitive to the aromatic character of the nanotubes. In the case of \(n\)-MWCNTs, the \(\pi-\pi^*\) intensity increases initially before decreasing after 15 min of O\(_3\) exposure, suggesting that amorphous carbon is removed to reveal the graphitic nanotube walls followed by sidewall functionalization. The intensity of the \(\pi-\pi^*\) peak simply decreases with treatment time for \(k\)-MWCNTs as the sidewall is oxidized immediately in the absence of amorphous carbon.
To complement surface functional group analysis by photoelectron spectroscopy, the amounts of acidic functionalities present on the surface of the MWCNTs were analyzed with chemical titration following the method of Boehm. Figure 2-10a summarizes the results of
titrating n-MWCNTs subjected to different O$_3$ treatment times. The results agree well with XPS in that the formation of -OH groups is favored for short reactions times, while carboxylic acids are generated after long exposure times. A similar trend is observed for k-MWCNTs, except that a greater number of lactonic species are formed early in the reaction, as shown in Figure 2-10b. As with FTIR and XPS analyses, these results suggest that hydroxyl groups formed at short exposure times may act as an intermediate species that is further oxidized into carbonyl and carboxylic acid groups upon further exposure.

![Figure 2-10](image)

**Figure 2-10.** Protic functional group concentrations obtained from Boehm titration of (a) n-MWCNTs and (b) k-MWCNTs.

### 2.4.6 Homogeneity of oxidation

To be suitable for industrial use, MWCNT functionalization reactions must produce relatively homogeneous oxidation levels throughout large sample volumes. This is a challenge for any gas-phase reaction, and previous work has shown that gaseous O$_3$ oxidation of CNTs is particularly difficult because oxidation is restricted to the outer surface of a CNT conglomerate.[19] This section will compare the variance in the oxidation levels achieved in
the present study with those previously reported for both traditional liquid-phase acid treatments and other gas-phase routes. Here we define homogeneity as the uniform composition of small volumes of nanotubes within a larger volume subjected to the same treatment.

Despite extensive published research, literature reports of oxidation variance within a given experiment are scarce. This may be due to the fact that, to date, most oxidation is done in solution with acids and the scatter is relatively small. The few reported error ranges for acid oxidized CNTs seem to support this assertion. Using nitric acid to oxidize MWCNTs, Andrade and coworkers found only a 2.9% relative standard deviation of the mean oxidation level of 3.5 at%, as determined by EDS.[33] While each EDS measurement probes a relatively large volume of nanotubes, the consistency of the results across the samples suggests that the nanotubes were homogeneously oxidized. Similarly, Wang et al. reported relative standard deviations on the order of 1%-9% for triplicate titration measurements of the acidic functional groups present in MWCNTs that had been refluxed in nitric acid and washed with NaOH.[34]

In contrast, gas-phase reactions tend to be much less homogeneous. Byl and coworkers found that O_3 oxidation of SWCNTs is highly dependent on their geometrical surface area but nearly independent of specific surface area.[19] Upon exposure to gaseous O_3, only SWCNTs on the outermost geometric surface of the nanotube agglomerate were oxidized. An early attempt to thermally oxidize MWCNTs in air also resulted in a broad distribution of oxidation levels. Ajayan and coworkers reported a relative standard deviation of 49% for thermogravimetric measurements of the nanotubes after 9.9 wt% loss to oxidation at 700
°C.[35] They attributed this large variation partially to differences in the availability of oxygen to samples with different geometric surface areas.

In this study, XPS and Boehm titration were used to characterize the extent of oxidation through measurements of many small aliquots of MWCNTs taken from the larger oxidized volume. While XPS is a surface sensitive technique, it has limited spatial resolution, so each measurement probes many MWCNTs at once. Therefore, both titration and XPS results give a measure of the bulk functionalization homogeneity but not necessarily the uniformity of oxidation along any given nanotube. The XPS and titration measurements performed in this study have relative standard deviations in the range of 2-5% and 1-12%, respectively, for samples with appreciable levels of oxidation. These figures are similar to those reported for liquid-phase acid reactions and suggest that fluidization of the MWCNTs in O₃ produces relatively homogeneous levels of oxidation.

2.5 Conclusions

Fluidizing MWCNTs in gas-phase O₃ proved effective at uniformly functionalizing the MWCNT sidewalls without destroying the nanotube structure and without the use of any solvents or additional purification steps. Comparison of two nominally similar MWCNTs with different defect structures revealed that this treatment can also purify MWCNTs from amorphous carbon in short periods of time. We suggest that this defect removal causes the apparent oxidation rate of n-MWCNTs to be lower than k-MWCNTs. Characterization of oxidized MWCNTs revealed that oxidation proceeds through the formation of predominantly -OH groups initially, which become further oxidized to C=O and COOH groups upon greater O₃ exposure. While the exact mechanism of oxidation was not determined, the presence of
aliphatic defects seems to play a significant role. Because the fluidized O₃ reaction reported herein is solvent-free, simple, and does not destroy the nanotube structure, we believe it offers an attractive route for functionalizing MWCNTs on an industrial scale.

2.6 References


CHAPTER 3: EFFECT OF SILANE STRUCTURE ON THE PROPERTIES OF SILANIZED MULTIWALLED CARBON NANOTUBE-EPOXY NANOCOMPOSITES

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3.1 Abstract

Multiwalled carbon nanotubes (MWCNTs) were functionalized with aminosilanes via an aqueous deposition route. The size and morphology of siloxane oligomers grafted to the MWCNTs was tuned by varying the silane functionality and concentration and their effect on the properties of a filled epoxy system was investigated. The siloxane structure was found to profoundly affect the thermo-mechanical behavior of composites reinforced with the silanized MWCNTs. Well-defined siloxane brushes increased the epoxy $T_g$ by up to 19 °C and significantly altered the network relaxation dynamics, while irregular, siloxane networks grafted to the MWCNTs had little effect. The addition of both types of silanized MWCNTs elicited improvements in the strength of the nanocomposites, but only the well-defined siloxane brushes engendered dramatic improvements in toughness. Because the silanization reaction is simple, rapid, and performed under aqueous conditions, it is also an industrially attractive functionalization route.

3.2 Introduction

Polymer nanocomposites offer an exciting avenue for dramatically changing the properties of polymers with very low filler loadings. Substantial improvements in electrical, thermal, mechanical, and barrier properties have been reported for composites made with a variety of nanoparticles including nanoclays,[1, 2] carbon nanotubes,[3-5] and graphene.[6, 7] These observed enhancements are due in part to the properties of the nanofiller, and, perhaps more importantly, to the good dispersion of nanofiller in the matrix, which creates an enormous amount of interfacial area at even low loading levels.[8, 9] The thermal and mechanical behavior of polymer nanocomposites is particularly sensitive to interfacial volume. Both experimental and theoretical work suggests that polymer chains adjacent to nanofiller experience accelerated or retarded dynamics compared to the bulk if the filler-matrix interactions are repulsive or attractive, respectively.[10-14] These changes are manifested macroscopically by changes in the glass transition temperature, a parameter that is important both fundamentally as a link to polymer physics and practically for use in engineering applications.[15] Despite receiving considerable attention in recent years, the study of the basic physical relationships between nanoparticles and polymers remains in its infancy. Linking changes in nano-scale structure to macro-scale properties will enable nanocomposites with tunable and multifunctional properties to be realized in their full potential.

Among nanofillers, carbon nanotubes (CNTs) have been studied extensively because of their outstanding electrical, mechanical, and thermal properties.[16, 17] Composites filled with CNTs often fall short of expected improvements due to poor dispersion and interfacial bonding.[4, 18] Covalent functionalization of the nanotube surface can mitigate both of these...
issues by changing the interaction of the nanotubes with solvents and polymers. Judicious matching of the moieties grafted to the CNT surface with a polymer matrix can significantly improve the mechanical properties of the resulting composite by limiting nanotube agglomeration and allowing for covalent bonding of CNTs with the matrix.[19-23] Furthermore, functionalization can elicit marked changes in the glass transition temperature ($T_g$) of composites containing even low loadings of CNTs as a result of altered chain dynamics.[5, 13, 15, 24-28] In the case of thermosetting polymers, functionalized CNTs may also affect the curing reaction. Different functionalities and structures grafted to the nanotube surface may result in steric and reactivity differences, which alter the cross-link topology of the network, leading to changes in macro-scale properties of the composite.[29] Thus, understanding the effect that the structure and chemistry of the moieties decorating the nanotube surface have on the structure of the polymer is paramount to developing composites with tunable properties.

To date, much of the work to functionalize CNTs has utilized reagents that are convenient in the laboratory but not amenable to industrial-scale use. Recent commercial expansion has enabled the production of high quality MWCNTs in huge quantities at low cost, and forecasts predict that 12,800 metric tons of MWCNTs will be on the market by 2016 with concomitant price declines.[30] For MWCNT-reinforced composites to realize their potential in engineering applications, new strategies must be devised to decorate MWCNTs with a variety of matrix-specific moieties rapidly and inexpensively. Coupled with continued growth in the MWCNT synthesis industry, this would enable the widespread manufacture of low-cost, MWCNT-reinforced composites in the near future.
Organosilanes represent one versatile, inexpensive, and commercially available solution. These silicon-bearing monomers contain two different types of reactive groups—a hydrolyzable group (Si-OR) that can condense with hydroxyl functionalities on the surface of a filler and another type of functional group that is compatible or capable of reacting with the matrix material (X). Thus, the two functionalities allow silanes to “couple” dissimilar materials together, and significant improvements in filler-matrix bond strengths are often achieved. For this reason silanes have long been used as adhesion promoters in composite manufacturing and are available with functionalities to match nearly any polymer matrix material.[31, 32] Silanes are often deposited in aqueous solution, during which the Si-OR bonds rapidly hydrolyze into silanols that can condense with hydroxyl groups on the filler surface or self-condense to form very stable Si-O-Si bonds. Because the self-condensation reaction is favored, aqueous deposition leads to grafting of oligomeric or polymeric siloxane molecules to the filler surface, the size and structure of which can profoundly alter the polymer-filler interactions after subsequent processing into a composite. When the siloxane and polymer matrix have little mismatch in solubility parameters, they are thought to form interpenetrating networks at the boundary interphase, which leads to excellent adhesion.[33] Deposition reactions can also be performed in organic solvents under anhydrous conditions to graft silane monomers onto filler through a direct condensation of the Si-OR group with hydroxyl groups on the particle’s surface. Monolayer grafting of silanes onto oxidized MWCNTs has been reported.[34] However, this approach requires that the MWCNTs be refluxed in organic solvents for very long periods of time and does not allow for tuning of the silane structure.
This work uses a simple aqueous route similar to that used in industrial glass fiber treatments to graft silanes of varying morphology and MW onto oxidized MWCNTs. Alkoxy silanes with two different Si-OR functionalities were used to attach both well-defined, siloxane brushes and irregular, cross-linked siloxane molecules to the MWCNTs and their MW was tuned by changing the concentration of silane in solution during the reaction. These silanized MWCNTs were then incorporated into a model epoxy system, and the effect of the silane structure and size on the crosslink topology and thermo-mechanical properties of the cured composite were investigated. Using thermal analysis to probe the MWCNT-epoxy interactions, we attempt to link the nano-scale structural changes in the epoxy to macro-scale property changes.

3.3 Experimental Details

3.3.1 Materials

Multiwalled carbon nanotubes (MWCNTs) with an average diameter of 10 nm and purity greater than 90% were supplied by Kumho Petrochemical Co (Seoul, South Korea). Two methoxy silanes, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane (ADMS) and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (ATMS), were purchased from Gelest, Inc. (Morrisville, PA). Composites were fabricated with a diglycidyl ether of bisphenol A, Epon 828, and triethylenetetramine (TETA) curing agent supplied by Momentive Specialty Chemicals (Houston, TX).

3.3.2 Methods

Functionalization of MWCNTs

Pristine MWCNTs (p-MWCNTs) were oxidized with gas-phase ozone in a fluidized bed to obtain primarily hydroxyl functionality (o-MWCNT) using an optimized reaction similar to Ref [35]. Silanization was conducted by dispersing 200 mg of o-MWCNTs in 200
mL Millipore water via bath sonication for 10 min before adding ADMS or ATMS to the suspension in concentrations of 0.1, 0.5, or 1.0% wt/wt of silane in water. The solution was stirred at room temperature for 20 min, after which the MWCNTs were filtered and washed copiously with water. The resulting filtrate was heated to 110°C in an oven and held isothermally for 60 min to promote condensation of the silanols with hydroxyl groups on the nanotube surface. Samples functionalized with ATMS and ADMS will be referred to as ts-MWCNTs and ds-MWCNTs, respectively. The concentration of silanes in solution used to functionalize the MWCNTs will be denoted in parentheses. For instance, a sample coded (0.1)ds-MWCNTs refers to o-MWCNTs reacted in a 0.1 wt% ADMS aqueous solution. Figure 3-1 schematically shows the expected morphology of siloxane oligomer grafted to MWCNTs after reactions with both types of silane monomer. ADMS, with only two methoxy groups, tends to form well-defined brushes with linear branches upon self-condensation while ATMS, with three methoxy groups per molecule, can form irregular, three-dimensional networks.
Preparation of nanocomposites

Composites were prepared according to the following procedure. MWCNTs were weighed and added to Epon 828 resin. In the case of functionalized MWCNTs, TGA measurements of the siloxane weight fraction were used to determine the amount of MWCNTs needed to achieve a given loading. The epoxy-MWCNT mixture was first sonicated with a horn (Fisher, sonic dismembrator model 100) in 30 second intervals for a total of 8 min at a power of 80W before it was sonicated in a bath (Bransonic) at 60 °C for 30 min. The mixture was allowed to cool, and a stoichiometric amount of TETA hardener was added. The resin mixture was then placed in a planetary mixer and subjected to high speed shear mixing and degassing steps. After mixing, the resin was cast into a mold and allowed to
cure at room temperature for 3 hours. The gelled solid was then isothermally held at 80°C for 1 hour followed by a post-cure at 120°C for 1 hour.

Characterization

The amount of silane grafted onto the surface of functionalized MWCNTs was determined by thermogravimetric analysis (TGA, Q50, TA Instruments) in air at 20 °C/min heating rate. Fourier-transform infrared spectroscopy (FTIR) was used to identify functional groups present in as-received and treated MWCNTs. The nanotubes were thoroughly mixed with potassium bromide and pressed into a pellet before data acquisition with a Bruker IFS66V spectrometer utilizing a Michelson interferometer. Changes in the surface chemistry of silanized MWCNTs were monitored with X-ray photoelectron spectroscopy (XPS). Measurements were carried out in a Physical Electronics 5500 Multitechnique system with a monochromatic Al Kα radiation source, and CasaXPS software was employed for data processing. The thermo-mechanical behavior of composites filled with MWCNTs was characterized by dynamic mechanical analysis (DMA, Q800, TA Instruments) in three-point bending mode. Samples with dimensions of 25 mm x 6 mm x 1.5 mm were tested at a fixed frequency of 1 Hz during temperature sweeps from 20 to 200 °C with a heating rate of 3 °C/min. The glass transition temperature ($T_g$) of each sample was determined by the peak of the tan δ curve obtained from DMA. Heat capacity measurements were conducted by differential scanning calorimetry (DSC, Q2000, TA Instruments) at 10 °C/min in nitrogen using a sapphire standard for calibration. The mechanical properties of nanocomposites at room temperature were evaluated by tensile testing with an Instron universal testing machine (Model 5569) equipped with a 50 kN load cell and video extensometer. Dog-bone shaped samples were machined according to the recommendations in ASTM D638 (Type V) and
tested at a crosshead speed of 5 mm/min. At least 5 samples were tested per batch to determine average properties. The fracture surfaces of samples were examined post-tensile testing with a scanning electron microscopy (SEM, FEI Quanta 200) to evaluate the nanotube dispersion and correlate the fracture morphologies with mechanical properties. Images were collected at 8 kV accelerating voltage and 10 mm working distance.

3.4 Results and Discussion

3.4.1 MWCNT functionalization

MWCNTs grafted with siloxanes having two different morphologies were prepared by reacting o-MWCNTs with di-functional and tri-functional silanes in order to elucidate the effect of siloxane structure on nanocomposite properties. With only two methoxy groups, ADMS forms brushes having linear chains upon self-condensation, while ATMS, with three methoxy groups can form a variety of networked, three-dimensional structures. Furthermore, the MW of each type of siloxane was controlled by varying the concentration of silane in solution during the reaction in order to determine the influence of siloxane size on nanocomposite properties. During deposition, higher concentrations of silane monomer in solution generally produce greater rates of self-condensation, and, as a result, the MW of siloxanes that grow from or graft to a hydroxylated substrate increases as well.[36] The three complimentary techniques of TGA, FTIR, and XPS were employed to characterize the nature of siloxane oligomer grafted to MWCNTs post-reaction.

Figure 3-2a shows the thermal degradation behavior of p-MWCNTs, o-MWCNTs, and ds-MWCNTs. p-MWCNTs exhibit almost no weight loss up to 450 °C and o-MWCNTs experience a minor weight loss of about 2%. In contrast, ds-MWCNTs display significant weight losses of 6.0%, 7.6%, and 8.7% for (0.1)ds-MWCNTs, (0.5)ds-MWCNTs, and
(1.0)ds-MWCNTs, respectively, in the temperature range from 200-400 °C. Figure 3-2b shows the degradation behavior of ts-MWCNTs. (0.1)ts-MWCNTs, (0.5)ts-MWCNTs, and (1.0)ts-MWCNTs experience weight losses of 5.8%, 8.1%, and 13.8%, respectively, in the temperature range from 200-400 °C. This mass loss is attributed to the decomposition of siloxane molecules and confirms that increasing the concentration of silane during the reaction increases the amount of siloxane grafted to the MWCNTs. The higher degree of silane grafting in ts-MWCNTs than ds-MWCNTs for a given concentration likely stems from the fact that with three reactive sites, ATMS can self-condense more rapidly than ADMS.
Figure 3-2. Thermogravimetric analysis of a) ds-MWCNTs and b) ts-MWCNTs

Figure 3-3 illustrates differences in the FTIR spectra of o-MWCNTs, ds-MWCNTs, and ts-MWCNTs. The OH bending peak centered at 1384 cm$^{-1}$ that is prominent in the spectrum
of o-MWCNTs diminishes significantly in relative intensity after reactions with both ADMS and ATMS at all concentrations. This suggests that hydroxyl groups on the nanotube surface are consumed as a result of reactions with silanol molecules. Other notable peaks appearing exclusively in the silanized MWCNT spectra include those at 880, 1020, 1110, and 1260 cm\(^{-1}\), which correspond to Si-OH, Si-O-Si, Si-O-C, and Si-CH\(_3\) vibrations, respectively. In addition, the band at 1560 cm\(^{-1}\), which is attributed to N-H stretching of a primary amine, becomes more pronounced at higher silane concentrations. The two bands at 2850 cm\(^{-1}\) and 2918 cm\(^{-1}\) and the broad band centered around 3450 cm\(^{-1}\) present in all samples are attributed to aliphatic defects in the nanotube sidewall and adsorbed water, respectively.
Figure 3-3. FTIR spectra of a) ds-MWCNTs and b) ts-MWCNTs

Figure 3-4 shows the XPS survey spectra of ds-MWCNTs and ts-MWCNTs reacted under different silane concentrations. The peaks at 533, 286, 401, 154, and 103 eV correspond to O1s, C1s, N1s, Si2s, and Si2p electrons, respectively, and the peaks in each spectrum have been normalized to the C1s peaks to allow for direct comparison of peak
intensities among all spectra. Clearly the intensities of the O1s, N1s, and both Si peaks increase with increasing silane concentration for both ds-MWCNTs and ts-MWCNTs. This corroborates the TGA findings that increasing the silane concentration increases the amounts of siloxane on the MWCNT surfaces. Table 1 summarizes the elemental surface composition of oxidized and silanized MWCNTs obtained by quantification of the XPS spectra. Because XPS is a surface sensitive technique, composition changes will not vary linearly as the thickness of the siloxane layer increases, and, as a result, the quantities of N and Si cannot be used to determine the thickness of the silane layer precisely. However, high resolution scans of the Si2p peaks of ds-MWCNTs and ts-MWCNTs can reveal qualitative trends by comparison of the areas of two peaks centered at 103.1 eV and 102.1 eV, which correspond to Si-O-Si and Si-O-C bonds, respectively. As depicted in Figure 3-5, the fraction of Si-O-Si bonds increases with increasing silane concentration for both ds-MWCNTs and ts-MWCNTs, which indicates that the increased number of silane molecules grafted to the MWCNT were the result of the attachment of siloxanes having greater MW and not merely from the attachment of a greater number of silane monomers.

Table 3-1. Elemental surface composition of o-MWCNTs and silanized MWCNTs as determined by XPS

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>ADMS</th>
<th></th>
<th></th>
<th></th>
<th>ATMS</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O %</td>
<td>N %</td>
<td>Si %</td>
<td>O/Si</td>
<td>O %</td>
<td>N %</td>
<td>Si %</td>
<td>O/Si</td>
</tr>
<tr>
<td>-</td>
<td>8.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.1</td>
<td>6.32</td>
<td>2.46</td>
<td>1.39</td>
<td>4.55</td>
<td>9.65</td>
<td>4.16</td>
<td>2.50</td>
<td>3.86</td>
</tr>
<tr>
<td>0.5</td>
<td>7.52</td>
<td>3.59</td>
<td>2.87</td>
<td>2.62</td>
<td>10.62</td>
<td>5.04</td>
<td>3.50</td>
<td>3.03</td>
</tr>
<tr>
<td>1.0</td>
<td>7.50</td>
<td>4.30</td>
<td>2.93</td>
<td>2.56</td>
<td>10.98</td>
<td>5.95</td>
<td>4.46</td>
<td>2.46</td>
</tr>
</tbody>
</table>
Figure 3-4. XPS survey scans of a) $ds$-MWCNTs and b) $ts$-MWCNTs
Figure 3-5. High resolution scans of the Si2p peaks of ds-MWCNTs and ts-MWCNTs reacted under silane concentrations of 0.1, 0.5, and 1.0%. Fits of the Si-O-Si peak (---), Si-O-C peak (-----), and their sum (---) are shown superimposed over each raw spectrum.
The properties of any filled composite depend on the degree of dispersion, and nanocomposites are particularly sensitive because of the fillers’ large surface area. Often the effects of nanoparticle functionalization and dispersion are convoluted. For instance, the glass transition temperature \((T_g)\) has been found to depend on both the surface chemistry and dispersion of nanoparticles,[37] so an understanding of the MWCNT distribution in the epoxies in this study is warranted. Figure 3-6 gives representative TEM images of neat epoxy and composites made with 0.2 wt% loading of ds-MWCNTs and ts-MWCNTs. Imaging of large areas of composites prepared with all types of MWCNTs revealed generally good levels of dispersion. While some degree of agglomeration was observed in composites prepared with p-MWCNTs (see Figure 3-6a), fine dispersion of both ds-MWCNTs and ts-MWCNTs were achieved at the low loading levels of 0.1 wt% and 0.2 wt%.
Figure 3-6. TEM images of composites made with 0.2 wt% loading of a) p-MWCNTs, b) ds-MWCNTs, and c) ts-MWCNTs. Insets provide higher magnification views of the dispersion state and structure of MWCNTs in the epoxy.

3.4.3 Dynamic mechanical analysis of nanocomposites

Dynamic mechanical analysis (DMA) is a powerful probe of interfacial interactions in filled polymer systems, and damping spectra, in particular, have been found to be good indicators of the efficiency of load transfer and chain mobility at the polymer-nanoparticle interface.[38-41] Figure 3-7 illustrates the thermo-mechanical behavior of the neat resin and composites made with 0.1 wt% loading of pristine, oxidized, and silanized MWCNTs. The
inset in Figure 3-7 compares the damping behavior (tan δ) of the samples, and Table 2 summarizes the features of tan δ peaks for all samples in the study. Increases in glass transition temperature ($T_g$) from about 136 °C for the neat epoxy to 142 °C and 145 °C are observed when pristine and oxidized MWCNTs are added to the resin, respectively. However, the addition of ts-MWCNTs at the same loading increases the $T_g$ very little relative to the neat epoxy. Notably, ts-MWCNTs with different siloxane grafting densities display similar thermo-mechanical behavior. In contrast, composites prepared with ds-MWCNTs have much higher $T_g$s relative to the neat epoxy, indicating significant confinement of network segments. (0.1)ds-MWCNTs produce the greatest $T_g$ increase up to 149 °C while (0.5)ds-MWCNTs and (1.0)ds-MWCNTs yield more moderate gains with $T_g$s of 143 °C and 142 °C, respectively. Changes in the height and width of the tan δ peak are also observed with the addition of MWCNTs. The tan δ peak height is a measure of interfacial load transfer in filled composites, with small values resulting from relatively elastic behavior (efficient stress transfer) and large values arising from relatively viscous (lossy) responses to stress.[29, 42, 43] The tan δ peak height of composites loaded with p-MWCNTs is similar to that of the neat epoxy while the peaks of o-MWCNT and ds-MWCNT composites are slightly lower. Reactions between the resin and both o-MWCNTs and ds-MWCNTs are possible, and covalent bonding of the MWCNTs to the matrix may be responsible for the increased stiffness of the composites. In contrast, ts-MWCNT additions increase the peak height despite also presumably bonding with the epoxy network. In the case of both ds-MWCNT and ts-MWCNTs composites, increasing the MW of grafted siloxane increases the height of the damping peak, likely due to the introduction of a greater number of very flexible Si-O-Si linkages at the MWCNT-epoxy interface. Differences in the tan δ width with variations in the
MWCNT surface chemistry are also apparent. The damping peaks of ds-MWCNTs are narrower than those of the neat resin or other composites, which indicates that the brush-like siloxane chains on the nanotube surface engender a more homogeneous distribution of segmental relaxation times in the network.

Table 3-2. Summary of tan δ peak features observed from dynamic mechanical analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)a</th>
<th>Peak Height</th>
<th>FWHM (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>136.0 ± 0.6</td>
<td>0.64 ± 0.02</td>
<td>18.03 ± 0.26</td>
</tr>
<tr>
<td>p-MWCNT</td>
<td>141.7 ± 3.1</td>
<td>0.61 ± 0.02</td>
<td>16.86 ± 0.07</td>
</tr>
<tr>
<td>o-MWCNT</td>
<td>144.7 ± 2.5</td>
<td>0.59 ± 0.01</td>
<td>16.91 ± 0.03</td>
</tr>
<tr>
<td>(0.1)ds-MWCNT</td>
<td>149.1 ± 1.5</td>
<td>0.59 ± 0.01</td>
<td>15.62 ± 0.08</td>
</tr>
<tr>
<td>(0.5)ds-MWCNT</td>
<td>143.4 ± 3.3</td>
<td>0.60 ± 0.02</td>
<td>15.67 ± 0.10</td>
</tr>
<tr>
<td>(1.0)ds-MWCNT</td>
<td>141.7 ± 1.4</td>
<td>0.62 ± 0.02</td>
<td>15.80 ± 0.04</td>
</tr>
<tr>
<td>(0.1)ts-MWCNT</td>
<td>135.5 ± 2.9</td>
<td>0.69 ± 0.01</td>
<td>17.40 ± 0.05</td>
</tr>
<tr>
<td>(0.5)ts-MWCNT</td>
<td>134.5 ± 1.9</td>
<td>0.71 ± 0.01</td>
<td>17.62 ± 0.07</td>
</tr>
<tr>
<td>(1.0)ts-MWCNT</td>
<td>134.8 ± 2.4</td>
<td>0.73 ± 0.01</td>
<td>17.29 ± 0.09</td>
</tr>
<tr>
<td>p-MWCNT</td>
<td>143.6 ± 3.2</td>
<td>0.62 ± 0.01</td>
<td>16.79 ± 0.25</td>
</tr>
<tr>
<td>o-MWCNT</td>
<td>147.4 ± 3.6</td>
<td>0.59 ± 0.01</td>
<td>16.57 ± 0.18</td>
</tr>
<tr>
<td>(0.1)ds-MWCNT</td>
<td>155.3 ± 0.9</td>
<td>0.56 ± 0.01</td>
<td>13.81 ± 0.02</td>
</tr>
<tr>
<td>(0.5)ds-MWCNT</td>
<td>153.8 ± 0.7</td>
<td>0.59 ± 0.01</td>
<td>15.65 ± 0.08</td>
</tr>
<tr>
<td>(1.0)ds-MWCNT</td>
<td>147.5 ± 1.3</td>
<td>0.63 ± 0.01</td>
<td>15.31 ± 0.15</td>
</tr>
<tr>
<td>(0.1)ts-MWCNT</td>
<td>141.0 ± 1.9</td>
<td>0.67 ± 0.01</td>
<td>17.14 ± 0.03</td>
</tr>
<tr>
<td>(0.5)ts-MWCNT</td>
<td>141.5 ± 1.5</td>
<td>0.69 ± 0.01</td>
<td>17.08 ± 0.15</td>
</tr>
<tr>
<td>(1.0)ts-MWCNT</td>
<td>141.5 ± 0.3</td>
<td>0.70 ± 0.02</td>
<td>17.64 ± 0.34</td>
</tr>
</tbody>
</table>

a Numbers after the ‘±’ sign represent a 95% confidence interval.
Figure 3-7. Dynamic mechanical analysis of composites containing 0.1 wt% loading of a) ds-MWCNTs and b) ts-MWCNTs. The main graphs display storage modulus while insets show tan δ.

Figure 3-8 depicts the thermo-mechanical behavior of composites made with 0.2 wt% loading of pristine, oxidized, and silane functionalized MWCNTs. Higher loadings of pristine and oxidized MWCNTs increase the $T_g$ of the epoxy further to 144 °C and 147 °C, respectively. Composites containing higher loadings of ts-MWCNTs also exhibited minor increases in $T_g$, and as with 0.1 wt% composites, the $T_g$ remained nearly independent of
The addition of higher loading of ds-MWCNTs elicited marked $T_g$ gains to 155 °C, 154 °C, and 148 °C for (0.1)ds-MWCNTs, (0.5)ds-MWCNTs, and (1.0)ds-MWCNTs, respectively. As with the lower loading level, ds-MWCNT composites exhibit shorter and narrower tan δ peaks than their ts-MWCNT analogs, clearly reflecting a difference in their interactions with the network.

Figure 3-8. Dynamic mechanical analysis of composites containing 0.2 wt% loading of a) $ds$-MWCNTs and b) $ts$-MWCNTs. The main graphs display storage modulus while insets show tan δ.
The interactions among polymers and nano-scale fillers are complex and vary greatly for different matrix-filler systems. This in turn leads to a wide variety of glass transition behaviors. Several mechanisms have been proposed to explain both increases and decrements in $T_g$. $T_g$ elevation follows from positive filler-polymer interactions such as van der Waals, hydrogen, or covalent bonding, which alter the chain mobility near the nanoparticle and lead to a reduction in free volume. Depression of the $T_g$ can stem from many sources. Negative filler-polymer interactions lead to an increased mobility of polymer chains near the nanoparticle, which increases free volume. In thermosetting systems, nanoparticles can also cause network disruption in several ways by: (i) providing a barrier to cure by physically blocking functional group diffusion, (ii) causing local phase separation due to selective positive or negative interactions with resin components, or (iii) changing the resin heat capacity, which can cause incomplete curing if the cure schedule is not adjusted.[44]

In the present case, the minor $T_g$ increases found upon addition of p-MWCNTs may be attributed to positive $\pi-\pi$ stacking interactions among the MWCNTs and the aromatic rings of the EPON 828 molecules contained in the epoxy network. The slightly higher $T_g$ of the o-MWCNT composites may be due to the reaction of some phenols on the o-MWCNTs with the epoxide groups of EPON 828 or the formation of amide linkages from the reaction of COOH groups on the o-MWCNTs with amines from the TETA hardener. $T_g$ elevation in ds-MWCNT composites is attributed to covalent bonding of amines on the siloxane chains with oxirane groups of the epoxy resin. The well-ordered structure of the ds-MWCNT siloxane oligomers and the flexiblity of the Si-O-Si bonds may afford epoxy groups from the matrix easy access to amines on the silane oligomers, facilitating the formation of a covalently bonded interpenetrating network with the epoxy matrix. Dramatic increases in the
$T_g$ of other nanocomposite systems on the same order as observed here have been attributed to the formation of percolating interphases.[5, 45] In contrast, the disordered, cross-linked siloxane layer grafted to the surface of ts-MWCNTs does not allow for easy amine accessibility, and thus, would limit interactions with the epoxy matrix. This conclusion is consistent with our experimental observations that limited increases in $T_g$ and relatively large tan δ peak heights are found with ts-MWCNTs additions. The decrease in $T_g$ with increasing siloxane MW in ds-MWCNT composites is likely due to the fact that the chains are flexible, and increasing their length increases the free volume of the system. Another possible explanation for the decreased $T_g$ is that increasing the siloxane MW produces an excess of amine groups, which alter the curing stoichiometry and decreases cross-link density. However, the low loadings of MWCNTs used in this study do not introduce significant numbers of amine groups (less than 0.08 mol% increases) and the rubbery plateau moduli in Figures 3-7 and 3-8 do not indicate dramatic differences in cross-link density. For both ts-MWCNT and ds-MWCNT systems, increasing the MWCNT loading amplified the $T_g$ increase, which is likely due to an increase in the MWCNT-polymer interfacial area.

3.4.4 DSC analysis of CRR

To further elucidate the effect of MWCNT functionalization on segmental confinement in the epoxy network, the cooperatively rearranging region (CRR) size was determined by DSC. The structural relaxation of glassy polymers depends on cooperative motion of chains or network segments. This behavior can be rationalized through the concept of a CRR, which Adam and Gibbs defined as a subsystem capable of rearranging its configuration independently of its environment upon sufficient thermal fluctuation.[46] A bulk thermoset can be conceptually divided into many CRR subsystems, the number and size of which are heavily temperature dependent. At $T_g$, the average size of a CRR can be described by a
characteristic volume \((\xi^3)\) and length \((\xi)\), which define the number of polymer segments involved in the cooperative glass relaxation. A convenient method of measuring \(\xi\) via changes in heat capacity at \(T_g\) has been proposed by Donth:[47]

\[
\xi^3 = \frac{k_B T_g^2 \Delta (1/C_v)}{\rho (\delta_T)^2}
\]

where \(\delta_T\) represents the thermal fluctuation of an average CRR at \(T_g\), \(\rho\) is density, \(k_B\) is the Boltzmann constant, and \(C_v\) is the heat capacity at constant volume. In practice, \(C_v\) is approximated by the constant pressure heat capacity, \(C_p\), measured by DSC. Detailed explanations of CRR measurement with DSC have been previously reported and are employed in the current work.[48, 49]
Figure 3-9. CRR of neat epoxy and nanocomposites loaded with 0.2 wt% MWCNTs.

Figure 3-9 depicts the variation in $\xi$ with nanotube surface functionality for composites loaded with 0.2 wt% MWCNTs. The characteristic relaxation length of the neat resin is about 2.2 nm and remains unchanged with the addition of p-MWCNTs and ts-MWCNTs of all MW. However, composites containing ds-MWCNTs have significantly larger CRR lengths. The degree of cooperativity is directly related to interphase-induced $T_g$ changes, and larger CRRs allow nanoparticle-polymer interfacial effects to propagate over greater length scales.\cite{44} Several studies have investigated the effect of nanofiller on cooperativity size, and increases in CRR with low nanoclay loadings have been observed for PMMA,\cite{50} PS,\cite{51} poly(ethylene-terephthalate)/poly(cyclohexane-dimethanol terephthalate) copolymer\cite{52}, and epoxy\cite{53} composites. In all cases, the increased
cooperativity was attributed to “nanoconfinement” of polymer chains by positive interactions with well-dispersed clay particles. In the case of PS-clay composites, organic modification of the clay surface with brush-like PS produced further increases in $\xi$ and $T_g$.\cite{51, 54}

Figure 3-10. Schematic drawing illustrating the proposed microstructure evolution in the neat epoxy with $ds$-MWCNT and $ts$-MWCNT additions based on CRR and DMA measurements.

In the present work, changes in chain dynamics of the resin are clearly dependent on the structure of siloxane grafted to the nanotube surface. Based on CRR and tan $\delta$ data, an explanation of the differences in network-MWCNT interactions for $ds$-MWCNTs and $ts$-MWCNTs is schematically proposed in Figure 3-10. Addition of $ds$-MWCNTs causes the tan
δ peak to narrow and CRR volume to increase relative to the neat resin, suggesting that the brush-like siloxane chains increase the connectivity of the network while producing a more homogeneous cross-link topology.[55] This behavior is consistent with the formation of a percolating interphase in which the siloxane brushes form an interpenetrating network with the resin. Covalent bonding of the interconnected chains significantly reduces their mobility, causing an increase in $T_g$. As the MW of siloxane grafted to the nanotube surface increases, the composite $T_g$ is reduced slightly as the result of an increase in flexibility from the incorporation of more Si-O-Si bonds. In contrast to ds-MWCNTs, ts-MWCNT additions do not elicit large increases in $T_g$ and $\xi$, and the damping spectra reveal relatively lossy behavior. This suggests that cross-linked siloxane chains grafted to the surface of ts-MWCNTs do not interact as favorably with the network, possibly as a result of sterically limited amine accessibility.

3.4.5 Nanocomposite mechanical properties

Tensile tests were performed to determine the effect of nano-scale morphology on macroscopic mechanical properties. Figure 3-11 shows representative stress-strain curves of composites loaded with 0.1 wt% pristine and functionalized MWCNTs and Table 3 summarizes data from several samples (at least 5 per data entry). The addition of all types of MWCNT increased the tensile strength slightly, though the modulus remained largely unchanged within error. Composites containing ds-MWCNTs were markedly tougher than the neat resin as a result of high failure strengths and strains, and toughness was observed to increase with the MW of grafted siloxane on the ds-MWCNTs. Additions of ts-MWCNTs yielded properties similar to those of p-MWCNTs and o-MWCNTs.
Table 3-3. Tensile properties of neat epoxy and nanocomposites prepared with 0.1 wt% loading of MWCNTs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Failure Strain (%)</th>
<th>Toughness (MJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>3.01 ± 0.07</td>
<td>79.2 ± 3.7</td>
<td>3.58 ± 0.33</td>
<td>1.47 ± 0.17</td>
</tr>
<tr>
<td>p-MWCNT</td>
<td>3.15 ± 0.08</td>
<td>86.1 ± 4.9</td>
<td>5.12 ± 0.25</td>
<td>2.96 ± 0.10</td>
</tr>
<tr>
<td>o-MWCNT</td>
<td>3.14 ± 0.10</td>
<td>90.6 ± 3.6</td>
<td>4.78 ± 0.46</td>
<td>2.83 ± 0.12</td>
</tr>
<tr>
<td>(0.1)ds-MWCNT</td>
<td>3.17 ± 0.07</td>
<td>93.0 ± 2.7</td>
<td>5.30 ± 0.27</td>
<td>3.31 ± 0.22</td>
</tr>
<tr>
<td>(0.5)ds-MWCNT</td>
<td>3.12 ± 0.10</td>
<td>89.2 ± 2.6</td>
<td>6.08 ± 0.43</td>
<td>3.73 ± 0.14</td>
</tr>
<tr>
<td>(1.0)ds-MWCNT</td>
<td>3.09 ± 0.15</td>
<td>88.5 ± 1.9</td>
<td>6.34 ± 0.39</td>
<td>4.06 ± 0.31</td>
</tr>
<tr>
<td>(0.1)ts-MWCNT</td>
<td>3.13 ± 0.05</td>
<td>95.6 ± 3.5</td>
<td>4.82 ± 0.32</td>
<td>2.95 ± 0.19</td>
</tr>
<tr>
<td>(0.5)ts-MWCNT</td>
<td>3.11 ± 0.03</td>
<td>91.4 ± 2.7</td>
<td>4.60 ± 0.44</td>
<td>2.86 ± 0.23</td>
</tr>
<tr>
<td>(1.0)ts-MWCNT</td>
<td>3.05 ± 0.12</td>
<td>93.8 ± 3.0</td>
<td>5.02 ± 0.20</td>
<td>3.07 ± 0.09</td>
</tr>
</tbody>
</table>

* Numbers after the ‘±’ sign represent a 95% confidence interval
* Toughness calculated from the area under the stress-strain curve

Table 3-4. Tensile properties of neat epoxy and nanocomposites prepared with 0.2 wt% loading of MWCNTs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Failure Strain (%)</th>
<th>Toughness (MJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>3.01 ± 0.07</td>
<td>79.2 ± 3.7</td>
<td>3.58 ± 0.33</td>
<td>1.47 ± 0.17</td>
</tr>
<tr>
<td>p-MWCNT</td>
<td>3.18 ± 0.07</td>
<td>88.4 ± 6.3</td>
<td>5.60 ± 0.47</td>
<td>3.37 ± 0.12</td>
</tr>
<tr>
<td>o-MWCNT</td>
<td>3.18 ± 0.04</td>
<td>94.5 ± 3.4</td>
<td>4.88 ± 0.51</td>
<td>3.01 ± 0.10</td>
</tr>
<tr>
<td>(0.1)ds-MWCNT</td>
<td>3.27 ± 0.12</td>
<td>94.4 ± 4.3</td>
<td>5.46 ± 0.56</td>
<td>3.48 ± 0.12</td>
</tr>
<tr>
<td>(0.5)ds-MWCNT</td>
<td>3.22 ± 0.10</td>
<td>92.3 ± 2.6</td>
<td>5.63 ± 0.22</td>
<td>3.80 ± 0.07</td>
</tr>
<tr>
<td>(1.0)ds-MWCNT</td>
<td>3.19 ± 0.12</td>
<td>89.5 ± 8.3</td>
<td>6.00 ± 0.38</td>
<td>4.00 ± 0.13</td>
</tr>
<tr>
<td>(0.1)ts-MWCNT</td>
<td>3.13 ± 0.22</td>
<td>93.8 ± 3.9</td>
<td>4.62 ± 0.50</td>
<td>2.77 ± 0.54</td>
</tr>
<tr>
<td>(0.5)ts-MWCNT</td>
<td>3.18 ± 0.11</td>
<td>91.8 ± 4.8</td>
<td>4.62 ± 0.42</td>
<td>2.73 ± 0.41</td>
</tr>
<tr>
<td>(1.0)ts-MWCNT</td>
<td>3.13 ± 0.05</td>
<td>90.9 ± 3.6</td>
<td>4.93 ± 0.29</td>
<td>3.00 ± 0.29</td>
</tr>
</tbody>
</table>

* Numbers after the ‘±’ sign represent a 95% confidence interval
* Toughness calculated from the area under the stress-strain curve
Figure 3-11. Stress-strain curves of composites made with 0.1 wt% loading of a) $ds$-MWCNTs and b) $ts$-MWCNTs.
Figure 3-12. Stress-strain curves of composites made with 0.2 wt% loading of a) $ds$-MWCNTs and b) $ts$-MWCNTs.
Table 4 summarizes data from samples loaded with 0.2 wt% MWCNTs, and representative stress-strain curves are provided in Figure 3-12. The increased loading of p-MWCNT and o-MWCNTs produced slightly higher composite strengths, ultimate strains, and toughness. Composites prepared with 0.2 wt% ds-MWCNTs exhibited moderately higher strength and lower failure strain than their 0.1 wt% counterparts while very little change was observed for the higher loadings of ts-MWCNTs. While ds-MWCNT composites contain a large fraction of confined network segments, dramatic improvements in the strength and modulus of the composite are not observed. This is due to the fact that the neat resin is a highly cross-linked thermoset, and as such, significant improvements in the mechanical properties will only result with the introduction of a large proportion of filler. The low loading levels of MWCNTs used in this study would not be expected to dramatically improve strength and modulus, even with efficient load transfer. However, changes in toughness are reflective of the resin-MWCNT interactions and structure. In the case of ds-MWCNTs, composite toughness is dramatically affected by siloxane MW. The increased strain at break with MW is likely the result of a larger fraction of network segments bonding to flexible siloxane chains that are intimately incorporated into the network. Such a structure of hard nanofiller surrounded by a percolating, tough interphase presents a tortuous path for crack propagation.[40, 41] In contrast, the mechanical properties of ts-MWCNTs are nearly independent of siloxane MW, which suggests that the siloxane structure develops in a manner similar to that depicted in Figure 3-10. Because the irregular siloxane oligomer is composed of several cross-linked molecules, the number of accessible amines at the resin interface grows slowly with MW, and the final composite consists of islands of MWCNTs coated with siloxane layers that do not intimately interact with the resin during curing. As a
result, composites containing ts-MWCNTs are not as tough as those filled with the same loading of ds-MWCNTs.

![Figure 3-13. SEM images of the fracture surfaces of a) neat epoxy and b) 0.1 wt% loading of p-MWCNTs. Scale bars represent 10 µm.](image)

Differences in toughness are further delineated by variations in the topology of the composite fracture surfaces. Figure 3-13 shows representative SEM images of the fracture surfaces of the neat resin and a composite filled with 0.1 wt% p-MWCNTs. The samples were fractured at room temperature in pure tension. The flat and nearly featureless fracture surface of the neat resin is characteristic of a brittle failure with limited modes of plasticity. Figure 3-13b shows that the addition of a small amount of p-MWCNTs significantly increases the density of river markings. Furthermore, the rounded ends of the stripes indicate some degree of crack blunting by the p-MWCNTs. Further changes in the character of the fracture surface were observed with the addition of silanized MWCNTs as shown in Figure 3-14. Composites containing ds-MWCNTs produced fractures surfaces with very closely spaced river markings, indicating that many crack deflection events occurred before final fracture. The rough, rounded river markings of ts-MWCNT composites are spaced further
apart and appear similar to those of p-MWCNTs. While indicative of plasticity, these wider stripes provide evidence of fewer crack deflection events during fracture than ds-MWCNTs.

Figure 3-14. SEM images of the fracture surfaces of 0.1 wt% loading of a) (0.1)ds-MWCNTs, c) (0.5)ds-MWCNTs, and e) (1.0)ds-MWCNTs as well as b) (0.1)ts-MWCNTs, d) (0.5)ts-MWCNTs, and f) (1.0)ts-MWCNTs. Scale bars represent 10 µm

3.5 Conclusions
We have demonstrated that functionalization of MWCNTs using an aqueous silane solution is possible, which could have important commercial applications because the reaction is fast, free of organic solvents, and requires only inexpensive reagents. Furthermore, we show that the structure of the oligomers grafted to the MWCNT have a significant impact on the chain confinement in an epoxy composite. MWCNTs grafted with irregular, three dimensional siloxane oligomers (ts-MWCNTs) tended to interact poorly with the matrix, while MWCNTs coated with well-defined, linear siloxane brushes (ds-MWCNTs) interact strongly with the network. DMA and DSC analyses revealed that ds-MWCNT additions dramatically limited the mobility of network segments and promoted a more homogeneous cross-link topology, which translated to large increases in $T_g$ relative to the neat resin at low loading levels. The toughness of the resin was found to improve with the addition of all varieties of MWCNT; however composites containing ds-MWCNTs produced the greatest effect, seemingly due to crack deflection by a highly connected percolating interphase formed around the nanotubes.

3.6 References


4.1 Abstract

Supercritical carbon dioxide was employed as the solvent for the functionalization of multiwalled carbon nanotubes (MWCNTs) with an epoxy-capped silane. The silanization protocol was found to be a suitable green alternative to traditional routes that rely on organic solvents for grafting nearly monolayers of silane molecules onto the nanotube surfaces. The addition of silanized MWCNTs to a model epoxy markedly increased its $T_g$, and measurements of the network cooperativity length scale linked this change to a reduction in polymer segment mobility. Composites filled with low loading levels of both pristine and silanized MWCNTs exhibited significantly higher strain at break and toughness than the neat epoxy, and the greatest improvements were observed at low loading levels. SEM analysis of the composite fracture surfaces revealed that nanotube pullout was the primary failure mechanism in epoxy loaded with pristine MWCNTs while crack bridging predominated in

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composites containing silanized MWCNTs as the result of strong interfacial bonding with the matrix. The elevated $T_g$ and toughness achieved with small additions of silanized MWCNTs promise to extend the engineering applications of the epoxy resin.

### 4.2 Introduction

Carbon nanotubes (CNTs) possess extraordinary electrical, mechanical, and thermal properties, which, coupled with their extremely high aspect ratios, makes them ideal candidates for the reinforcing phase in polymer nanocomposites. A tremendous amount of research has been devoted to processing and characterizing CNT composites with mixed results. Dramatic increases in the thermo-mechanical and electrical properties of thermosets and thermoplastics have been observed.[1-5] However, CNT additions have also been reported to have minor or even deleterious effects on polymer properties as the result of poor dispersion.[6-8] Covalent functionalization of the nanotube surface has emerged as a popular method of not only improving dispersion, but also promoting a strong interface between the CNT and matrix. Hundreds of functionalization reactions have been developed, and incorporation of these modified nanotubes into polymer matrices with compatible reactive sites has produced composites with outstanding thermo-mechanical properties. Recent expansion in the industrial synthesis of multi-walled carbon nanotubes (MWCNTs) has led to a dramatic decrease in price, and today huge quantities of high quality MWCNTs are available for less than $200/kg. The changing economic situation has opened the door for pervasive use of MWCNT composites in many engineering applications; however, challenges in dispersing the nanotubes uniformly in matrix materials on a large scale remains an unresolved problem. While covalent functionalization of MWCNTs represents a rational solution, almost all of the reactions developed to date are not well-suited for large scale
operations due to long processing times, poor yield, safety hazards, and environmental concerns. As a result, alternative functionalization strategies are needed for MWCNTs to find widespread application in polymer composites.

One potential solution involves the use of organosilanes, which have two different types of reactive groups per molecule—a hydrolyzable group (Si-OR) that can condense with hydroxyl functionalities on the surface of a filler and another type of functional group capable of reacting with the matrix material (X). Silanes have been used as adhesion promoters in composite manufacturing for decades because they are inexpensive, non-toxic, and available with functionalities to match nearly any polymer matrix material.[9, 10] Traditional silanization is performed in aqueous solution, during which the Si-OR bonds rapidly hydrolyze into silanols, which can condense with hydroxyl groups on the filler surface or self-condense to form stable Si-O-Si bonds. Because the self-condensation reaction is favored, aqueous deposition leads to grafting of oligomeric or polymeric siloxane molecules onto the filler surface. This can be problematic for nanoparticles because the deposited oligomer can approach the size scale of the nanoparticle and significant entanglement of adjacent siloxane chains causes particle agglomeration.[11] As a result, monolayer deposition is often preferred when the nanoparticles are to be used in composite applications. This is usually achieved through a direct condensation reaction of the Si-OR group with hydroxyl groups on the particle’s surface under anhydrous conditions in an organic solvent. Such an approach for monolayer grafting of silanes onto oxidized MWCNTs has been reported.[12] While this route affords the versatility of silane end-group chemistry, it requires that the MWCNTs be refluxed in organic solvents for very long periods of time making it undesirable for industrial reactions.
Supercritical carbon dioxide (scCO$_2$) has emerged as an alternative to organic solvents for silanization reactions and offers the benefits of being non-flammable, non-toxic, naturally abundant, relatively inert, and a good solvent.[13] It is especially attractive for reactions involving nanoparticles because scCO$_2$ has low viscosity and lacks surface tension, allowing it to wet out even complicated and porous structures including the interstitial surfaces of an agglomerate.[14-19] Successful monolayer silanization of several inorganic nanoparticles including hydroxyapatite,[19, 20] TiO$_2$,[19-21] and hectorite[20] have been reported. In addition to being simple, these reactions do not produce any solvent waste because the CO$_2$ is removed upon depressurization post-reaction. Since 60-80% of the capital and operating costs of industrial chemical reactions are typically tied to purification and separation of the desired product from solvents and byproducts,[22] the ease of solvent removal is a serious advantage. This paper presents a new strategy for MWCNT functionalization that is free of organic solvents and acids and requires only non-toxic reagents. A two-step approach of oxidizing the MWCNTs with gas-phase O$_3$ followed by silanization in scCO$_2$ is employed to graft silane monomers to the nanotube surface. A solventless processing route is then used to incorporate the silanized MWCNTs (s-MWCNTs) into a model epoxy and the effects of functionalization on the network structure and thermo-mechanical properties are investigated.

4.3 Experimental Details

4.3.1 Materials
Multiwalled carbon nanotubes (MWCNTs) with an average diameter of 10 nm and purity greater than 90% were supplied by Kumho Petrochemical Co (Seoul, South Korea). An epoxy-capped silane, 3-(Glycidyloxypropyl) trimethoxysilane (GPTMS), was purchased from Gelest, Inc. (Morrisville, PA). Composites were fabricated with a diglycidyl ether of
bisphenol A, Epon 828, and triethylenetetramine (TETA) curing agent supplied by Momentive Specialty Chemicals (Houston, TX).

4.3.2 Methods

MWCNT functionalization

As-received MWCNTs were first oxidized with gas-phase ozone in a fluidized bed for 10 min to obtain primarily hydroxyl functionality using an optimized reaction reported previously.[23] The oxidized MWCNTs (o-MWCNTs) were further functionalized according to Figure 4-1. Reactions were conducted by placing 100 mg o-MWCNTs, 100 µL GPTMS, and 200 g scCO\textsubscript{2} into a Parr reactor (model 452HC3), heating the contents to 60°\textdegree{}C (pressure ~ 1500 psi), and stirring for 20 hours. Post-reaction, the MWCNTs were washed with toluene to remove any excess silane, a step which would could be omitted during industrial production through the design of a reaction chamber which allows for filtration and washing with liquid or supercritical carbon dioxide. The treated MWCNTs were then heated to 110°\textdegree{}C in an oven and held isothermally for 30 min to promote condensation of the silanols with hydroxyl groups on the o-MWCNT surface. Samples functionalized in this manner will be hereafter referred to as s-MWCNTs.
Nanocomposite processing

Epoxy nanocomposites were prepared with p-MWCNTs and s-MWCNTs using the following procedure. MWCNTs were weighed and added to Epon 828 resin. In the case of s-MWCNTs, TGA measurements were performed to determine the MWCNT weight fraction, which was used to correct for the actual weight of MWCNTs needed to achieve a given loading. The epoxy-MWCNT mixture was subjected to sonication with a horn (Fisher, sonic dismembrator model 100) in 30 second intervals for a total of 2 min at a power of 40W and 2 min at 80 W followed by sonication in a bath (Emerson, Bransonics Model 1800) at 60°C for 30 min. The mixture was allowed to cool, and a stoichiometric amount of TETA hardener was added. A two-axis planetary mixer (Kurabo, Mazerustar) was then used to thoroughly mix the resin components and remove trapped air bubbles before the resin was cast into a mold and allowed to cure at room temperature for 3 hours. The gelled solid was subsequently heated to 80°C for 1 hour followed by a post-cure at 120°C for 1 hour.

Characterization
Thermogravimetric analysis (TGA, Q50, TA Instruments) in air at 20 °C/min heating rate was used to determine the amount of silane grafted onto the surface of functionalized MWCNTs. Functional groups present in as-received and silanized MWCNTs were identified with Fourier-transform infrared spectroscopy (FTIR). The nanotubes were thoroughly mixed with potassium bromide and pressed into a pellet before data acquisition with a Bruker IFS66V spectrometer utilizing a Michelson interferometer. Changes in the surface chemistry of s-MWCNTs were probed with X-ray photoelectron spectroscopy (XPS) using a Physical Electronics 5500 Multitechnique system with a monochromatic Al Kα radiation source, and CasaXPS software was employed for data processing.

The rheological properties of epoxy/MWCNT suspensions were measured using an AR2000ex stress-controlled rheometer (TA Instruments) configured with 25 mm diameter parallel plates. All tests were performed with a 0.75 mm gap size at 25 °C according to the following procedure. MWCNTs were sonicated in Epon 828 using the same protocol outlined for nanocomposites processing. After cooling, 0.3 mL of the nanotube dispersion was transferred to the parallel plates and held for 3 min at 25 °C before a stepped steady state flow test was conducted from 0.01 to 100 s⁻¹.

Dynamic mechanical analysis (DMA, Q800, TA Instruments) of nanocomposite samples was performed in three-point bending mode to probe thermo-mechanical properties. Samples with dimensions of 25 mm x 6 mm x 1.5 mm were tested at a fixed frequency of 1 Hz during temperature sweeps from 20 to 200 °C with a heating rate of 3 °C/min. The glass transition temperature ($T_g$) of each sample was determined by the peak of the tan δ curve. Heat capacity measurements of cured samples were conducted by differential scanning calorimetry (DSC, Q2000, TA Instruments) at 10 °C/min in nitrogen using a sapphire
standard for calibration. The mechanical properties of nanocomposites at room temperature were evaluated by tensile testing with an Instron universal testing machine (Model 5569) equipped with a 50 kN load cell and video extensometer. Dog-bone shaped samples were machined according to the recommendations in ASTM D638 (Type V) and tested at a crosshead speed of 5 mm/min. At least 5 samples were tested per batch to determine average properties. The fracture surfaces of samples were examined post-tensile testing with a scanning electron microscopy (SEM, FEI Quanta 200) to evaluate the nanotube dispersion and correlate the fracture morphologies with mechanical properties. Images were collected at 8 kV accelerating voltage and 10 mm working distance.

4.4 Results and Discussion

4.4.1 Silanization

Functionalization of the nanotubes was confirmed by TGA, FTIR, and XPS analyses. Figure 4-2 shows the thermal degradation behavior of p-MWCNTs, o-MWCNTs, and s-MWCNTs. While p-MWCNTs and o-MWCNTs are stable up to 400 °C, s-MWCNT exhibit weight loss (~ 6 wt%) from 200-400 °C corresponding to the decomposition of silane molecules. FTIR confirmed reaction of the methoxy group of the silane monomer with hydroxyl groups on the MWCNTs, and a comparison of p-MWCNT, o-MWCNT, and s-MWCNT spectra is given in Figure 4-3. The band at 1384 cm⁻¹, which is prominent in the o-MWCNT spectrum, is attributed to bending of hydroxyl groups. After silanization, the intensity of this peak decreases significantly, signifying reaction of methoxy groups with hydroxyl moieties on the nanotube surfaces. Three other bands appear after silanation in the range from 880-1110 cm⁻¹ that are not present in the p-MWCNT or o-MWCNT. Theses peaks at 880 cm⁻¹, 1020 cm⁻¹, 1110 cm⁻¹, are attributed to absorption by Si-OH, Si-O-Si, and
Si-O-C bonds, respectively. While the reaction was run using dry CO$_2$, the presence of Si-O-Si and S-OH moieties suggests that some water was present, likely on the surface of the MWCNTs.

![Thermogravimetric analysis of p-MWCNTs, o-MWCNTs, and s-MWCNTs.](image)

**Figure 4-2.** Thermogravimetric analysis of p-MWCNTs, o-MWCNTs, and s-MWCNTs.

XPS was used to further characterize the silane grafting process. The survey scans presented in Figure 4-4a show the average surface composition of p-MWCNTs, o-MWCNTs, and s-MWCNTs. The peaks in each spectrum have been normalized to their respective C1s bands at 285 eV to allow for direct comparison. Almost no oxygen (~0.5 at%) is present on the surface of p-MWCNTs, as can be seen from the low intensity of the O1s band at 532 eV. Oxidation introduces a significant number of hydroxyl groups and yields an overall composition of about 7.5 at% oxygen on the MWCNT surfaces. Silanization further increases the oxygen content and peaks appear at 102 eV and 152 eV due to Si2p and Si2s photoelectrons, respectively, which confirms the presence of silane molecules.
Figure 4-3. FTIR spectra of p-MWCNTs, o-MWCNTs, and s-MWCNTs.

High resolution scans of the Si2p peak were obtained to better understand the bonding environment of the silanes and a representative spectrum is given in Figure 4-4b. Two peaks centered at 102.1 eV and 103.1 eV were required to fit the spectrum, indicating two distinct chemical states of silicon. The band at 102.1 eV corresponds to silicon bonded to oxygen and the MWCNT surface while the peak at 103.1 eV derives from silicon bonded to oxygen and the silicon atom of another silane monomer. The presence of Si-O-Si bonds indicates that partial hydrolysis of the silane molecules occurred and is in agreement with the FTIR results discussed earlier. However, only a small number of silane monomers underwent self-condensation relative to the number of GPTMS molecules that reacted with the o-MWCNT surface. Comparison of the fitted peak areas reveals that approximately 77% of the Si atoms were grafted to the MWCNT surface while 23% were bonded to another silane molecule.
Rheological measurements indicate that functionalization affects the interaction of nanotubes with epoxy resin. Figure 4-5 compares the viscosity of neat Epon 828 with that of resin containing 0.5 wt% p-MWCNTs and s-MWCNTs as a function of shear rate. The neat resin behaves as a Newtonian fluid with viscosity independent of shear rate. The addition of
both p-MWCNTs and s-MWCNTs increases the resin viscosity and induces shear thinning behavior. However, the higher viscosity of epoxy containing s-MWCNTs suggests that these nanotubes are either more highly dispersed or interact more favorably with the resin than p-MWCNTs.[24, 25]

![Rheological behavior of neat resin as well as resin containing 0.5 wt% p-MWCNTs and s-MWCNTs.](image)

**Figure 4-5.** Rheological behavior of neat resin as well as resin containing 0.5 wt% p-MWCNTs and s-MWCNTs.

4.4.2 Nanocomposite thermo-mechanical properties

In order to test the effectiveness of functionalization in improving nanocomposite properties, composites were prepared using model epoxy system consisting of Epon 828 and TETA. Figure 4-6 and 4-7 summarize the thermo-mechanical behavior of nanocomposites made with p-MWCNTs and s-MWCNTs, respectively. The addition of p-MWCNTs increased the glassy modulus of the epoxy slightly at all loading levels while the rubbery modulus plateaued at nearly the same value for the neat epoxy and all composites.
Composites containing s-MWCNT also exhibited marginally higher glassy moduli than the neat epoxy, but had significantly higher rubbery moduli. The elevated rubbery plateau modulus of s-MWCNT composites may be due to increased cross-linking density. While a stoichiometric ratio of amine to epoxide groups was maintained in the resin mixture, the addition of s-MWCNTs introduces a slight excess of epoxide groups, which can react with –OH moieties present in cured portions of the network. Such a reaction would increase the cross-link density relative to the neat epoxy.

Figure 4-6. Dynamic mechanical analysis of nanocomposites made with different loadings of p-MWCNTs.

The insets in Figure 4-6 reveal the significant changes observed in tan δ of the nanocomposites, and the tan δ peak temperature was used to define the $T_g$. The $T_g$ of the epoxy increased from 136 °C to around 142 °C upon introduction of 0.1 wt% and 0.2 wt% p-MWCNTs. Higher loading levels caused only minor increases in the $T_g$, which may be due to
limited polymer-MWCNT interaction as the result of agglomeration of the nanotubes. Dramatic increases in the $T_g$ of composites containing s-MWCNTs were seen at low loading levels. At 0.1 wt% s-MWCNT loading, the composite $T_g$ increased 18 °C relative to the neat epoxy to 154 °C. The addition of greater amounts of s-MWCNTs led to progressively lower $T_g$s, though they were still much higher than the neat epoxy with values of 149 °C, 147 °C, and 143 °C for 0.2 wt%, 0.5 wt%, and 1.0 wt% loading, respectively.

Figure 4-7. Dynamic mechanical analysis of nanocomposites made with different loadings of s-MWCNTs.

The dramatic increase in the $T_g$ of the epoxy with small MWCNT additions suggests that strong, positive interactions exist among the MWCNTs and polymer network. To further probe the nature of these confinement effects, the nanocomposite heat capacities were measured with DSC and polymer cooperativity length scales calculated according to the method of Donth.[26, 27] Within this framework, an inhomogeneous glass composed of
spatially fluctuating network mobility can be conceptually divided into several subsystems capable of rearranging their configurations independently of surrounding subsystems upon thermodynamic fluctuation. These subsystems, called cooperatively rearranging regions (CRRs), represent the number of segments that must cooperatively move in order for network relaxation to occur and their size strongly depends on temperature. The CRR volume at the glass transition, $\xi^3$, can be estimated from the mean temperature fluctuation ($\delta_T$) of an average CRR at the glass transition according to:

$$
\xi^3 = \frac{k_B T_g^2 \Delta (1/C_v)}{\rho \delta_T^2}
$$

where $k_B$ is the Boltzmann constant, $\rho$ the density, $T_g$ the glass transition temperature, and $C_v$ the heat capacity at constant volume of the composite. In practice, $C_v$ is approximated by the constant pressure heat capacity, $C_p$, measured by DSC. For all measurements, samples were first heated to 200 °C to erase thermal history, cooled at 10 °C/min to 30 °C, and finally heated to 200 °C at 10 °C/min. The heat capacity measured during the final heating cycle was used to calculate all parameters. The mean temperature fluctuation at $T_g$ was estimated using Donth’s approach, in which $\delta_T = \Delta T/2.5$ with $\Delta T$ defined as the temperature interval over which $C_p(T)$ varies by one standard deviation of the total $C_p$ change at $T_g$.[28]

The effect of various loadings of p-MWCNT and s-MWCNT on the CRR of epoxy nanocomposites is presented in Figure 4-8. The neat epoxy has a slightly lower average CRR length ($\xi \sim 2.18$ nm) than composites prepared with p-MWCNTs at all loading levels ($\xi \sim 2.32$ nm). However, composites filled with s-MWCNTs exhibit a fundamentally different behavior, with $\xi$ values of 3.50 nm, 3.46 nm, 3.15 nm, and 2.79 nm for loadings of 0.1 wt%, 0.2 wt%, 0.5 wt%, 1.0 wt%, respectively. The large CRR size of the composites prepared
with s-MWCNTs is attributed to covalent bonding of the silanized nanotubes with the epoxy network, which greatly restricts the mobility of its segments and necessitates the coordinated movement of many chains for relaxation to occur. The increased connectivity of the network produces a larger activation energy barrier for chain motion, which is manifested in a relatively large $T_g$.

![Figure 4-8](image.png)

**Figure 4-8. Changes in the cooperatively rearranging region length with p-MWCNT and s-MWCNT additions.**

Tensile testing was performed to evaluate the effect of nanotube additions on the epoxy mechanical behavior. Figure 4-9 summarizes the results and reveals that optimal properties are realized at low loadings. The addition of 0.2 wt% s-MWCNTs markedly increases the ultimate tensile strength of the resin, while the same loading of p-MWCNTs has little effect. Both types of MWCNTs increase the strain at break and toughness of the epoxy, though the greatest improvements are observed for s-MWCNTs composites. Functionalization has a less pronounced impact on the Young’s modulus, and Figure 4-9b shows that the modulus of s-
MWCNT composites is nearly the same as those of p-MWCNTs at all nanotube loadings. Elevating the loading levels of any type of MWCNT above 0.2 wt% has a deleterious effect on toughness, likely due to agglomeration of the nanotubes. The fracture surfaces of tensile test specimens were examined with SEM to compare the failure mechanisms of the neat epoxy and nanocomposites prepared with both types of nanotubes.

![Graphs showing tensile properties](image)

Figure 4-9. Tensile properties of neat epoxy as well as p-MWCNTs and s-MWCNT/epoxy nanocomposites: (a) Young’s modulus, (b) tensile strength, (c) fracture strain, and (d) toughness

4.4.3 Fracture surface analysis

Large differences in the fracture behavior of p-MWCNT and s-MWCNT composites reflect the increased toughness that was observed for composites containing silanized
nanotubes. Figure 4-10 shows the surfaces of neat epoxy and p-MWCNT composite samples fractured via tensile testing. The neat epoxy fracture surface is smooth with few river markings, indicative of brittle failure. p-MWCNT composites contain agglomerations even at 0.1 wt% loading that become larger as the nanotube concentration is increased to 0.5 wt%. Inspection at high magnification reveals significant nanotube pullout, which is indicative of poor bonding at the MWCNT-epoxy interface. In contrast, s-MWCNT composites contained fewer agglomerations at low loadings, and microcracks were bridged with nanotubes, as shown in Figure 4-11. Therefore, the increased toughness observed for s-MWCNT composites is likely due to the increased energy required to open cracks, in an analogous fashion to crazing-induced toughening in thermoplastics.
Figure 4-10. Fracture surfaces of (a) neat epoxy and composites filled with (b) 0.1 wt% p-MWCNT and (c) 0.5 wt% p-MWCNT. A higher magnification image of the 0.5 wt% p-MWCNT composite (d) shows significant nanotube pullout.
scCO$_2$ was found to be a suitable solvent for the functionalization of o-MWCNTs with GPTMS and offers a green alternative to organic solvents for grafting nearly monolayers of silane molecules onto the nanotube surfaces. The addition of s-MWCNTs to a model epoxy system markedly increased its $T_g$, and measurements of the network cooperativity length scale confirmed that silanized nanotubes restrict polymer mobility. Composites filled with p-MWCNTs and s-MWCNTs exhibited significantly higher strain at break and toughness than

4.5 Conclusions

Figure 4-11. Fracture surfaces of composites filled with (a) 0.1 wt% s-MWCNT and (b) 0.5 wt% s-MWCNT. A higher magnification image of the 0.5 wt% s-MWCNT composite (c) shows nanotube crack bridging.
the neat epoxy, and the greatest improvements were observed at low loading levels. SEM analysis of the composite fracture surfaces revealed that nanotube pullout was the primary failure mechanism in epoxy loaded with p-MWCNT while crack bridging predominated in s-MWCNT composites as the result of covalent bonding of silanated nanotubes with the matrix. The elevated $T_g$ and toughness achieved with small additions of s-MWCNTs promise to extend the engineering applications of the epoxy resin.

4.6 References


CHAPTER 5: ANISOTROPIC BUCKYPAPER THROUGH SHEAR-INDUCED MECHANICAL ALIGNMENT OF CARBON NANOTUBES IN WATER

A paper submitted to Carbon

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5.1 Abstract

A simple method for aligning nanotubes in BP with a modified Taylor-Couette system is reported. Using shear forces produced by a rotating cylinder to orient MWCNTs in an aqueous dispersion, the suspended nanotubes are simultaneously aligned and filtered to produce BP with preferential nanotube orientation in the direction of flow. The aligned BP has anisotropic electrical and mechanical properties, which are both enhanced parallel to the direction of orientation. The technique presented here is simple and versatile in that it can be adapted for use with any type of CNT synthesized by any method. In addition, large BP sheets can be easily fabricated by increasing the length and diameter of the cylinders in the setup. As a result, this approach is more scalable than current techniques and offers an attractive route for producing large quantities of oriented BP at relatively low cost.

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5.2 Introduction

Carbon nanotubes (CNTs) have been studied extensively over the last two decades because of their outstanding electrical, mechanical, and thermal properties, which makes them ideal candidates for use as reinforcement in multifunctional composites among other applications.[1, 2] However, composites fabricated by mixing CNTs into a resin are limited to low loading levels because the large increases in viscosity that occur at higher loadings encumber processing. This, in turn, limits the effect that CNTs can have on the composite properties, and new methods must be developed if the true potential of CNT composites is to be realized. One way to achieve high loadings of CNTs in a resin is through the use of buckypaper (BP), which is a free-standing mat of tightly packed CNTs formed by the controlled filtration of a CNT dispersion. BP can be handled in a manner similar to glass and carbon fiber mats, and traditional composite processing techniques such as compression molding and vacuum-assisted resin transfer molding can be used to infiltrate resin into the pores of the BP mat and bind several plies together into composites.[3, 4] Using this approach, composites containing up to 60 wt% MWCNTs have been achieved[5] and outstanding mechanical,[6, 7] thermal,[8] electrical,[7] and electromagnetic shielding properties[9] have been realized in BP-reinforced polymers. Most BP is composed of CNTs that are randomly aligned. However, as with any fiber-reinforced composite, optimal properties are realized when the fiber alignment is unidirectional within each ply and the composite layup is judiciously tailored to match the expected stress state of its application.

Several methods to align CNTs within BP films have been reported recently, which can be broadly classified as alignment through (i) mechanical stretching of cross-linked CNT mats, (ii) pushing or pulling vertically-aligned carbon nanotubes (VACNTs), and (iii) the
application of large magnetic fields. Mechanical stretching involves uniaxially straining randomly aligned multi-walled carbon nanotube (MWCNT) BP and then impregnating the stretched nanotube film with resin. Bismaleimide (BMI)/BP composites made with this process possessed outstanding mechanical and electrical properties,[5] and, when the MWCNTs in the BP were functionalized with epoxide groups, the resulting composites exhibited unprecedentedly high strength (3081 MPa) and modulus (350 GPa), surpassing even high-performance carbon fiber composites.[10] However, the MWCNTs used in this study were cross-linked together through a specialized synthesis process necessary to prevent the BP from tearing at high strains, which excludes the method from widespread industrial use in the near future.

Highly aligned BP can also be produced from VACNT arrays, which consist of forests of densely-packed and highly aligned nanotubes. By pulling on a VACNT forest, van der Waals attraction among neighboring nanotubes causes the CNTs to assemble into continuous yarns or BP mats.[11-19] In addition to being spun by pulling action, VACNT forests can also be “pushed” down like dominos to form BP. This method has been implemented for vertically aligned MWCNTs using a cylinder to physically roll over and flatten the nanotube forest, and the BP produced in this manner exhibited higher electrical and thermal conductivity in the direction of alignment.[20] However, this method is also not amenable to large-scale use, as MWCNT forests with very high degrees of vertical alignment must be grown, a process that is currently only possible in a few laboratories.

Magnetic alignment is another nanotube orientation technique developed by Smalley[21] and refined by Liang and coworkers.[22] This method involves filtering CNTs in the presence of an applied magnetic field. Because CNTs have anisotropic magnetic
susceptibilities, they tend to align with the direction of applied magnetic field lines in order to minimize energy. If a sufficiently strong magnetic field is applied to MWCNTs that are very well dispersed in solution, the MWCNTs will become oriented, and subsequent filtering will lead to the formation of aligned BP. Individual nanotubes within a MWCNT can be metallic or semiconducting depending on their structure with paramagnetic or diamagnetic responses to applied magnetic fields, respectively, both of which tend to align the MWCNT in the same direction and with nearly the same force.[23-25] However, huge magnetic fields on the order of 10-30 T are required to produce observable degrees of alignment.[21] The cryogenically-cooled electromagnets needed to achieve those massive magnetic fields render this method unfit for the production of aligned BP on any appreciable scale.

An alternative approach for aligning nanotubes in BP is outlined in this paper. When subjected to shear forces in a fluid, CNTs align along the direction of flow. Using a modified Taylor-Couette system, an aqueous MWCNT dispersion is simultaneously sheared and filtered to produce BP with preferential nanotube orientation in the direction of flow. The aligned BP has anisotropic electrical and mechanical properties, which are both enhanced parallel to the direction of orientation. The technique presented here is simple and versatile in that it can be adapted for use with nanotubes synthesized by any method. In addition, the size of the BP can easily be increased using cylinders with larger dimensions. As a result, this approach is more scalable than current techniques and offers an attractive route for producing large quantities of oriented BP at relatively low cost.
5.3 Experimental Details

5.3.1 Materials
NC7000 MWCNTs with an average diameter of 10 nm and purity of 90% were supplied by Nanocyl, S.A. (Belgium). A surfactant, Triton X-100, was purchased from Fisher Scientific (Waltham, MA, USA). Nanotube dispersions were prepared by sonicating a mixture of 1.5 g MWCNTs, 15 mL surfactant, and 750 mL DI water with a horn (Fisher, sonic dismembrator model 100) for 2 hours. The resulting dispersion was allowed to settle for 24 hours, and the well-dispersed supernatant was used to prepare BP films with a setup shown schematically in Figure 5-1.

![Figure 5-1. Schematic of modified Taylor-Couette system used to simultaneously shear and filter MWCNT dispersions](image-url)
5.3.2 Methods

The modified Taylor-Couette apparatus was constructed from an acrylic outer cylinder with an inner diameter of 31.15 mm and a high-density polyethylene Porex (Fairburn, GA, USA) inner cylinder having an outer diameter of 26.00 mm and an average porosity of 60 µm. The inner cylinder was sealed with adhesive tape along its length, except over an 8 cm long section. An electric stirring motor (Caframo, Ontario, Canada) with rpm control of ± 1 rpm was used to rotate the outer cylinder at speeds up to 2000 rpm. Compression fitted PTFE bushings secured to the inner cylinder maintained the inner rod parallel to the outer cylinder while allowing the two to be separated easily. A small fill tube was inserted into a slit milled in the top bushing to provide fresh dispersion during filtration, and a vacuum in the inner cylinder was created by a belt-driven pump (Welch, Niles, IL, USA). In all experiments, the top of the inner cylinder was clamped to prevent rotation.

To fabricate BP using the setup, a 9 cm x 8 cm strip of nitrocellulose filter paper (Osmonics, Inc.) with an average pore size of 45 µm was affixed to the exposed porous section of the inner rod by pulling the paper tautly around the cylinder and bonding the overlapping ends of the paper with a small amount of adhesive. After the adhesive had cured, the inner cylinder was inserted into the outer cylinder and the gap was filled with dispersion. The outer cylinder was rotated at a constant rate to shear the fluid, and vacuum was subsequently applied to the fixed inner cylinder to force the dispersion through the filter paper. A BP sheet formed on the filter, and the separated water was collected in a series of traps. Fresh dispersion was continually added via the fill tube during filtration to maintain a constant fluid level.
After filtration, the inner cylinder was removed from the setup and the filter paper was cut along the overlapped edge to produce a rectangular sheet, which was dried in a vacuum oven at 100°C for 12 hr. The dried BP was then separated from the filter paper by gently folding and peeling the nanotube mat free from the filter. The resulting freestanding film of MWCNTs was soaked in isopropanol overnight to remove any residual surfactant before drying once more in a vacuum oven at 80°C for 4 hr. Figure 5-2 shows a representative sample of BP after processing.

Figure 5-2. Optical image of dried BP sheet formed under a shear rate of 1000 s$^{-1}$.

5.3.3 Characterization

The viscosity of the MWCNT dispersions was measured as a function of shear rate using an AR2000ex rheometer equipped with a Peltier temperature control stage and a 40 mm diameter cone ($\alpha = 1^\circ,0^\prime,11^\prime\prime$). Measurements were performed by placing 0.2 mL of dispersion on the Peltier stage and equilibrating at 25°C before performing a constant temperature, steady-state flow test at shear rates ranging from 1 to 1200 s$^{-1}$. The degree of
nanotube alignment in BP samples was monitored with scanning electron microscopy (SEM, FEI Quanta 200) operating at 8 kV accelerating voltage. Electrical conductivity measurements were performed using a linear four point probe (Jandel model RM2). For each test, a 1 cm x 3 cm strip was cut from the BP either perpendicular or parallel to the direction of alignment, and conductivity measurements were made with the four probes oriented parallel to the long axis of the strip. The thickness of each sample was averaged from 10 measurements taken along the length of the BP using a digital micrometer (Mitutoyo). The anisotropic mechanical properties of BP samples were evaluated by tensile testing 0.5 cm x 3 cm strips cut either parallel or perpendicular to the direction of alignment. For each test, the BP strip was mounted in a flat-faced fixture and elongated with an Instron universal testing machine following a procedure similar to ASTM D882.

5.4 Results and Discussion

5.4.1 Rheological behavior of the MWCNT dispersion

Figure 5-3 depicts the rheological behavior of the MWCNT dispersion used in this study. In a similar manner to previous reports on aqueous nanotube dispersions,[26, 27] the viscosity was observed to decrease significantly with increasing shear rate. This shear-thinning behavior is due to the fact that MWCNTs align under shear, which lowers their resistance to flow. The viscosity of the dispersion used in this study plateaus at ~ 800 s\(^{-1}\), indicating that the nanotubes reach their maximum degree of alignment at shear rates above this value.
Figure 5-3. Rheological behavior of the aqueous MWCNT dispersion used in this study.

5.4.2 Fabrication of aligned BP

The Taylor-Couette setup is a classic method for studying fluid behavior under shear. By rotating the outer and/or inner cylinder, shear forces develop in the fluid trapped between the two cylinders, the magnitude of which is determined by both their radii and relative speeds.[28] Rotation of the outer cylinder is desirable for aligning fibers in solution as it avoids turbulent transitions that can occur from instabilities associated with rotation of the inner cylinder.[29] The modified Taylor-Couette setup used in this study was designed to produce shear rates from 0 s⁻¹ to 1200 s⁻¹. By shearing the dispersion while simultaneously applying a vacuum to the inner cylinder, the suspended nanotubes were circumferentially aligned and then forced onto filter paper. Progressive build-up of MWCNT layers led to the formation of BP comprised of nanotubes with a preferential orientation parallel to the circumference of the cylinders. In this paper, the direction of flow is referred to as “∥”, and the direction perpendicular to flow (the axial cylinder direction) is referred to as “⊥”. The morphology of samples produced at various shear rates is depicted in Figure 5-4. With no
cylinder rotation (0 s$^{-1}$), the nanotubes are randomly oriented. As the shear rate is increased to 640 s$^{-1}$, the nanotubes become partially oriented in the // direction. At an even higher shear rate of 825 s$^{-1}$, the MWCNTs are highly aligned in the direction of flow. Shear rates above 825 s$^{-1}$ also produced BP with MWCNTs oriented in the // direction, although a higher degree alignment is not discernible.

Figure 5-4. Scanning electron micrographs of BP formed at shear rates of 0 s$^{-1}$, 640 s$^{-1}$, 825 s$^{-1}$, and 1000 s$^{-1}$.
5.4.3 Electrical conductivity of BP

While SEM indicates alignment of MWCNTs in BP produced at elevated shear rates, it is a qualitative measure. To better quantify the degree of anisotropy, the electrical conductivity of BP samples was measured in different directions. Figure 5-5 shows representative current-voltage curves obtained from four point probe measurements of ~100 µm thick BP produced at shear rates of 0 s⁻¹ and 1000 s⁻¹. BP formed at all shear rates displays Ohmic behavior. However, random BP fabricated in the absence of shear exhibits very little directional dependence, while BP formed at a shear rate of 1000 s⁻¹ has markedly lower slope (V/I) in the // direction and higher slope when measured ⊥ to alignment as a result of higher and lower conductivity, respectively. Figure 5-6 summarizes the electrical behavior of BP produced in this study as a function of shear rate and measurement direction. At low shear rates, the electrical anisotropy, defined as the ratio of conductivity measured // and ⊥ to alignment, is ~ 1. With increasing shear rate, the conductivity steadily increases // to alignment while decreasing in the ⊥ direction, and the anisotropy ratio reaches a plateau of ~ 2 around 825 s⁻¹. This behavior coincides with a plateau in shear thinning observed by rheology, and suggests that viscosity measurements are a convenient method for determining the minimum shear rate needed to maximize nanotube alignment.
Figure 5-5. Representative I-V curves for BP samples produced in the absence of shear (red) and at $\dot{\gamma} = 1000 \text{ s}^{-1}$ (blue) measured both parallel and perpendicular to the direction of flow.

Figure 5-6. Summary of electrical conductivity measurements performed on BP in directions parallel and perpendicular to the direction of flow at various shear rates.
Conductivity in BP is generally dictated by nanotube-nanotube junctions, which limit the mean free paths of electrons and lower the conductivity.[30, 31] The BP produced in this study does not contain perfectly aligned MWCNTs, and as a result, nanotube-nanotube junctions play a role in the conductivity in all directions. However, electrons traveling in the // direction of aligned BP samples will encounter far fewer junctions than electrons traveling in the transverse direction, and, as a result will experience less resistance. Anisotropic electrical conductivity has been observed in aligned BP samples produced by other methods, and Table 5-1 compares the results of this study with a select number of those previously reported in the literature. Here we report a maximum anisotropy of ~ 2, which is lower than that achieved using magnetic alignment and pulling of VACNTs, but similar to the value found by “domino pushing” MWCNT forests.

The lower levels of anisotropy found in this study may be due to the presence of a higher number of misaligned nanotubes than by magnetic alignment. Because the relaxation time of water is very short, the aqueous dispersions used in this study may have allowed some MWCNTs to relax and coil upon removal of shear forces, especially on the upper few layers, which are less constrained by neighboring nanotubes. The use of higher viscosity fluids may limit such relaxation and improve nanotube alignment and packing density. Greater levels of alignment might also be achieved by tuning the interaction among the nanotubes, surfactant, and filter paper, and greater electrical properties could be realized by extending the approach to other varieties of CNTs such as high aspect ratio SWCNTs.
Table 5-1. Literature reports of electrical anisotropy in aligned BP at room temperature

| Method                   | $\sigma_{||}$ (S/cm) | $\sigma_{\perp\perp}$ (S/cm) | $\sigma_{||}/\sigma_{\perp\perp}$ | Reference |
|-------------------------|----------------------|-------------------------------|------------------------------------|-----------|
| Magnetic Alignment      |                      |                               |                                    |           |
| SWCNT                   | 1100                 | 138                           | 8.0                                | [32]      |
| SWCNT                   | 1210                 | 200                           | 6.1                                | [33]      |
| Pushing/pulling VACNT   |                      |                               |                                    |           |
| MWCNT                   | 209                  | 110                           | 1.9                                | [34]      |
| MWCNT                   | 403                  | 56                            | 7.2                                | [31]      |
| Mechanical Stretching   |                      |                               |                                    |           |
| Nanocomp MWCNT*         | 600                  | -                             | -                                  | [5]       |

* Study did not report $\sigma_{\perp\perp}$ but did find that $\sigma_{||}$ was 40% higher than randomly oriented BP

Figure 5-7. Representative stress-strain curves for BP produced in the absence of shear and at $\dot{\gamma} = 1000$ s$^{-1}$ in directions both parallel and perpendicular to flow.

5.4.4 Mechanical properties of BP

The anisotropic mechanical properties of BP produced in the absence of shear and at a shear rate of 1000 s$^{-1}$ were also investigated to test the efficacy of BP for composite
applications. Figure 5-7 shows representative stress-strain curves for BP tested at both shear rates in different directions. The results of testing many samples are summarized in Fig. 8. Randomly oriented BP has a modulus of ~0.4 GPa, ultimate tensile strength near 4 MPa, and a strain at break of 1% with no directional dependence within experimental error. In contrast, BP produced under high shear shows strong anisotropy, with moduli and tensile strengths 2.8 and 2.2 times higher in the direction of alignment, respectively. However, even in the direction of alignment, the mechanical properties are modest, and further improvements are likely needed before the BP can be considered for use as reinforcement in composites.

Figure 5-8. Summary of mechanical properties for BP prepared in the absence of shear and at in directions both parallel (□) and perpendicular to flow (□).
5.5 Conclusions

A simple method for aligning nanotubes in BP with a modified Taylor-Couette system has been reported. Simultaneous shear-alignment and filtration of an aqueous MWCNT dispersion yielded BP with preferential nanotube orientation in the direction of flow. The BP exhibited anisotropic electrical and mechanical properties, which were both enhanced parallel to the direction of orientation and maximized at high shear rates. While the highest degree of anisotropy was found to be lower than some previously reported methods, such as magnetic alignment, the technique presented here is simple and versatile in that it can be adapted for use with any type of CNT synthesized by any method. In addition, large BP sheets can be easily fabricated by increasing the length and diameter of the cylinders in the setup, making this approach an attractive route for the producing large quantities of oriented BP at relatively low cost.

5.6 References


CHAPTER 6: A NOVEL MICROWAVE-ASSISTED CARBOtherMIC ROUTE FOR THE PRODUCTION OF COPPER-CARBON NANOTUBE METAL MATRIX COMPOSITES DIRECTLY FROM COPPER OXIDE

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6.1 Abstract

Cu\textsubscript{2}O was reduced to copper via a microwave-assisted carbothermic route using multi-walled carbon nanotubes (MWCNTs) as the carbon source. The reaction atmosphere as well as the degree of mixing of Cu\textsubscript{2}O and MWCNTs was varied, and the resulting products were characterized as a function of microwave exposure time. Irradiation of thoroughly mixed Cu\textsubscript{2}O and MWCNTs under argon for 45 s produced Cu-MWCNT composites with high MWCNT loading and high hardness. This new approach for fabricating carbon nanotube-reinforced metal matrix composites eliminates many of the challenges associated with traditional methods while requiring a fraction of the time and energy.

6.2 Introduction

The discovery of carbon nanotubes (CNTs) and their extraordinary mechanical, thermal, and electrical properties has sparked significant effort to develop lightweight composites using CNTs as reinforcement. To date, the vast majority of CNT-filled composites employ a polymer matrix. However, the same advantages CNTs afford polymer matrix composites (PMCs) apply to metal matrix composites (MMCs) as well. In particular, CNTs exhibit higher strength, stiffness, thermal conductivity, and electrical conductivity than the matrix phase while having lower density. A major reason CNT-MMCs are not as well established as PMCs lies in the fact that metals are more difficult to process than polymers, because high temperatures and/or large forces are usually needed to introduce reinforcement into the metal matrix. Current CNT-MMC fabrication processes generally can be categorized as powder metallurgy, electrodeposition, electroless deposition and molten mixing, all of which require specialized equipment.

In recent years, novel implementations of these basic techniques have emerged for the fabrication of MWCNT-reinforced MMCS and Cu-MWCNT MMCS, in particular, with a focus on maximizing mechanical and thermal properties. Kim et al. used a combination of electroless plating and hot press sintering to form Cu MMCS reinforced by Ni-SWCNTs, which exhibited excellent mechanical and tribological qualities. In an effort to improve dispersion, Chu et al. developed a new technique for making Cu-MWCNT composites by dry impact blending Cu powder and MWCNTs together before consolidating the particles via spark plasma sintering. Working at the extremes of mechanical mixing, Kang et al. formed Cu-MWCNT MMCS by spraying a mixture Cu powder and MWCNTs onto a substrate at supersonic velocities. While these pursuits have produced composites with
promising properties, new processing methods must be developed in order for CNT-reinforced MMCs to move out of the realm of the laboratory and gain widespread usage.

The reduction of metal oxides using carbon represents one of the oldest and most versatile extractive metallurgy processes, and economically important metals such as iron, tin and zinc are still produced in large tonnages using this method. Recently a new twist on this ancient technology has been reported in the literature; here, carbon and metal oxide are heated by microwaves.\textsuperscript{[16]} Using charcoal, coke, and graphite as carbon sources, iron,\textsuperscript{[16]} copper,\textsuperscript{[17]} and nickel\textsuperscript{[18]} have been obtained from their respective oxides. These early studies have shown that microwave reactions proceed rapidly with high efficiency and may require decreased activation energy relative to their traditional counterparts. A key to microwave carbothermic reactions lies with carbon’s ability to intensely absorb microwaves, which leads to rapid heating of the carbon and oxide. However, the microwave heating behavior of carbon depends strongly on its structure, and allotropes with sp$^2$ hybridized bonding exhibit enhanced microwave heating due to the Maxwell–Wagner effect.\textsuperscript{[19]} This form of Joule heating endows CNTs with a much higher microwave frequency dielectric loss tangent than coal\textsuperscript{[20]} and charcoal\textsuperscript{[21]}.

Here, we report for the first time the use of multi-walled carbon nanotubes (MWCNTs) as a carbon source for the microwave-assisted reduction of a metal oxide. In addition, while previous investigations used a nearly stoichiometric ratio of carbon to oxygen in order to produce pure metals, this study uses an excess amount of MWCNTs to produce MMCs. We show that Cu-MWCNT MMCs can be made directly from Cu$_2$O in very short times with a simple experimental setup, and that these composites exhibit increased hardness relative to pure copper.
6.3 Experimental

6.3.1 Materials
Cu₂O (99 % purity, 200 mesh powder) was purchased from Alfa Aesar (Ward Hill, MA, USA). Commercially available NC7000 MWCNTs were obtained from Nanocyl (Nanocyl S.A., Sambreville, Belgium).

6.3.2 Methods
Metal samples were prepared using the following procedure. First, 0.40 g MWCNTs were placed into a high form alumina crucible. Then, 0.35 g Cu₂O was placed in the middle of the MWCNT bed, and the crucible was shaken lightly to sink the Cu₂O powder just below the surface of the MWCNTs. For some experiments, the powder was mixed with the MWCNTs using a spatula. The crucible was then placed in a domestic microwave (1.3 kW, Emerson, Parsippany, NJ, USA) and irradiated at high power for a set time. Figure 6-1 shows a schematic depiction of the experimental setup used in this study. For experiments conducted in an inert atmosphere, the glass chamber was flooded with argon for 1 minute prior to microwave irradiation, and a steady gas flow was maintained until the crucible had cooled to room temperature.
6.3.3 Characterization

The phases present during different stages of Cu₂O reduction in air were studied using XRD. To obtain fine particles for these powder diffraction experiments, samples were abraded with a steel file, and the filings were collected for analysis. A strong magnet was subsequently passed over the copper powder to ensure that no steel filings remained in the sample, and diffraction data were collected on a SCINTAG XDS2000 multi-purpose powder diffractometer at room temperature with CuKα radiation. Samples selected for optical, hardness, and SEM analyses were mounted in Bakelite, ground, and polished. The microstructures of partially reduced copper oxide and Cu-MWCNT composites were examined optically with an Olympus GX51 inverted metallurgical microscope and images were collected with an Olympus D12 digital camera system. The mechanical properties of Cu-MWCNT composites were evaluated using Vickers microhardness measurements, which were performed at 10 locations per sample with a LECO LM247AT microhardness tester.
applying a load of 100 gf over 13 s dwell time. Micro-Raman spectroscopy was employed to determine the location and structural integrity of MWCNTs within the copper matrices of Cu-MWCNT MMCs. These measurements were collected using a Renishaw inVia spectrometer operating with a 488 nm Ar laser. SEM micrographs of Cu-MWCNT MMCs were acquired with an FEI Quanta-250 SEM operating at 10 kV under high vacuum, and EDS mapping was performed under the same conditions.

6.4 Results and Discussion

In this study, Cu$_2$O powder was reduced in both air and argon environments after different degrees of mixing of the oxide powder and MWCNTs prior to microwave irradiation. In the following discussion, “unmixed” refers to the experimental condition of Cu$_2$O placed in the middle of a bed of MWCNTs and “mixed” refers to the condition in which MWCNTs and Cu$_2$O were nearly homogeneously mixed prior to irradiation. To elucidate the reduction process of Cu$_2$O under these different conditions, reactions were run at short time intervals and the products were analyzed with optical microscopy and XRD. Figure 6-2 gives a representative set of micrographs for samples obtained after unmixed Cu$_2$O was microwaved in air for progressively longer times. After 5 s of irradiation, relatively large pieces of porous, brittle Cu$_2$O with reduced copper shells were removed from the MWCNT bed. The large size of the particles indicates that the initially very fine Cu$_2$O particles sintered together quickly after microwave exposure. As shown in Figure 6-2a, the reduction mainly occurred at the edges of the Cu$_2$O particles. This suggests that reduction occurred in the solid state, where slow diffusion would only allow the reaction to proceed in areas of intimate contact between oxide and carbon. Close inspection of Figure 6-2a reveals some small areas of copper in the interior of the large Cu$_2$O particle. These copper particles
are likely the result of the oxidation of carbon nanotubes (and, correspondingly, the reduction of copper oxide) trapped between Cu$_2$O particles as they sintered together. After 10 s of irradiation, the particles still had porous Cu$_2$O cores, but the outer core of reduced copper was much larger and contained several dendrites of Cu$_2$O, indicative of melting. Furthermore, a eutectic structure of fine Cu$_2$O lamellae in a copper matrix was observed between the large dendrites. As the oxide and copper formed a melt, diffusion of carbon and oxygen were much faster than in the solid state, and the reduction reaction was accelerated. Irradiation for 30 s resulted in particles with only small amounts of Cu$_2$O. Figure 6-2c reveals that these particles were composed primarily of copper dendrites with an interdendritic eutectic structure of Cu$_2$O and copper (Figure 6-2e); this microstructure is again indicative of melting. Notably, several agglomerations of CNTs were also incorporated into the melt. Microwave exposure for 60 s resulted in spherical copper particles devoid of Cu$_2$O and containing small clusters of CNTs, as shown in Figure 6-2d. Etching of samples irradiated for 60 s and subsequent micro-Raman measurements revealed that the majority of these CNT agglomerations were located on grain boundaries.
Figure 6-2. Microstructural evolution of the unmixed Cu$_2$O exposed to microwaves in air for 5 s (a), 10 s (b), 30 s (c), and 60 s (d). A higher magnification image of the 30 s sample is given in (e) to better resolve the eutectic structure. A representative micrograph of an etched 60 s sample is shown in (f).

XRD was used to confirm the identity of the phases at different exposure times. Figure 6-3 reveals the presence of small copper peaks after 5 s of irradiation that become
much more intense as the irradiation time is increased. Conversely, the Cu$_2$O peaks become less intense and sharp with exposure time. The absence of CNT peaks in the XRD spectra of the 30 s and 60 s irradiation time samples should be noted, because relatively large agglomerations of CNTs were observed both optically and with micro-Raman spectroscopy. However, the XRD pattern of the NC7000 CNTs resulted in very weak and broad peaks that were difficult to distinguish, consistent with XRD data of Nanocyl CNTs previously reported in the literature.[22]

![XRD spectra of mixed Cu$_2$O samples irradiated in air as a function of microwave exposure time.](image)

**Figure 6-3.** XRD spectra of mixed Cu$_2$O samples irradiated in air as a function of microwave exposure time.

Figure 6-4 summarizes the results of experiments conducted in air using mixed Cu$_2$O and MWCNTs. After a short exposure time of 10 s, very fine copper particles were observed to be evenly distributed in the MWCNT bed. Figure 6-4a illustrates the spherical nature of
these particles, which indicates that melting occurred. The absence of Cu$_2$O is also notable, but expected if melting occurred due to the high surface area of the droplet and rapid diffusion in the liquid state. Microwave irradiation for 30 s resulted in much larger spherical copper particles with a few agglomerated MWCNTs and no Cu$_2$O, as confirmed by micro-Raman and XRD measurements. The curved line seen near the top right quadrant of the copper sphere in Figure 6-4b was a commonly observed feature of particles formed after microwave exposure for 30 s or longer. These may be the result of welding of molten copper onto a partially solidified sphere during cooling. Copper particles formed after 60 s exposure time were even larger than those formed after 30 s and contained large MWCNT agglomerations, as shown in Figure 6-4c. These experiments, using mixed Cu$_2$O and MWNCTs in air, suggest that molten copper droplets are formed early on, which then wick together to form progressively larger spheres. MWCNTs trapped in the melt likely agglomerate due to van der Waals forces.
Experiments using unmixed and mixed Cu$_2$O were also performed in an argon environment. Figures 6-5a and 6-5c show micrographs of the products obtained when unmixed Cu$_2$O was irradiated for 15 and 45 s, respectively. Similar to the case of unmixed Cu$_2$O in air, a large sintered mass of Cu$_2$O with a thin layer of surface reduction was formed after short exposure time. Further irradiation led to a reduction of the sintered Cu$_2$O, but at a much slower rate than in air. The slower rate likely resulted from the lower temperatures reached under argon due to the lack of oxidation of MWNCTs by ambient O$_2$, a highly exothermic event.
Irradiation of mixed Cu$_2$O for 15 s in argon resulted in much smaller pieces of reduced Cu$_2$O, analogous to the case of mixed Cu$_2$O in air. However, as depicted in Figure 6-5b, the particles were not spherical, which indicates that melting did not occur. The large surface area of oxide in contact with carbon likely allowed for rapid reduction, even in the solid state. After 30 s of irradiation, brittle, porous structures composed of many sintered
particles of fully reduced copper were obtained from the bottom of the crucible, as shown in the left image of Figure 6-5e. Further microwave exposure caused consolidation and partial melting of these structures, and a representative micrograph of a sample irradiated for 45 s is shown in Figure 6-5d. Because the reaction was run in an inert atmosphere, the absence of oxygen in the system inhibited extensive oxidation of the MWCNTs, as was the case when the reaction was carried out in air. As a result, samples produced under irradiation in argon contain many more MWCNTs than those irradiated in air.

The relative stability of MWCNTs incorporated into the reduced copper under argon compared to those incorporated in air is further evidenced by R-values obtained from micro-Raman spectroscopy. R-values are defined as the ratio of the intensity of the D peak (~1350 cm\(^{-1}\)) to the G peak (~1575 cm\(^{-1}\)) and are indicative of the defect density within a MWCNT structure. Figure 6-6 shows a Raman spectrum of pristine MWCNTs, as well as spectra taken of MWCNTs embedded in copper matrices during reactions in air and argon (Cu\(_2\)O mixed with the MWCNTs, also referred to as mixed condition). Pristine MWCNTs have an R value of 0.95. Irradiation of MWCNTs for progressively longer times in both air and argon produced increasing R values, though the MWCNTs heated in air had significantly higher defect concentrations for the same exposure time. Heating in air produced R values of 1.08 and 1.11 after 30 and 45 s, respectively, compared with R values of 0.99 and 1.06 for MWCNTs heated in argon for the same amounts of time. The copper-Cu\(_2\)O eutectic temperature has been reported as 1067 °C,\(^{[23]}\) which is about twice the temperature needed to rapidly oxidize MWCNTs in air. Therefore, any MWCNTs subjected to such high temperatures in air are expected to have significant numbers of oxidized defect sites, and hence, high R-values. MWCNTs found in copper samples produced under argon have higher
defect densities than pristine MWCNTs, which could be due to oxidation from oxygen dissolved in the molten copper or from residual atmospheric oxygen in the reaction chamber.

Figure 6-6. Raman spectra of MWCNTs subjected to different irradiation times in air and argon. From bottom to top: pristine MWCNTs, air 30 s, air 45 s, air 60 s, argon 30 s, and argon 45 s. The dashed lines are a guide for the eyes to distinguish relative peak heights.

Table 6-1. Vickers microhardness measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atmosphere</th>
<th>Exposure Time (s)</th>
<th>Average Hardness (HV)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>air</td>
<td>5</td>
<td>62.1</td>
<td>3.7</td>
</tr>
<tr>
<td>2</td>
<td>air</td>
<td>60</td>
<td>72.5</td>
<td>4.6</td>
</tr>
<tr>
<td>3</td>
<td>argon</td>
<td>45</td>
<td>121.0</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Microhardness measurements were used to determine the mechanical properties of the Cu-MWCNT composites prepared under different conditions. As a baseline, hardness
measurements were taken of the pure copper shells found in samples microwaved for 5 s in air. Hardness tests were also performed on the MWCNT-copper composites made in the mixed condition and irradiation for 60 s in air and for 45 s in argon, and the results are summarized in Table 1. The copper shells formed after 5 s of microwave exposure did not contain any MWCNTs, as reduction occurred in the solid state. The average hardness of these shells was 62.1 HV. The Hall-Petch relationship for the hardness of pure copper is given as \cite{24}:

\[ H = 13.40 + 16.50d^{-1/2} \]

where \( H \) is Vickers hardness and \( d \) is grain size in mm. The average grain size of samples made by irradiation in air for 60 s was determined to be 98.1 \( \mu \)m by the linear intercept method. The hardness of pure copper with that grain size is predicted to be 66.1 HV by the Hall-Petch equation, though an average hardness of 72.5 HV was observed. Accounting for error in the hardness measurement, good agreement exists with the Hall-Petch relation, as is to be expected based on the small amount of MWCNTs incorporated into the copper. The grain size of the sample produced under argon in 45 s irradiation time was more difficult to determine. However, a markedly increased average hardness of 121.0 was observed. This high hardness value is likely caused by a combination of grain refinement and strengthening from MWCNT reinforcement. Area fraction analysis with ImageJ was performed to estimate the volume fraction of MWCNTs in 45 s argon composites, and an average value of 25.6 vol \% was determined with a standard deviation of 2.9. This analysis treated all black areas in optical micrographs as 100% MWCNTs, so it gives an upper bound on the possible vol \% MWCNTs. The actual figure is likely lower due to the fact that the black regions contain some copper as well as small voids between individual MWCNTs.
Figure 6-7. Backscattered SEM image (a) and corresponding EDS maps (b and c) of sample irradiated for 45 s in argon. An overlay of the copper and carbon maps on the backscattered image is shown in the bottom right figure (d).

Reported hardness values for Cu-MWCNT composites vary widely in the literature. Kim et al. used a molecular level mixing process together with spark plasma sintering to form composites having hardness of 110 HV at 10 vol % MWCNTs, an 80% increase relative to pure copper.[25] Dong et al. used a traditional powder metallurgy sintering technique to produce Cu-MWCNT composites with 119 HV at 15 vol % MWCNTs and 91
HV at 25 vol % MWCNTs.\textsuperscript{[26]} With a combination of electroless deposition and spark plasma sintering, Daoush et al. fabricated composites having an average hardness of 141 HV at 20 vol % MWCNTs, which was 22\% greater than copper without MWCNTs.\textsuperscript{[27]} Very recently Kang et al. employed a kinetic spraying method to achieve values of 162 HV hardness for composites containing only 4 vol % MWCNTs.\textsuperscript{[15]} However, pure copper processed under these same conditions had a high hardness of 129 HV due to grain refinement and extensive plastic deformation. Composites from the present study have an average hardness of 121 HV at approximately 25 vol % MWCNT loading, which is comparable to figures reported in the literature for composites made by sintering and spark plasma sintering. When performed under argon, the microwave-assisted carbothermic approach reported herein involves reduction of copper oxide followed by sintering and partial melting of the resulting fine copper particles. Thus, the final consolidation process is similar in some ways to established sintering processes, absent applied pressure. It is, however, very different in nature from methods such as kinetic spraying, which rely on large dynamic forces to plastically deform and consolidate copper powder together with MWCNTs, and the measured hardness values reflect this difference in the degree of strain hardening. Electron microscopy was employed to further examine the structure of Cu-MWCNT composites produced by irradiation in the mixed condition under argon. Figure 6-7a represents a typical backscattered SEM image of a 45 s argon sample, and Figures 6-7b and c are corresponding EDS elemental maps of copper and carbon. The copper and carbon elemental maps indicate that the black regions of the backscattered image are carbon rich, and that these regions, which contain MWCNT agglomerations, are uniformly distributed throughout the copper matrix. A representative secondary electron image of one of these MWCNT agglomerations is given in Figure 6-8b,
in which individual MWCNTs can be seen bundled next to one another and surrounded by the copper matrix. The purple areas in Figure 6-7d denote areas with strong carbon and copper signatures, and a secondary electron image of such a region is presented in Figure 6-8a. Red arrows in this figure were added to demarcate individual MWCNTs emerging from the copper matrix. Previous reports of Cu-MMCs with similar degrees of CNT-copper mixing as observed in Figure 6-6 attributed the composites’ excellent mechanical properties to the presence of MWCNTs.\textsuperscript{[4, 27]} While difficult to separate the effects of grain refinement from MWCNT-induced strengthening, the Cu-MWCNT composites produced in the current study exhibited excellent hardness and contained significant amounts of MWCNTs.

Figure 6-8. Secondary electron SEM images of mixed Cu\textsubscript{3}O irradiated for 45 s in argon. Image (a) was taken from an area appearing to be predominantly copper (light phase in backscattered image), and (b) was captured in an area appearing to be a CNT agglomeration (dark phase in backscattered image). Individual CNT ends emerging from the copper matrix are indicated with red arrows in (a).
6.5 Conclusions

This study has shown that MWCNTs are a very effective carbon source for a new type of microwave-assisted carbothermic reduction of Cu$_2$O. When exposed in ambient air, the reaction produced nearly pure copper regardless of the degree of oxide-MWCNT mixing, and a similar result was obtained for unmixed Cu$_2$O in an inert argon atmosphere. However, when Cu$_2$O was intimately mixed with MWCNTs, Cu-MWCNT MMCs with markedly increased hardness relative to pure copper were made directly from Cu$_2$O in very short times. Because the carbothermic reduction reaction is one of the most versatile means of producing metals from their oxides, the process reported here can likely be adapted to other systems, and such studies are currently under way. Moreover, current methods to produce MWCNT-reinforced MMCs often necessitate the use of expensive, specialized equipment and require metal powders that must be carefully handled to prevent oxidation. The microwave-assisted carbothermic route presented here uses metal oxide as a starting material and requires only a low power magnetron as a heating source. Thus, raw materials for the process are inexpensive and stable in air, and the reaction itself requires a fraction of the energy needed to produce Cu-MMCs using traditional methods.

6.6 References


CHAPTER 7: GENERAL CONCLUSIONS

7.1 General Discussion

A major goal of this work was to develop a versatile and scalable method to functionalize carbon nanotubes using a protocol of consecutive oxidation and silanization. Several oxidation strategies were explored, including plasma treatment, thermal oxidation, and oxidation by UV-irradiation. Ultimately, a gas-phase O$_3$ oxidation route was found to be the most efficacious means of introducing oxygen-bearing functional groups onto the surface of multi-walled carbon nanotubes (MWCNTs). Using a fluidized bed with a mixture of O$_2$ and O$_3$ as the bubbling gas, significant oxidation of the MWCNT sidewalls was achieved without destroying their structure. Because the method did not require any solvents, no additional purification steps were necessitated, which is a significant advantage over most functionalization reactions reported in the literature. Comparison of two nominally similar MWCNTs with different defect structures revealed that gas-phase O$_3$ oxidation can also purify MWCNTs from amorphous carbon in short periods of time. Characterization of oxidized MWCNTs with XPS, FTIR, and Boehm titration revealed that oxidation proceeds through the formation of predominantly hydroxyl groups initially, which become further oxidized to carbonyl and carboxylic acid groups upon further O$_3$ exposure. While the exact mechanism of oxidation was not determined, the presence of aliphatic defects seems to play a significant role. The simplicity, speed, and uniformity of oxidation achieved through the use of a fluidized bed makes gas-phase O$_3$ oxidation an attractive route for functionalizing MWCNTs on an industrial scale.

After developing a successful oxidation protocol, silanization routes were explored to endow the nanotubes with other functionalities using the oxygen-bearing functional groups
as a platform. The first silanization protocol involved reacting the oxidized MWCNTs in an aqueous silane solution at room temperature in a fashion analogous to industrial treatment of glass fibers. Aqueous silane deposition leads to the formation of oligomeric siloxanes as a result of self-condensation, and the functionality (in terms of hydrolysable groups) affects the morphology of the oligomers. We tuned the structure and size of the oligomers grafted to the MWCNT by controlling the silane monomer functionality and concentration in solution and found that the siloxane structure, in particular, significantly impacts chain confinement in an epoxy composite. MWCNTs grafted with irregular, three dimensional siloxane oligomers (ts-MWCNTs) interacted weakly with the matrix, while MWCNTs coated with well-defined, linear siloxane brushes (ds-MWCNTs) interacted strongly with the network. DMA and DSC analyses revealed that ds-MWCNT additions dramatically limited the mobility of network segments and promoted a more homogeneous cross-link topology, which translated to large increases in $T_g$ relative to the neat resin at low loading levels. The toughness of the resin was found to improve with the addition of all varieties of MWCNT; however composites containing ds-MWCNTs produced the greatest effect, seemingly due to crack deflection by a highly connected percolating interphase formed around the nanotubes. In terms of engineering applications, this reaction was deemed attractive because it is fast, free of organic solvents, requires only inexpensive reagents, and composites fabricated with silanized nanotubes have dramatically improved thermo-mechanical properties.

While the aqueous silanization route was attractive, it still required the use of water as a solvent and generated waste containing MWCNTs. In an effort to eliminate all solvents from the silanization reaction, supercritical carbon dioxide (scCO$_2$) was explored as an alternative reaction medium. Furthermore, scCO$_2$ allowed for grafting nearly monolayers of silane
molecules onto the nanotube surfaces because of the absence of hydrolysis and self-condensation that result from the presence of water. Using a high pressure reactor, oxidized MWCNTs were successfully reacted with an epoxy-capped silane as confirmed by TGA, FTIR, and XPS analyses. The addition of the silanized MWCNTs (s-MWCNTs) to a model epoxy system markedly increased its $T_g$, and measurements of the network cooperativity length scale confirmed that silanized nanotubes restrict polymer mobility. Composites filled with p-MWCNTs and s-MWCNTs exhibited significantly higher strain at break and toughness than the neat epoxy, and the greatest improvements were observed at low loading levels. SEM analysis of the composite fracture surfaces revealed that nanotube pullout was the primary failure mechanism in epoxy loaded with p-MWCNT while crack bridging predominated in s-MWCNT composites as the result of covalent bonding of silanated nanotubes with the matrix. Therefore, scCO$_2$ silanization was found to be a suitable, green solvent for the functionalization of o-MWCNTs, and small additions of s-MWCNTs were effective in extending the engineering applications of a common epoxy resin elevating its $T_g$ and toughness.

While the previous efforts to functionalize MWCNTs were found to improve the properties of epoxies at low loading levels, higher loadings led to agglomeration of nanotubes, an increase in the resin viscosity, and a reduction in the nanocomposite mechanical properties. This observation is common to all melt or resin blended carbon nanotube dispersions, and loading restrictions prevent composites from achieving properties remotely close to those of individual CNTs. In an effort to overcome such limitations, we explored methods of producing macroscopic mats of MWCNTs called buckypaper (BP), and attempted to orient nanotubes within the paper to achieve anisotropic properties. Using a
modified Taylor-Couette system, the nanotubes in an aqueous MWCNT dispersion were simultaneously shear-aligned and filtered to yield BP with preferential nanotube orientation in the direction of flow. The BP exhibited anisotropic electrical and mechanical properties, which were both enhanced parallel to the direction of orientation and maximized at high shear rates. While the highest degree of anisotropy was found to be lower than some previously reported methods, such as magnetic alignment, the technique we developed was simple and versatile in that it can be adapted for use with any type of CNT synthesized by any method. In addition, it is scalable, as large BP sheets can be easily fabricated by increasing the length and diameter of the cylinders in the setup.

The advent of low-cost, commercially available MWCNTs has opened the door to a variety of new applications. During the course of research on MWCNT composites, an ancillary study was performed to examine the potential of MWCNTs as the heating medium for chemical reactions conducted under microwave irradiation. We found that MWCNTs are a very effective carbon source for a new type of microwave-assisted carbothermic reduction of metal oxides. \( \text{Cu}_2\text{O} \) was chosen as a candidate oxide for study because copper has a uniquely low solubility for carbon. When \( \text{Cu}_2\text{O} \) was heated in a bath of MWCNTs in ambient air, the reaction produced nearly pure copper regardless of the degree of oxide-MWCNT mixing, and a similar result was obtained for unmixed \( \text{Cu}_2\text{O} \) in an inert argon atmosphere. However, when \( \text{Cu}_2\text{O} \) was intimately mixed with MWCNTs, and reacted in argon, Cu-MWCNT MMCs with markedly increased hardness relative to pure copper were made directly from \( \text{Cu}_2\text{O} \) in very short times. This new method of producing Cu-MWCNT composites is attractive because it does not require the use of expensive, specialized equipment or finely divided metal powders that current methods to produce MWCNT-
reinforced MMCs necessitate. Instead, it uses metal oxide as a starting material and requires only a low power magnetron as a heating source. Thus, raw materials for the process are inexpensive and stable in air, and the reaction itself requires a fraction of the energy needed to produce Cu-MMCs using traditional methods.

7.2 Recommendations for Future Work

The fluidized $\text{O}_3$ oxidation treatment we developed proved to be very effective at producing a few grams of homogeneously oxidized MWCNTs, making it an attractive industrial oxidation route. However, the reaction is exothermic, and an important consideration for scale-up is the removal of heat. Therefore, a logical next step to validate the efficacy of the process would be to construct a much larger fluidized bed and monitor the internal temperature. It is anticipated that the steady flow of $\text{O}_3$ and $\text{O}_2$ through the reactor would help to actively cool the MWCNTs, but the relationship between the amount of MWCNTs in the reactor, the flow rate, and temperature must be established.

MWCNTs silanized with di-functional silanes were found to dramatically improve the thermo-mechanical properties of epoxy nanocomposites at low loading levels. In particular, the increased $T_g$ and toughness make these nanocomposites ideal candidates for use as the matrix phase in a hierarchical composite reinforced with traditional materials such as carbon or glass fiber. However, tri-functional silanes have traditionally been favored for use in macroscopic fiber treatment for their increased hydrolytic stability.[1] Before the nanocomposites we developed can be used in engineering applications, tests must be conducted to determine the effects of moisture on mechanical properties. MWCNTs have a much greater surface area for bonding with the matrix compared to macroscopic fibers,
which may slow, but not eliminate hydrolytic degradation. However, only experimental observations can confirm this hypothesis.

The method for producing aligned buckypaper (BP) described in Chapter 5 offers several opportunities for improvement. Because the relaxation time of water is very short, the aqueous dispersions used in this study may have allowed some MWCNTs to relax and coil upon removal of shear forces, especially on the upper few layers, which are less constrained by neighboring nanotubes. The use of higher viscosity fluids may limit such relaxation and improve nanotube alignment and packing density. Greater levels of alignment might also be achieved by tuning the interaction among the nanotubes, surfactant, and filter paper, and greater mechanical and electrical properties could be realized by extending the approach to other varieties of CNTs such as high aspect ratio SWCNTs. Furthermore, composites could be fabricated using the BP, which would likely improve the mechanical properties by allowing efficient stress transfer among the nanotubes in contrast the weak van der Waals forces among nanotubes in the resin-free BP.

One potentially easy method of attaining better alignment of nanotubes in the BP while simultaneously making composite prepregs would be to prepare a dispersion of CNTs in a viscous resin, such as an epoxy, and then filter it under shear in the modified Taylor-Couette setup. Higher viscosity dispersions would increase the MWCNT relaxation time and limit recoiling of the nanotubes, though filtration may be quite slow. Some solvent or reactive diluent could be added to the dispersion to tune the viscosity and achieve a balance of stability against relaxation and filtration speed. Of course curing of the resin must be avoided during the filtration, and a system with a suitably long pot life must be selected. By making several BP prepregs in this manner, a composite could be produced by stacking the
prepreg sheets and consolidating them while heating under pressure to produce a laminate composite. Such composites may be useful for applications demanding multifunctional roles such as for electromagnetic shielding or structural capacitors.

Finally, the method of producing metal-matrix composites from metal oxides using MWCNTs as both a heating element and carbon source in a microwave-assisted carbothermic reduction outlined in Chapter 6 produced several interesting avenues of future research. While determining the reducing potential of MWCNTs using a series of metal oxides with various oxidation potentials, it was discovered that a variety of nanostructure can form upon microwave irradiation. For instance, MgO nanocubes with edge lengths ranging from 30-200 nm were produced when MgO powder consisting of irregular, micron-sized particles were heated with MWCNT in the presence of ammonium hydroxide, as shown in Figure 7-1. AlN nanorods were produced when unpurified MWCNTs (containing residual iron catalyst particles) were heated in the presence of Al₂O₃ under ambient atmosphere. As can be seen in Figure 7-2, the ends of some of these nanorods were capped by iron-rich bulbs, and the segmented nature of the body of the rod suggests that they grew through a step-wise precipitation process such as the vapor-liquid-solid (VLS) mechanism. Because MWCNTs heat so quickly to high temperatures (over 1000°C in a few seconds) when irradiated with microwaves, they offer an exciting heating media for the production of materials far from equilibrium. We are currently collaborating with researchers at Letourneau University to heat metal oxides in the presence of MWCNTs using a close-looped, directional microwave apparatus with controllable atmosphere in an effort to carefully control the formation of nanostructures and elucidate their growth mechanisms.
Figure 7-1. MgO nanocubes formed under microwave heating in the presence of MWCNTs for 30 s (a) and higher magnification image of the nanocubes highlighting their dimensions (b).

Figure 7-2. AlN nanorods formed by heating Al₂O₃ for 60 s in the presence of MWCNTs (a) and the end of a rod capped with an iron-rich sphere (b).

7.3 References

APPENDIX A: EFFECT OF MULTI-WALLED CARBON NANOTUBE FUNCTIONALIZATION ON THE CURING BEHAVIOR OF EPOXY NANOCOMPOSITES

A.1 Objectives

The surface chemistry of filler introduced into a thermoset can alter the curing behavior of the resin. The changes can be especially pronounced with nano-scale filler as a result of their large surface areas. Knowledge of the speed and extent of reaction of a resin system is vitally important for practical use. This work aims to determine the effect that pristine and functionalized multiwalled carbon nanotubes (MWCNTs) have on the cure kinetics of a model epoxy.

A.2 Materials and Characterization

All experiments described in the current report have been carried out using Kumho MWCNTs. Oxidized MWCNTs (o-MWCNTs) were prepared by fluidizing pristine MWCNTs (p-MWCNTs) in ozone for 10 min. Silane functionalized MWCNTs were prepared according to procedures in Chapters 3 and 4. Table 1 summarizes the samples included in the present cure kinetics study as well as the abbreviation conventions used herein.
Table A-1. Naming conventions adopted for the samples investigated in this study

<table>
<thead>
<tr>
<th>MWCNT Variety</th>
<th>Abbreviation</th>
<th>Loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>p-MWCNTs</td>
<td>0.1, 0.2, 0.5</td>
</tr>
<tr>
<td>Oxidized</td>
<td>o-MWCNTs</td>
<td>0.1, 0.2, 0.5</td>
</tr>
<tr>
<td>Dimethoxy silanated (low MW)*</td>
<td>0.1ds-MWCNTs</td>
<td>0.1, 0.2</td>
</tr>
<tr>
<td>Dimethoxy silanated (high MW)†</td>
<td>1.0ds-MWCNTs</td>
<td>0.1, 0.2</td>
</tr>
<tr>
<td>Trimethoxy silanated (low MW)*</td>
<td>0.1ts-MWCNTs</td>
<td>0.1, 0.2</td>
</tr>
<tr>
<td>Trimethoxy silanated (high MW)†</td>
<td>1.0ts-MWCNTs</td>
<td>0.1, 0.2</td>
</tr>
<tr>
<td>GPTMS [functionalized in scCO₂]</td>
<td>scCO₂-MWCNTs</td>
<td>0.1, 0.2, 0.5</td>
</tr>
</tbody>
</table>

*A* Amine-capped silanes  
† Epoxy-capped silane

### A.3 Methods

The effect of MWCNT additions and surface functionality on the curing behavior of a model epoxy (Epon 828 + TETA) was investigated using non-isothermal differential scanning calorimetry (DSC). Because the epoxy cure reaction occurs at room temperature, the following sample preparation procedure was adopted to minimize the degree of cure before DSC testing. First, MWCNTs were sonicated in Epon 828 until well-dispersed and then allowed to cool to room temperature. 1.5 g of the resin mixture was poured into a biological culture dish whose shallow walls allowed for easy stirring with minimal container surface area for resin to stick to. At this point, a stoichiometric amount of TETA was added and the resin system was stirred vigorously for 30 s before the whole dish was quenched in liquid nitrogen. The frozen resin mixture was stored in a cooler full of dry ice and immediately characterized by DSC. For each run, 7-10 mg of frozen resin was placed in a Tzero aluminum pan, which was subsequently crimped and placed in a pre-cooled Q20 DSC (TA Instruments). After equilibrating at -50°C, the uncured resin was heated to 250 °C at a rate of 2, 5, 10, 15, or 20 °C/min. Five experiments (one at each heating rate) were performed.
for each composite sample and kinetic analysis of the curing exotherms was performed with Netzsch’s Thermokinetics software.

A.4 Cure Kinetic Modeling

Model-based Method

Kinetic analysis is based on the following general equation describing the rate of conversion:

\[
\frac{d\alpha}{dt} = k(T)f(\alpha)
\]

\[= A \exp\left(-\frac{E}{RT}\right)f(\alpha)\]

where \(d\alpha/dt\) is the rate of reaction, \(f(\alpha)\) is a reaction model, and \(k(T)\) is the temperature-dependent rate constant, which is often described by the Arrhenius equation in terms of the activation energy \((E)\), pre-exponential factor \((A)\), and universal gas constant \((R)\). DSC provides one method for determining the degree of cure \((\alpha)\) as a function of time or temperature. Comparison of the enthalpy of reaction at any time, \(H(t)\), with the total enthalpy of reaction, \(H_R\), gives the degree of cure according to:

\[
\alpha(t) = \frac{H(t)}{H_R}
\]

At a constant heating rate of \(\beta = dT/dt\), the explicit time dependence in \(d\alpha/dt\) can be eliminated:

\[
\frac{d\alpha}{dt} = \frac{d\alpha}{dt} \cdot \frac{dT}{dt} \cdot \frac{dT}{dt} = \frac{d\alpha}{dT} \cdot \frac{dT}{dt} \cdot \beta
\]

\[= \left(\frac{d\alpha}{dT}\right)\beta\]
Then
\[ \frac{d\alpha}{dt} = \left( \frac{d\alpha}{dT} \right) \beta = A \exp \left( - \frac{E}{RT} \right) f(\alpha) \]
\[ \ln \frac{d\alpha}{dT} / f(\alpha) = \ln \left[ \frac{A}{\beta} \right] - \frac{E}{RT} \]

The last equation is linear in 1/T, so optimal values for the kinetic parameters can be determined via multiple linear regression on data obtained at different heating rates. Model-based analysis requires an expression for \( f(\alpha) \) and a variety of models have been developed. Table 2 summarizes some of the models and their kinetic parameters. In this study, 17 models were evaluated in total for each sample.

**Table A-2. Examples of reaction models**

<table>
<thead>
<tr>
<th>Reaction Model Name</th>
<th>( f(\alpha) ) equation</th>
<th>Parameters to be Solved for</th>
</tr>
</thead>
<tbody>
<tr>
<td>First order</td>
<td>(1- ( \alpha ))</td>
<td>A, E</td>
</tr>
<tr>
<td>Second order</td>
<td>(1- ( \alpha ))^2</td>
<td>A, E</td>
</tr>
<tr>
<td>nth order</td>
<td>(1- ( \alpha ))^n</td>
<td>A, E, n</td>
</tr>
<tr>
<td>nth order with autocatalysis</td>
<td>(1- ( \alpha ))*(1- ( K_{cat} \alpha ))</td>
<td>A, E, n, ( K_{cat} )</td>
</tr>
<tr>
<td>Prout-Tompkins equation</td>
<td>(1- ( \alpha ))^m ( \alpha^m )</td>
<td>A, E, n, m</td>
</tr>
<tr>
<td>One-dimensional diffusion</td>
<td>0.5/( \alpha )</td>
<td>A, E</td>
</tr>
<tr>
<td>Two-dimensional diffusion</td>
<td>-1/ln(1-( \alpha ))</td>
<td>A, E</td>
</tr>
</tbody>
</table>

**Model-free Method**

An alternative approach to modeling cure kinetics is the isoconversional model-free method. While model-based methods provide one average activation energy for the cure reaction, model-free analysis assumes that both the activation energy and pre-exponential factor vary with conversion. Determination of these parameters can be performed following the method of Friedman with the logarithmic form of the general rate equation

\[ \ln [\beta_i \left( \frac{d\alpha}{dT} \right)_{\alpha,i}] = \ln [A_{\alpha} f(\alpha)] - \frac{E_{\alpha}}{R T_{\alpha,i}} \]
where the subscripts $\alpha$ and $i$ represent the degree of cure and heating rate of an experiment, respectively. Linear regression from a plot of $\ln(\beta \cdot \frac{da}{dT})_{\alpha,i}$ vs $1/T_{\alpha,i}$ yields $E_\alpha$ and $A_\alpha$.

**A.5 Results**

Both model-free and model-based methods were employed to fit the experimental cure data. Figure 1 shows the exothermic peaks obtained by DSC for the uncured epoxy resin heated at various rates, and Figure 2 gives the corresponding degree of cure-temperature relationships obtained by integration of the raw exotherms.

![Figure A-1. Raw DSC curves for neat epoxy](image)

17 different models were used to fit the data by multivariate linear regression and compared based on an F-test statistical analysis. An example of such a comparison is given in Table 3 for the neat epoxy. With this analysis, models having $F_{\text{exp}} < F_{\text{crit}}$ provide good fits of the experimental data while those with $F_{\text{exp}} > F_{\text{crit}}$ do not. In the present study, the Prout-Tompkins autocatalytic model (designated Bna, $f(\alpha) = (1-\alpha)^n \alpha^a$) provided the best fit for all samples studied and no other models were statistically significant according to the F-test.
Table A-3. Comparison of model fits for neat epoxy

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<th>Type 1</th>
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<td>1.00</td>
<td>1.04</td>
<td>8576</td>
<td>Ena</td>
</tr>
<tr>
<td>1</td>
<td>s:</td>
<td>2.66</td>
<td>1.04</td>
<td>8576</td>
<td>Cn B</td>
</tr>
<tr>
<td>2</td>
<td>s:</td>
<td>4.96</td>
<td>1.04</td>
<td>8577</td>
<td>Fn</td>
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<td>1.04</td>
<td>8578</td>
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<tr>
<td>4</td>
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<td>12.14</td>
<td>1.04</td>
<td>8577</td>
<td>An</td>
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<tr>
<td>5</td>
<td>s:</td>
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<tr>
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<td>s:</td>
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<td>1.04</td>
<td>8578</td>
<td>D4</td>
</tr>
<tr>
<td>14</td>
<td>s:</td>
<td>73.09</td>
<td>1.04</td>
<td>8578</td>
<td>D2</td>
</tr>
<tr>
<td>15</td>
<td>s:</td>
<td>121.32</td>
<td>1.04</td>
<td>8578</td>
<td>D1</td>
</tr>
<tr>
<td>16</td>
<td>s:</td>
<td>132.07</td>
<td>1.04</td>
<td>8578</td>
<td>A3</td>
</tr>
<tr>
<td>17</td>
<td>s:</td>
<td>672.46</td>
<td>1.04</td>
<td>8578</td>
<td>B1</td>
</tr>
</tbody>
</table>

Figure A-2. Degree of cure as a function of temperature and heating rate for neat epoxy
Figure A-3. Model fit of DSC data for the neat epoxy. Solid lines represent raw data while the colored symbols represent predictions from the Prout-Tompkins model.

Figure 3 shows the fit obtained from the Prout-Tompkins model for the neat epoxy. Generally good fitting was found for all samples in the study, with correlation coefficient coefficients ranging from 0.9952-0.9993. Table 4 summarizes the kinetic parameters and correlation coefficients for every sample obtained from linear regression. The addition of every type of MWCNT had little effect on the overall activation energy and the reaction order remained nearly constant with a value of \( n \sim 1.6 \). The autocatalytic parameter, \( a \), varied somewhat. Small values of \( a \) correspond to higher reaction rates. While MWCNTs functionalized with epoxy-capped silanes in scCO2 have generally low values for \( a \), they are of the same magnitude as the other samples observed in the study.
Table A-4. Summary of kinetic parameters and fit obtained by Prout-Tompkins model for all samples in study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Loading (wt %)</th>
<th>$E_a$ (kJ/mol)</th>
<th>Log ($A_1/s^{-1}$)</th>
<th>n</th>
<th>a</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>--</td>
<td>52.43</td>
<td>5.44</td>
<td>1.58</td>
<td>0.34</td>
<td>0.9987</td>
</tr>
<tr>
<td>p-MWCNT</td>
<td>0.1</td>
<td>60.57</td>
<td>6.60</td>
<td>1.62</td>
<td>0.23</td>
<td>0.9985</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>63.15</td>
<td>6.92</td>
<td>1.67</td>
<td>0.20</td>
<td>0.9988</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>64.33</td>
<td>7.06</td>
<td>1.63</td>
<td>0.11</td>
<td>0.9983</td>
</tr>
<tr>
<td>o-MWCNT</td>
<td>0.1</td>
<td>57.66</td>
<td>6.15</td>
<td>1.61</td>
<td>0.23</td>
<td>0.9993</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>51.76</td>
<td>5.38</td>
<td>1.52</td>
<td>0.29</td>
<td>0.9977</td>
</tr>
<tr>
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<td>0.5</td>
<td>52.08</td>
<td>5.42</td>
<td>1.57</td>
<td>0.33</td>
<td>0.9958</td>
</tr>
<tr>
<td>0.1ts-MWCNT</td>
<td>0.1</td>
<td>55.83</td>
<td>5.95</td>
<td>1.62</td>
<td>0.30</td>
<td>0.9952</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>65.46</td>
<td>7.26</td>
<td>1.63</td>
<td>0.14</td>
<td>0.9986</td>
</tr>
<tr>
<td>1.0ts-MWCNT</td>
<td>0.1</td>
<td>54.74</td>
<td>5.81</td>
<td>1.58</td>
<td>0.30</td>
<td>0.9989</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>61.16</td>
<td>6.68</td>
<td>1.65</td>
<td>0.22</td>
<td>0.9992</td>
</tr>
<tr>
<td>0.1ds-MWCNT</td>
<td>0.1</td>
<td>55.74</td>
<td>5.92</td>
<td>1.59</td>
<td>0.28</td>
<td>0.9991</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>56.12</td>
<td>5.97</td>
<td>1.60</td>
<td>0.28</td>
<td>0.9991</td>
</tr>
<tr>
<td>1.0ds-MWCNT</td>
<td>0.1</td>
<td>63.47</td>
<td>6.98</td>
<td>1.61</td>
<td>0.17</td>
<td>0.9986</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>63.71</td>
<td>7.01</td>
<td>1.61</td>
<td>0.17</td>
<td>0.9986</td>
</tr>
<tr>
<td>sc-CO$_2$-MWCNT</td>
<td>0.1</td>
<td>62.88</td>
<td>6.83</td>
<td>1.58</td>
<td>0.17</td>
<td>0.9990</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>61.25</td>
<td>6.65</td>
<td>1.54</td>
<td>0.20</td>
<td>0.9991</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>66.47</td>
<td>7.31</td>
<td>1.61</td>
<td>0.13</td>
<td>0.9989</td>
</tr>
</tbody>
</table>

Model-free fitting of the data was performed using Friedman’s method. Figure 4 shows examples of the Friedman plots used to calculate kinetic parameters from isoconversional lines in the logarithmic graphs. The black lines in the plots represent isoconversional lines. At low conversion levels, the slopes of the raw data are steeper than the isoconversional lines, which suggests that the reaction is accelerated in comparison to an $n^{th}$ order reaction. This is in good agreement with the model-based fitting, which found an
autocatalytic (accelerated) model to provide the best fit. Friedman plots of every sample in the study exhibited similar behavior at low degrees of cure.

![Friedman plots](image)

**Figure A-4.** Friedman plots used to determine model-free kinetic parameters as a function of conversion for the neat resin as well as composites containing 0.1 wt% loadings of p-MWCNTs, 0.1ts-MWCNTs, and 1.0ts-MWCNTs

The activation energy and pre-exponential factor of each sample was determined from the Friedman plots and examples of their dependence on the degree of cure are given in Figure 5. Accounting for error, the neat epoxy and p-MWCNT samples exhibited nearly constant activation energies throughout the cure. While amino-functionalized MWCNTs had similar average activation energies as the neat epoxy, they had higher initial values of $E_a$. Greater grafting densities of aminosilanes on the MWCNTs led to higher initial activation energies as can be seen by comparison of the 1.0ts-MWCNT and 0.1ts-MWCNT composites. The high initial $E_a$ values for the amino silanized MWCNTs may be due to the fact that epoxy monomers reacted with amines on the nanotube surface during sonication (before the
TETA hardener was added) so the confined epoxy monomers have a reduced mobility compared to the neat epoxy. MWCNTs functionalized with epoxy-capped silanes did not appreciably increase $E_a$ at low conversion. Since epoxy groups would not react with the Epon 828 during sonication, this is consistent with the idea proposed above. Table 5 summarizes the kinetic parameters obtained for all samples at low conversion. All types of amino functionalized MWCNTs exhibited slightly higher activation energies relative to the neat epoxy while p-MWCNTs, o-MWCNTs, and scCO$_2$-MWCNTs had little effect at all loadings.

Figure A-5. Dependence of model-free kinetic parameters on conversion for the neat resin as well as composites containing 0.1 wt% loadings of p-MWCNTs, 0.1ts-MWCNTs, and 1.0ts-MWCNTs
Table A-5. Summary of kinetic parameters obtained by model free analysis at low levels of conversion for all samples in study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Loading (wt %)</th>
<th>(E_a) (kJ/mol) @ 2% Conversion</th>
<th>(\log (A_1/s^{-1})) @ 2% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat Epoxy</td>
<td>--</td>
<td>57.81</td>
<td>5.74</td>
</tr>
<tr>
<td>p-MWCNT</td>
<td>0.1</td>
<td>62.07</td>
<td>6.47</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>64.06</td>
<td>6.76</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>65.43</td>
<td>7.03</td>
</tr>
<tr>
<td>o-MWCNT</td>
<td>0.1</td>
<td>60.90</td>
<td>6.29</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>55.09</td>
<td>5.42</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>60.48</td>
<td>6.19</td>
</tr>
<tr>
<td>0.1ts-MWCNT</td>
<td>0.1</td>
<td>67.93</td>
<td>7.36</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>72.48</td>
<td>8.10</td>
</tr>
<tr>
<td>1.0ts-MWCNT</td>
<td>0.1</td>
<td>70.97</td>
<td>7.87</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>77.67</td>
<td>8.93</td>
</tr>
<tr>
<td>0.1ds-MWCNT</td>
<td>0.1</td>
<td>66.46</td>
<td>7.16</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>67.92</td>
<td>7.29</td>
</tr>
<tr>
<td>1.0ds-MWCNT</td>
<td>0.1</td>
<td>69.97</td>
<td>7.70</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>70.28</td>
<td>7.75</td>
</tr>
<tr>
<td>sc-CO\textsubscript{2}-MWCNT</td>
<td>0.1</td>
<td>63.29</td>
<td>6.62</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>64.38</td>
<td>6.78</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>65.43</td>
<td>6.92</td>
</tr>
</tbody>
</table>
A.6 Conclusions

The functionalized MWCNTs used in this study were not found to substantially affect the curing behavior of the model epoxy. Seventeen models were fit to dynamic DSC data, and the Prout-Tompkins autocatalytic model provided the best fit for the neat resin and all resin-nanotube composites. Minor changes in the overall activation energy of the resin upon the introduction of nanotubes at various loadings suggests that the MWCNTs do not appreciably hinder or accelerate the cure. Model-free analysis revealed that while amino-functionalized MWCNTs do not change the average activation energy, they do increase $E_a$ at low conversion levels. This phenomenon may be due to the fact that during processing, the MWCNTs are first sonicated in Epon 828, and amines bonded to the nanotube are able to react with and immobilize epoxy monomers on the MWCNT surface. The reduced mobility of the monomers may initially increase the activation energy of the resin system relative to the neat epoxy.

Summaries of model-based and model-free kinetic analyses for each type of functionalized MWCNT used in this study are provided in the following section. Each page contains (from top to bottom) a Friedman plot, the activation energies and pre-exponential factors found from the Friedman analysis as a function of conversion, and a plot of the raw data together with the predictions of model-based fitting using the Prout-Tompkins autocatalytic model.
A.7 Friedman and Model-based Prout-Thompkins Analyses

Figure A-6. Neat epoxy
Figure A-7. 0.1 wt% p-MWCNT
Figure A-8. 0.2 wt% p-MWCNT
Figure A-9. 0.5 wt% p-MWCNT
Figure A-10. 0.1 wt% o-MWCNT
Figure A-11. 0.2 wt% o-MWCNT
Figure A-12. 0.1 wt% 0.1ds-MWCNT
Figure A-13. 0.2 wt% 0.1ds-MWCNT
Figure A-14. 0.1 wt% 1.0ds-MWCNT
Figure A-15. 0.2 wt% 1.0ds-MWCNT
Figure A-16. 0.1 wt% 0.1ts-MWCNT
Figure A-17. 0.2 wt% 0.1ts-MWCNT
Figure A-18. 0.1 wt% 1.0ts-MWCNT
Figure A-19. 0.2 wt% 1.0ts-MWCNT
Figure A-20. 0.1 wt% sc-CO2 MWCNTs
Figure A-21. 0.2 wt% sc-CO2 MWCNTs
Figure A-22. 0.5 wt% sc-CO\(_2\) MWCNT
APPENDIX B: EFFECT OF FUNCTIONALIZATION ON THE RHEOLOGICAL BEHAVIOR OF MWCNT/EPOXY DISPERSIONS

B.1 Objectives

In addition to affecting the cure reaction, filler additions can also impact a resin’s rheological behavior. Increases in resin viscosity can present challenges to processing and must be characterized in order for suitable applications of the thermoset to be established. The goal of this work is to characterize the rheological behavior of epoxy/multi-walled carbon nanotube (MWCNT) dispersions prepared with pristine and functionalized nanotubes.

B.2 Materials and Characterization

All experiments described in the current report have been carried out using *Kumho* MWCNTs. Oxidized MWCNTs (o-MWCNTs) were prepared by fluidizing pristine MWCNTs (p-MWCNTs) in ozone for 10 min. Silane functionalized MWCNTs were prepared according to procedures in Chapters 3 and 4. Table 1 summarizes the samples included in the present study as well as the abbreviation conventions used herein.

<table>
<thead>
<tr>
<th>MWCNT Variety</th>
<th>Abbreviation</th>
<th>Loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>p-MWCNTs</td>
<td>0.1, 0.5</td>
</tr>
<tr>
<td>Oxidized</td>
<td>o-MWCNTs</td>
<td>0.1, 0.5</td>
</tr>
<tr>
<td>Dimethoxy silanated (low MW) †</td>
<td>0.1ds-MWCNTs</td>
<td>0.1, 0.5</td>
</tr>
<tr>
<td>Dimethoxy silanated (medium MW) †</td>
<td>0.5ds-MWCNTs</td>
<td>0.1, 0.5</td>
</tr>
<tr>
<td>Dimethoxy silanated (high MW) †</td>
<td>1.0ds-MWCNTs</td>
<td>0.1, 0.5</td>
</tr>
<tr>
<td>Trimethoxy silanated (low MW) †</td>
<td>0.1ts-MWCNTs</td>
<td>0.1, 0.5</td>
</tr>
<tr>
<td>Trimethoxy silanated (medium MW) †</td>
<td>0.5ts-MWCNTs</td>
<td>0.1, 0.5</td>
</tr>
<tr>
<td>Trimethoxy silanated (high MW) †</td>
<td>1.0ts-MWCNTs</td>
<td>0.1, 0.5</td>
</tr>
<tr>
<td>GPTMS [functionalized in scCO₂] †</td>
<td>scCO₂-MWCNTs</td>
<td>0.1, 0.5</td>
</tr>
</tbody>
</table>

* Amine-capped silanes
† Epoxy-capped silane
B.3 Methods

The effect of MWCNT additions and surface functionality on the viscosity of an epoxy resin (Epon 828) was investigated using a nonoscillatory rheological method. To avoid the effects of curing, all measurements were made on dispersions of MWCNTs in epoxy resin without any hardener; however, the results are expected to be similar to that of the full resin system (e.g. Epon 828 + TETA). For each measurement MWCNTs (3 mg or 15 mg) were dispersed in 3 g of Epon 828 via sonication with a horn (Fisher, sonic dismembrator model 100) in 30 second intervals for a total of 2 min at a power of 40W and 2 min at 80 W followed by sonication in a bath (Emerson, Bransonic Model 1800) at 60 °C for 30 min. The mixture was allowed to cool to room temperature and rheological properties were measured using an AR2000ex stress-controlled rheometer (TA Instruments) configured with a 40 mm diameter cone (α = 1°,0′,11″) and plate geometry in which the bottom plate was a Peltier stage. For each test, 0.3 mL of the nanotube dispersion was transferred to the Peltier stage and held for 3 min at 25 °C to reach thermal equilibrium before a stepped steady state flow test was conducted from 0.01 to 100 s⁻¹ at a constant temperature of 25 °C.

B.4 Results

The effect of MWCNT additions on the resin viscosity are summarized below. Figure B-1 shows the viscosity of the neat resin and resin loaded with 0.1 wt% and 0.5 wt% p-MWCNTs and o-MWCNTs. The neat resin behaves as a Newtonian fluid with a nearly shear rate-independent viscosity of about 10 Pa·s. The addition of both p-MWCNTs and o-MWCNTs increases the resin viscosity and induces shear thinning behavior. An increase in the loading level increases the viscosity of both varieties of MWCNTs at low shear rates, and
the viscosity of resin containing o-MWCNTs is higher than that of p-MWCNTs for a given loading level.

Figure B-1. Rheological behavior of neat resin as well as resin containing p-MWCNTs and o-MWCNTs at low and high loading levels.
As shown in Figure B-2, resin containing MWCNTs functionalized with 3-glycidoxypropyltrimethoxysilane (GPTMS) in supercritical CO$_2$ has higher viscosity than that with p-MWCNTs, although the values are still on the same order of magnitude. The elevated viscosity of scCO$_2$-MWCNTs at low shear rates may be due to the fact that the nanotubes are either more highly dispersed or interact more favorably with the resin than p-MWCNTs.[1, 2]
Resin containing 0.1 wt% ds-MWCNTs also had a slightly elevated viscosity compared to p-MWCNT dispersions. The MW of the silane oligomers attached to the MWCNTs does not seem to have an impact on the rheological behavior of the dispersions, as can be seen in Figure B-3.
Increasing the loading of ds-MWCNTs to 0.5 wt% increased the viscosity of the resin slightly compared to the 0.1 wt% systems. Again, the MW of the silane oligomer grafted to the MWCNTs did not appear to greatly influence the viscosity profile, as can be seen in Figure B-4.
Figure B-5. Rheological behavior of resin loaded with 0.1 wt% ts-MWCNTs.

Figure B-5 depicts the effect of incorporating 0.1 wt% ts-MWCNTs into Epon 828. Unlike ds-MWCNT additions, ts-MWCNT dispersions do not increase the viscosity much relative to p-MWCNTs. The reasons for this are not entirely clear, although it may be due to the fact that the brushlike ds-MWCNT oligomers present a greater surface area than their cross-linked ts-MWCNT counterparts, which would increase internal friction in the resin.
As with all other types of MWCNTs, increasing the loading level of ts-MWCNTs from 0.1 wt% to 0.5 wt% increases the viscosity of the dispersion. Figure B-6 summarizes the rheological behavior of ts-MWCNTs with different MWs. The viscosity of dispersions containing 0.5 wt% ts-MWCNTs did not vary with oligomer MW and were similar to that of p-MWCNTs.

**B.5 Conclusions**

In summary, the addition of small amounts of all types of MWCNTs to the resin do not dramatically increase the viscosity. While ds-MWCNTs and scCO$_2$-MWCNT elicit the
greatest change in the room temperature resin viscosity, the magnitude of the increase will likely not encumber processing.

**B.6 References**
