CONTROLLING DISPERSION AND ELECTRIC-FIELD-ASSISTED ALIGNMENT OF CARBON NANOTUBES AND NANOFIBERS FOR MULTI-FUNCTIONAL EPOXY COMPOSITES

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Abstract

The objective of this investigation is to enhance the elastic modulus and tailor the electrical conductivity of nanoreinforced epoxy composites. The resin employed in this investigation is a bisphenol F epoxide with an aromatic diamine curative, extensively used for high performance composites. The nanofillers are unfunctionalized and functionalized carbon nanofibers (CNFs) and multi-walled carbon nanotubes (MWCNTs). The objectives are achieved by controlling the dispersion and alignment of unfunctionalized and functionalized CNFs and CNTs. The process of ultrasonic agitation was used to disperse nanofillers in epoxy resin. The dispersed nanofillers were aligned using alternating current electric field (AC).

Continuous use of ultrasonic agitation reduced the lengths, and increased the degree of dispersion of CNFs and CNTs. The parameters of the ultrasonic agitation process were optimized to minimize the reduction in CNF and CNT lengths while achieving good dispersion of CNFs and CNTs in the resin. The composites manufactured with well dispersed CNFs and CNTs increased the elastic modulus as expected based on the theory of short fiber reinforced composites.

The alignment and chaining of CNFs and CNTs dispersed in resin were investigated by experiments and modeling. The assembly of chains was found to depend on the frequency of AC electric field used. The mechanism of CNF/CNT chain assembly and growth in a low viscosity epoxy was investigated by developing a finite element model of a chain attached to an electrode. The model includes the combined effects of electrostatic and electro-hydrodynamic forces on chain morphology. The electro-hydrodynamic forces are modeled using the theory of AC electroosmosis. Predictions of the model are compared to experimental results. The experiments were conducted on a CNF/epoxide/curative mixture by applying an AC field at frequencies ranging from 100 – 100,000 Hz. Predictions of the model qualitatively capture the variations of chain morphology and growth rate as functions of AC frequency. Higher frequencies promote a more uniform and denser network of chains. The rate of growth of chains is highest at an intermediate frequency. A uniform network of chains was observed at frequencies of 1 kHz and greater in the experiments. The rate of growth of chains was maximized at a frequency of 1 kHz for a liquid viscosity of 0.03 Pa·s.

Based on the knowledge of chaining mechanisms, networks of aligned CNFs and CNTs were developed over a 25-mm distance in CNF and CNT epoxy composites. This distance is roughly an order of magnitude greater than previously reported distances obtained with AC electric fields and was accomplished without highly sophisticated electrical equipment. A wide range of anisotropy in direct current (DC) resistivity of CNT/epoxy and CNT/glass fiber/epoxy composites was engineered by using electric fields at different frequencies. The use of AC and DC electric fields in manufacturing buckypapers of aligned CNFs and CNTs was explored. The methods developed to use DC and AC electric fields were found unsuitable for making functional buckypapers with aligned CNFs and CNTs.
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1 Introduction

1.1 Background and motivation
Carbon nanotubes and nanofibers represent a potentially unique type of filler for improving the physical properties of polymeric resin systems. The extraordinary mechanical, electrical, and thermal properties of carbon nanotubes (CNTs) include a tensile strength of 11-63 GPa [1], Young’s modulus over 1 TPa, fracture strains up to 20%, electrical conductivity of $10^7$ S/m [2-3], and a thermal conductivity up to twice that of diamond. As produced, CNTs have diameters in the range of 1-50 nm and lengths of several microns. Carbon nanofibers (CNFs) are significantly larger, with diameters of 60-300 nm and lengths of 30-1000 µm. Typical properties of CNFs include a tensile strength of 3 GPa [4], tensile modulus of 600 GPa [6], electrical conductivity of $10^6$ S/m [6], and a thermal conductivity of 1000 W/m-K [6]. Though CNFs do not have a property set as impressive as CNTs, it is cheaper to produce CNFs than CNTs with current manufacturing capabilities, making CNFs competitive fillers for numerous exploratory investigations underway to enhance mechanical properties of polymeric materials.

The effective reinforcement of polymeric resins by CNTs/CNFs is hindered mainly by the difficult dispersion of CNTs/CNFs in the resin and the poor interfacial adhesion between the CNTs/CNFs and the matrix. Due to CNT/CNF processing procedures and strong van der Waals forces, CNTs/CNFs tend to form tight bundles or ropes which, in turn, agglomerate into entangled networks or webs [7]. Ropes and webs do not exhibit the same outstanding mechanical properties as individual CNTs and CNFs, because of CNTs/CNFs slipping within the ropes and webs. Considerable efforts have been done in the past decade to effectively disperse CNTs and CNFs and to improve the interface between CNTs/CNFs and polymer matrices. However, these efforts have resulted in improvements in mechanical properties with varying degree of success. As a result, efforts are still underway to develop dispersion procedures and interfacial bond between CNTs/CNFs and matrix.

The efforts to disperse CNTs and CNFs can be broadly classified as physical and chemical in nature. The physical processes use shear forces only to disperse CNTs and CNFs in polymers, whereas chemical processes utilize combination of shear forces and chemicals. Based on the
previous statements, it is safe to say that the shear intensive methods are almost always used to disperse CNTs and CNFs in polymers, be it a physical or chemical process. The reason for the ubiquitous use of shear forces lies in the effectiveness of shear forces to break the strong van der Waals forces holding CNTs and CNFs together in agglomerates. However, shear intensive methods are known to reduce the lengths of CNTs and CNFs [8]. From the viewpoint of micromechanics, the aspect ratio of CNTs and CNFs should be greater than 100 to effectively reinforce polymers. Therefore, controlling the aspect ratio of dispersed CNTs and CNFs is critical to improving the mechanical properties of polymer composites. To be able to control the lengths of CNTs and CNFs, the mechanism of CNT/CNF scission by shear forces needs to be identified. Based on the mechanism of scission, appropriate parameters for dispersing CNTs and CNFs in the polymers can be selected. However, the micromechanics predictions assume a perfect bond between CNTs/CNFs and the polymer matrix. To achieve a good bond, CNTs and CNFs functionalized with appropriate chemicals should be used because the bond between the surface of a pristine CNT and matrix is thought to be weak due to the lack of defect sites where polymer molecules can attach themselves to CNTs [9]. Amine functionalization of CNT/CNF surfaces is known to provide a strong bond between CNTs/CNFs and matrix. Any of the amine functionalization routines available in the literature can be used to obtain amine functionalized CNTs and CNFs. Alternatively, amine functionalized CNTs and CNFs can be purchased directly from vendors for making composites.

Since it is anticipated that dispersed CNTs and CNFs will be shortened, additional ways of improving the mechanical performance of composites are desired. One of the ways to improve mechanical properties in the direction of loading is to align CNTs and CNFs in the load bearing direction. Due to the small size of CNTs and CNFs, manipulation of CNTs/CNFs orientations in composites is a challenging task. Recently, the use of electric field to align and chain CNTs and CNFs in epoxy composites has shown promise in manipulating the orientation of CNTs and CNFs [10]. The chaining of CNTs and CNFs is understood based on the dipole-dipole interaction. CNTs and CNFs polarize in electric field and the interaction of their polarization charge with electric field results in mutual forces of attraction. Under these forces of attraction, CNTs and CNFs assemble in chains oriented in the field direction.
Due to the high viscosity and low conductivity (low ionic concentration) of a medium, the theory of dipole-dipole interaction to explain the assembly of particles is considered adequate. At high viscosities, the suppressed ionic movement produces insufficient electro-hydrodynamic forces to influence the assembly of particles. Moreover, the Brownian forces on the particles are insignificant at high viscosities. However, with the increasing use of low viscosity epoxy systems for making high performance composites, there is a need to consider the effects of ions and Brownian forces on particle assembly. Ions can be introduced during the manufacture of composites with CNTs and CNFs. The increased mobility of ions due to reduced resin viscosity at elevated temperatures can shield electric fields up to frequencies as high as 10 kHz. Such shielding produces nonuniformities in the field distribution which, in turn, changes the electrokinetics of particles [11]. Due to the hydrodynamic effects resulting from the increased mobility of ions, it becomes difficult to theoretically predict the response of particles using the theory of dipole-dipole interaction alone, as has been commonly observed in the literature on particles suspended in various solvents [12-13]. Due to the increasing use of low viscosity resin for making high performance composites, there is a need to develop a theoretical framework to understand the mechanism of CNT/CNF chaining in low viscosity resins.

Out-of-plane properties of continuous fiber/epoxy composites can also benefit from alignment of CNTs. The weakest link in continuous fiber composites is the resin rich area between the fibers. Due to the low strength and modulus of epoxy matrices, the load carrying capacity of continuous fiber composites is limited in the transverse direction. Introducing CNTs in between fibers, on account of their small size, offers a solution to reinforce the resin rich areas between the fibers. However, the-less-than 2 μm gap typically observed between fibers puts a limit on the length of CNTs that can be used to infiltrate the fibers successfully. Following the micromechanics theory for short fiber composites, CNTs with aspect ratios greater than 100 would reinforce the matrix well. This puts an upper limit on the diameter of the CNTs that can be used to be 20 nm to obtain the aspect ratio of 100. Based on the argument of large aspect ratio, single-walled carbon nanotubes (SWCNTs) should provide the best alternative on account of their 1 nm diameter. However, dispersion of SWCNTs has proven difficult because of the high van der Waals forces that hold the SWCNTs tightly together. Moreover, purification and functionalization of SWCNTs is difficult and increases the overall cost of composite manufacturing. Table 1.1
compares the prices of unfunctionalized and functionalized SWCNTs and MWCNTs. Clearly, SWCNTs are more expensive than MWCNTs and functionalized CNTs than unfunctionalized CNTs. The most expensive of all the CNTs are the amine functionalized SWCNTs. Due to low cost, multi-walled carbon nanotubes (MWCNTs) with diameters in the range 8-20 nm are commonly used.

Table 1.1 Comparison of the unit cost of unfunctionalized and functionalized CNTs

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Type</th>
<th>Functionalization</th>
<th>Purity by TGA, wt%</th>
<th>Dia., nm</th>
<th>Length, µm</th>
<th>Price $/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cheaptubes Inc.¹</td>
<td>SWCNTs</td>
<td>None</td>
<td>90</td>
<td>1-2</td>
<td>5-30</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>MWCNTs</td>
<td>None</td>
<td>95</td>
<td>&lt; 8</td>
<td>10-30</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>MWCNTs</td>
<td>None</td>
<td>95</td>
<td>8-15</td>
<td>10-50</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>MWCNTs</td>
<td>None</td>
<td>95</td>
<td>10-20</td>
<td>10-30</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>SWCNTs</td>
<td>-OH &amp; -COOH</td>
<td>90</td>
<td>1-2</td>
<td>5-30</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>MWCNTs</td>
<td>-OH &amp; -COOH</td>
<td>95</td>
<td>&lt; 8</td>
<td>10-30</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>MWCNTs</td>
<td>-OH &amp; -COOH</td>
<td>95</td>
<td>8-15</td>
<td>10-50</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>MWCNTs</td>
<td>-OH &amp; -COOH</td>
<td>95</td>
<td>10-20</td>
<td>10-30</td>
<td>25</td>
</tr>
<tr>
<td>Nano-lab²</td>
<td>SWCNTs</td>
<td>Amine</td>
<td>95</td>
<td>1-2</td>
<td>1-5</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>MWCNTs</td>
<td>Amine</td>
<td>95</td>
<td>10-20</td>
<td>1-5</td>
<td>160</td>
</tr>
</tbody>
</table>

¹ www.cheaptubes.com
² www.nano-lab.com

The mechanical properties of epoxy composites also depend on the weight fractions of CNTs used. However, increase in viscosity of liquid epoxy prevents use of higher concentrations of CNTs in liquid epoxy for making continuous fiber composites. Typically, resins with MWCNTs weight fractions more than 0.5 wt% have been found to pose difficulties in infusing preforms of continuous fibers [14]. Due to the limitation on using amounts of CNTs, it makes more sense to orient CNTs to maximize the enhancement in transverse direction properties. CNTs oriented perpendicular to crack plane are envisioned to increase resistance to crack propagation. The considerably high improvement in interlaminar fracture toughness obtained by placing CNTs normal to the surface of plies in a laminated composite was due to the perpendicular placement
of CNTs to the interlaminar crack plane [15]. However, having CNTs at the interfaces between plies is not the same as uniformly reinforcing the entire volume of composites.

CNTs in the matrix are also used as pass-fail sensors for detecting damage in composites. The randomly dispersed CNTs form conducting pathways in the matrix. These conducting pathways, when severed by cracks, change the resistance of composites indicating damage in the matrix [16]. In order for these pathways to indicate damage, the change in resistance of the composites should be significant enough to be detected by electrical equipments. The random orientation of CNTs can provide redundancy in conducting pathways. The redundancy in conducting pathways would minimize the change in resistance due to damage, thereby making it difficult to clearly detect damage. This redundancy in conducting pathways would further increase for higher weight fractions of CNTs [17]. The use of electric field can assemble CNTs in orderly fashion by forming chains to minimize redundancy in conducting pathways for better damage detection.

1.2 Overall objectives
The overall goal of this investigation is to tailor the elastic modulus and electrical conductivity of CNT and CNF reinforced epoxy composites by controlling the dispersion, lengths, functionalization, and alignment of CNTs and CNFs in epoxy composites. The focus of this investigation is on the use of CNFs and CNTs in a low viscosity epoxy resin used for high performance composites. More specifically, the dispersion and lengths of CNTs and CNFs is controlled by identifying and selecting appropriate dispersion parameters through the understanding of ultrasonic agitation mechanism, by evaluating the effects of covalent and non-covalent functionalization of CNTs and CNFs on dispersion and interfacial bonding, and by studying the electrokinetics of CNTs and CNFs using numerical and experimental techniques to develop capabilities for manipulating the orientation and assembly of CNTs and CNFs in epoxy composites using electric fields. The combined knowledge from numerical and experimental investigations is used to develop procedures for making continuous fiber composites with tailored alignment of CNTs.
1.3 Organization of thesis

The work presented in this thesis can be essentially broken down into four sections. The four sections are dispersion and functionalization of CNFs and CNTs in liquid epoxy, development of theoretical framework to understand the electrokinetics of CNFs and CNTs in liquid epoxy, manufacturing fully cured epoxy composites with controlled alignment of CNFs and CNTs, and manufacturing fully cured continuous fiber/epoxy composites with aligned CNTs. Some of the chapters in this thesis are already published in various journals and conferences. The first section which comprises Chapter 2, develops the dispersion and functionalization procedures to obtain well dispersed and chemically modified CNTs and CNFs in liquid epoxy with controlled lengths. The second section, which comprises Chapter 3, is based on the work published in references [18-19]. Chapter 3 develops a theoretical framework to understand the electrokinetics of CNTs and CNFs in liquid epoxy and experiments to corroborate the predictions. The third section, which comprises Chapter 4, is based on the work published in references [20-21]. Chapter 4 presents a method for tailoring the conductivity of CNT/CNF epoxy composites using electric fields. The last section, comprising Chapters 5 and 6, concerns the manufacturing of continuous fiber/epoxy composites with aligned and randomly oriented CNTs to assess the effectiveness of electro-chemical tailoring capabilities developed in this thesis.
1.4 References


2 Effective Reinforcement of Epoxy Based Composites by Controlling the Dispersion, Lengths, and Functionalization of Carbon Nanotubes and Nanofibers

2.1 Introduction
To be able to utilize the full potential of CNTs and CNFs in improving the mechanical properties of epoxy based composites, good dispersion and strong interface bond between CNTs/CNFs and epoxy matrices are thought to be essential. Shear intensive methods are commonly used to disperse CNTs and CNFs in liquid epoxies, and chemical functionalization of CNT/CNF surfaces is used to improve the bond with the matrix. However, action of shear forces can reduce lengths of CNTs and CNFs. From mechanics standpoint, shorter fibers do not reinforce composites as effectively as longer fibers do. Therefore, to enhance the properties of the host polymer it is not sufficient to only disperse and functionalize CNTs and CNFs, but care should be taken to preserve the lengths of dispersed CNTs and CNFs. This chapter describes the efforts made to disperse CNTs and CNFs in epoxy while controlling CNT/CNF lengths, and then functionalizing the dispersed particles to enhance the interface bond between CNTs/CNFs and the epoxy matrix. In the following paragraphs, literature on CNT/CNF dispersion, effects of shear intensive forces of the physical attributes of dispersed CNTs and CNFs, and functionalization routines available to specifically improve the bonds with epoxy matrices are discussed. After reviewing the literature, areas of potential improvements are identified and objectives of this investigation are stated. The experiments performed to fulfill the objectives are discussed next. The outcome of these experiments is discussed in the section on results, which is followed by the conclusions drawn from this investigation.

2.2 Literature survey
The effective reinforcement of polymeric resins by carbon nanotubes (CNTs) and nanofibers (CNFs) is hindered mainly by the difficult dispersion of CNTs and CNFs in the resin, and the poor interfacial adhesion between the matrix and CNTs and CNFs. Due to CNT processing procedures and strong van der Waals forces, CNTs tend to form tight bundles or ropes which, in turn, agglomerate into entangled networks or webs [1]. Ropes and webs do not exhibit the same outstanding mechanical properties as individual CNTs because of CNTs slipping within the bundles. To facilitate dispersion, various surfactants have been used. The surfactant molecules adsorb on the surface of the dispersed nanoparticles, providing electrostatic or steric repulsion to
segregate nanoparticles and prevent their reaggregation. Various surfactants used to disperse CNTs in aqueous and organic mediums are polyoxyethylene 8 lauryl (C12EO8) [2-4], Triton X-100 (Bio World, Dublin, OH) [3,5], sodium dodecyl sulfate (SDS) [6-10], sodium dodecylbenzenesulfonate (NaDDBS) [11-15], dimethylformamide (DMF) [16], gum Arabic [17], deoxyribonucleic acid (DNA) [18], and poly(diallyldimethylammonium chloride) (PDMA) [19].

The use of surfactants to disperse nanoparticles is almost always accompanied with mechanical agitation. The most common form of mechanical agitation is produced by ultrasonic devices or shear mixers. The shear stresses produced by mechanical agitation break agglomerates of nanoparticles to promote uniform dispersion of individual nanoparticles in the resin. The CNTs and CNFs in agglomerates are held together by van der Waals forces and mechanical entanglement. Start et al. [20] investigated the stress needed to break an agglomerate of MWCNTs using a microfluidic device. The correlation between the aggregate size and critical stress resembled that for the breakup of aggregates comprised of spherical particles. A power-law inverse relationship was observed between the size of agglomerate and critical stress. The power-law dependence showed a strong dependence of agglomerate strength on the local particle density. The local CNT density in agglomerates depends on the manufacturing methods and would therefore require different amount of stresses to break CNT agglomerates obtained from different manufacturing processes.

The shear stresses break agglomerates and also cut individually suspended CNTs [21-22]. In an attempt to determine the best method for dispersing the CNTs in epoxy, Liao et al. [23] found the use of tip sonication most promising in achieving good dispersion and improved mechanical properties. Hilding et al. [24] investigated the use of sonication to achieve uniform dispersion of CNTs in various liquids. The process of sonication effectively dispersed MWCNTs but reduced their lengths. The reduction in length was found to be dependent on the time of sonication, however the most shortening in length occurred after the first few minutes of sonication. Not only CNT shortening, but also degradation of the side walls is reported due to sonication. Lu et al. [25] observed considerable damage in SWCNTs dispersed in CH2Cl2 using a low power ultrasonic horn (~17 W). The damage to CNTs increased with increasing sonication time and was verified using transmission electron microscopy (TEM) and Raman spectroscopy. However,
O’Connell et al. [26] discovered that the side walls of SWCNTs were not substantially damaged after subjecting them to high power sonication (540 W) in water for 10 minutes. The differences in these two investigations were in the solvent, power level, and the time of sonication used. These differences can produce substantially different results as the process of sonication depends on the input power, viscosity of the solvent, and the time of sonication. The process of sonication produces shear stresses due to the rapid movement of the fluid resulting from the creation and implosion of bubbles. The creation and implosion of bubbles is commonly referred to as cavitation. Based on the recent experiments and theoretical models developed to understand the process of cavitation, it is estimated that strain rates as high as $10^9$ s$^{-1}$, high pressure, and temperatures in excess of 15,000 K are produced close to the imploding bubbles [27]. Ultrasonic cavitation occurs if a threshold energy density of 10 W/cm$^3$ is exceeded by an acoustic compression wave [27]. While cavitation produces high enough shear stresses to break CNT agglomerates, it also cuts and damages individual CNTs. A damaged CNT has lower stiffness and is much weaker in strength [28]. Moreover, short CNTs with low aspect ratio do not reinforce composites effectively [22, 29-30].

Manufacturing processes usually result in CNTs of different lengths. CNT composites are analogous to short fiber reinforced composites on account of their shape and size. The elastic properties of short fiber reinforced composites depend on the residual lengths and orientations of short fibers [31-32]. Jiang et al. [33] have shown based on numerical modeling that, if the length distribution of CNTs is not symmetric about the average length value, then the modulus predictions made using the average length could be as high as 30% in comparison to those predicted using the length distribution. This difference was shown to magnify for low aspect ratio CNTs. Another well recognized and important fiber parameter that controls the overall modulus of the composites is the orientation of fibers [31-32, 34]. Typically, the fibers orient randomly in composites after resin casting or infusion processes which, in turn, could result in wide range of elastic modulus values [31-32, 34].

To effectively reinforce polymeric composites using CNTs, it is not enough to minimize damage, preserve the lengths, and control the orientations of CNTs, but the interfacial adhesion between the CNTs and matrix should also be improved. The interfacial bond strength of as-processed
CNT/polymer interface is thought to be weak due to the lack of defect sites where polymer molecules can attach themselves to the reinforcement [31-32]. The interfacial bond can be enhanced by functionalizing the surface of CNTs.

Various chemical functionalization techniques have been developed to improve the interfacial bond between CNTs and epoxy matrix [33-36]. Since both CNTs and CNFs have side walls that resemble basal plane of graphite, the chemical functionalization techniques developed for CNTs can be used for functionalizing CNFs as well. The most common procedure to functionalize CNTs is to treat them with acids. The acids oxidize CNTs introducing carboxylic, hydroxyl, ester, and carbonyl groups on the ends and side walls of the CNTs. CNTs can be oxidized using boiling nitric acid [37-39] or mixture of nitric and sulphuric acids [37], gaseous oxygen [40], or ozone [41]. In addition to oxidizing the CNTs, the process of oxidation removes traces of metal catalysts and amorphous carbon, a byproduct of most processing methods [42]. Oxidation can also be used for cutting and shortening CNTs by controlling the rate and the extent of reaction [42]. Hong et al. studied the effects of oxidation time and temperature on the change in properties of MWCNTs [43]. The length of MWCNTs decreased dramatically on increasing the oxidation time and temperature. Based on the experimental results, a phenomenological model was suggested to predict the length of MWCNTs as a function of oxidation time and temperature. Furthermore, it was observed that oxidatively shortened MWCNTs dispersed very well in polypropylene composites.

The introduction of carboxylic acid group, −COOH, on CNTs provides access to further tailor the surface chemistry. From carboxylic acids, carboxamides can be formed via carboxylic acid chlorides. Most commonly, the carboxylic groups are converted into acyl chloride groups by reacting with thionyl chloride (SOCl₂). The chloride groups can further react with various chemical compounds to provide different functionalities to CNTs [44]. By grafting the right kind of chemical group on CNTs, compatibility, dispersion and solubility in organic solvents and in polymers can be improved [45]. Amine functionalized CNTs have been used to covalently integrate with epoxy resins [46-47]. The multiple amino groups on the surface of CNTs form heavily crosslinked structure with the surrounding matrix, thereby facilitating the transfer of load from matrix to CNTs.
Using the acid-thionyl procedure, Wang et al. [48] grafted triethylenetetramine (TETA) on the surfaces of MWCNTs. TETA is a very popular curative for many epoxy systems. A homogeneous dispersion of amino functionalized MWCNTs was achieved in the composite along with improved mechanical, thermal and optical properties. The use of 0.5 wt% amino-functionalized MWCNTs doubled the charpy impact strength, increased the glass transition temperature ($T_g$) by 15°C, and increased the initial decomposing temperature of cured epoxy. Following the chemical route of thionyl chloride, Shen et al. [49] reacted acyl-chlorinated MWCNTs with ethylene diamine to graft amine derivatives on the MWCNTs. Use of 1 wt% amino-functionalized MWCNTs in bisphenol-A epoxy composite increased the thermal and mechanical performance of the composite. An increase of 19% in Young’s modulus and 100% in flexural modulus was observed. Using carboxylated SWCNTs as precursors, Zhu et al. [50] grafted amine groups by reacting oxidized SWCNTs with diamines. The use of 1 wt% amine functionalized SWCNTs increased the modulus of a bisphenol-F epoxy composite by 24%. Ramanathen et al. [51] used amide-functionalized SWCNTs prepared by directly coupling ethylene diamine with oxidized SWCNTs. Using poly(methyl methacrylate) (PMMA) as the matrix, addition of 1 wt% amino-functionalized SWCNTs doubled the Young’s modulus and increased the $T_g$ by 30°C. Despite the improvement in mechanical properties observed by some researchers, there are also reports of no improvement in Young’s modulus or strength on using amine functionalized CNTs [47].

The process of oxidation is known to damage the side walls of CNTs which might reduce the physical properties of CNT/epoxy composites. Considering the degrading effects of oxidation on the properties of CNTs, alternative functionalization procedures are of interest. Realizing the similarity between the basal plane of graphite and the side walls of CNTs, researchers have tried the techniques developed for the fluorination of graphite and fullerenes to functionalize CNTs with fluorine. The fluorine functionalized CNTs are used as precursors for further functionalization with amine terminations [52-54]. The fluorinated CNTs can be easily dissolved in alcohols which would help to disperse them in polymers. However, fluorination remarkably reduces the thermal and electrical conduction [55]. Some functionalization routines using free radical addition have also been tried to graft different chemical species on the CNTs [56-57]. The
free radical functionalization causes less damage to CNTs, but requires longer time for functionalization.

To eliminate the need of oxidation for grafting amines on the CNTs, Wang et al. [58] directly functionalized SWCNTs with amines through diazotization. The curing agent, EPIcure W, was first reacted with isoamyl nitrile to form intermediate diazonium salt, which being unstable rapidly releases nitrogen to convert into carbo-cations. The carbo-cations deposited on the CNTs easily extract electrons to attach on the surface of the CNTs. Using 0.5 wt% EPIcure W grafted SWCNTs, Wang et al. showed an increase of 24% in the Young’s modulus of Epon 862 (bisphenol-F)/EPIcure W composite system. Another form of functionalization is called the noncovalent functionalization, where the CNTs are wrapped with long polymer chains. The helical structure of poly (m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene)(PmPV) is found useful in wrapping SWCNTs [59]. PmPV wrapped SWCNTs are shown to disperse well in thermoset epoxies.

To maximize the benefits from functionalization, it is desired that each individual CNT is functionalized. Most commonly, as-manufactured CNTs are used for functionalization and require ultrasonic agitation for breaking the agglomerates to obtain individually suspended CNTs. Individually suspended CNTs have a better chance of participating in the chemical reaction than those in the agglomerates. Ultrasonication is also needed after the step of functionalization to disperse functionalized CNTs in polymers because CNTs are commonly obtained in dry powdered form after the process of functionalization. Therefore, ultrasonication is almost always involved in manufacturing CNT/epoxy composites. To optimize composite manufacturing, it is important to investigate the effects of ultrasonication. The main parameter determining the dispersion process is the strain rate caused by ultrasonic cavitation. The strain rate depends on the bubble dynamics which is a function of the surface tension of the liquid, vapor pressure, the liquid viscosity, the polytropic index of the gas phase, static pressure, the initial radius of the bubble, acoustic pressure, and the probability of agglomerates or individual CNTs to be in the vicinity of the collapsing bubbles [60, 61]. The probability of CNTs to be in the vicinity of the bubble can be controlled by the time and power of sonication. Lucas et al. [61] have shown that lengths of CNTs depend on the energy supplied by the process of sonication.
The length of CNT reduces with increasing amount of energy. The energy is defined as the product of sonication power and time. Thus similar length CNTs can be obtained using high power short duration or low power long duration sonication.

A good dispersion necessitates breakup of all the agglomerates to the level of individual CNTs and CNFs. Often it is difficult to know and control majority of the parameters governing the bubble dynamics, except for solvent viscosity, sonication power, and time of sonication. Therefore this investigation primarily focuses on the effects of viscosity of the solvent and time of sonication to achieve good dispersion while maintaining high aspect ratio of the nanoparticles. Also, the well dispersed and long CNFs and CNTs are functionalized to enhance the interfacial bond between the matrix and CNTs and CNFs. The effects of length and functionalization are evaluated by measuring the elastic modulus of fully cured CNT/epoxy and CNF/epoxy composites.

2.3 Theory
The theory presented in this section is used to determine the expected improvement in elastic modulus of nanoparticle/epoxy composites. Since the composite manufacturing process is anticipated to result in CNTs and CNFs with unequal lengths, it is essential to use the measured length and orientation distribution of CNFs and CNTs to improve the predictions. The predictions of elastic modulus based on the measured length and orientation distributions will assist in optimizing the manufacturing process for making composites with improved elastic properties.

2.3.1 Fiber length distribution
The length distribution of CNTs and CNFs after processing can be described by a probability density function given by [62],

\[ f(l) = abl^{b-1}e^{-alt^b}, \text{for } l > 0 \]  \( (2.1) \)

where \( l \) is the fiber length and \( a \) and \( b \) are scale and shape parameters, respectively. The parameters can be obtained by numerically fitting equation (2.1) to the actually measured
distribution of CNTs and CNFs. Once the parameters are known from curve fitting, the mean fiber length can be obtained as follows,

\[ l_{\text{mean}} = a^{-1/b} \Gamma(1/b+1) \]  

(2.2)

where \( \Gamma(\ ) \) is the gamma function. Also, the most probable length can be obtained by differentiating equation (2.2) with respect to \( l \) and setting it equal to zero.

\[ l_{\text{mod}} = \left[ \frac{1}{a} - \frac{1}{(ab)} \right]^{1/b} \]  

(2.3)

2.3.2 Fiber angle distribution

Similar to fiber length distribution, fiber angle probability distribution can be estimated using a two-parameter exponential function given by [62],

\[ g(\theta) = \frac{\sin(\theta)^{2p-1}\cos(\theta)^{2q-1}}{\sin(\theta)^{2p-1}\cos(\theta)^{2q-1}d\theta} \]  

(2.4)

where, \( p \) and \( q \) are curve fitting parameters, \( \theta \) is the angle fibers make from the direction of modulus measurement, and \( \theta_{\text{max}} \) and \( \theta_{\text{min}} \) represent the range of fiber angle distribution. Since it is difficult to measure the orientation distribution of fibers in a three dimensional space, the parameters are usually assumed based on the best guess of fiber angle distribution in the composite. The value of \( p \) and \( q \) for a random orientation of fibers is \( \frac{1}{2} \) and \( \frac{1}{2} \), respectively.

2.3.3 Elastic modulus of short fiber composite

2.3.3.1 Paper-Physics Approach (PPA)

According to the paper-physics approach (PPA), the elastic modulus of short fiber composites can be expressed as follows [63],

\[ E_c = \chi_1 \chi_2 E_f V_f + (1 - V_f) E_m \]  

(2.5)

where \( E_c \), \( E_f \), and \( E_m \) are the modulus of composite, fiber, and matrix, respectively, \( V_f \) is the fiber volume fraction. \( \chi_1 \) and \( \chi_2 \) are the fiber length and orientation factors given as follows,
\[ \chi_1 = \frac{1}{l_{\text{mean}}} \int_{l_{\text{mean}}}^{l_{\text{max}}} \left[ 1 - \frac{\tanh \left( \frac{1}{2} \right)}{\frac{1}{2}} \right] l f(l) dl \]  

(2.6)

\[ \chi_2 = \int_{\theta_{\text{min}}}^{\theta_{\text{max}}} (\cos^2 \theta - v_{12} \sin^2 \theta) (\cos \theta)^2 g(\theta) d\theta \]  

(2.7)

\[ \beta = \left( \frac{E_m}{E_f(1+\nu_m) \rho^{2} \ln \left( \frac{R}{r} \right)} \right)^{1/2} \]  

(2.8)

where, \( r \) is the radius of the fiber, and \( R' \) is the mean separation of the fibers normal to their length. The relationship between \( r \) and \( R' \) for a hexagonal fiber packing arrangement in the composite is given by,

\[ \ln \left( \frac{R'}{r} \right) = \frac{1}{2} \ln \left( \frac{2\pi}{\sqrt{3}V_f} \right) \]  

(2.9)

The value of fiber orientation factor, \( \chi_2 \), for randomly oriented fibers ranging between 0 and 90 deg. is 0.325. This value is obtained using \( p \) and \( q \) equal to \( \frac{1}{2} \) in equation (2.7), and setting the values of \( \theta_{\text{min}} \) and \( \theta_{\text{max}} \) equal to 0 and \( \pi/2 \), respectively.

### 2.3.3.2 Halpin-Tsai model

The elastic modulus of short fiber composites can be predicted by the Halpin-Tsai equations shown below:

\[ \frac{E_c(l)}{E_m} = \frac{1+\gamma V_f}{1-\gamma V_f} \]  

(2.10)

where

\[ \gamma = \frac{\left( \frac{E_f}{E_m} - 1 \right)}{\left( \frac{E_f}{E_m} + \xi \right)} \]  

(2.11)

\[ \xi = \frac{L}{d} \]  

(2.12)

where \( d \) is the diameter of the fibers and \( E_c(l) \) is the modulus of composite. In the Halpin-Tsai equations, fibers are assumed to have a uniform length. Since in a realistic composite the fibers are not of the same length, a modified Halpin-Tsai prediction can be made by combining the
length distribution, \( f(l) \), with Halpin-Tsai equations as follows [64]. The mean value of composite modulus with fiber length distribution given by \( f(l) \) can then be written as

\[
E_{c,\text{mean}} = \frac{\int_0^\infty E_c(l) f(l) \, dl}{\int_0^\infty f(l) \, dl}
\]  

(2.13)

2.4 Materials

2.4.1 Resin materials
Specimens for this investigation were prepared by adding nanoparticles to an epoxy resin system. The resin system was Epon 862 with curative W, a bisphenol F/aromatic diamine system. This resin system was chosen because of its extensive use in making high performance aerospace structures. The low viscosity of this resin system makes it useful for manufacturing process such as wet-filament winding, resin transfer molding, and vacuum assisted resin transfer molding to name a few. The resin system was mixed at a ratio of 100:26.4 epoxide to curative, and this mixture (epoxide+curative) was used for determining the weight percentages of nanoparticles added to the mixture.

2.4.2 Resin additives
The additives used in dispersing nanoparticles in liquid epoxide were a non-ionic surfactant and in some cases acetone. The surfactants used were nonionic surfactants commercially known as Triton-X 100 (Bioworld, Dublin, OH) for dispersing CNFs and BYK-9076 (BYK Chemie USA, Washington, CT) for dispersing MWCNTs. These surfactants were chosen based on their successful use in dispersing CNTs and CNFs in epoxy polymers demonstrated in literature [3, 23]. The surfactants were used to disperse unfunctionalized CNFs and CNTs only. Following the recommendations in the literature, the surfactants were mixed at 76 weight percent of the nanoparticle weights. The air release agent used in processing of all the composites was BYK A 501 (BYK-Chemie USA inc. Wallington, CT), mixed at 0.5 wt% of the total weight of the epoxy system (epoxide+curative), to aid in elimination of air bubbles during a degassing phase.
2.4.3 Nanoparticles

2.4.3.1 Unfunctionalized nanoparticles
For investigating the effects of solvent viscosity and sonication time on dispersion, unfunctionalized CNFs and two types of unfunctionalized MWCNTs were used. The CNFs are a commercial product designated Pyrograf\textsuperscript{©}-III PR-24 HHT (Applied Sciences Inc., Cedarville, OH) with diameters in the range of 60–150 nm and lengths of 30–100 µm. These CNFs are referred to as u-CNFs. The two types of MWCNT investigated were obtained from Cheaptubes (Brattleboro, VT). The main difference between the two types was in the physical assembly of CNTs in the agglomerates, one type had entangled CNTs whereas the other had CNTs grown aligned to each other in the length direction with minimal entanglement. The entangled CNTs are referred to as e-MWCNTs and are shown in Figure 2.1. The e-MWCNTs have a purity of >95 wt%, diameters in the range of 10-20 nm and lengths of 10-20 µm. The CNTs that are grown aligned in the length direction are referred to as a-MWCNTs and are shown in Figure 2.2. The a-MWCNTs have a purity of >95 wt%, diameters in the range of 8-15 nm and lengths 20-100 µm. a-MWCNTs were delivered in a dry powder form by the manufacturer. On visual inspection of the two types of CNT powders, it was observed that the powder of e-MWCNT was denser than a-MWCNT.

![Figure 2.1](image-url)  
Figure 2.1 SEM micrograph showing networks of entangled MWCNTs.
2.4.3.2 Functionalized nanoparticles

To investigate the effect of chemical functionalization of nanoparticles on dispersion and mechanical properties of the fully cured composites, five different types of functionalized MWCNTs and one type of functionalized CNFs were used. The types of functionalizations investigated for MWCNTs were covalent and non-covalent in nature. In a covalent type of functionalization, the polymer is grafted on CNTs by forming a covalent bond between the atoms of the polymer and CNT, whereas in a non-covalent type of functionalization the polymer is adsorbed on the surface without forming a covalent bond. Four different kinds of covalently functionalized MWCNTs were investigated. Three out of four covalent functionalizations were with amine and one was with carboxylic acid (–COOH). Out of the three amine-functionalized CNTs, one type was purchased from the vendor Nanolab (Newton, MA) and two were prepared in-house using procedures available in literature (see Sections 2.5.4 and 2.5.5). The CNTs bought from Nanolab have a purity >95wt% after functionalization and lengths in the range 5-20 µm. The –COOH functionalized CNTs were purchased from Cheaptubes Inc. (Brattleboro, VT) and have a purity >95wt% after functionalization and diameter of 8-15 nm and lengths in the range 0.5-2 µm. The non-covalently functionalized CNTs were purchased from Zyvex Performance Materials, LLC (Columbus, OH).
and were delivered pre-dispersed in Epon 862 at a weight fraction of 2 wt% of the epoxide weight. Table 2.1 gives descriptions of all the nanoparticles used in this investigation.

2.5 Experiments

2.5.1 Effect of CNFs and CNTs entanglement on dispersion
The CNTs and CNFs were dispersed in epoxide and epoxide diluted with acetone at a mix ratio of 20 ml to 10 ml, epoxide to acetone. A 2.5 oz. steel container was used for dispersing nanoparticles using ultrasonic horn. The volume of the liquids subjected to sonication was kept constant at 30 ml for all the experiments performed in this section. The amount of nanoparticles used for in this section was 0.005 g. No surfactant was used to stabilize the suspension of dispersed particles. Since surfactant was not used, it was anticipated that dispersed particles will reagglomerate over time. The rate of reagglomeration depends on the distance between the particles or simply on the concentration of particles. The particles will reagglomerate faster if the concentration is higher. If the particles reagglomerate before the observation is made to determine the extent of dispersion, it would give a false impression of the efficacy of the dispersion process. Therefore, the use of small amount of nanoparticles to slow down reagglomeration provides sufficient time to make the observations. The sonication was performed with a 900-W, 20-kHz, ultrasonic horn (Branson, Danbury, CT). Sonication was carried out at 900 W power-level for up to 5 min. The degree of dispersion was characterized by taking photographs of the mixture after every 1 min. A digital camera was used to take the pictures.
Table 2.1 Various nanoparticles used in this investigation.

<table>
<thead>
<tr>
<th>Name</th>
<th>Vendor</th>
<th>Type of functionalization</th>
<th>Polymer</th>
<th>Dia. nm</th>
<th>Surfactant for dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>e-MWCNT</td>
<td>Cheaptubes (Brattleboro, VT)</td>
<td>Unfunctionalized</td>
<td>Not applicable</td>
<td>10-20</td>
<td>Not used</td>
</tr>
<tr>
<td>a-MWCNT</td>
<td>Cheaptubes (Brattleboro, VT)</td>
<td>Unfunctionalized</td>
<td>Not applicable</td>
<td>8-15</td>
<td>BYK -9076</td>
</tr>
<tr>
<td>Amino1-MWCNT</td>
<td>NanoLab (Newton, MA)</td>
<td>Covalent/amine</td>
<td>Not known</td>
<td>15-50</td>
<td>Not used</td>
</tr>
<tr>
<td>Amino2-MWCNT</td>
<td>In-house using a-MWCNT</td>
<td>Covalent/amine</td>
<td>4,4’-diaminodiphenylmethane</td>
<td>8-15</td>
<td>Not used</td>
</tr>
<tr>
<td>PEI-MWCNT</td>
<td>In-house using a-MWCNT</td>
<td>Covalent/amine</td>
<td>Polyethyleneimine (PEI)</td>
<td>8-15</td>
<td>Not used</td>
</tr>
<tr>
<td>COOH-MWCNT</td>
<td>Cheaptubes (Brattleboro, VT)</td>
<td>Covalent/-COOH</td>
<td>Not known</td>
<td>10-20</td>
<td>Not used</td>
</tr>
<tr>
<td>Z-MWCNT</td>
<td>Zyvex Performance Materials, LLC (Columbus, OH)</td>
<td>Non-covalent</td>
<td>Not known</td>
<td>15-50</td>
<td>Not used</td>
</tr>
<tr>
<td>u-CNFS</td>
<td>Applied Sciences Inc., Cedarville, OH</td>
<td>Unfunctionalized</td>
<td>Not applicable</td>
<td>60-150</td>
<td>Triton-X 100</td>
</tr>
<tr>
<td>PEI-CNFS</td>
<td>In-house using u-CNFS</td>
<td>Covalent/amine</td>
<td>polyethyleneimine</td>
<td>60-150</td>
<td>Not used</td>
</tr>
</tbody>
</table>

2.5.2 Raman spectroscopy
To investigate the damage caused by sonication to u-CNFS, e-MWCNTs, and a-MWCNTs, raman spectra of as-received CNFs and CNTs before and after sonication were collected under ambient conditions with a WITec CRM200 Confocal Raman spectrometer (MCL, 132 MRI Building). Excitation was produced by 488 nm laser at 1-3 mW incident power. A 100X lens was used to focus the beam on the samples. The spectra were collected at three different spots on each specimen. Specimens were collected after 1 to 15 min. of sonication. CNFs/CNTs were obtained from the solvents (epoxide or mixture of epoxide and acetone) by filtration. After desired amount of sonication, the suspensions were diluted with excess of acetone and stirred for 10 min. using a magnetic stirrer. After stirring, the diluted suspension was filtered using a 10 µm PTFE filter membrane (DeWAL Industries, Saunderstown, RI) to collect CNFs and CNTs. The precipitate was re-dispersed in acetone using magnetic stirrer for 10 min. The process of
dispersion and filtration was repeated three times to remove any epoxy adhering to the nanoparticles. The resulting precipitate after the third time was dried for 48 hours at 60°C. The dried precipitate was transferred to a microscope glass slide by pressing the glass slide against the precipitate formed on the filter membrane. The specimens for investigating the effect of no sonication were prepared by first soaking the nanoparticles in the mixture of epoxide and acetone for 3 min. before collecting them on a glass slide. Table 2.2 lists the types of specimens prepared for Raman spectroscopy.

Table 2.2  Specimens for Raman spectroscopy

<table>
<thead>
<tr>
<th>Type of nanoparticles</th>
<th>Type of solvent</th>
<th>Sonication @ 900W, 20k Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received u-CNFs</td>
<td>Epoxide/acetone (20ml/10ml)</td>
<td>No sonication</td>
</tr>
<tr>
<td>As-received a-MWCNTs</td>
<td>Epoxide/acetone (20ml/10ml)</td>
<td>No sonication</td>
</tr>
<tr>
<td>As-received e-MWCNTs</td>
<td>Epoxide/acetone (20ml/10ml)</td>
<td>No sonication</td>
</tr>
<tr>
<td>u-CNFs</td>
<td>Epoxide/acetone (20ml/10ml)</td>
<td>3min. &amp; 5 min.</td>
</tr>
<tr>
<td>a-MWCNTs</td>
<td>Epoxide/acetone (20ml/10ml)</td>
<td>1min.</td>
</tr>
<tr>
<td>e-MWCNTs</td>
<td>Epoxide/acetone (20ml/10ml)</td>
<td>3 min. &amp; 5 min.</td>
</tr>
<tr>
<td>a-MWCNTs</td>
<td>Epoxide</td>
<td>3 min. &amp; 5 min.</td>
</tr>
</tbody>
</table>

2.5.3 Effect of sonication time on dispersion and residual lengths of CNFs

u-CNFs were used to investigate the effects of sonication time on the residual lengths and degree of dispersion of nanoparticles. Since CNFs are visible in white light, it was easier and more importantly quicker to make observations using an optical microscope. It is important to observe the degree of dispersion quickly after sonication to correctly characterize the effectiveness of the process. For this investigation, the amount of CNFs used was 0.2 g. This amount is equivalent to 1.0 wt% of resin (epoxide+curative) and corresponds to amounts used later in the investigation for manufacturing composites. The surfactant used to stabilize the suspension of dispersed CNFs was Triton-X 100, and was added in an amount equal to 0.76 times the weight of CNFs. The sonication was done at 900 W power-level for a total of 5 min. A small amount of sample was taken from the container and placed in between two microscope glass slides for measuring the lengths of CNFs using an optical microscope. Confining the suspension between glass slides reduces the mobility of suspended particles, thereby preventing reagglomeration. The measured
length distribution of CNFs was used to determine the expected improvement in elastic modulus using theoretical models discussed in Section 2.3. Predictions of elastic modulus together with observed state of dispersion were analyzed to make recommendations for manufacturing CNF and CNT composites.

2.5.4 Functionalization using polyethyleneimine (PEI)
To improve the interfacial bond between nanoparticles and the matrix, u-CNFs and a-MWCNTs were functionalized using polyethyleneimine (PEI) polymer with molecular formula H(NHCH₂CH₂)ₙNH₂ and an average molecular weight of 10,000 g/mol (Sigma-Aldrich, Inc.) [65]. First, 10 g of PEI was mixed with 100 ml of N,N-dimethylformamide (DMF) in a glass beaker. After PEI was completely dissolved in DMF, 2 g of u-CNFs or a-MWCNTs was added to the mixture. The suspension was sonicated for 5 min. at 900 W using 20k Hz ultrasonic horn. After sonication, the mixture was continuously stirred using a magnetic stirrer at 60-70°C for 3 days. The resulting suspension was filtered through a 0.2 μm PTFE membrane (Sterlitech Corp., Kent, WA) and the precipitate was washed with 1 molar HCl, 1 molar NaOH, and de-ionized water to remove any excess PEI. The washed precipitate was dried for two days at room temperature. After drying, 1.8 g of the product was obtained. The functionalized CNFs and CNTs are referred to as PEI-CNFs and PEI-MWCNTs, respectively.

2.5.5 Functionalization using 4,4′-diaminodiphenylmethane
The procedure described in reference [66] was used with slight modifications for the functionalization of a-MWCNTs. The CNTs were dispersed using sonication in DMF as opposed to using fuming sulphuric acid. The remaining chemicals used for functionalization are the same as used in reference [66]. The a-MWCNTs were dispersed in DMF using an ultrasonic horn for 5 min. The suspension had 50 mg of CNTs in 50 ml of DMF. The suspension was heated to 80°C and 2.7 ml of isoamyl nitrite (4 equiv/mol of carbon) (VWR International) was added slowly to the suspension. A syringe pump was used to slowly add isoamyl nitrite over a period of 10 min. The suspension was continuously stirred while adding isoamyl nitrite. After 2 min. of mixing, 0.137 g of AIBN (0.2 equiv/mol of carbon) (Sigma-Aldrich Inc.) was added to the suspension. The mixture was kept at 80°C under an argon blanket and stirred for 3-4 hours. The resulting suspension was diluted with an excess of DMF and filtered through a 0.2 μm cellulose membrane (0.2 μm, Whatman Nuclepore). The precipitate was repeatedly washed with de-
ionized water to remove any excess DMF. The dried precipitate was kept at 70°C for 24 hrs to remove water. The functionalized MWCNTs are referred to as Amine2-MWCNT.

2.5.6 Manufacturing composites
Composites were made using functionalized and unfunctionalized CNFs and MWCNTs. The weight fractions used for making CNF and CNT composites were 1.0 and 0.5 wt%, respectively. As will be discussed later in Section 2.6.1, the use of acetone was found better to disperse unfunctionalized CNFs and CNTs in epoxide. The reduced viscosity of epoxide resulted in longer lengths of CNFs and CNTs. Therefore, u-CNFs, a-MWCNTs, and COOH-MWCNTs were dispersed in a mixture of epoxide and acetone. The amine functionalized CNFs and CNTs were dispersed in a mixture of curative and acetone. Since amine functionalized CNFs and CNTs would cross link with the epoxide during the dispersion process and hinder dispersion in unknown ways, CNFs and CNTs with amine functionalization were first dispersed in curative. Recall that curative is an amine compound, and the amine functionalized CNTs would not cross link with the curative. Though the viscosity of curative is 3 orders of magnitude smaller than epoxide viscosity at room temperature, the reason for using acetone with curative was to reduce the increased viscosity due to dispersion of high loading of CNTs and CNFs in curative. Since the amount of curative is 1/5th of the total weight of epoxide/curative mixture, the amounts of CNFs and CNTs to be added in curative is 5 times of that in the mixture of epoxide and curative. With such high loadings of CNTs and CNFs in curative, the increase in viscosity of the mixture would result in inadequate dispersion. Therefore, acetone was used to reduce the viscosity of CNF/CNT/curative mixture.

The mix ratio for epoxide and acetone was 20 ml to 10ml, epoxide to acetone, whereas the mix ratio for curative and acetone was 10 ml to 20 ml, curative to acetone. Sonication was performed for 4 min. at 900 W and 20k Hz. After dispersing CNTs and CNFs in epoxide or curative, the acetone was removed by stirring the suspension at 60°C for 24 hrs using a magnetic stirrer. After removing the acetone, the curative or epoxide (as the case may be) and air-release agent were added and mixed manually using a plastic stirrer for 5 min. Acetone was not used to prepare Z-MWCNT composites. Z-MWCNTs were manually mixed in an appropriate amount of epoxide using a plastic stirrer for 5 minutes. After manually stirring the mixture, sonication was performed for 15 min. at a power level of 270 W. The mixture was continuously cooled to
minimize excessive heating due to sonication. After manually mixing the curative or epoxide, the mixture of nanoparticle/epoxide/curative was sonicated for 1 min. at 900 W power-level. The freshly sonicated mixture was then placed in a vacuum oven at elevated temperature (~65°C) and a pressure less than 1000 millitorr to eliminate air bubbles in the mixture. The mixture was degassed for 30-45 min.

The degassed mixture was carefully poured in between two glass slides pre-treated with mold release agent Monocoat E-340 (Chem-Trend, Howell, MI). The slides were separated by roughly 1.9 mm and were 10×3.8×0.1 cm in size. These slides were placed horizontally on a hot plate for curing the resin. The curing schedule employed was 121°C for 1 hour followed by 177°C for 2.5 hours. Composite specimens of dimensions 6.5×3.8×0.19 cm were obtained after curing. Two rectangular specimens of dimensions 5.5×1×0.19 cm were then cut from the fully cured composite part using a water cooled diamond saw.

2.5.7 Scanning electron microscopy
To determine the dispersion of CNFs and CNTs in fully cured composites, specimens were machined appropriately for SEM analysis. The quality of CNT or CNF dispersion was determined by examining freshly fractured surfaces of the materials in a Philips XL 30 (FEI, Hillsboro, OR) scanning electron microscope. The specimens were fractured at room temperature. A gold layer of approximately 50 Å was coated over the fracture surface of the SEM specimen to prevent charging.

2.5.8 Flexural testing
Two rectangular specimens of dimensions 5.5×1×0.19 cm were used to measure the flexural modulus of composites using a dynamical mechanical analyzer (DMA). Testing was conducted using a dual cantilever clamp. The tests were done at a temperature of 35°C and a frequency of 1 Hz. The strain amplitude used for obtaining the data was set at 500 µε (peak surface strain).

2.6 Results

2.6.1 Effect of entanglement of CNFs and CNTs on dispersion
The three kinds of nanoparticles studied in this section are u-CNFs and two types of CNTs with different entanglement states as shown in Figures 2.1 and 2.2. Amongst all the nanoparticles investigated, a-MWCNTs dispersed quickly when subjected to sonication. The a-MWCNTs
required only 1 min. of sonication to disperse in the mixture of epoxide and acetone, whereas e-MWCNTs and u-CNFs needed at least 5 min. as shown in Figures 2.3-2.6. However, a-MWCNTs took 15 min. of sonication when added directly in liquid epoxide (Figure 2.7). An explanation for the longer sonication time needed in the case of liquid epoxide is presented later in this section. A possible reason for nanoparticles to require different amounts of time to disperse in the mixture of epoxide and acetone could be the entangled state of nanoparticles in the agglomerates. The CNTs in an agglomerate of a-MWCNTs are not tangled and are held together by van der Waals forces only, whereas the particles are physically entangled with each other as well in agglomerates of e-MWCNTs and u-CNFs. Based on the observations in Figures 2.4-2.7, it appears that entangled particles require more work to disperse than untangled particles.

Since the CNTs and CNFs used here are essentially different, a direct comparison of the results presented in the previous paragraph to draw conclusions on the relative ease of dispersing untangled nanoparticles is not entirely correct. Therefore to verify the hypothesis that entangled nanoparticles require more work to disperse than untangled particles, entangled CNFs (u-CNFs) were cut short to prepare a powder of untangled CNFs in which the particles were held together by the van der Waals forces only. u-CNFs were cut short by sonicating them in de-ionized water for 30 min. After sonication, the short and untangled CNFs were collected by evaporating water. The untangled CNFs were prepared by dispersing 0.1 g of u-CNFs in 30 ml of de-ionized water. A 2.5 oz. steel cup was used for dispersion. Water was added from time to time to maintain the volume of the suspension. To verify the dispersion of CNFs in water, a small sample of the suspension was taken from the container and placed between two glass slides for optical observation using a microscope. Figure 2.8 shows the dispersion of CNFs in water after 30 min. of sonication. CNFs dispersed very well but were shortened considerably in length due to extended sonication. Once it was confirmed that CNFs were dispersed to the level of individual CNFs, water was evaporated by placing the container on a hot plate maintained at 60°C for 24 hrs. The dried and untangled CNFs were then dispersed in the mixture of epoxide and acetone (20ml:10ml) using ultrasonic horn operating at 900 W and 20 kHz. The amount dispersed was 0.005 g in 30 ml of the mixture. It was observed that 2 min. sonication was sufficient to disperse short and untangled CNFs in the mixture of epoxide and acetone (Figure 2.9). In comparison,
entangled CNFs needed 5 min. of sonication. This confirms the hypothesis that entangled particles require more work to disperse than untangled particles.

**Figure 2.3** a-MWCNTs in mixture of epoxide and acetone before sonication (0.005 g of CNTs in 30 ml of epoxide/acetone mixture (20 ml/10 ml).

**Figure 2.4** a-MWCNTs in mixture of epoxide/acetone after 1 min. of sonication. a-MWCNTs have dispersed to the level where no agglomerates are visible.
Figure 2.5 e-MWCNTs in mixture of epoxide/acetone after sonication.

Figure 2.6 CNFs in mixture of epoxide/acetone after sonication.
Figure 2.7 a-MWCNTs in epoxide after sonication.

Figure 2.8 CNFs dispersed in de-ionized water after 30 min. of sonication at 900 W power level.
Figure 2.9 Dispersion of untangled CNFs in mixture of epoxide/acetone after 2 min. sonication (epoxide/acetone: 20 ml/10 ml, CNF wt. =0.005 g, sonication @ 900 W, 20 kHz).

The stresses produced in the process of sonication are not uniform throughout the volume of suspension. The maximum strain rate occurs at the wall of an imploding bubble and decays rapidly on moving away from the bubble (Figure 2.10) [27]. The breakup of particles and agglomerates therefore depends on their relative position from the bubble wall. Since not all the agglomerates and particles experience same stresses, the dispersion becomes a time dependent process. Continuous sonication for longer time would ensure all the particles and agglomerates experience similar stresses. Therefore, a physical model is proposed to understand the dispersion process based on the knowledge that strain rate decays on moving away from the bubble. An effective region around the bubble can be defined where the stresses are sufficient to break the agglomerates as shown in Figure 2.10. The agglomerates present in this region will break and disperse into individual particles. If this effective region is not equal to the entire volume of the suspension, it will take some time for all the agglomerates to translate in this region due to the agitation produced by cavitation. This means that larger the effective region, smaller the time needed to disperse particles.

The size of the effective region can be increased by either reducing the viscosity of the suspension or by reducing the agglomerate strength such that agglomerates positioned far away from the bubble can be disintegrated. From the forgoing analysis, it is known that the strength of the agglomerates can be reduced by using untangled CNFs and CNTs. The dependency of the size of effective region on viscosity is not straightforward but can be understood by this simple
explanation. The strain rate in the suspension is generated by the movement of the bubble wall. The velocity of the bubble wall decreases with an increase in viscosity of the suspension due to higher hydrodynamic forces. As a result of reduced bubble wall velocity, the strain rate in the suspension decreases. Also, the agitation produced by cavitation decays rapidly due to more dissipation of the energy in a more viscous medium. As a result of the reduced strain rate and more dissipation of the acoustic energy in viscous solvents, the size of effective region is reduced considerably. The reduction in size of the effective region leads to increase in sonication time for achieving dispersion. This could be a potential reason for needing 15 min. of sonication to disperse a-MWCNTs in liquid epoxide as opposed to 1 min. in mixture of epoxide and acetone (Figures 2.4 & 2.7). The higher viscosity of liquid epoxide at room temperature reduces the strain rate thereby requiring longer sonication time to achieve dispersion.

Figure 2.10 Variation of strain rate around an imploding cavitation bubble after [27]. $(R=10 \, \mu m, \frac{dR}{dt}=5000 \, m/s)$
2.6.2 Raman spectra
Raman spectroscopy of the CNTs and CNFs is done to determine the extent of damage caused by sonication. Figures 2.11-2.14 show Raman spectra of u-CNFs, e-MWCNTs, and a-MWCNTs before and after various amounts of sonication times. The Raman spectra of CNFs and CNTs did not change appreciably after sonication. The positions of D- and G-lines are almost the same as reported in literature [67]. The D- and G-lines occur around 1345 and 1570 cm\(^{-1}\), respectively. The G-line corresponds to the tangential stretching mode of highly pyrolytic graphite and indicates the presence of crystalline graphitic carbon in CNFs and CNTs. The D-line is caused by defects in the graphite crystals and by the finite sizes of graphite crystallites in the material. The strength of the D-line relative to the G-line is a measure of the amount of disorder in graphitic material [67]. A lower ratio of D- to G-line intensities indicates less damage. The D to G ratio is small in case of CNFs and is around 0.46. No change in D to G ratio was observed for CNFs. The u-CNFs are reported to be high heat treated for increasing the content of crystalline carbon. A lower D to G ratio observed here in this investigation confirms that these CNFs indeed have highly crystalline graphitic carbon. CNTs on the other hand have a D to G ratio in the range 0.87-0.95. Such a high ratio indicates CNTs obtained from the manufacturer are of inferior quality. However, the D to G ratio values reported in the literature for MWCNTs range from 0.7 to 1.5. No change in D to G ratio was observed for e-MWCNTs, however the ratio changed slightly from 0.87 to 0.92 for a-MWCNTs dispersed in epoxide/acetone mixtue and 0.87 to 0.95 for a-MWCNTs subjected to 15 min. of sonication in epoxide. The increase in D to G ratio indicates accumulation of defects or reduced size of graphite crystallites in CNTs (reduced length). Based on a larger increase in D to G ratio, it appears that the lattice structure of a-MWCNTs changed more during sonication in epoxide than in the mixture of epoxide and acetone. This change could result from either the extended period of sonication or due to the higher viscosity of liquid epoxide in comparison to mixture of epoxide and acetone. Overall, from the foregoing analysis it can be concluded that less amount of sonication in diluted epoxide is a better way of dispersing nanoparticles for manufacturing composites.
Figure 2.11 Raman spectra of CNFs that were dispersed in epoxide/acetone mixture.

Figure 2.12 Raman spectra of e-MWCNTs that were dispersed in the epoxide/acetone mixture.
Figure 2.13 Raman spectra of a-MWCNTs that were dispersed in epoxide/acetone mixture.

![Raman spectra of a-MWCNTs dispersed in epoxide/acetone mixture](image1)

Figure 2.14 Raman spectra of a-MWCNTs that were dispersed in epoxide.

![Raman spectra of a-MWCNTs dispersed in epoxide](image2)
2.6.3 Effect of sonication time on dispersion and residual lengths of CNFs

The process of sonication is known to cut CNTs and CNFs [24, 27]. The residual lengths of CNTs and CNFs play an important role in determining the mechanical properties of composites. It is important to note that not only the final length of nanoparticles but also their dispersion will affect the final properties of composites. Since the viscosity of the suspension changes as nanoparticles disperse, the change in strain rate would affect the extent of dispersion. In the analysis presented in Section 2.6.1, the viscosity of the suspension did not change due to the use of very small weight fractions of CNTs and CNFs (~0.05 wt%). Therefore, all the conclusions drawn from the previous analysis cannot be directly used for dispersing higher weight fractions.

The amount of CNFs used in this section is equivalent to 1 wt% in resin added to a mixture of epoxide and acetone mixed at a ratio of 20ml:10ml epoxide to acetone. In this section, the focus is to simultaneously investigate the degree of dispersion and residual lengths of nanoparticles subjected to ultrasonication in the mixture of epoxide and acetone. u-CNFs are used as model reinforcements for this investigation because they are visible using an optical microscope which allows for quicker observations. Figure 2.15 shows the effect of sonication time on the length distribution and dispersion of CNFs in the mixture of epoxide and acetone. The degree of dispersion increased, or in other words, the size and occurrence of agglomerates reduced with increase in sonication time. The average length of dispersed CNFs reduced with sonication time as shown in Figure 2.16. It is observed that sonication for 4-5 min. dispersed CNFs fairly well, though some agglomerates are still left. The average length of CNFs after 5 min. is around 6.1 µm. A length of 6.1 µm in this case corresponds to an average aspect ratio of 61. Sonication done for extended period of time (≥15 min.) resulted in well dispersed CNFs with shorter lengths (ave. length ~ 3.5 µm). It appears that a terminal length of CNFs (~3.5 µm) is reached after 15 min. of sonication. The scission of CNFs by ultrasonication will cease if the shear forces exerted by the solvent equals the strength of CNFs. Assuming that the strength of CNFs is around 3 GPa [69], the average strain rate generated by cavitation can be calculated using the following expression given in reference [29].

\[
l_{\text{lim}} = \sqrt{\frac{d^2 \sigma^*}{\eta 2(\frac{dR}{dt} / R)}}
\]

(2.14)

where, \(l_{\text{lim}}\) is the limiting length of CNFs, \(d\) is the diameter of the CNFs, \(\sigma^*\) is the strength of CNFs, \(\eta\) is the viscosity of the solvent, and \(2(dR/dt/R)\) is the strain rate at the surface of
cavitation bubble. Using 0.01 Pa·s for the viscosity of epoxy/acetone mixture, the strain rate is determined to be around $2 \times 10^8 \text{ s}^{-1}$. The strain rate reported in the literature for solvents with viscosity around 0.001 Pa·s is $10^9 \text{ s}^{-1}$ [27]. An order of magnitude smaller strain rate determined in this investigation is expected on account of an order of magnitude higher viscosity of the epoxide/acetone mixture. The strain rate is expected to be less in high viscosity solvents. The value of strain rate determined in this investigation provides confidence in the physical description of the dispersion process proposed based on the theory of cavitation.

![Image of dispersion after 1 min. of sonication](image1)

**a)** Dispersion after 1 min. of sonication

![Image of dispersion after 2 min. of sonication](image2)

**b)** Dispersion after 2 min. of sonication
c) Dispersion after 3 min of sonication.

\[ l_{\text{mean}} = 7.5 \mu m \]

\text{Curve fit parameters} \\
\[ a = 0.0081; b = 2.2579 \]

\[ l_{\text{mean}} = 6.8 \mu m \]

\text{Curve fit parameters} \\
\[ a = 0.0386; b = 1.6010 \]

d) Dispersion after 4 min. of sonication
e) Dispersion after 5 min. of sonication

f) Dispersion after 15 min. of sonication.
g) Dispersion after 60 min. of sonication.

**Figure 2.15** Probability density distribution of u-CNF lengths after sonication in epoxide/acetone mixture mixed at 20 ml:10 ml, epoxide to curative. The amount of CNFs is equivalent to 1 wt% in resin (epoxide+curative). Sonication performed at 900 W, 20 kHz. Probability density = (No. of counts/(Total no. of counts×histogram bin width)). Histogram bin width = 2 µm.

**Figure 2.16** Average length of u-CNFs after various sonication times. Sonication performed at 900 W, 20 kHz on a mixture of epoxide and acetone mixed at a ratio of 20 ml:10 ml, epoxide to curative, containing CNFs equivalent to 1 wt% in resin (epoxide+curative)

**2.6.4 Elastic modulus predictions**
For making composites with well dispersed u-CNFs, sonication times of 4, 5, 15 and 60 min. provided the best alternatives as shown in Section 2.6.3. Theoretical models discussed in Section 2.3 were used to predict the expected improvement in elastic modulus of composites using the
measured length distributions after 4, 5, 15, and 60 min. The two assumptions in using equations (2.5)-(2.9) are the perfect bond between CNFs and the matrix, and the CNFs are perfectly straight. Table 2.3 lists the parameters used for making predictions using equations (2.2)-(2.9).

Table 2.3  Values of parameters used to predict improvement in elastic modulus of randomly oriented and aligned CNF/epoxy composites using equations (2.2)-(2.9).

<table>
<thead>
<tr>
<th>Sonication time, min.</th>
<th>a</th>
<th>b</th>
<th>( t_{\text{mean}} ), µm</th>
<th>Random orientation</th>
<th>Aligned</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>p</td>
<td>q</td>
</tr>
<tr>
<td>4</td>
<td>0.0386</td>
<td>1.6010</td>
<td>6.8</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>0.0507</td>
<td>1.5528</td>
<td>6.1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>15</td>
<td>0.0809</td>
<td>1.8330</td>
<td>3.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>60</td>
<td>0.0614</td>
<td>1.8611</td>
<td>3.9</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure 2.17 shows the comparison of elastic modulus values for randomly oriented CNF composites predicted using the length distributions obtained after 4, 5, 15, and 60 min. sonication. The predictions are made for 1 wt% CNF/epoxy composites. The modulus of the baseline epoxy was experimentally determined by DMA to be 2.36 GPa, and the modulus of CNFs used in the calculations was 200-300 GPa [69]. CNF/epoxy composite modulus increases with increase in average aspect ratio of CNFs. The increase in modulus value also depends on the modulus of CNFs. However for a small aspect ratio, the difference in predicted elastic modulus does not depend significantly on the modulus of CNFs. The length distribution obtained after 4 to 5 min. of sonication is estimated to improve the modulus by 11-14%, whereas longer sonication times that result in smaller aspect ratios will increase the modulus by 7-10% at best. However, the models discussed in Section 2.3 predict that elastic modulus of the composites can be further increased if all the CNFs are aligned in the loading direction. Using the same length distributions, the elastic modulus of composites with aligned CNFs is shown in Figure 2.18. The two models predict different values for the increase in elastic modulus. This could be because of the assumptions made to develop these models. Out of the two models considered here, modified Halpin-Tsai model is widely used to predict the improvement in elastic modulus of short fiber
composites. Based on modified Halpin-Tsai model, aligning CNFs can increase the modulus of baseline epoxy composite by 20-23% for $l/d$ ratio of 35 and 30-37% for $l/d$ ratio of 61.

**Figure 2.17** Elastic modulus predictions for randomly oriented CNF/epoxy composites using length distributions obtained after 4, 5, 15, and 60 min. of sonication (wt% of CNF = 1%; CNF dia.= 100 nm)

**Figure 2.18** Elastic modulus predictions for random and aligned CNF/epoxy composites using length distributions obtained after 4, 5, 15, and 60 min. of sonication (wt% of CNF = 1%; CNF dia.= 100 nm).

**2.6.5 SEM micrographs of fully cured composites**
From the above analysis, it was determined that a sonication time of 5 min. is the best alternative to disperse u-CNFs for making composites. Also from previous analysis, a-MWCNTs were found to be better than e-MWCNTs for dispersing. Therefore, for making composites with unfunctionalized MWCNTs, only a-MWCNTs are used. **Figures 2.19-2.26** show the dispersion
of CNFs and CNTs in fully cured composites. u-CNFs dispersed as expected after 5 min. of sonication. Occasionally, there were agglomerates which appeared not dispersed after sonication as shown in Figure 2.19c. The dense packing of CNFs in the observed agglomerates is an indication that particles in the agglomerates never separated. These agglomerates of undispersed CNFs were expected after 5 min. of sonication as observed in Figure 2.15e. However, an unexpected observation was the reagglomeration of dispersed CNFs as shown in Figure 2.19d. No reagglomerated CNFs are seen in Figure 2.15e. The reagglomeration of dispersed CNFs results in a highly non-uniform dispersion that might adversely affect composite properties. This reagglomeration of CNFs is believed to occur during the step of acetone evaporation. It is known that well dispersed CNTs reagglomerate on mildly shearing the suspension of CNTs in epoxy [21]. Since the mixture of CNF/epoxide/acetone was continuously stirred as acetone evaporated, there is a possibility that the CNFs reagglomerated under the influence of shearing forces. The state of PEI-CNFs dispersion was similar to u-CNFs. Agglomerates and reagglomerated PEI-CNFs were observed on the fractured surfaces. However, PEI-CNFs formed a strong bond with the matrix as can be seen in Figure 2.20c. The PEI-CNFs pulled out of the fractured surface still have matrix bonded to the surface. The good adhesion between the matrix and PEI-CNFs indicates that the interface bond is stronger than the strength of the matrix which is typically in the range of 70-100 MPa. In comparison, the clean surface of unfunctionalized CNFs hanging out of the fractured surface indicates poor bond between the fiber and matrix (Figure 2.19c, d). A better bond between fibers and matrix is anticipated to improve elastic modulus of the composite.

All the CNTs investigated dispersed well after 5 min. of sonication except for PEI-MWCNTs (Figures 2.21-2.26). Occasionally, reagglomerated PEI-MWCNTs were observed on the fractured surface (Figure 2.22). Also the amount of PEI-MWCNTs observed on the fractured surface is considerably less in comparison to a-MWCNTs. The functionalized CNTs are expected to be heavier than unfunctionalized CNTs due to the presence of polymer on their surface. The PEI polymer adsorbed on the surface of CNTs is reported to be 6-8% by weight of CNTs. Since the MWCNTs were added on a wt% basis, the total number of CNTs is less for functionalized CNTs than unfunctionalized CNTs. A similar observation is made for Amine2-MWCNTs (Figure 2.23). The number of Amine2-MWCNTs visible per unit area is less than a-
MWCNTs (Figure 2.21). However, in case of Amine2-MWCNTs the exact amount of CNT to polymer weight ratio is not known. Amine1-, Z- and COOH-MWCNTs dispersed well in the matrix as can be seen in Figures 2.24-2.26.

On analyzing the dispersion of CNFs and CNTs, it appears that PEI polymer does not act as a good dispersant. Both PEI-CNFs and PEI-CNTs reagglomerated after dispersion. The reagglomeration appears to have resulted due to the use of acetone. The nanoparticles reagglomerated during the step of acetone evaporation. Use of acetone is necessary to obtain CNFs and CNTs with longer lengths. In dispersing procedures where acetone is used, the PEI polymer appears to be not useful as a dispersant but can definitely provide a strong link between the matrix and nanoparticles. Therefore, use of PEI polymer along with acetone can be expected to improve the interfacial bond between the fibers and matrix and not dispersion. Also, the use of Triton-X 100 resulted in poor dispersion of u-CNFs. However, Triton-X 100 has been successfully used to disperse u-CNFs as shown in reference [3]. The procedure used to disperse u-CNFs in reference [3] did not use acetone. It is possible that the acetone evaporation procedure reagglomerated CNFs. A similar observation is made for Amine2-MWCNTs. The CNTs appear to have dispersed well, but reagglomerated during the evaporation of acetone.

On the other hand, the well dispersed a-, Amine1-, COOH-MWCNTs indicates that BYK 9076 as a surfactant, and Amine1- and COOH- functionalizations, work well with acetone and can maintain the dispersion under the influence of mild shear forces.
Figure 2.19 SEM micrographs of fractured surfaces of 1 wt% u-CNF/epoxy composite.
Figure 2.20 SEM micrographs of 1 wt% PEI-CNF/epoxy composite’s fractured surface.

a) Region with well dispersed CNFs

b) Region showing a CNF agglomerate

c) Wetting of CNF by epoxy

d) CNF with PEI coating

Figure 2.20 SEM micrographs of 1 wt% PEI-CNF/epoxy composite’s fractured surface.
Figure 2.21 SEM micrographs of 0.5 wt% a-MWCNT/epoxy composite’s fractured surface.

Figure 2.22 SEM micrographs of 0.5 wt% PEI-MWCNT/epoxy composite’s fractured surface.
Figure 2.23 SEM micrographs of 0.5 wt% Amine2-MWCNT/epoxy composite’s fractured surface.

Figure 2.24 SEM micrographs of 0.5 wt% Amine1-MWCNT/epoxy composite’s fractured surface.
2.6.6 Elastic modulus of fully cured composites

Figure 2.27 compares the measured elastic modulus of CNF/epoxy composites. Also plotted on the same graph are the expected values based on the length distribution of CNFs after 5 min. of sonication. Two specimens from the same batch for each kind of CNF/epoxy materials were tested and are reported in Figure 2.27. However, two specimens each from two different batches
were tested to obtain the baseline epoxy modulus. The use of unfunctionalized CNFs improved the measured elastic modulus of baseline epoxy by 5%. This increment is within the scatter observed in the measured values of the baseline epoxy. Moreover, the increment is less than the 11-14% increment predicted by the model. The less-than-expected increase in modulus could be a result of the poor bonding and non-uniform dispersion seen in the u-CNF/epoxy composite (Figure 2.19). However, the PEI-CNF composites clearly show improvement in modulus and the measured values agree well with model predictions. The better bond formed by the functionalized CNFs with the matrix (Figure 2.20c) could be the reason for this improvement.

Figure 2.27 Experimentally measured elastic modulus for 1 wt% CNF/epoxy composites. The scatter bar shows the difference between two specimens from the same batch for CNF/epoxy composites, and a total of four specimens for baseline epoxy. Model predictions were made using the following assumptions, dia of CNFs = 100 nm, CNF modulus = 200 & 300 GPa.

In order to predict the modulus of MWCNT/epoxy composites, the residual lengths of a-MWCNTs were measured from SEM micrographs of MWCNTs collected on a glass plate after 5 min. of sonication in the mixture of epoxide and acetone. The weight fraction of a-MWCNTs in epoxide/acetone mixture was equivalent to 0.5 wt% in resin. At the end of 5 min., a small amount of mixture (~ 5 ml) from the suspension of a-MWCNT/epoxide/acetone was transferred
in a 250 ml beaker containing 100 ml of acetone. The diluted mixture was stirred for 2 min. using a magnetic stirrer at slow speed (~100-200 rpm). After stirring, roughly 0.5 ml sized drops were placed at 5 to 6 locations on glass slides coated with indium tin oxide (ITO). The size of ITO glass slides was 2.5×2.5×0.1 cm. Only one surface of the glass slides was coated with ITO. The ITO coated glass slide was kept at room temperature for 24 hours to allow acetone to evaporate. The deposit of CNTs on the glass slide was then imaged using SEM. Three glass slides with CNT deposits were prepared for measuring the lengths of a-MWCNTs. The lengths of a-MWCNTs were later measured from the SEM micrographs using ImageJ software (http://rsbweb.nih.gov/ij/). The length distribution is shown in Figure 2.28. This length distribution is used for predicting the improvement in elastic modulus of the composite using CNTs as reinforcements. The parameters used for predicting the elastic modulus of MWCNT/epoxy composite are given in Table 2.4.

Figure 2.28 Probability density distribution of a-MWCNT lengths after 5 min. of sonication in epoxide/acetone mixture. Sonication done at 900 W, 20 kHz on a mixture of epoxide and acetone mixed at a ratio of 20 ml:10 ml, epoxide to curative, containing a-MWCNTs equivalent to 0.5 wt% in resin (epoxide+curative). Probability density = (No. of counts/(Total no. of counts× histogram bin width)). Histogram bin width = 0.1 µm. SEM micrograph shows a-MWCNTs deposited on ITO glass slides.
Table 2.4  Values of parameters used to predict improvement in elastic modulus of randomly oriented MWCNT/epoxy composite using equations (2.2)-(2.9).

<table>
<thead>
<tr>
<th>Sonication time, min.</th>
<th>$a$</th>
<th>$b$</th>
<th>$l_{mean}$, µm</th>
<th>Random orientation</th>
<th>Aligned</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$p$</td>
<td>$q$</td>
</tr>
<tr>
<td>5</td>
<td>1.2807</td>
<td>1.6856</td>
<td>0.77</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

All of the CNT composites except for COOH-MWCNT showed improvement in elastic modulus over the baseline epoxy modulus (Figure 2.29). The maximum increment in elastic modulus was achieved for Amine2-MWCNTs, and was around 33%. The a-MWCNTs also showed a large improvement in modulus of about 31%. The other CNTs, except for COOH-MWCNTs, improved the elastic modulus by 20%. A 22% improvement was predicted by the model for CNT/epoxy composites. The agreement between the measured values and predicted values is fairly good and indicates a good bond between the CNTs and the matrix, except for COOH-MWCNTs. The increase in modulus obtained using COOH-MWCNTs is only 4%. Such a negligible increase in the modulus indicates poor bonding between the reinforcement and the matrix.

![Figure 2.29](image-url)  

Figure 2.29  Experimentally measured elastic modulus for random 0.5wt% CNT/epoxy composites. The dotted line shows the expected modulus value. Predictions were made using the following assumptions, CNT modulus = 1 TPa, ave. dia. = 10 nm.
It should be noted that in some of the cases, the measured value of modulus was more than expected modulus value. A possible reason for that could be the limitations of the model used for predictions. It is important to note that the model takes into account only the effects of length distribution and not the diameter distribution. An average value of diameter was used for making the predictions. The effective reinforcement due to a fiber like particle actually depends on the aspect ratio (length/diameter ratio) of the particles and not on the lengths. Using models that can take into account the effects of aspect ratio distribution would further enhance the correlation between the experiments and the theory.

2.7 Conclusions
This section is broken down to reflect the effects of type of nanoparticles, viscosity of the suspension, time of sonication, and functionalization of nanoparticles on dispersion and elastic modulus of the fully cured composites.

Type of nanoparticles
a-MWCNTs dispersed readily in comparison to e-MWCNTs. A longer sonication time was needed to disperse e-MWCNTs in comparison to a-MWCNTs. The reason for that is the highly entangled state of e-MWCNTs. A similar effect was observed for entangled and untangled CNFs. The as-received u-CNFs required more sonication time as compared to shortened and untangled CNFs. More work is needed to disperse entangled than untangled CNFs and CNTs.

Viscosity of suspension
Use of diluted epoxide was found to be better than plain epoxide in dispersing CNFs and CNTs. The process of sonication can be adequately described by the theory of cavitation. A physical explanation based on the decaying strain rate around a cavitation bubble captures the effect of suspension viscosity on particle dispersion. The rate of dispersion of particles decreases with an increase in suspension viscosity.

Time of sonication
The length of CNFs decreases and the degree of dispersion increases with an increase in sonication time. The length decreases rapidly in the first few minutes of sonication, but reaches a terminal length beyond which no reduction in length occurs. For the investigation conducted here, the strain rate generated by ultrasonication in mixture of epoxide and acetone is determined
to be $10^8 \text{s}^{-1}$. For a mix ratio of 20 ml to 10 ml, epoxide to acetone, 5 min. of sonication was found to be adequate to disperse CNTs and CNFs. An aspect ratio close to 60 was obtained after sonication for both CNFs and CNTs. A similar aspect ratio of MWCNTs is reported in the literature for dispersion using a three roll mill [21]. The expected improvement in elastic modulus for this aspect ratio is 20-30% for randomly oriented CNF and CNT composites.

Dispersion of CNFs and CNTs

Amine1-, Z- and COOH-MWCNTs dispersed well in epoxy composites. The use of Amine1 and COOH functionalizations provided better stability to CNT suspensions against mild shearing forces. On the other hand, PEI functionalization for CNFs and CNTs did not work well as a dispersant against mild shearing forces. The process of acetone evaporation reagglomerated PEI functionalized CNFs and CNTs. Use of Triton-X 100 resulted in reagglomeration of u-CNPs dispersed using acetone, whereas BYK 9076 provided stable dispersion of a-MWCNTs using the same dispersion procedure as u-CNFs. It can be concluded that BYK 9076 is a better choice in comparison to Triton-X 100 for dispersing nanoparticles in mixture of liquid epoxide and acetone.

Elastic modulus

A 20-30% improvement observed for Amine1- and Z-MWCNTs indicates a strong bond between CNTs and matrix. However, COOH-MWCNTs did not improve the modulus as expected. CNFs and CNTs functionalized with PEI polymer did not disperse well. However, PEI functionalization improved the bond between nanoparticles and matrix. The modulus increased by 20% on using PEI functionalized CNFs and CNTs. Amine2-MWCNTs also did not disperse well in the epoxy matrix, however an increase of 31% in the modulus was observed on testing the composites.

Overall, the dispersion of CNFs and CNTs must be done in diluted epoxide as opposed to plain epoxide, if longer lengths of CNFs and CNTs are desired. Sonication should not be performed for an extended period of time. Using an ultrasonic horn for about 5 min. at 900 W and 20 kHz should disperse nanoreinforcements adequately while giving an average aspect ratio of around 60. CNFs and CNTs should be functionalized with amine polymers to improve the interfacial bond between nanoreinforcements and matrix. To achieve good dispersion while using acetone
as a dispersion aid, either Amine1 functionalization or BYK 9076 surfactant should be used. An alternative to using amine functionalization or surfactant is to use non-covalently functionalized Z-MWCNTs. A good dispersion and expected improvement in elastic modulus was observed using Z-MWCNTs. Based on the predictions of the model, an additional improvement of elastic modulus can be achieved by aligning CNFs and CNTs in the direction of loading.
2.8 References


30. Bai, J. B., and A. Allaoui. 2003. “Effect of the length and the aggregate size of MWNTs on the improvement efficiency of the mechanical and electrical properties of


3 Electrokinetics of Carbon Nanofibers and Nanotubes in Liquid Epoxy

The analysis presented in this chapter provides a theoretical framework to understand the alignment and chaining of CNFs in liquid epoxide using electric fields. Due to the low viscosity of epoxy resin at elevated temperature, the high mobility of ions develops hydrodynamic forces on account of ion-electric field interactions. The hydrodynamic forces might interfere with alignment and chaining of CNTs and CNFs in epoxide. In the following paragraphs, literature review pertinent to use of electric field to align CNTs and CNFs in epoxy based composites is presented. After reviewing the literature, gaps in understanding are identified and the objectives of this investigation are stated. A theoretical framework is described to study the process of CNF chaining in liquid epoxide. Experiments designed to corroborate the predictions of theoretical framework are discussed next. Results are discussed in the following paragraphs, and in the end, conclusions are drawn and recommendations are made on manufacturing composites with aligned CNFs.

3.1 Literature review

High aspect ratio carbon nanoparticles such as carbon nanotubes (CNTs) and nanofibers (CNFs) show great promise as multifunctional nanofillers for thermoset epoxy composites due to their exceptional mechanical, electrical and thermal properties. As in high performance fiber reinforced polymeric composites, it is desired to control the orientation of CNFs and CNTs for enhancing direction-specific material properties. CNTs and CNFs can be used for tailoring polymer epoxy properties such as the elastic modulus, strength, and damping, particularly if well aligned [1-2]. Well connected networks of CNTs and CNFs can render polymeric composites sufficiently electrically conducting to be used in various applications as well [3-4]. Figure 3.1 shows networks of CNFs formed in between electrodes on application of AC electric field. Due to the high aspect ratio of CNTs and CNFs, such composites can be realized with less than 1 wt% nanofiller content [4-5].

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1The work presented in this chapter is based on the following two papers,
Recently, the use of alternating current (AC) or direct current (DC) electric fields to align nanoparticles in epoxy has shown promise [1, 6]. CNTs and CNFs suspended in liquid epoxy are polarized by the electric field and experience electrostatic torque due to the interaction of their charge and the applied field. Furthermore, oriented and polarized particles experience attraction towards each other and can form a network of chains between the electrodes. Based on these electrostatic effects, CNTs and CNFs have been aligned and assembled into conducting networks in thermoset epoxies [6-7]. The use of AC electric fields has been found to be superior to DC fields for achieving alignment and network formation in epoxy composites [7]. A uniform network of aligned nanofillers and a higher electrical conductivity in the cured composite is achieved using an AC electric field.

**Figure 3.1** Network formation of 0.2 wt% CNF dispersed in the amine curing agent in an AC electric field of 400 V/cm and 1 kHz, after 30 min. of field application. Distance between electrodes = 500 µm (Source of the image: Figure 4(c) from reference [3]).

Park et al. [6] investigated the effect of AC field strength, frequency, and application time on the alignment of single-walled carbon nanotubes (SWCNTs) in a photopolymerizable polymer. Electrical conductivity and Raman spectroscopy were used to assess the degree of SWCNT alignment in the cured resin. The aligned SWCNTs caused anisotropy in the electrical and dielectric properties of the composite material. In a related investigation involving the same materials [8], a large improvement in electrical conduction was achieved by selecting an appropriate AC frequency during composite manufacturing. Although the conductivity values in
the direction of alignment and transverse to it both increased with frequency, the conductivity in
the direction of alignment showed greater variation with frequency, resulting in increased
anisotropy in electrical conduction at higher frequencies.

Commonly, the concept of dipole-dipole interaction is used to understand the alignment and
chaining of nanoparticles in an electric field. The primary reason for using the theory of dipole-
dipole interaction to explain the assembly of particles in a nonpolar medium like epoxy is the
high viscosity and low conductivity (low ionic concentration) of that medium. Ionic movement is
suppressed at high viscosity and insufficient electro-hydrodynamic forces are present to
influence the assembly of particles. Moreover, the Brownian forces on the particles are
insignificant at high viscosities. The minute electrical currents flowing through liquid epoxy
eliminate the need to consider the effects of joule heating, as well. However, in considering the
low viscosity epoxy systems used for making high performance fiber-reinforced composites,
there is a need to consider the effects of ion mobility and Brownian forces on particle assembly.
Ions can be introduced by the use of surfactants, for example, during the manufacture of
composites with nanofillers. At elevated cure temperatures, the reduced resin viscosity increases
the mobility of the ions, shielding the applied electric field up to frequencies as high as 10 kHz.
Such shielding produces nonuniformities in the field distribution, thus changing the
electrokinetics of particles due to dielectrophoresis (DEP), induced charge electrophoresis, and
AC electroosmosis (ACEO) [9]. With the increasing use of CNFs and CNTs in engineering
applications, a wide variety of experimental observations has been reported on the assembly of
particles that cannot be satisfactorily explained by the theory of dipole-dipole interaction alone
[10-11]. The assembly of conducting particles in an electric field is influenced by various forces
such as electrostatic, electro-hydrodynamic, gravity, Brownian, electro-thermal, and van der
Waals, to name a few. Under the combined influence of aforementioned phenomena, it becomes
difficult to theoretically predict the response of particles using the theory of dipole-dipole
interaction alone, as has been commonly observed in the literature.

Although the assembly of particles in an electric field is influenced by various forces as
discussed above, the focus of this investigation is to model only the effects of electrostatic and
electro-hydrodynamic forces on particle assembly in an attempt to better understand the CNF
and CNT chain assembly in low viscosity epoxy systems typically used to manufacture high-performance fiber-reinforced composites. A finite element model of the process was developed to study the effects of AC frequency on CNF or CNT chain assembly in liquid epoxy system. The process of chain growth is analyzed by studying a conducting chain attached to an electrode. The results of modeling are corroborated with experimental observations. Such insight on the assembly of chains is expected to lead to better ways of tailoring the morphology of CNFs and CNTs at the nano-scale to enhance the multi-functionality of epoxy-based composites.

3.2 Theory

3.2.1 Dielectrophoresis

The force exerted on an uncharged, elongated particle in a non-uniform electric field can be approximated using the point dipole approximation. Such a force approximation can be justified if the scale of the spatial nonuniformity of the electric field is large compared to particle dimensions. For calculating the dipole moment, the effective moment method is commonly used [12]. The analysis presented here can be used for studying suspensions of CNFs or CNTs in a dielectric medium such as liquid epoxide/amine system. It is assumed that CNFs and CNTs are straight, have a high aspect ratio (length/diameter ~30-60) and are highly conducting in comparison to the liquid epoxy/amine system considered here. The theory discussed in the following paragraphs is equally applicable to CNFs and CNTs.

Using the effective moment method, the time-averaged electric force exerted on a CNF, commonly known as the dielectrophoretic (DEP) force, can be approximated as [13],

$$\langle \vec{F}_{DEP} \rangle = \frac{\pi r^2 l}{6} \varepsilon_f \text{Re} \left[ \frac{\vec{\varepsilon}_p - \vec{\varepsilon}_f}{\vec{\varepsilon}_f} \right] \nabla | \vec{E} |^2 \tag{3.1}$$

where $\langle \rangle$ indicates the time-averaged quantity in the brackets, $\vec{E}$ is the applied electric field at a frequency of $\omega$, $\vec{\varepsilon}_p = \varepsilon_p - i \frac{\sigma_p}{\omega}$ and $\vec{\varepsilon}_f = \varepsilon_f - i \frac{\sigma_f}{\omega}$ are the complex dielectric constants of particle and fluid respectively, $\varepsilon$ and $\sigma$ are the real dielectric constant and conductivity of the particle and the fluid, Re stands for the real part of the complex number, and $r$ and $l$ are the
radius and length of the CNF, respectively. The expression \[ \text{Re} \left( \frac{\bar{\varepsilon}_p - \bar{\varepsilon}_f}{\bar{\varepsilon}_f} \right) \], also known as the polarization factor or the Clausius-Mossotti (CM) factor, shows the influence of material properties and frequency on the magnitude and direction of the DEP force. The magnitude and direction of the DEP force also depends on the gradient of electric field magnitude. For a positive CM factor, the particle will translate towards increasing gradient of electric field magnitude. At low frequencies, the force primarily depends on the conductivities of the particle and the medium, but at higher frequencies the difference in permittivities governs the behavior of the force. For conducting particles like CNFs in epoxy, the CM factor is always positive and the particles experience a force towards a higher gradient of electric field.

Particles in a uniform electric field distort the local field due to self polarization. These polarized particles can be considered as minute dipoles initially uniformly distributed in a dielectric medium that are free to move under the influence of electric forces. The nonlinearity in the electric field around a particle attracts nearby particles to form chain-like structures. In turn, a chain distorts the field at a larger scale and grows in size by attracting neighboring chains or individual particles.

### 3.2.2 Electrorotation

The torque on a point dipole is

\[ \vec{\tau} = \vec{P} \times \vec{E} \]  

where \( \vec{P} \) is the dipole moment of the particle. Approximating CNT or CNF as a prolate spheroid, the torque acting on a particle to align the longest axis parallel to the electric field can be given by [12],

\[ \langle \vec{\tau} \rangle = 4\pi^2 \varepsilon_0 \varepsilon_f \text{Re}\{K(\omega)\} |\vec{E}|_{rms}^2 \sin \theta \]  

\[ \text{Re}\{K(\omega)\} = \text{Re} \left( \frac{\varepsilon_p - \varepsilon_f}{\varepsilon_f (\varepsilon_p + \varepsilon_f)} \right) \]  

where \( \theta \) is the acute angle between the electric field direction and CNF’s long axis.

### 3.2.3 Alternating current electroosmosis

Liquid epoxy contains ions that are introduced during the manufacturing of epoxy polymer or through chemical compounds added to aid the dispersion of particles. This is not to say that
liquid epoxy has a net charge; the polymer is electrically neutral. These ions are present as ion pairs and dissociate in the presence of an appropriate chemical or electric field. The dissociated ions can then form a layer around electrically charged surfaces, commonly referred to as the double-layer. Given the high concentration of one kind of ion in the double-layer, it is possible to translate the fluid in the double-layer by applying an electric field. Such a motion of the fluid in the double layer due to the action of the electric field on ions is known as electroosmosis. Ions can be moved by the application of DC or AC electric fields. The fluid motion generated by a DC electric field is known as DC electroosmosis and that by an AC field as AC electroosmosis (ACEO). The fluid flow referred to in ACEO is the time-averaged motion and not the instantaneous response of the fluid. In ACEO, the electric field acts on its own induced double-layer charge at electrically charged surfaces. Since both the charged layer and the electric field reverse sign simultaneously in case of ACEO, the net fluid flow direction is unchanged [14-15]. The fluid flow generated by AC fields is studied extensively in the field of microfluidics, where the focus is on transporting water through micron sized channels.

The magnitude of the fluid velocity in ACEO is frequency dependent and is expected to influence particle chaining under various electric field frequencies. Following the work of Levitana et al. in [16], the assumptions made to model the growth of chains in liquid epoxy/amine system are: liquid is considered neutral in the bulk with thin, charged double layers at polarizable surfaces. The bulk and the double layers are represented by linear circuit elements. Using this ubiquitous approximation, the problem simplifies to a leaky dielectric (the bulk), and a thin capacitor skin (the double layer) on charged surfaces of the electrodes and chains. Assuming no significant ionic variations in the bulk, the electrostatic potential in the bulk, $\phi$, satisfies Laplace’s equation, $\nabla^2 \phi = 0$. For the capacitor, the usual “RC” boundary condition equates the ionic bulk current to the double-layer charging. On all the charged surfaces,

$$\sigma_f \hat{n} \cdot \nabla \phi = C_D \frac{d\zeta}{dt} \quad (3.5)$$

where $\hat{n}$ is the unit normal to the surface, $\sigma_f = \varepsilon_\text{f} D / \lambda^2$ is the bulk conductivity, $C_D = \varepsilon_\text{f} / \lambda$ is the capacitance of the diffuse part of the double layer, $\varepsilon_\text{f}$ is the permittivity of liquid epoxy, $D = k_B T/6\pi \eta a$ is the ion coefficient of diffusion, $k_B$ the Boltzmann constant, $T$ is the absolute temperature, $\eta$ is the dynamic viscosity of liquid epoxy, $a$ is the diameter of the hydrated ions,
\[ \lambda = \sqrt{\frac{\varepsilon_f D}{\sigma_f}} \] is the thickness of ionic double-layer, and \( \zeta \) is the local zeta potential (voltage drop across the diffuse part of the double layer), which is non-uniform in time and space. The zeta potential is related to the total voltage across the double-layer by:

\[ \zeta = \phi_0 - \phi \]  

(3.6)

where \( \phi_0 \) is the potential of the charged surface and \( \phi \) is the potential in the bulk just outside the double-layer. It should be noted that the Stern layer at charged surfaces is not considered in this analysis. Additionally, the double-layer is considered only around the chains and on the electrodes, but not around individual particles. The double-layer around individual particles is ignored because of its size in comparison to the minimum dimension of CNFs. The size of the double layer is typically of the order of the CNF diameter and plays an insignificant role in the hydrodynamics of CNF [9].

Use of an equivalent circuit model decouples the electrochemical charging dynamics of the double-layer from the fluid mechanics of the bulk. This means that the electrostatic body force on the fluid acts only in the double-layer, and is included in an effective slip velocity boundary condition on the charged surfaces.

For the type of microsystem considered in this study, the Reynolds number is usually very small. With typical velocity around 10 \( \mu \)m/s, characteristic dimension less than \( 10^{-3} \) m, viscosity around 0.03 Pa-s, and fluid density of 1200 kg/m\(^3\) the Reynolds number is less than \( 10^{-3} \). Due to such a low Reynolds number, the fluid velocity, \( \vec{u} \), satisfies Stokes’ equations,

\[ \eta \nabla^2 \vec{u} = \nabla p, \quad \nabla \cdot \vec{u} = 0 \]  

(3.7)

where \( \eta \) is the dynamic viscosity of liquid epoxy, and \( p \) is the pressure field. The effective tangential slip velocity on charged surfaces is used as the boundary condition for solving Stokes’ equations, and is given by the Helmoltz-Smoluchowski formula,

\[ u_\| = \frac{\varepsilon \zeta}{\eta} \nabla_\| \phi \]  

(3.8)

where \( \zeta \) is related to \( \phi \) by equation (3.6) and \( \nabla_\| \) is the tangential gradient of potential on the surface just outside the double-layer.
3.3 Finite element analysis

The analysis is conducted on a single chain attached to the electrode. The chain is approximated as a conducting ellipse with its longer axis equal to 100 µm and shorter axis equal to 20 µm. The thickness of the chains observed in experiments is roughly around 5 - 10 µm. For the purpose of analysis, the electrode not touching the chain and the side walls are considered sufficiently far from the chain so as to not affect the fluid flow generated in the vicinity of this chain. Without losing generality of the analysis, the chain is attached to the ground electrode giving the value of $\phi_0 = 0$ in equation (3.6). Due to the low concentration of particles (~0.05 vol% or 0.1 wt%) in the mixture of liquid epoxy and curative, it is assumed that the freely suspended particles do not alter the electric field and the dielectric properties of the mixture of liquid epoxy/amine system can be used to model the region around the chain. The region near a chain is represented in a simplified form as a two-dimensional domain of unit thickness (Figure 3.2).

![Figure 3.2 Schematic of a CNF chain attached to an electrode.](image)

To solve the Laplace’s equation for the potential in the bulk, $\Phi$ with a sinusoidal electric field with angular frequency, $\omega$, the potential is represented as

$\Phi(x,y,t) = Re\left((\Phi_R(x,y) + i\Phi_I(x,y))e^{i\omega t}\right)$, where the subscripts $R$ and $I$ represent the real and imaginary part of the complex number, and $i$ represents $\sqrt{-1}$. The boundary conditions on all the charged surfaces can then be written as,

$\hat{n} \cdot \nabla(\Phi_R + i\Phi_I) = i\omega(\Phi_R + i\Phi_I)$  \hspace{1cm} (3.9)
At the insulating boundaries, the normal component of the bulk current is set to zero \( (\hat{n} \cdot \nabla \phi = 0) \). The boundary conditions are shown in Figure 3.3.

After solving for the potential in the bulk (i.e outside the double-layer), the slip velocities at the charged surfaces are calculated using equation (3.8). These slip velocities then are used as the boundary conditions on the charged surfaces to solve Stokes’ equations. A no-slip velocity condition is applied on insulating boundaries as shown in Figure 3.3. The slip velocity at the charged surfaces is given by,

\[
\begin{align*}
\frac{\epsilon}{2\eta} (\Phi_R \frac{d\Phi_R}{dx} + \Phi_I \frac{d\Phi_I}{dx}) &= u \\
\frac{\epsilon}{2\eta} (\Phi_R \frac{d\Phi_R}{dy} + \Phi_I \frac{d\Phi_I}{dy}) &= v
\end{align*}
\]  

Equations (3.10) and (3.11) are more general form of the equation for slip velocity in equation (3.8). To solve Stokes’ equations, the pressure at the corner farthest from the chain is set equal to zero (Figure 3.3). Since the fluid flow mostly occurs close to the chain, the pressure developed due to fluid flow at the farthest corner can be assumed zero. A prescribed value of pressure is needed for the numerical solution to converge.

**Figure 3.3** Boundary conditions used for the single chain FEA model.
The equations given above are solved numerically using COMSOL Multiphysics (Burlington, MA) finite element software. The domain is meshed with an unstructured triangular mesh, with a fine mesh near the chain. The electric field away from the chain is uniform and does not require a fine mesh to capture the behavior. The system is solved using a combination of the Partial Differential Equation (PDE) and the Incompressible Navier-Stokes modes. The domain is meshed using 42115 elements. Since the model solves only for the electric potential, the values for other variables in equations (3.5)-(3.11) were considered constant. Table 3.1 shows the values of the assumed variables and constants used in the electrostatic and electro-hydrodynamic force calculations. It should be noted that the assumed values reported in Table 3.1 are temperature sensitive. Out of all the assumed values listed in Table 3.1, the liquid epoxide/curative viscosity and conductivity were measured, whereas typical values available in the literature were used for other variables. The variables were determined for a temperature of 121°C because the epoxy/curative system used in this investigation was cured at 121°C and the nanoparticles were aligned at this temperature before the system viscosity increased due to curing.

The assumptions of ion radius and diffusion constant are based on the typical values of ion mobility reported in the literature for epoxy/amine systems. The ion mobility is of the order of $10^{-6.2}$ cm$^2$/N·s for viscosities in the range of 0.05-0.1 Pa·s [17]. The well-known Einstein relationship between ion mobility, $\mu$, and ion diffusion constant, $D$ is given by:

$$\mu = D \frac{q}{k_B T}$$

(3.12)

where, $q$, is the charge carried by each ion and rest of the terms in the equation are as described earlier. From this equation the value of ion diffusion constant can be assumed to be $1.9\times10^{-12}$ m$^2$/s. With this value of ion diffusion constant, the value of hydrated ion radius can be determined using the relationship $D = k_B T / 6\pi \eta a$, and the thickness of double layer using $\lambda = \sqrt{\varepsilon_f D / \sigma_f}$. The FEA modeling steps used to generate all the numerical results in this chapter are given in the Appendix A.
3.4 Materials
Specimens for this investigation were prepared by adding CNFs, surfactant, and an air-release agent to an epoxy resin system. The surfactant used was Triton X-100 (Bioworld, Dublin, OH) with the molecular formula (C\textsubscript{28}H\textsubscript{58}O\textsubscript{9}). The air-release agent used was BYK A 501 (BYK Chemie USA, Washington, CT), and the epoxy/amine system used was Epikote 862 with curative W, a bisphenol F/aromatic diamine system (Hexion Specialty Chemicals, Columbus, OH). The epoxy/amine system was mixed at a ratio of 100:26.4 epoxy to amine, and this mixture (epoxy+amine) was used for determining all the weight percentages of particles used in this investigation. The unfunctionalized CNFs are a commercial product designated Pyrograf\textsuperscript{®}-III PR-24 HHT (Applied Sciences Inc., Cedarville, OH), with diameters in the range of 60–150 nm and as-received lengths of 30–100 \( \mu \)m, according to the manufacturer. The concentration of CNFs used varied between 0.005-0.1wt%.

Table 3.1 Values of variables and constants used in the FEA model.

<table>
<thead>
<tr>
<th>Constants</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF conductivity(^1)</td>
<td>( \sigma_p )</td>
<td>( 10^4 ) S/m</td>
</tr>
<tr>
<td>CNF permittivity(^1)</td>
<td>( \epsilon_p )</td>
<td>(-10^3 \times 8.854 \times 10^{-12} ) s(^4)A(^4)/m(^3)kg</td>
</tr>
<tr>
<td>Liquid epoxy w/ curative conductivity(^2)</td>
<td>( \sigma_f )</td>
<td>( 0.5 \times 10^{-7} ) S/m</td>
</tr>
<tr>
<td>Liquid epoxy w/ curative permittivity(^1)</td>
<td>( \epsilon_f )</td>
<td>( 10 \times 8.854 \times 10^{-12} ) s(^4)A(^4)/m(^3)kg</td>
</tr>
<tr>
<td>Hydrated ion radius(^3)</td>
<td>( a )</td>
<td>5 nm</td>
</tr>
<tr>
<td>Liquid epoxy w/ curative dynamic viscosity(^2)</td>
<td>( \eta )</td>
<td>( 30 \times 10^3 ) Pa\cdot s</td>
</tr>
<tr>
<td>Boltzmann constant(^4)</td>
<td>( k_b )</td>
<td>( 1.38065 \times 10^{-23} ) m(^3)kg/s(^2)K</td>
</tr>
<tr>
<td>Temperature</td>
<td>( T )</td>
<td>393 K</td>
</tr>
<tr>
<td>Diffusion constant(^3)</td>
<td>( D )</td>
<td>( 1.919 \times 10^{-12} ) m(^2)/s</td>
</tr>
<tr>
<td>Double-layer thickness(^1)</td>
<td>( \lambda )</td>
<td>58 nm</td>
</tr>
</tbody>
</table>

\(^1\) Assumed based on typical values reported in literature [13]
\(^2\) Measured experimentally
\(^3\) Estimated based on typical values reported in literature [17]
\(^4\) Universal constant
3.5 Experiments

3.5.1 Mixing procedure
The CNFs were dispersed in epoxy alone with the aid of ultrasonic agitation and surfactant for about an hour. The sonication was performed with a 900-W, 20-kHz, ultrasonic horn (Branson, Danbury, CT). Sonication was performed at 450 W for 60 min. while continuously stirring the suspension with magnetic stirrer. Mixing was done in a 2.5 oz steel container immersed in ice-cooled water bath to prevent excessive heating due to sonication. After dispersion, the curative and air-release agent were added and mixed manually using a plastic stirrer for 5 minutes. The mixture was then placed in a vacuum oven at elevated temperature and a pressure less than 1000 millitorr for 60 minutes to eliminate air bubbles in the mixture. Figure 3.4 shows CNFs dispersed in the liquid epoxy/amine mixture. The well dispersed CNFs have lengths in the range of 1-10 µm, and are nearly straight. It should be noted that the lengths of CNFs after dispersion are considerably shorter than the lengths reported by the manufacturer. This shortening of CNF length occurs due to the scission of CNFs induced by ultrasonication [18].

Figure 3.4 Optical micrograph of CNFs dispersed in liquid epoxy/amine mixture (CNF wt% = 0.1).
3.5.2 Cell description
The cell used for the visual observation of rotation and chaining of CNFs consisted of a glass microscope slide with two parallel electrodes as shown in Figure 3.5. As voltage was applied to the electrodes with an AC power supply, a microscope mounted on a positioning stage and equipped with a CCD camera was used to record the movement of CNFs in the cell. For measuring the rate of rotation of CNFs in liquid epoxy, 2-mm-thick pieces of aluminum sheet were used as electrodes. The electrodes were bonded to the glass slides using epoxy adhesive. To investigate the process of chain development, the electrodes were segments of 100-μm-thick aluminum adhesive tape. The cell for this investigation was 22-mm wide and was as thick as the electrodes. The gap between the electrodes was varied between 0.5 and 25 mm.

Figure 3.5 Schematic of the experimental setup for studying particle chaining.

3.5.3 Rate of rotation of CNFs
To investigate the rate of rotation of CNFs, electrodes were spaced 0.5 mm apart and the cell was filled with liquid CNF/epoxy/amine mixture having 0.005 wt% of CNFs. The experiments were performed at 121°C. Use of such a small amount of CNFs provided better optical clarity and precise particle tracking. The rate of rotation is calculated by post analyzing the videos recorded at a speed of 30 frames per second. The videos were analyzed frame by frame to track the motion of CNFs. The software used for analyzing the videos is called VirtualDub, and is available for free download from multiple websites on the internet.

3.5.4 Morphology of chains
For investigating the morphology of chains, electrodes were spaced 1 mm apart and the space between the electrodes was filled with liquid CNF/epoxy/amine mixture having 0.1 wt% of CNFs. The experiments were performed at an elevated temperature of 121°C. As the degree of cure advances, the viscosity of the resin increases and hinders the process of alignment. Therefore, it is important to determine the time available for achieving alignment. For this
purpose, the viscosity of the epoxy/amine system without CNFs was measured as a function of time using Brookfield viscometer (Figure 3.6). At this temperature the viscosity of epoxy/amine system was measured to be 0.03 Pa·s. The chaining of CNFs was achieved prior to gelling of the epoxy/amine system. The epoxy/amine system gels in about 1 hour at 121°C. The electric field was applied at 50 Vrms until the CNFs aligned and formed chains spanning the electrode gap. The chains formed within 5 minutes.

![Figure 3.6 Viscosity of Epikote 862/curative W system at T = 121°C as a function of time after mixing.](image)

3.5.5 Rate of chain growth
For determining the rate of chain growth, a 25-mm spacing was chosen between the electrodes and a voltage of 50 Vrms was applied. The electric field was applied for 30 minutes, and the average length of the chains was measured. The experiments were done at 121°C. The range of frequencies investigated was from 100 – 100,000 Hz. For the durations electric field was applied, the viscosity of epoxy/amine system did not change due to curing (Figure 3.6).

3.5.6 Extension of chains
To investigate the extension of chains, the gap between the electrodes was varied between 1 and 2 cm. Plain epoxide with no curing agent was used for the case of 1 cm gap between the electrodes, while curing agent was added to epoxide at 26.4 pph for the second experiment where the gap between the electrodes was 2 cm. After the gap was filled with plain epoxide or mixture
of epoxide and curing agent, a 5-mg drop of CNF/epoxide solution was added into the cell in a localized position near one electrode. On account of the viscous nature of liquid epoxide (approximately 30 cP at the test temperature of 121°C), the CNFs did not diffuse far from the location of drop during the experiments. After all the materials were added to the cell, a cover glass was placed on top, as shown in Figure 3.5.

3.6. Results
In this section, the results of the numerical analysis are presented first. Using these results, the chain morphology and rate of chain growth are predicted and later corroborated by comparing them to experimental observations.

3.6.1 Electrorotation
The electric torque experienced by particles in an AC field is frequency dependent. The frequency dependence of electric torque is plotted in Figure 3.7. The torque is dependent on frequency through the factor $K(\omega)$. The value of $K(\omega)$ decreases with increasing frequency. This implies the torque on CNFs decreases with increasing frequency. Assuming that the viscous drag does not change with frequency, CNFs will take more time to align at higher than lower frequencies. To verify these predictions, experimentally measured times for aligning 4±0.5 μm long CNFs oriented at an angle of 45±5 deg. to the electric field direction are plotted in Figure 3.8. Clearly, it can be seen that more time is taken at 1 MHz in comparison to 100 Hz. Since the measured values qualitatively follow the trend predicted by equations (2.3) and (2.4), a point dipole description of individual CNFs is considered as a suitable approximation for predicting the DEP force on CNFs.
The DEP force depends on the dielectric properties of the medium and the particles and the parameters of the applied electric field. The gradient in electric field and the mismatch in dielectric properties between the particles and the medium determine the direction of the DEP force. For the results presented below, the permittivities of conducting CNF particles and liquid

**Figure 3.7** Variation of $1/K(\omega)$ with frequency. $1/K(\omega)$ is directly proportional to the time required to orient CNFs in the direction of an electric field.

**Figure 3.8** Time to align $4\pm0.5$ μm long CNFs oriented at an angle of $45\pm5$ deg. to the electric field direction. ($T=120^\circ$C, wt% = 0.005). The scatter bars represent the variation observed between 5 particles.

### 3.6.2 Effect of DEP force

The DEP force depends on the dielectric properties of the medium and the particles and the parameters of the applied electric field. The gradient in electric field and the mismatch in dielectric properties between the particles and the medium determine the direction of the DEP force. For the results presented below, the permittivities of conducting CNF particles and liquid
epoxy are assumed to be constant for frequencies up to 100,000 Hz. The chain of CNFs is assumed to have conductivity equal to that of a CNF with perfectly conducting inter-CNF contacts. The value of uniform electric field determined by dividing the voltage by the distance between the electrodes is 100 V/cm. The convergence of the FEA results was verified by increasing the number of elements till the variation in the results was within ±5%. The automatic mesh-refine feature of the software was used to increase the number of elements throughout the domain. The difference in results was found to be within 5% on almost doubling the number of elements. **Figure 3.9** shows the direction of increasing electric field magnitude. These arrows also show the direction of the DEP force around the chain because the CM factor is a positive number (equation (3.1)). The light and dark colored areas represent the regions of attractive and repulsive DEP forces, respectively. If the horizontal component of the DEP force is towards the chain, the force is considered attractive. Otherwise, it is repulsive. It should be noted that this distribution of electric field captures the effect of double-layer charging around the chain and the electrodes. Due to the dependence of double-layer charging on frequency, the ionic double-layer shields the charge with varying intensity, thus altering the magnitude of electric field gradient. For example, the variation of the square of electric field magnitude with frequency at point A in **Figure 3.9** is shown in **Figure 3.10**. The value of this magnitude increases with frequency due to the reduced shielding of the electric field by the incompletely charged double-layer, but the spatial distribution remains same for all the frequencies. At higher frequencies (>1000 Hz), the restricted movement of the ions prevents complete charging. This configuration of the chain provides a DEP force on the particles that is attractive in front of the tip, but repulsive near the root where the chain touches the electrode. The repulsion around the root of the chain tends to reduce the concentration of particles close to the electrode, thereby diminishing the chances of a new chain formation in this region. The magnitude of this repulsion determines the spacing between chains originating at the electrodes. That is, all else the same, a stronger repulsive force at the root of a chain would tend to give a larger spacing between the chains as compared to a weaker force.
Figure 3.9 Direction of increasing electric field magnitude, which corresponds to the direction of DEP force on CNFs because the CM factor is positive in this case.

Figure 3.10 Variation of the square of electric field gradient at point A (coordinates of point A, x = 0.5×10^{-4} m, y = 1.5×10^{-4} m). Points are calculated values; straight line between points added to show trend.
Since both the gradient of electric field and the CM factor are dependent on the frequency, a plot of the product of CM factor and the square of electric field gradient versus frequency for point A in Figure 3.9 is shown in Figure 3.11. The value of this product decreases with frequency. Realizing that the spatial distribution of the electric field does not change with frequency, the numerical value of this product will decrease with increase in frequency for any point around the chain. It is therefore anticipated that the decrease in the repulsive DEP force around the chain with increased frequency would increase the density of chains attaching to the electrode and growing parallel to each other.

The alignment and structure of CNF chains formed in the epoxy/amine system held at a constant temperature of 121°C was investigated as functions of the applied AC frequency to validate the FEA model. It was observed that the chains initially grew from the electrodes and their morphology is dependent on the frequency of electric field. As can be seen in Figure 3.12, the higher tested frequencies (10 kHz and 100 kHz) resulted in denser chain patterns or, in other words, more chains per unit area of the cell. An increasing chain density with frequency indicates a decreasing force of repulsion between any given chain and nearby particles being attracted to the electrode to initiate a new chain, as predicted by the model. An outcome of closely spaced chains is that the quantity of cross-links between the chains increases, as shown in

Figure 3. 11 Variation of the frequency dependent part of the DEP force at point A in Figure 3.9. Points are calculated values; curved line between points added to show trend.
Figure 3.12. These cross-links provide conducting pathways transverse to the applied electric field direction, thereby increasing the conductivity in the transverse direction. The cross-links are formed by shorter chains branching off at an angle or two larger chains collapsing together due to chain coarsening as explained in [6].

3.6.3 Effect of fluid flow due to ACEO
When electric field is applied to a suspension of conducting particles, the movement of particles is influenced by the electro-hydrodynamic motion of the fluid as explained in Section 3.2.3. Figure 3.13 shows the direction of fluid flow around a chain attached to an electrode based on a finite element simulation. As in Figure 3.9, the light and dark colored areas represent the regions of attractive and repulsive ACEO forces, respectively. The fluid moves towards the tip and runs along the length of the chain generating a viscous drag that pushes the chain towards the
electrode. The directions of fluid motion and DEP force are similar at the tip and root of the chain, bringing CNFs close to the tip and repelling them near the electrode.

![Diagram showing fluid flow and forces around a CNF chain](image)

**Figure 3.13** Direction of fluid flow around a conducting chain attached to an electrode ($E = 100$ V/cm, $f = 100$ Hz)

The magnitude of fluid velocity at the tip of the chain, as a function of electric field strength, is plotted in **Figure 3.14**. The quadratic dependence of fluid velocity on field strength is a result of the nonlinearity generated by the action of electric field on its own induced double-layer charge, as shown by equations (3.7) and (3.8). **Figure 3.15** shows the dependency of fluid velocity at the tip on the frequency of the applied electric field. The fluid velocity decreases with increasing frequency. This is commonly observed in ACEO flows as the double-layer charging is inversely proportional to the applied field frequency [16].

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3.6.4 Forces on the chain

The movement of fluid generates hydrodynamic drag on the chain and is calculated by integrating the hydrodynamic stress tensor along the outer boundary of the chain. The result of hydrodynamic force vs. frequency is plotted in Figure 3.16. As expected, the hydrodynamic

Figure 3. 14 Fluid velocity at the tip of the chain as a function of electric field strength ($f = 100$ Hz). Points are calculated values; the curved line between the points is added to show the trend.

Figure 3. 15 Fluid velocity at the tip of the chain as a function of electric field strength ($E = 100$ V/cm). Points are calculated values; the straight lines between the points are added to show the trend.
force on the chain decreases with frequency. A slow moving fluid induced by high frequencies exerts less drag on the chain as opposed to a fast moving fluid induced by lower frequencies. The hydrodynamic force is plotted with a negative value to indicate that it resists chain stretching. Also shown in Figure 3.16 is the electrostatic force on the chain as function of frequency. This electrostatic force is calculated by integrating the Maxwell’s stress tensor along the outer boundary of the chain just outside the double-layer. In the thin double-layer assumption, the forces just outside the double-layer are assumed to act on the charged surface. The force is constant for frequencies ranging from 100 to 100 kHz. The electrostatic force is positive and assists in chain stretching, and is higher in magnitude than hydrodynamic force. As a result, the chain always stretches for the range of frequencies investigated, but at different rates. The chain breaks if the stretching force overcomes the force of attraction holding the particles together in a chain. In order for the chains to grow due to stretching, the point of breakage needs to be repaired by fresh particles. The position where chain breaks becomes a nucleus for the addition of fresh CNFs on account of dipole-dipole interactions and fluid flow.

![Figure 3.16](image)

*Figure 3.16* Electrostatic and hydrodynamic forces as a function of frequency ($E = 100$ V/cm)
3.6.5 Rate of chain growth
The rate of chain growth can be broken down into two fundamental processes: particle addition, and chain stretching. The addition of particles at the tip and at the broken part of a chain is governed by the magnitude of the DEP and hydrodynamic forces. Since the directions of DEP and hydrodynamic forces (as shown by the direction of fluid flow in Figure 3.13) on the particles around the tip of the chain are the same, the net force on the particles is in the same direction. Although it is not shown here, the directions of DEP and hydrodynamic forces around a break in a chain are also the same. The decrease in the DEP and hydrodynamic forces with frequency, as shown in Figure 3.11 and Figure 3.16, decreases the rate of particle addition with frequency. Since both the particle addition and chain stretching are frequency dependent, it is anticipated that the growth of chains is also frequency dependent.

It is assumed that the rate of chain growth is a summation of the rate of particle addition at the tip and the rate of stretching. The rate of stretching, in turn, depends on the rate of chain breakage and particle addition where the chain breaks. As a first approximation, the rate of breakage is assumed to be proportional to the net force on the chain and the rate of particle addition due to DEP and hydrodynamic forces on the particles. The rate of stretching is then assumed to be proportional to the product of the DEP and hydrodynamic forces on the particles in the vicinity of the chain break and the net force on the chain. If the rate of particle addition at the tip is defined by function $CT(\omega)$, the rate of particle addition at the point of chain break by $CB(\omega)$, and the rate of chain breakage by $CS(\omega)$, then the rate of chain growth, $CG(\omega)$, can be written as,

$$CG(\omega) = CT(\omega) + CB(\omega) \times CS(\omega)$$  \hspace{0.5cm} \text{(3.13)}$$

Figure 3.17 shows plots qualitatively describing the rate of chain growth as predicted by equation (3.13). It is anticipated that the rate of chain growth will be maximum at an intermediate frequency. The reason for that is the combined effect of particle addition and stretching, which shows opposing trends with frequency.

To verify the predictions of equation (3.13) via experimental data, CNF chains were grown for 30 minutes between electrodes 25-mm apart, at frequencies ranging from 100 to 100 kHz. The
lengths of the three longest partial chains grown from each electrode were measured and averaged. Since the chains are visible only at 10X or higher magnifications, the chain lengths were measured using the horizontal dimension of the field of view (~160 µm) as a scale. The field of view was scrolled horizontally along the chains to measure their lengths. The comparison for different frequencies is shown in Figure 3.18. It can be seen that a 1 kHz frequency resulted in the longest chains. The overall trend (e.g., intermediate peak) in the chain growth vs. frequency graph matches the qualitative prediction shown in Figure 3.17. Therefore, based on the analytical and empirical evidence presented in this paper, it is concluded that a combination of electrostatic and electro-hydrodynamic forces governs the rate of CNF chain growth in liquid epoxy.

Figure 3.17 Series of graphs showing chain growth as a function of frequency.
On carefully analyzing the equation for rate of chain growth, it can be seen that chains can grow even if there is no addition of particles at the tip of the chain. This is to say that $CT(\omega)$ is zero in equation (3.13). Following the predictions of equation (3.13), chains of CNFs were grown in region of liquid epoxide where there were initially no CNFs. On application of 200 V$_{pk-pk}$ at a frequency of 100 Hz, the CNFs were observed to assemble in chains. On continued application of the electric field, the chains extended into the regions of epoxide where there were initially no CNFs (Figure 3.19), eventually spanning the distance between the electrodes. The chains that extended into plain epoxide had CNFs aligned in the direction of the applied electric field. The majority of the chains formed by this process are chains of individual CNFs as shown in Figure 3.19. It took 10-15 min. for the chains to span the 1-cm distance between the electrodes when grown from one electrode. The chains were spaced equally and did not touch each other. The extension of chains in regions with no CNFs corroborates the predictions of equation (3.13) because the chains grow due to stretching and addition of particles at the point of chain break only.

Figure 3.18 Average length of three longest partial chains on each electrode after 30 minutes at various frequencies, $V = 50$ Vrms, $T = 121^\circ$C. The scatter bars show the longest and the shortest of the three chains. The straight lines between the points are added to show the trend.

3.6.6 New method of chaining CNFs in liquid epoxy

On carefully analyzing the equation for rate of chain growth, it can be seen that chains can grow even if there is no addition of particles at the tip of the chain. This is to say that $CT(\omega)$ is zero in equation (3.13). Following the predictions of equation (3.13), chains of CNFs were grown in region of liquid epoxide where there were initially no CNFs. On application of 200 V$_{pk-pk}$ at a frequency of 100 Hz, the CNFs were observed to assemble in chains. On continued application of the electric field, the chains extended into the regions of epoxide where there were initially no CNFs (Figure 3.19), eventually spanning the distance between the electrodes. The chains that extended into plain epoxide had CNFs aligned in the direction of the applied electric field. The majority of the chains formed by this process are chains of individual CNFs as shown in Figure 3.19. It took 10-15 min. for the chains to span the 1-cm distance between the electrodes when grown from one electrode. The chains were spaced equally and did not touch each other. The extension of chains in regions with no CNFs corroborates the predictions of equation (3.13) because the chains grow due to stretching and addition of particles at the point of chain break only.
In the second experiment, curative was added to the epoxide to make rigid composites with parallel chains of aligned CNFs in a roughly 2-cm electrode gap. A voltage of 200 V<sub>pk-pk</sub> at 100 Hz was applied to grow the chains from the CNF/epoxy mixture placed in a strip-shaped region along one electrode. A frequency of 100 Hz was chosen to make fully cured composites because of the following two reasons; high voltages can be applied at 100 Hz easily using a power supply that is commonly available. Moreover, the response of CNFs to 100 Hz would be similar to 60 Hz thus allowing the use of simple transformers that operate at 60 Hz to apply high voltages. Using a step-up transformer in place of a power supply would reduce the overall cost of composite manufacturing. The other reason is that if the chains can be assembled at a frequency of 100 Hz where the hydrodynamic forces are high, then it can be expected that chains can be easily assembled at higher frequencies due to suppressed hydrodynamic interactions between the fluid and chains. The chains were assembled at the 121°C curing temperature of the epoxy. The chains had to be grown before the viscosity of the system markedly increased due to crosslinking. Chaining parameters were therefore selected to complete chain extension across the 2-cm gap in 30 minutes—the time required to double the viscosity of the Epon 862/curative W system at 121°C. **Figure 3.20** shows multiple parallel chains grown over a distance of 2 cm in the fully cured epoxy. It was observed that the growth of some of the chains ceased or slowed down due to the depletion of CNFs close to the electrodes. This limitation can be easily overcome by using a higher concentration of CNFs in the solution.
This new process requires that only a small region of epoxy between the electrodes contain CNFs, with the bulk of the region through which chains are developed being initially devoid of CNFs. It is proposed that the observed mechanism of chain assembly and growth depends on the conductive nature of CNFs and the self-repairing ability of these chains. A clear advantage of this new technique is that unidirectional conducting chains of CNFs can be assembled in regions where there are no CNFs, thus providing a means to fabricate CNF/epoxy composites with tailored anisotropy in nano-scale morphological texture leading to anisotropy in electrical, mechanical, thermal, and photonic properties. Using this technique, chains of aligned CNFs up to 2 cm long have been grown in liquid epoxy, adding to the significance of the technique for the manufacture of multi-functional structural materials.

3.7 Conclusions
The effect of AC field frequency on CNF chain assembly in liquid epoxide/amine curative system was studied by developing a FEA model for a single chain attached to an electrode and comparing the predictions with experimental observations. Two forces, electrostatic and electro-hydrodynamic, are included in the model. The assembly of chains close to the electrode is primarily governed by the DEP force experienced by neighboring particles. The chain density
increases with increase in AC frequency. With the increase in chain density, the spacing between the chains decreases, resulting in higher cross-links between chains. By using an appropriate AC frequency, it is anticipated that the electrical anisotropy in the composite can be tailored. AC frequency also affects the rate of chain growth. An intermediate frequency of 1 kHz was found to be optimal for the most rapid assembly of long chains in liquid epoxy at a viscosity of 0.03 Pa·s. The growth of chains was found to be adequately explained by considering it to be a function of chain stretching and particle addition. The stretching of chain is affected by the hydrodynamic forces generated by the fluid flow due to ACEO, demonstrating the importance of considering hydrodynamic forces in assembling CNF chains in liquid epoxy.

Based on the understanding developed on chain stretching and particle addition, a new method of chaining CNFs in liquid epoxide was discovered. Chains of aligned CNFs were assembled and extended into regions where there were no CNFs. The observed stretching of chains into regions of no CNFs revealed a new mechanism of chain growth that is different from the well-known assembly of polarized particles at the tip of the growing chain in a nonpolar medium. By contacting the chains with the electrodes, the process of chain growth was expedited and well-ordered parallel chains were grown up to large distances (∼2 cm). These chains of CNFs can be potentially used at μm to cm scales for applications in structures with electrical, thermal and photonic functions. The new understanding of chain assembly revealed in this investigation will lead to improved manufacturing capabilities for creating various nano-scale morphologies and enhanced multi-functionalities in CNF/CNT-epoxy composites.

These results can be used for understanding the mechanism of CNT chains assembly as well. Since the conductivity of CNTs is also much higher in comparison to the conductivity of liquid epoxide or mixture of liquid epoxide and curative, CNTs would essentially assemble just like CNFs. However, due to the small size of CNTs, a higher strength electric field would be required to drive CNT chain assembly. The expression for DEP force given by equation (3.1) shows the dependence of particle size on DEP force. The DEP force on a particle is directly proportional to particle’s volume. Since CNTs are smaller than CNFs, the DEP force for a given electric field strength would be less for CNTs. The growth of chains depends on particle addition which, in
turn, depends on DEP force, and thus the growth of chain rate for CNTs is expected to be slower in comparison to CNFs for a given electric field strength.
3.8 References


4 Tailoring Alignment of Functionalized and Unfunctionalized Carbon Nanotubes and Nanofibers in Epoxy Composites

4.1 Literature survey

CNTs and CNFs have been used as fillers to make otherwise insulating materials conducting. The addition of a small amount of CNTs, less than 0.1 wt%, can make epoxy composites conducting enough for electrostatic charge dissipation. Composites filled with conducting fillers show a characteristic percolation threshold [1]. At the percolation threshold, the conductivity of composite increases many fold due to the formation of a conducting network. Close to the percolation threshold, the electrical conductivity of the composite follows a power law of the form

\[ \sigma_0 \propto (\phi_V - \phi_C)^t \quad \phi_V > \phi_C, \]

where \( \sigma_0 \) is the conductivity of the composite, \( \phi_V \) is the volume fraction of the particles, \( \phi_C \) is the critical mean volume fraction for electrical percolation, and \( t \) is the exponent which is determined empirically from curve fitting the experimental data. The percolation threshold depends on the shape and aspect ratio of the particles, and can be predicted, given the volume fraction and the orientation parameters of fillers [2]. Due to the large aspect ratio and high conductivity, CNTs exhibit a lower percolation threshold than CNFs. However, the maximum conductivity is limited by the contact resistance between the particles [3]. Sandler et al. [4] reported an ultra-low electrical percolation threshold in CNT/epoxy composites using CVD-grown MWCNTs with. The resin system used was a bisphenol-A epoxy with an amine hardener. The composite’s bulk conductivity followed a percolation scaling law given by equation (3.1) with \( \phi_C \) approximately 0.0015 vol% and \( t \) around 1.2. Kim et al. [5] found a percolation threshold around 0.046 vol% of SWCNTs with a value of 1.3 for \( t \). The SWCNTs were produced by the arc-discharge method and purified by thermal oxidation and chemical treatments. On

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The work presented in this chapter is based on the following papers,


increasing the weight fraction of CNTs above 0.063 vol%, the composites exhibited ohmic conduction over a broad range of frequencies. Ounaies et al. [6] investigated the AC and DC conductivities of polyimide composites containing various concentrations of SWCNTs. The bulk conductivity of the composite was found to obey a percolation-like power law with relatively low percolation threshold of 0.05 vol.%. In order to investigate the effect of using nanofilled epoxy on the properties of conventional glass fiber reinforced composites, Gojny et al. [7] used unfunctionalized double-walled carbon nanotubes (DWCNTs) and amine-functionalized DWCNTs. The composites exhibited anisotropy in the conductivity, with higher conductivity in-plane than out of plane. A more dramatic increase in the specific conductivity of the composites was obtained using unfunctionalized DWCNTs.

The capability of using carbon nanotubes (CNTs) to sense strains and damage in fiberglass-reinforced polymeric composites has been demonstrated in recent years [8-9]. The randomly dispersed CNTs in the matrix form conducting networks providing electrical percolation at low weight fractions of CNTs [10]. By monitoring the changes in electrical conductivity of the composite, the strains, onset of cracks, and severity of damage in the matrix can be detected. As with metals and graphite, conducting CNTs undergo a change in electrical resistance with deformation and can therefore be used to sense strain in a structural element [10-11]. Not only strains, but damage inside polymeric composites can be detected using continuous conducting networks of CNTs as pass/fail sensors. The severed networks of CNTs due to the formation of cracks and delaminations alter the conductivity of the composite irreversibly [8]. This irreversible change indicates permanent damage in the composite. By simply measuring the direct current (DC) conductivity of the composite during loading, changes in strain state and severity of damage can be monitored in-situ.

The change in DC conductivity of the composites before considerable damage accumulates is commonly reported to be around 5% [12]. This change in conductivity to detect strain in the composite is even less—around 1% [9]. The small change in conductivity is because of the much higher weight fractions of CNTs used in manufacturing composites than is required to obtain electrical percolation (\( \leq 0.1 \text{ wt\%} \)). Higher weight fractions of randomly oriented CNTs provide redundant conducting pathways and multiple points of contact between CNTs. Because of higher
amount of contacts, the CNT network is presumed to be electrically less sensitive to mechanical strains. Böger et al. [9] conducted a comparative study using 0.3 wt% MWCNTs and carbon black (CB) to investigate the sensitivity of DC conductivity to mechanical strain. The change in conductivity was much higher using CB than MWCNTs. The reason for higher sensitivity was fewer points of contact between CB particles as they are spherical in shape.

In a conducting network, the CNTs are either physically in contact with each other and/or are positioned sufficiently close for electrons to tunnel through the gap between the CNTs. Based on numerical simulations, the tunneling resistance is shown to play an important role in determining the conductivity of composites [13]. The gap between the CNTs is modeled as the space between the parallel plates of a capacitor. The resistance provided by the material occupying the gap is modeled using quantum mechanics arguments and predicts an exponential increase in tunneling resistance with increase in gap size between CNTs. The cut-off distance between CNTs that would cease tunneling, and make composites insulating, is suggested to be 2 nm or more. Another factor that could potentially control the tunneling resistance is the overlap area between the CNTs. The conducting electrons hop from one CNT to another from within this overlap area. An increase in the overlap area would reduce the tunneling resistance thereby increasing the effective conduction through the gap between the CNTs. The distance, overlap area, and the points of contact between the CNTs can be controlled by manipulating the orientation of CNTs in the composites.

Efforts have been made to align and chain unfunctionalized carbon nanotubes and carbon nanofibers (CNFs) using alternating (AC) and direct current (DC) electric fields [14-17]. CNTs and CNFs have been aligned and assembled into conducting networks in thermoset epoxies over the range of a micrometer to a few millimeters using interdigitated or parallel plate electrodes [14]. In order to better realize the potential of aligned carbon nanofillers for enhancing the stiffness, strength, and electrical conductivity of structural composites, there is a need to align and network nanofillers over distances greater than a few millimeters. To be able to utilize the full potential of aligned CNFs and CNTs for increasing the stiffness and strength, it is necessary to ensure good transference of load from the matrix to CNTs. The effective reinforcement of polymeric resins by nanotubes is hindered mainly by the poor interfacial adhesion between the
nanotubes and the matrix in the absence of surface functionalization. The capability to transfer load can be enhanced by functionalizing the surface of CNTs. A wide range of functionalization methods have been attempted to increase the ability of polymers to bond to nanotubes [18-19]. Most common are covalent and non-covalent types of functionalizations. If the covalently attached or physically adsorbed chemical groups contain derivatives of amine, the functionalized nanotubes can be covalently integrated with the epoxy matrix [20-21]. The multiple amino groups on the nanotubes will form a heavily crosslinked structure between the nanotubes and the matrix, thereby facilitating the transference of load. This advantage from functionalized nanotubes can be further enhanced by aligning the nanotubes in the epoxy composites. However, chemical modification of a nanotube affects its dielectric properties. The change in dielectric properties of the particle alters its response to applied electric fields [22].

The objective of the research presented in this chapter is to extend by an order of magnitude the distance of alignment and network formation of CNFs using AC electric fields with moderate electrical requirements and to investigate the effects of electric field frequency and strength on the direction-dependent low-frequency electrical behavior of unfunctionalized and covalently and non-covalently functionalized MWCNTs composites. The underlying theory is that electric field parameters applied during processing and the chemical nature of the nanoreinforcements and surrounding medium will affect the alignment and networking of the nanoreinforcements, thereby affecting electrical behavior of the cured composite. The strength and frequency of the electric field were varied to achieve the desired objectives. The electrical properties of aligned, cured composites were evaluated to assess the effects of alignment.

4.2 Specimen preparation and testing

4.2.1 Materials

4.2.1.1 Resin material
Specimens for this investigation were prepared by adding nanoparticles to an epoxy resin system. The resin system was Epon 862 with curative W, a bisphenol F/aromatic diamine system. The resin system was mixed at a ratio of 100:26.4 epoxide to curative, and this mixture (epoxide+curative) was used for determining the weight percentages of nanoparticles added to the mixture.
4.2.1.2 Resin additives
The additives used in dispersing and making nanoreinforced epoxy composites were a non-ionic surfactant and an air release agent. The surfactant used is commercially known as Triton-X 100 (Bioworld, Dublin, OH), and was mixed at 76 weight percent of the nanoparticles. The surfactant was used to disperse unfunctionalized nanoparticles only. No surfactant was used to disperse covalently and non-covalently functionalized nanoparticles. The air release agent used in processing of all the composites was BYK A 501 (BYK-Chemie USA Inc., Wallington, CT), mixed at 0.5 wt% of the total weight of the epoxy system (epoxide+curative), to aid in elimination of air bubbles during a degassing phase.

4.2.1.3 Nanoreinforcements
MWCNT investigated are α-MWCNTs purchased from Cheaptubes Inc. (www.cheaptubes.com), non-covalently functionalized Z-MWCNTs purchased from Zyvex Performance Materials, LLC (Columbus, OH), and amine-functionalized Amine1-MWCNTs purchased from NanoLab (Newton, MA). The CNFs, referred as u-CNFs, are a commercial product designated Pyrograf® III PR-24 HHT (Applied Sciences Inc., Cedarville, OH). And the two in-house functionalized nanoparticles, PEI-CNFs and PEI-MWCNTs, were functionalized with amine polymer. The polymer used for functionalization was polyethyleneimine (PEI). The functionalization procedure is detailed in Section 2.5.4 of Chapter 2.

4.2.2 Procedure for dispersing nanoparticles
The procedure recommended for dispersing nanoparticles in epoxy in Chapter 2 was not used in this investigation because; the occasional agglomerates and reagglomerates left after sonication might interfere with alignment and chaining. By increasing the time of sonication, the nanoparticles were dispersed to the level of individual nanoparticles.

4.2.2.1 Unfunctionalized CNFs (u-CNFs) and α-MWCNTs
CNFs and surfactant were added in liquid epoxide at the desired weight percentage and mixed manually for 5 min. using a plastic stirrer. Sonication was then performed using ultrasonic horn (Branson, Danbury, CT) operating at 450 W (50% power level) and 20 kHz to disperse nanoparticles. The sonication was done for 60 min. while continuously stirring the suspension using a magnetic stirrer. Mixing was done in a 2.5 oz steel container immersed in an ice-cooled water bath to prevent excessive heating. The temperature of the mixture during sonication was around 80°C. After dispersion, the curative and air-release agent were added and mixed...
manually using a plastic stirrer for 5 minutes. The mixture was then placed in a vacuum oven at elevated temperature and a pressure less than 1000 millitorr to eliminate air bubbles in the mixture. The mixture in the steel container was degassed for 30-45 min.

4.2.2.2 Amine1-MWCNT, Z-MWCNT, PEI-MWCNT, and PEI-CNFs
Z-MWCNTs were manually mixed in an appropriate amount of epoxide using a plastic stirrer for 5 minutes. Amine1-MWCNT, PEI-MWCNT, and PEI-CNFs were mixed similarly with curative, diluted as needed using acetone to lower the viscosity of the mixture. After manually stirring the mixtures, sonication was performed with a 900-W, 20-kHz, ultrasonic horn (Branson, Danbury, CT). Amine1-MWCNTs, PEI-MWCNTs and PEI-CNFs were sonicated for 60 min. at 450 W, whereas the Z-MWCNTs were sonicated for 30 min. at a power level of 270 W. The mixtures were continuously cooled to minimize excessive heating due to sonication.

After sonication, the curative or resin (as the case may be, depending on the type of nanoparticles) was added and mixed manually using a plastic stirrer for 5 minutes. Whenever acetone was used, it was removed prior to adding the resin by keeping the mixture at 70°C for 12-24 hours. No stirring was performed while removing the acetone. Once the acetone was removed, epoxide was added to the mixture and hand mixed for another 5 min. The mixtures of nanoparticles, epoxide, and curative were then placed in a vacuum oven set to 70°C and a pressure less than 1000 millitorr to help eliminate air bubbles in the mixture. The mixtures were degassed for an hour at 70°C.

4.2.3 Experiments with CNFs to investigate the morphology of chains
To provide deeper insight on the conductivity behavior of composites, observations of the alignment and networking of the particles in liquid epoxy under the influence of electric fields would be the ideal approach. However, since the MWCNTs used here are too small to see with optical equipment, CNFs were selected on the basis of their similar aspect ratio and conductivity in comparison to MWCNTs. The conductivity of CNFs are reported to be around $2 \times 10^6$ S/m [23], while the conductivity of MWCNTs are in the range of $10^4$ to $10^7$ S/m [24]. Moreover, the response of conducting particles suspended in an insulating liquid primarily depends on the difference in the conductivities of particles and medium [22]. The conductivity of the epoxide used in this investigation is in the range of $10^{-6}$ to $10^{-8}$ S/m.
The experiments with CNFs were designed to visually determine the effect of frequency on CNF assembly. Experiments were performed at 121°C using electric field strength of 300 V/cm at frequencies ranging from 100 Hz – 100 kHz. The electric field was applied for 30 minutes before taking photographs of CNF assemblies. To observe the electrokinetic response of CNFs, an inverse microscope equipped with a CCD camera was used. A mixture of CNF and Epon 862 epoxide was used to study the electrokinetics of CNFs. Since these experiments were strictly for observations of assembly, the CNF/epoxide mixtures were not cured. CNFs were used at a concentration of 0.1 wt% to preserve optical transparency of the mixture. The electrodes were 5 mm wide by 100 µm thick and separated from each other by 5 mm. A cover glass was placed on top of the electrodes. The purpose of cover glass was to provide uniform thickness in between the electrodes.

4.2.4 Process for creating 25-mm-long u-CNF chains
The degassed mixture was carefully poured between parallel aluminum electrodes mounted on a microscope slide pre-treated with a dry PTFE release spray. The electrodes were 25 mm wide, 300 µm thick, and 25 mm apart. The electrodes were connected to an AC power supply. An inverse microscope equipped with a CCD camera was used to record the observations. The curing schedule employed was 121°C for 1 hour followed by 177°C for 2.5 hours. The electric field was applied up to 1 hour during the 121°C segment of the curing schedule. The concentrations of CNFs used to make composites ranged from 0.1 to 2 wt%.

From the results of Chapter 2, it was observed that a voltage of 50 Vrms was insufficient to assemble chains across a gap of 25 mm in 30 min. Since the frequencies of 1 kHz and 10 kHz resulted in the longest chains. It was decided to further investigate the 1 kHz and 10 kHz frequencies at higher voltages with the aim of growing chains over the entire 25-mm gap. Recall that lower frequencies enable the use of higher voltages with a given power supply. However, as mentioned earlier, different frequencies will have an effect on the morphology of the chains. The electric field was applied for 30 minutes, which was the time required for the viscosity of the resin to increase by a factor of 2. As the CNFs aligned to form chains under a constant applied voltage, the current flowing through the specimens across the electrodes was also recorded. The change in current was used as an indicator of the network formation. Using the same batch of material, control specimens were also prepared without applying an electric field in order to
evaluate the effect of the field on the electrical resistance of the CNF/epoxy composite. After curing the composites, rectangular specimens of approximate dimensions 25×25×0.3 mm were removed from the mold.

4.2.5 Manufacturing a-, Amine1-, and Z-MWCNT/epoxy composites
The degassed mixtures were carefully poured between parallel aluminum electrodes mounted on a microscope slide pre-treated with a dry PTFE release spray. The electrodes for investigating the effects of functionalization on alignment were 5 mm wide by 400 µm thick and separated from each other by 5 mm. The reason for choosing three different kinds of MWCNTs is that these three represent the most popular types of MWCNT reinforcements available for making composites.

Once the cell was completely filled with the mixture of nanoparticles and resin, controlled voltages were applied to the electrodes of the cell. The electrodes were connected to an AC power supply and the microscope slide with the mixture was placed on a hot plate. The curing schedule employed for making MWCNT composites was 121°C for 1 hour followed by 177°C for 2.5 hours. The electric field was applied up to 1 hour during the 121°C segment of the curing schedule. The concentrations of MWCNTs used to prepare specimens in this investigation were 0.5 wt%.

Since the MWCNT experiments were aimed at determining the effects of electric field frequency and strength on subsequent direction-dependent electrical behavior of the cured composite, electric fields were applied at frequencies ranging from 100 Hz – 100 kHz and strengths of 100 and 300 V/cm. An open molding process was used for the MWCNT specimens because the combination of an opaque material and a cover glass over the top of the material would have made it difficult to remove entrapped air from the mold. After fully curing the MWCNT composites, rectangular specimens were prepared for electrical measurements by grinding the thickness of the specimens to 0.4 mm using a water-cooled silicon carbide wheel. This eliminated the convex curvature resulting from the open molding process. Using the same batch of materials, control specimens were also prepared without applying an electric field in order to evaluate the effect of the field on the electrical resistance of the composites.
4.2.6 Electrical measurements of composites
DC resistances and AC impedances were measured using the 2-point measurement technique. Since the measured resistances were anticipated to be more than thousands of ohms, the contact resistances were believed to play a negligible role in determining the sample resistance. The two opposite edges were polished using a 600 grit abrasive paper and then coated with a conducting silver based solution (containing acrylic as the binder) to provide good electrical contacts. Thin copper wires were then soldered to the conducting faces. This silver based solution is commercially available under the brand name “CircuitWriter Pen” from RadioShack (www.radioshack.com). From the measured resistance, the volume resistivity of the specimen, $\rho_{DC}$, was determined using the formula,

$$\rho_{DC} = RA/L,$$  \hspace{1cm} (4.2)

where $R$ is the resistance of the specimen measured by dividing the applied voltage by the current, $L$ is the length of the specimen between the electrical contacts, and $A$ is the cross-sectional area of the specimen. Similarly for measured AC impedances, specific AC impedance is defined using the formula,

$$\rho_{AC} = |Z_{rms}| A/L,$$  \hspace{1cm} (4.3)

where $|Z_{rms}|$ is the root mean squared (rms) value of the impedance determined by dividing the rms value of the voltage with the rms value of current.

4.2.7 Manufacturing aligned CNF and CNT/epoxy composites for mechanical testing
The nanoparticles used for investigating the effect of CNF/CNT alignment on elastic modulus of epoxy composite were, u-CNFs, PEI-CNFs, PEI-MWCNTs, and Z-MWCNTs. CNFs were mixed at a ratio of 1 wt% and the concentrations of MWCNTs in the composites were 0.5 wt%. The choice of type and concentration of nanoparticles for alignment was governed by the conductivity of the CNF/CNT suspension. Electric field could not be applied to highly conducting suspensions because of excessive flow of current causing the suspension to burn due to joule heating.
The electrodes for aligning CNFs and CNTs were separated by 6 cm and were placed on a glass slide pretreated with mold release Monocoat E-340. Two 1.9-mm-thick pieces of aluminum sheet were used as electrodes. After pouring the suspension of nanoparticles/epoxide/curative between the electrodes, another glass slide was placed on top of the electrodes. The cell was left open on two edges. The surface tension of the suspension prevented the resin from flowing out of the cell. The electrodes were connected to a power supply and electric field strength of 100 V/cm was applied at a frequency of 1 kHz. The curing schedule employed for making MWCNT composites was 121°C for 1 hour followed by 177°C for 2.5 hours. The electric field was applied for 1 hour during the 121°C segment of the curing schedule.

After curing, fully cured composites of roughly 6×3×0.19 cm³ were obtained. Two rectangular specimens of dimensions 5.5×1×0.19 cm³ were then cut using water cooled diamond saw from the fully cured composite part. After cutting the specimens were immediately pat dried using paper towels and placed on a hot plat at 60°C for two hours. These specimens were tested using DMA. The tests were done at a temperature of 35°C at a frequency of 1 Hz. The strain used for obtaining the data was set at 500 με.

4.3 Results and discussion

4.3.1 Morphology of u-CNF chains
The alignment and structure of CNF chains formed in resin held at a constant temperature of 121°C were investigated as functions of the applied AC frequency. Various assemblies of CNFs obtained at different field frequencies are shown in Figures 4.1 and Figure 4.2. As can be seen in Figure 4.1, the higher tested frequencies (10 kHz and 100 kHz) resulted in denser chain patterns or, in other words, more chains per unit area of the cell. This observation is consistent with the predictions of the FEA model and experimental observations made in Chapter 3. Moreover, inspection at higher magnification reveals that the chains are cross-linked by shorter chains branching off at an angle less than 45 deg. (90 deg. being the maximum angle of a branched chain) as shown in Figure 4.2. These cross-links provide conducting pathways transverse to the applied electric field direction. At higher frequencies, the closely spaced chains develop more cross-linking between the chains (Figure 4.2). Based on these visual observations
enabled by the large size and low concentration of the CNFs, it can be expected that composites assembled at higher frequencies would demonstrate lower electrical anisotropy.

![Figure 4.1 Chains of CNFs in epoxide, assembled using various frequencies](image)

**Figure 4.1** Chains of CNFs in epoxide, assembled using various frequencies
4.3.2 Process for creation of 25-mm-long u-CNF chains
Using 145 Vrms across the 25-mm electrode gap (a value dictated by the capability of the available power supply), it was determined that, at 1 kHz, the chains of aligned CNFs spanned the gap within 6 min. On the other hand, at 10 kHz the chains did not completely bridge the gap in 30 min. The extent to which the chains grew at 10 kHz and 145 Vrms was 23 mm, which is still an order of magnitude improvement in the state-of-the-art and would render 10 kHz as an option for alignment distances less than 2 cm. Particle chains in the 145 Vrms field initiated close to the electrodes and grew in the direction of the electric field (Figure 4.3).

4.3.3 Electrical measurements on u-CNF/epoxy composites
The electrical current measured during cure can be used as an indicator of alignment and chain growth, which is a potentially valuable tool for specimens that are not optically transparent (eg., >0.2 wt% CNF). As CNFs align and form chains, the current flowing through the solution typically increases, as shown in Figure 4.3. A plateau in the current verses time curve is reached once the chains bridge the gap between the electrodes. As the resin starts to gel, a decrease in
the current is observed. The current at the end of the curing cycle is slightly lower than the maximum current value attained during the curing process.

CNFs added to epoxy at 0.1 and 0.2 wt% did not improve the conductivity of the composites within the measurement capability of the available equipment. For a low weight fraction of CNF/epoxy composite (≤0.2 wt%), the conductivity of fully cured composite is much less than the liquid mixture used to make composite. As a result, current could be measured while the mixture was curing but no current could be detected through the fully cured composite. No current at the level of nA or greater was detected at a DC voltage of 200 V. This implies a DC resistance ≥ 2×10$^{11}$ Ohms. However, the micrographs show a well aligned network of chains in the specimens (Figure 4.4). A similar behavior for a 0.2 wt% CNF/epoxy composite was obtained in Reference [15], though for a different resin system.

An increase in conductivity was observed in specimens with CNF contents of 0.5 wt% and more. Resistivities of random and aligned specimens are plotted together in Figure 4.5. Aligned specimens show resistivity anisotropy of 2. Resistivity anisotropy is an indicator of preferential alignment in the direction of electric field [14-15]. The resistivity values obtained in this
investigation are an order of magnitude lower than those reported in Reference [15], and are similar to that reported by Tibbetts et al. [25] for polypropylene/vapor grown CNF composites. It was anticipated that the resistivity of the composite in the direction of electric field applied during processing would decrease more than that in the transverse direction because of chain formation. However, only the 0.5 and 1 wt% specimens followed the anticipated behavior while the resistivity values are similar in both in-plane directions for 2 wt% composite.

4.3.4 DC resistivity of a-, Amine1-, and Z-MWCNT composites
The DC resistivities of random and aligned composites containing three different types of MWCNTs are plotted in Figures 4.6, 4.7 and 4.8. The electric field strength used for aligning MWCNTs in these composites was 100 V/cm. The DC resistivity of randomly oriented Z-MWCNT composite is $8.0 \times 10^9 \, \Omega\cdot\text{cm}$ while that achieved parallel to the electric field is roughly $1.5 \times 10^8 \, \Omega\cdot\text{cm}$. All the frequencies used at 100 V/cm resulted in similar values of DC resistivities in the parallel direction. Relative to the randomly oriented Z-MWCNT material, the transverse DC resistivity of materials prepared with electric fields were greater at lower frequencies (100 Hz to 10 KHz) and slightly less at the highest frequency (100 kHz). The transverse resistivity decreased from $1.0 \times 10^{11}$ to $4.0 \times 10^9 \, \Omega\cdot\text{cm}$ as frequency increased from 100 to 100k Hz. The DC resistivity anisotropy ratio, defined as the transverse DC resistivity divided by the parallel DC resistivity, decreased from 650 to 30 on increasing the alignment frequency.

Figure 4. 4 Evidence of chain formation in 0.1 wt% and 0.2 wt% fully cured composites using optical observations (arrows indicate direction of electric field used for alignment). Electric field strength of 100 V/cm applied at 1k Hz.

4.3.4 DC resistivity of a-, Amine1-, and Z-MWCNT composites
The DC resistivities of random and aligned composites containing three different types of MWCNTs are plotted in Figures 4.6, 4.7 and 4.8. The electric field strength used for aligning MWCNTs in these composites was 100 V/cm. The DC resistivity of randomly oriented Z-MWCNT composite is $8.0 \times 10^9 \, \Omega\cdot\text{cm}$ while that achieved parallel to the electric field is roughly $1.5 \times 10^8 \, \Omega\cdot\text{cm}$. All the frequencies used at 100 V/cm resulted in similar values of DC resistivities in the parallel direction. Relative to the randomly oriented Z-MWCNT material, the transverse DC resistivity of materials prepared with electric fields were greater at lower frequencies (100 Hz to 10 KHz) and slightly less at the highest frequency (100 kHz). The transverse resistivity decreased from $1.0 \times 10^{11}$ to $4.0 \times 10^9 \, \Omega\cdot\text{cm}$ as frequency increased from 100 to 100k Hz. The DC resistivity anisotropy ratio, defined as the transverse DC resistivity divided by the parallel DC resistivity, decreased from 650 to 30 on increasing the alignment frequency.
from 100 to 100k Hz. This observation is consistent with the observed dependence of CNF chain cross-linking on the electric field frequency (Figure 4.2). Higher transverse cross-linking between the nanoreinforcement chains when the material is processed with higher electric field frequencies provides more conducting pathways in the transverse direction.

The DC resistivities of 0.5 wt% aligned a-MWCNT and Amine1-MWCNT composites are around 100 and $10^3$ Ω-cm, respectively, which is 5-6 orders of magnitude less than Z-MWCNT composites. However, no anisotropy is observed in the a-MWCNT and Amine1-MWCNT composites subject to electric fields during processing. For a-MWCNTs the variation in resistivity is 115±15 Ω-cm. No trend in resistivity of the final composite is seen with frequency. For Amine1-MWCNT composites the resistivities obtained by applying electric fields at 100 and 1k Hz frequencies are around 2840±40 Ω-cm, and those at 10k and 100k Hz are around 1780±5 Ω-cm. In comparison, the resistivity of a 0.5 wt% randomly oriented Amine1-MWCNT composite is 3250 Ω-cm.

Figure 4.5 DC resistivity of electrically aligned and unaligned (random) CNF composites
Figure 4. 6 DC resistivity of Z-MWCNT specimens prepared with various frequencies.

Figure 4. 7 DC resistivity of a-MWCNT specimens prepared with various frequencies.
4.3.5 AC Impedance of a-, Amine1-, and Z-MWCNT composites

The rms values of AC impedances were measured in the direction parallel to the alignment field for samples prepared at 100 V/cm. The rms value of AC impedance, $|Z_{\text{rms}}|$, was measured as a function of frequency. Figures 4.9, 4.10, and 4.11 show the specific AC impedances of Z-MWCNT, a-MWCNT, and Amine1-MWCNT specimens, respectively. The specific impedance of Z-MWCNT specimens decreases with increasing frequency, whereas the impedance is independent of the measurement frequency for a-MWCNT and Amine1-MWCNT specimens. The frequency-dependent AC impedance indicates a typical dielectric behavior. A possible reason for this could be the polymer that wraps around Z-MWCNTs in case of non-covalent functionalization [26]. The polymer introduces a capacitive nature at the junction between MWCNTs. On the other hand, a-MWCNTs and Amine1-MWCNT form conducting pathways which are ohmic in nature up to a frequency of 100k Hz. The ohmic nature indicates resistive contacts between a-MWCNTs and Amine1-MWCNT in the composites.

![Figure 4.8 DC resistivity of Amine1-MWCNT specimens prepared with various frequencies.](image)
Figure 4.9 Specific AC impedance of Z-MWCNT specimens prepared with various frequencies.

Figure 4.10 Specific AC impedance of α-MWCNT specimens prepared with various frequencies.
4.3.6 Effect of electric field strength on conductivity of Z-MWCNT composites

To investigate the effects of electric field strength, specimens were also manufactured using 300 V/cm and the electrical measurements were compared with those made using 100 V/cm. Application of high strength electric field aligned the Z-MWCNTs effectively, but ignited the mixture of a-MWCNT and Amine1-MWCNT within few minutes of application due to excessive current flow. Therefore, only Z-MWCNTs were used for investigating the effects of electric field strength. Figure 4.12 shows the effects of electric field strength on DC resistivities. The DC resistivities in the parallel direction of specimens prepared using 300 V/cm were similar to the DC resistivities obtained for the 100 V/cm specimens. As was the case when using 100 V/cm in processing, the parallel DC resistivity of the 300 V/cm specimens was essentially independent of alignment frequency. Also similar to the 100 V/cm case, the transverse DC resistivities and anisotropy ratios of the 300 V/cm case showed substantial dependence on the alignment frequency. Considering all the alignment field frequencies, it is seen that increasing the strength of the field did not change the DC resistance anisotropy consistently.
4.3.7 Electrical conduction at the interface of CNFs and CNTs

The effects of electric field on the resistivity of fully cured composites can be explained based on the mechanism of conduction at the interface of two particles in liquid epoxy. The following explanation is equally valid for CNTs and CNFs. The resistance between two CNTs is thought of as the sum of direct contact and tunneling resistances [13]. The electrons move from one conducting CNT to an adjacent one in direct contact or sufficiently close for electrons to tunnel through the gap between the CNTs. Especially in liquid epoxy suspensions with weight fractions of CNTs more than percolation threshold, the possibility of randomly oriented CNTs forming conducting pathways is high. That is, the conducting pathways pre-exist and are not formed by electric field. On application of electric field to high weight fraction CNT suspensions, the electrons freely flow through the pre-existing conducting pathways. As a result of continuous flow of electrons, the CNTs forming conducting pathways do not polarize.

Polarization of an isolated CNT occurs due to the mismatch of conductivity at the interface of CNT and the surrounding medium. On application of electric field, the conducting electrons in a
CNT move in the direction opposite to the field. On reaching the junction between CNT and epoxy, electrons experience resistance to their motion due to the extremely low conductivity of epoxy. As a result, the electrons accumulate at one end of the CNT rendering the other end positively charged. The interaction of electric field with this pair of opposite charges applies a torque to orient CNTs in the field direction. However, if CNTs do not polarize, they cannot align or form chains in the direction of electric field. The high conductivity of CNF and CNT suspensions might be a possible reason for not observing preferential alignment in 2 wt% CNF and 0.5 wt% α- and Amine1-MWCNT composites prepared using electric field (Figures 4.5, 4.7, and 4.8).

Building on the previous argument, if the CNTs are coated with an insulating material that increases the contact and tunneling resistances, some of the electrons will be trapped at the interface due to the mismatch in conductivity. As a result, CNTs will polarize and much higher weight fractions of polymer coated CNTs can be aligned using electric fields. The argument of reduced polarization due to increased medium conductivity can also be understood based on the Maxwell-Wagner polarization model. The polarization of a particle suspended in a medium is related to the conductivities of the particle and medium by the Claussius-Mossotti (CM) factor given by

\[
\text{Re} \left[ \frac{\tilde{\varepsilon}_p - \tilde{\varepsilon}_f}{\tilde{\varepsilon}_f} \right],
\]

where \(\tilde{\varepsilon}_p = \varepsilon_p - i \frac{\sigma_p}{\omega}\) and \(\tilde{\varepsilon}_f = \varepsilon_f - i \frac{\sigma_f}{\omega}\) are the complex dielectric constants of particle and medium respectively, \(\varepsilon\) and \(\sigma\) are the real dielectric constant and conductivity of the particle and the fluid, Re stands for the real part of the complex number, and \(\omega\) is the angular frequency of the applied electric field. A higher value of CM factor indicates stronger polarization and more torque on the particles. Figure 4.13 shows the variation of CM factor with the variation of surrounding medium conductivity. With increasing medium conductivity (which would result due to higher concentration of conducting particles) the value of CM factor decreases, thereby reducing the polarization and torque on the suspended particles. Since Z-MWCNTs are coated with a polymer [26], they polarize and assemble in chains to give frequency dependent anisotropic resistivity. These polarized Z-MWCNTs respond to electric field frequency and assemble in chains as predicted by the FEA model developed in Chapter 3. The distance between the chains decreases with increased frequency. As a result, closely spaced chains have more cross-links that result in lower electrical anisotropy at higher frequencies.
To corroborate the physical understanding developed in the previous paragraphs on creating anisotropic resistivity in a high weight fraction composite by lowering the conduction between particles, 2 wt% CNFs were used as model nanoparticles to make composites. The reason for choosing 2 wt% CNFs is that anisotropy in resistivity was not observed on using an electric field to manufacture the composites (Figure 4.5). The inability to generate anisotropy in 2 wt% composite is thought to be due to pre-existing conducting pathways in liquid epoxy that prevent polarization of CNFs. If anisotropic resistivity can be generated in 2 wt% CNF/epoxy composite by reducing the conduction between CNFs, it will corroborate the proposed hypothesis described in the previous paragraphs. The electrodes for this investigation were 5 mm apart and 400 µm thick. An electric field of 100 V/cm was applied at 1 kHz. A non-ionic surfactant was used to tailor the conductivity at the interface between two CNFs. The non-ionic surfactant used is a commercially available product known as Triton-X 100. The surfactant adsorbs on the surface of a CNF forming an insulating layer which is anticipated to reduce the electrical conduction
between CNFs. In this experiment, the amount of surfactant used was 15.2 wt% of total resin weight, which is ten times of that normally used to make 2 wt% composites. A higher amount of surfactant is anticipated to form a thicker layer that would prevent electrical percolation, thereby allowing CNFs to align and increase anisotropy in resistivity. Figure 4.14 shows the effect of surfactant amount on electrical anisotropy. The use of higher amount of surfactant clearly shows higher anisotropy. The resistivity in the direction of electric field alignment for both the cases is similar to that of randomly oriented composite. However, the resistivity in the transverse direction increased by a factor of 10 on using higher amount of surfactant. The thicker coating formed by higher concentration of surfactant effectively breaks the conducting pathways and allows CNFs to polarize and orient in the direction of electric field. Due to the preferential orientation of CNFs in the direction of electric field, the transverse resistivity increases due to the lower number of conducting pathways in the transverse direction. Coating CNTs and CNFs by insulating polymers provides a possible way to achieve alignment in high weight fraction composites. By using appropriately functionalized CNFs or CNTs, higher weight fraction composites can be made with tailored electrical conductivity.

4.4 Aligned CNF and CNT composites

To assess the degree of alignment in fully cured composites prepared for mechanical testing, DC resistivity of random and aligned composites was measured using a 2-point measurement technique. The resistivity of composites was determined using equation (4.1). Figure 4.15 shows the measured resistivity for various composites made with and without electric field. The change in resistivity for u-CNF composites was negligible. An anisotropy ratio of around 1.5 was obtained for PEI-MWCNT and PEI-CNF composites, and an anisotropy ratio of 79 was observed for Z-MWCNTs. Based on the resistivity measurements, it seems that only Z-MWCNTs aligned well. It appears that anisotropy in resistivity in high weight fraction composites cannot be obtained using covalently functionalized CNFs and CNTs. Recall that functionalization with PEI polymer is covalent in nature and no anisotropy was observed in the composites made with covalently functionalized Amine1-MWCNTs.
Figure 4.14 Effect of various amounts of Triton-X 100 on electrical anisotropy of a 2 wt% CNF/epoxy composite (E=100 V/cm, f=1k Hz, T=121°C, E-field time =1 hr)
Figure 4.15 DC resistivities of composites made for investigating the effect of CNF and CNT alignment on elastic modulus.

Figure 4.16 shows the effect of aligning CNFs and CNTs on elastic modulus. Also plotted with experimental values are the predicted values for aligned CNF and CNT composites. The modified Halpin-Tsai model was used for predictions. The length distribution after 60 min. of sonication was used for predicting CNF/epoxy composite modulus (Figure 2.15 g). The assumed value of CNF modulus was 300 GPa. For all the MWCNT composites, the length distribution shown in Figure 2.28 was used for predictions. The modulus of MWCNTs was assumed to be 1 TPa. The alignment of nanoparticles using electric field did not improve the modulus.
significantly in comparison to randomly oriented nanoparticles composite modulus. The improvement in modulus over random composite was in the range 3-10% for all the nanoparticles investigated. It should be noted that this improvement is within the range of experimental scatter. The improvement relative to the modulus of baseline epoxy was in the range 24-26%. In comparison, the expected improvement was in the range 26-35%. For composites made with CNFs, the average length of CNFs after 60 min. of sonication is expected to be low (l=3.5 μm), and is not expected to show much improvement in the modulus due to alignment. Moreover, the improvement in modulus is not expected on account of poor alignment indicated by electrical measurements. Based on the electrical measurements, it is not expected that PEI-MWCNTs will increase the modulus either. Z-MWCNTs on the other hand aligned well, but showed no improvement in modulus over randomly oriented Z-MWCNT composite. However, the expected improvement due to alignment over random orientation of CNTs is roughly 10%, and is within the experimental scatter expected in measuring elastic modulus of epoxy composites.

Figure 4.16 Effect of aligning CNF and CNT on the elastic modulus. The scatter bars represent the variation observed between two specimens tested for each case. The two specimens were obtained from the same batch of material, except for baseline epoxy where two specimens from two different batches were tested.
4.5 Conclusions

4.5.1 u-CNF/epoxy composites
The alignment and chaining of CNFs in epoxy using AC electric fields has been demonstrated for an electrode distance of 25 mm, which is an order of magnitude larger distance in comparison to the state-of-the-art. Different chain morphologies and rates of chain growth were observed for different frequencies. The spacing between chains decreased with increase in frequency. At higher frequencies, the closely spaced chains develop more cross-linking between the chains. The highest rate of chain growth occurred at a frequency of 1 kHz. An AC electric field of 58 Vrms/cm at 1 kHz was adequate for growing CNF chains of 0.1 to 1 wt% concentration over a gap of 25 mm. Evidence of alignment was observed directly using a microscope for 0.1 and 0.2% weight fractions. For 0.5 and 1 wt% CNFs, anisotropy in conductivity was used to indirectly indicate alignment. For 2 wt% CNF concentration, the applied electric field agglomerated the CNFs, forming equally strong conducting pathways in the directions parallel and transverse to the intended direction of alignment.

4.5.2 MWCNT/epoxy composites
The DC resistivities in the direction of alignment of 0.5 wt% a- and Amine1-MWCNT/epoxy composites were around $10^2$ and $10^3$ Ω-cm respectively, and around $10^8$ Ω-cm for Z-MWCNTs. The DC resistivities of Z-MWCNT specimens prepared at 100 and 300 V/cm were similar in the direction of alignment. Electric field strength of 300 V/cm could not be applied to a- and Amine1-MWCNT mixtures because of excessive joule heating due to high electric conduction.

The use of Z-MWCNT resulted in maximum DC resistivity anisotropy ratios of 650 and 730 using 100 and 300 V/cm, respectively, at a 100 Hz alignment frequency. Depending on the alignment frequency used, DC resistivity anisotropy could be significantly tailored. On increasing the frequency from 100 Hz to 100 kHz, DC resistivity anisotropy decreased from 650 to 30 using 100 V/cm, and from 730 to 10 using 300 V/cm. This variation in DC resistivity anisotropy is attributed to reductions in the DC resistivity transverse to the direction of the applied field, as the DC resistivity in the direction of alignment was observed to be nearly constant in all cases with applied field. The AC impedance of the composites was decreased with measurement frequency, indicating dielectric behavior.
For a-MWCNT and Amine1-MWCNT specimens, the application of electric field before curing did not change the resistivity of the specimens appreciably. The resistivities of specimens made with or without electric field were similar. Moreover, the AC impedance was constant up to 100 kHz, indicating ohmic conduction in the specimens.

The alignment of CNFs and CNTs by electric field primarily depends on the presence of pre-existing conducting pathways. The particles in a liquid suspension with conducting pathways will not align upon application of an electric field. Unfunctionalized and covalently functionalized 1 wt% CNFs and 0.5 wt% CNTs form conductive pathways in liquid epoxy that prevent the polarization of individual particles. As a result, no anisotropy in resistivity is obtained in composites manufactured using 1 wt% and 0.5 wt% unfunctionalized and covalently functionalized CNFs and CNTs, respectively. However, the use of non-covalent functionalization is found to facilitate alignment and chaining of particles. The polymer wrapped around non-covalently functionalized MWCNTs assists in polarizing MWCNTs, eventually leading to alignment and chaining of MWCNTs in a 0.5 wt% composite. Also, anisotropy in resistivity was created in a 2 wt% CNF composite, which otherwise showed isotropic conductivity, by wrapping the CNFs with excess of surfactant, Triton-X 100. Anisotropy of 10 in DC resistivity was obtained in the 2 wt% CNF composite by adding higher weight percent of surfactant (15.2 wt%). The surfactant, just like the polymer in case of non-covalent functionalization, adsorbs on the surface of nanoparticles to change the conduction at the particles interfaces.

4.5.3 Effect of CNF and CNT alignment on elastic modulus
Alignment could only be achieved in non-covalently functionalized Z-MWCNT composites. No improvement in elastic modulus was obtained due to the alignment of CNTs, which was expected based on the insignificant improvement of 10% predicted by modified Halpin-Tsai model. The reason for a small improvement in elastic modulus was due to the small lengths of CNFs and CNTs that result after the dispersion. The longer sonication time needed to achieve dispersion to the level of individual particles resulted in shorter nanoparticles, which in turn did not improve the elastic modulus of the composites despite of alignment.
In summary, using appropriate electric field parameters and functionalization, CNFs and MWCNTs can be aligned and networked using electric fields to engender a wide range of electric anisotropy ratios. Moreover, the nature of conduction through the composites (e.g., ohmic or dielectric) can be tailored by choosing the type of functionalization. Composites with such tailored electrical properties can find use in wide range of electrical applications.
4.6 References


5 Aligning Multiwalled Carbon Nanotubes in Glass Fiber Composites using AC Electric Field

5.1 Introduction
Continuous fiber composites have excellent load bearing capacity in the fiber direction, but are considerably weaker transverse to the fibers. The low modulus and strength of the matrix restricts the load carrying capacity of such continuous fiber composites transverse to the fiber direction. Various fiber reinforcements such as multidirectional laminates, 2-D fabrics, and advanced fabrics with 3-D fiber orientations have been used to reinforce composites in multiple directions. 2-D reinforcements provide high in-plane strength and stiffness, but do not improve the interlaminar or through-the-thickness properties which are dependent on the matrix. 3-D fabrics provide a solution to reinforce composites in the thickness direction, but the fiber waviness or crimp can lower the fiber properties making these reinforcements less attractive for certain high strength and stiffness applications [1]. In composites where it is not possible to provide continuous fibers in certain directions, there is a need to improve the properties of the matrix to enhance the load carrying capacity of continuous fiber composites.

CNTs on account of their size and exceptional properties have been used to enhance the mechanical, electrical, and thermal properties of the epoxy composites. It is envisioned that the use of nanoreinforced epoxy for continuous fiber composites can improve the load carrying capacity transverse to continuous fiber direction. In a composite with high volume fraction of continuous fibers, the gap between the fibers is less than 1 µm. The small size of CNTs makes them a promising candidate for infiltrating the gaps between continuous fibers, thus providing a uniform distribution of nanofillers in the continuous fiber composites. As in conventional polymeric composites, it is desired to control the orientation of these nanoparticles for enhancing direction-specific material properties. In the following paragraphs, the literature on the use of aligned CNTs in continuous fiber composites is reviewed. The focus is on methods of aligning CNTs and ways of incorporating aligned CNTs in continuous fiber composites.

After a literature review, the objectives of this investigation are stated. Next, finite element models used to investigate the distribution of electric field in continuous fiber composites and specimen manufacturing and testing procedures are discussed. The outcome of finite element
analysis and testing are reported next, followed by conclusions and recommendations for making composites

5.2 Literature review
Realizing that the interface is far more accessible than the interior of a laminate from the standpoint of manufacturing, Garcia et al. [2] and Blanco et al. [3] have integrated forests of aligned CNTs in the laminates by placing them at the interface. The forest of aligned CNTs were grown on a substrate and then transferred to one of the surfaces of the prepregs by the ‘transfer-printing’ technique. The prepregs were placed on a cylinder and then rolled over the CNT forest while applying pressure. Due to the tack of the prepregs, CNT forest fully transferred to the prepregs. The transferred CNTs did not lose alignment and were positioned vertically on the prepreg’s surface. Prepregs with CNT forest were then stacked together to make laminates. The laminates with CNT forest improved the Mode I fracture toughness by 1.5-2.5 times and Mode II fracture values by 3 times.

Reinforcing the interface has its advantages, but is not the same as uniformly reinforcing the entire laminate with aligned CNTs. In a composite, the damage can occur anywhere in between the fibers and is not always concentrated at the interface between plies. Especially in case of out-of-plane impact loading, the chance of damage appearing in between fibers is considerably increased. Realizing the importance of uniformly reinforcing laminates with CNTs, Garcia et al. [4] grew aligned CNTs directly on the fibers of a woven carbon fiber fabric. The carbon fiber preform was first dip-coated with a CNT growth catalyst; later this preform was subjected to atmospheric-pressure chemical vapor deposition to grow forests of aligned CNTs on the fibers of the preform. Preforms with aligned CNTs were then stacked together and infused with thermoset resin. This technique of preparing laminates not only provided reinforcements at the interface between plies, but also reinforced the regions between individual fibers. The laminates with aligned CNTs showed a 69% increase in the interlaminar shear strength.

The technique of growing CNTs directly on fibers provided CNTs aligned perpendicular to fiber surfaces, but the orientation of these CNTs in a global sense was still random. Having CNTs oriented perpendicular to fiber length is not the same as having CNTs oriented in a specific direction for improving direction specific matrix properties. Moreover, the techniques of
chemical vapor deposition are known to significantly degrade the tensile properties of carbon fibers [5-7]. Though the techniques using forest of aligned CNTs as interleaves and growing CNTs aligned to fiber surfaces are promising, there is still a need to device manufacturing procedures that can manipulate the orientation of CNTs dispersed throughout in the matrix. Electric fields have been found to be useful in aligning and chaining CNTs in CNT/epoxy composites as shown in previous chapters of this thesis. The focus of this chapter is to use electric fields to align and chain CNTs in continuous fiber composites. For aligning CNTs using electric fields, glass fiber preforms are used on account of their insulating nature. The use of electric field is limited to insulating or low conductivity fiber preforms to prevent joule heating due to high current flow.

5.3 Finite element analysis
The effective alignment of CNTs in continuous fiber composites depends on the spatial distribution of electric field. Knowledge of the distribution of electric field would help in aligning CNTs effectively in the composite. CNTs align and chain in the direction of electric field. The prediction of electric field using analytical techniques is not straightforward due to the presence of continuous fibers and the complex electrode geometry. The electric field distribution in a complex system such as the one dealt with here can be estimated using finite element analysis.

5.3.1 Modeling assumptions

5.3.1.1 Insignificant hydrodynamic forces
From the results of previous chapters, it was determined that electric field frequencies of 1 kHz and 100 Hz are suitable for aligning and chaining CNTs in CNT/epoxy composites. Also, the ease of applying high voltages at these frequencies is ideal for aligning CNTs over large distances. At 100 Hz and 1 kHz, the hydrodynamic forces on chains were shown to be relatively high in Chapter 2. However, the hydrodynamic forces on chains are not considered in this investigation. The reason for neglecting hydrodynamic forces on CNT chains is due to the increased hydrodynamic resistance provided to the fluid flow by the closely spaced continuous fibers. However, it is anticipated that the movement of individual CNTs will be restricted due to their vicinity to continuous fibers. Nevertheless, the CNTs are expected to chain because they do not have to translate large distances to form chains on account of high weight fraction used. The
distance between individually suspended CNTs was estimated using equation (2.9). The mean separation of CNTs normal to their lengths assuming hexagonal packing is approximated to be 170 nm for a weight fraction of 0.5% in the matrix. The CNTs are considered aligned in the hexagonal packing for estimating the mean separation. As a rough estimate, the distance between the CNTs for a random orientation should be of the same order of magnitude.

5.3.1.2 Strength of electric field
Typically, electric field strength of 100 V/cm can align and chain CNTs in a CNT/resin suspension (without continuous fibers) as shown in Chapter 3. However, it is anticipated that electric field strengths higher than 100 V/cm would be required on account of the hydrodynamic drag exerted by continuous fibers to the movement of CNTs. In reference [8], the drag torque due to wire-floor interaction on a rotating metallic nanowire of aspect ratio 40 was estimated to be 25% of the total drag torque. The total drag torque was considered as the sum of the drag torques experienced by rotating nanowires in a boundless medium and in a medium close to a wall. The drag torque due to the wall is inversely proportional to the distance of the wire from the wall. That is, the drag torque would increase with the decreasing distance between the wire and the wall. It is important to note that CNTs in a fiber preform can be positioned anywhere relative to the surfaces of continuous fibers. In such a scenario, the total drag force experienced by CNTs could vary widely. Therefore, a high enough electric field that can be applied without causing excessive flow of electric current through the uncured composite part should be used. The analysis is performed using 1000 V/cm electric field strength.

5.3.1.3 Resin and fibers properties
Due to the large difference in the sizes of CNTs (nm), continuous fibers (µm), and the distance between the electrodes (mm), the entire gap between the electrodes with continuous fibers and nanoparticles cannot be modeled. The analysis is limited by the number of nodes/elements that can be handled by the computer memory (roughly around 500,000 nodes). As a result, the effective properties of the CNT reinforced resin are used. Since the measured resistivity of Z-MWCNT/liquid resin mixture was $10^{10} \, \Omega\cdot\text{cm}$ and the conductivity of glass fiber is $10^{16} \, \Omega\cdot\text{cm}$, the system was considered insulating for modeling purposes. Due to the extremely low conductivity of the system, the models are solved considering dielectric fibers embedded in a dielectric medium. This is, the system is considered insulating and the problem is solved using the dielectric constants of glass fibers and liquid resin. The dielectric constant for CNT
reinforced resin was assumed to be around 100, and a dielectric constant value of 4.2 was used for glass fiber.

5.3.2 Modeling cases

5.3.2.1 Electrodes in contact with uncured composite
The models used to determine the electric field distribution for the case when electrodes are in direct contact with uncured composite are shown in Figure 5.1. A simple case where electrodes are parallel to each other is considered in this investigation. The space between the electrodes has continuous fibers embedded in liquid resin. Based on the geometry of the electrodes and the orientation of continuous fibers, the electric field distribution was not expected to change along the length of continuous fibers. As a result, the cross-section of a continuous fiber composite is modeled in 2-D space. The finite element software used in this investigation was COMSOL Multiphysics (Burlington, MA) finite element software. The Electrostatics module available in COMSOL was used for solving the electric potential. The Laplace’s equation for the electric potential is solved for the space in between the electrodes (Figure 5.1). The domain is meshed with an unstructured triangular mesh, with a fine mesh near the fibers. The mesh was generated using the automatic-mesh-generation feature available in the software. The boundary conditions for the models are shown in Figure 5.1. Table 5.1 lists the assumed dielectric constant values used for glass fibers and liquid resin. This case is solved for two fiber volume fractions. The volume fractions of continuous fibers investigated are 40 and 50%. The fibers are randomly distributed in the space between the electrodes.

5.3.2.2 PTFE release film in between electrodes and uncured composite
The electrodes used for aligning CNTs could bond to the composite part if not removed before curing. In some instances, the attached electrodes might not be desired in a fully cured part. To facilitate removal of composite parts from molds, a Teflon (PTFE) release film is commonly used. Therefore, the effects of having a release film in between the electrodes and the uncured part on the distribution of electric field is also investigated. The geometry used for investigating the effects of release film is shown in Figure 5.2. The boundary conditions used for modeling are also shown in Figure 5.2 and the material properties used for the release film, glass fibers and the resin are listed in Table 5.1. Just like the previous case, this case is also solved for two fiber volume fractions. The volume fractions of continuous fibers investigated are 40 and 50%. The fibers are randomly distributed in the space between the electrodes.
Figure 5.1 Boundary conditions used for the case of electrodes in contact with composite.
Figure 5.2 Boundary conditions used for the case of PTFE film inserted in between electrodes and composite.

Table 5.1 Assumed material properties for FEA model

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT reinforced resin(^1)</td>
<td>100</td>
</tr>
<tr>
<td>Glass fibers(^2)</td>
<td>4.2</td>
</tr>
<tr>
<td>PTFE release film(^2)</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^1\) Assumed based on values reported in [9]
\(^2\) Material property data base of COMSOL
5.4 Specimen preparation and testing

5.4.1 Materials
Specimens for this investigation were prepared by adding nanoreinforcements to an epoxy resin system. The resin system was Epon 862 with curative W, a bisphenol F/aromatic diamine system. The resin system was mixed at a ratio of 100:26.4 epoxide to curative, and this mixture (epoxide+curative) was used for determining the weight percentages of nanoreinforcements added to the mixture. The MWCNT nanoreinforcements investigated are non-covalently functionalized multi-walled carbon nanotubes (Z-MWCNTs) purchased from Zyvex Performance Materials, LLC (Columbus, OH). The Z-MWCNTs were pre-dispersed by the vendor in Epon 862 at a weight fraction of 2 wt% of the resin weight. The reason for choosing Z-MWCNTs for this study was based on the results of Chapter 4. Recall that the non-covalent functionalization reduced the electrical percolation in a CNT/resin mixture thereby allowing high weight fractions of CNTs to align and chain in the direction of electric field. Also, a wide range of DC resistivity anisotropy ratio could be generated in Z-MWCNT composites using different electric field frequencies. The concentration of MWCNTs used to prepare specimens in this investigation was 0.5 wt%. The as-received mixture of Z-MWCNTs/epoxide was diluted appropriately with liquid epoxide to obtain a concentration equivalent to 0.5 wt% in the resin.

Z-MWCNTs were manually mixed in an appropriate amount of epoxide using a plastic stirrer for 5 minutes. After manually stirring the mixtures, sonication was performed with a 900 W, 20-kHz, ultrasonic horn (Branson, Danbury, CT). Z-MWCNTs were sonicated for 30 min. at a power level of 270 W. The mixture was continuously cooled to minimize excessive heating due to sonication. No surfactant or degassing agent was used in preparing the composites. After sonication, the curative was added and mixed manually using a plastic stirrer for 5 minutes. The mixtures of Z-MWCNTs, epoxide, and curative were then placed in a vacuum oven set to 70°C and a pressure less than 1000 millitorr to help eliminate air bubbles in the mixture. The mixtures were degassed for an hour at 70°C.

5.4.2 Manufacturing continuous fiber composites
Since the primary aim of this investigation is to investigate electric field methods to align and chain CNTs in continuous fiber composites, a vacuum assisted resin transfer molding or wet-filament winding process can be used to make composites. However, the vacuum assisted resin
infusion of glass preforms could not be achieved with a resin containing 0.5 wt% CNTs. Although, preforms were successfully impregnated using 0.2 wt% CNT reinforced resin. In the case of 0.5 wt% CNT reinforced resin, the higher viscosity of the resin prevented flow through the glass preform. The difficulty in infusion is compounded due to the reduced permeability of the glass preforms. The fibers compact under atmospheric pressure, thereby reducing the permeability of the preforms. Due to the difficulty in infusing glass preforms, the composites were manufactured using the filament winding process.

The degassed mixture containing 0.5 wt% CNTs was used for wet-filament winding. The mixture was poured in a resin bath kept at room temperature, and a 12k tow of fiber glass was used for filament winding 10 layers on a flat mandrel with dimensions 14×6.5×1.2 cm. The fibers were wound along the 6.5-cm side of the mandrel in a circumferential pattern. The fibers were wound during the forward and backward stroke of the carriage. The filament winding speed was 5% which took about 3 min. to cover the distance of 12 cm. The winding was done using two orifice sizes to have different fiber volume fractions of continuous fibers in the composites. The orifice sizes used were 0.031 inch and 0.038 inch (size specified in US customary units) that provided fiber volume fractions of around 55 and 45 volume percent, respectively.

After winding 10 layers, the fibers were cut along the 14 cm edge of the mandrel. Two 12×6.5 cm resin impregnated fiber preforms, containing 10 layers, were obtained. These preforms were then put in a vacuum oven maintained at 70°C to remove air that might have been entrapped during the filament winding process. After degassing for 30 min., the preforms were further cut along the fiber directions to obtain eight pieces of 2×6.5 cm. The fibers were oriented in the 6.5-cm direction of these pieces. Electrodes were then placed on top and bottom surfaces of these pieces to apply electric field (Figure 5.3). The electrodes were pieces of aluminum foil sheet and were 2×2 cm². The electrodes were connected to an AC power supply for applying electric field at 100 and 1k Hz frequencies. The strength of electric field was 1000 V/cm and was determined by dividing the applied voltage with the distance between the electrodes. The curing schedule employed for making composites was 121°C for 1 hour followed by 177°C for 2.5 hours. The electric field was applied for 1 hour during the 121°C segment of the curing schedule.
5.4.3 DC resistivity measurements
Specimens for DC resistivity measurements were cut from the fully cured composite parts. Specimens were cut using a water cooled diamond saw. The specimens were dried at 60°C for 2-4 hours. Immediately after cutting, the specimens were pat dried using a paper towel and placed on a hot plate maintained at 60°C. The specimens were obtained from the region in between the electrodes. The electrodes were 2×2 cm in area. The thickness of the fully cured part was 1.5 mm. The electric field was applied in the through-thickness direction of the composite. DC resistances were measured in the direction of electric field, that is in the through-thickness direction, along the continuous fiber direction, and transverse to the direction of applied field. Figure 5.4 shows the schematics of the specimens cut from the composites to measure DC resistivities. A 2-point measurement technique was used for measuring resistivity. Since the measured resistances were anticipated to be more than thousands of ohms, the contact resistances were believed to play a negligible role in determining the sample resistance. The two opposite edges were polished using a 600 grit abrasive paper and then coated with a conducting silver based solution (containing acrylic as the binder) to provide good electrical contacts. Thin copper wires were then soldered to the conducting faces. This silver based solution is commercially available under the brand name “CircuitWriter Pen” from RadioShack (www.radioshack.com). From the measured resistance, the volume resistivity of the specimen, \( \rho_{DC} \), was determined using the formula,

\[
\rho_{DC} = RA/L
\]  (5.1)

**Figure 5.3** Schematic of experimental setup used for aligning CNTs in glass-fiber composites.
where \( R \) is the resistance of the specimen measured by dividing the applied voltage by the current, \( L \) is the length of the specimen between the electrical contacts, and \( A \) is the cross-sectional area of the specimen.

**Figure 5.4** Schematics of specimens prepared for DC resistivity measurement.

**5.5 Results**

In this section, the discussion of FEA results is followed by experimental results. FEA analysis provides insight into the alignment and chaining of CNTs in continuous fiber composites. Following the FEA results, appropriate electrode configuration was selected for aligning CNTs in continuous fiber composites. The outcome of experiments on aligning CNTs in continuous fiber composites is discussed next. The experimental results are understood based on the results of FEA analysis.

**5.5.1 Finite element analysis**

**5.5.1.1 Electrodes in contact with uncured composite**

Figures 5.5 and 5.6 show the electric field distribution in the 40 and 50 volume percent continuous fiber composites. The arrows show the direction of electric field lines in between the
electrodes. The electric field lines are not uniformly oriented everywhere in the resin. Since the CNTs align in the direction of electric field lines, it is expected that the CNTs will not be uniformly oriented in one direction. Also, it is observed that the magnitude (shown by the colored contours) of electric field is not uniform everywhere in the resin. A large variation in electric field strength is observed in the vicinity of fibers. In regions where fibers are close together, the variation in electric field strength is higher.

**Figure 5.5** Spatial distribution of electric field for the case of electrodes in contact with the composite. The fiber volume fraction is 40%, \(V/d\) is 1000 V/cm.
Due to the nonuniform electric field strength, the suspended CNTs are anticipated to experience DEP forces. Recall that a polarized CNT experiences a force along the gradient of electric field. The DEP force is directly proportional to the gradient of electric field square. The arrows in Figures 5.7 and 5.8 show the direction of gradient of electric field square. Since the CNTs are expected to experience a force in the direction of gradient of electric field square, it is expected that CNTs will drift in between the continuous fibers resulting in a distribution less homogeneous than randomly oriented CNTs. Especially the CNTs will drift out of the region ABCD shown in Figures 5.7 and 5.8 based on the directions of arrows. The translation of CNTs
in the transverse direction will increase spacing between the CNTs, resulting in a possible reduction of conducting pathways in transverse direction.

**Figure 5.7** Direction of gradient of electric field square for the case of electrodes in contact with the composite. The DEP force on CNTs is in the direction of gradient of electric field square. The fiber volume fraction is 40%, $V/d$ is 1000 V/cm.
Figure 5.8 Direction of gradient of electric field square for the case of electrodes in contact with the composite. The DEP force on CNTs is in the direction of gradient of electric field square. The fiber volume fraction is 50%, $V/d$ is 1000 V/cm.

5.5.1.2 PTFE release film in between electrodes and uncured composite
A trend similar to the case of electrodes touching the uncured composite is observed with respect to electric field lines, strength of electric field, and the direction of gradient of electric field square when using a PTFE release film (Figures 5.9-5.12). Additionally, it is seen that the strength of the electric field in the resin decreases when using PTFE release film. Figure 5.13 compares the electric field strength along the line A-A shown in Figures 5.5 and 5.9 for the cases of with and without release film. The electric field strength is non uniform along line A-A, and is high in PTFE film as compared to resin. This nonuniformity in electric field results due to the mismatch in dielectric properties of the film and the resin. The electrical quantity that
remains constant across the film/resin interface is the displacement current, given by the product of dielectric constant and the electric field. To maintain a constant displacement current across the interface, the electric field in the film with lower dielectric constant is higher in comparison to the resin with higher dielectric constant.

**Figure 5.9** Spatial distribution of electric field for the case of PTFE release film at the interface between electrodes and the composite. The fiber volume fraction is 40%, $V/d$ is 1000 V/cm.
Figure 5.10 Spatial distribution of electric field for the case of PTFE release film at the interface between electrodes and the composite. The fiber volume fraction is 50%, $V/d$ is 1000 V/cm.
Figure 5.11 Direction of gradient of electric field square for the case of PTFE release film at the interface between electrodes and the composite. The DEP force on CNTs is in the direction of gradient of electric field square. The fiber volume fraction is 40%, $V/d$ is 1000 V/cm.
Figure 5. Direction of gradient of electric field square for the case of PTFE release film at the interface between electrodes and the composite. The DEP force on CNTs is in the direction of gradient of electric field square. The fiber volume fraction is 50%, $V/d$ is 1000 V/cm.
Figure 5.13 Change in electric field strength due to insertion of PTFE release film between electrodes and the composite. Electric field magnitude plotted along line A-A in Figures 5.5 & 5.9. Fiber volume fraction = 40%, $V/d = 1000$ V/cm.
5.5.2 Experimental results

The formation of CNT chains in a composite lowers its DC resistivity in comparison to randomly oriented CNT composite. Due to the reorientation of CNTs to form chains, the DC resistivity transverse to the direction of chains increases on account of the fewer connections left after reorientation of CNTs. In the following paragraphs, the DC resistivities of composites prepared with electric field are compared to those prepared without electric field to evaluate the effects of electric field on CNT chaining. The resistivities were measured in three directions, the through-thickness, in-plane transverse to fibers, and in-plane along the fibers. Figures 5.14-5.17 show the effect of applying electric fields at 100 and 1k Hz on the DC resistivities of composites manufactured using two different orifice sizes. The DC resistivities obtained without electric field are also plotted for comparison in Figures 5.14-5.17. The through-thickness resistivity (in direction of electric field) of composites made with electric field was less than that of composites made without electric field. The resistivity in the through-thickness direction of composites with aligned CNTs reduced by an order of magnitude in comparison to composites with randomly oriented CNTs. The CNTs polarized by electric field drifted towards each other due to the mutual force of attraction to form chains in the field direction. The formation of chains thus reduced the resistivity in the through-thickness direction.

![Figure 5.14 DC resistivity of Z-MWCNT/continuous glass fiber/epoxy composite manufactured using orifice size 0.031 in. Electric field of 1000 V/cm was applied at 1 kHz.](image_url)
Figure 5.15 DC resistivity of Z-MWCNT/continuous glass fiber/epoxy composite manufactured using orifice size 0.031 in. Electric field of 1000 V/cm was applied at 100 Hz.

Figure 5.16 DC resistivity of Z-MWCNT/continuous glass fiber/epoxy composite manufactured using orifice size 0.038 in. Electric field of 1000 V/cm was applied at 1 kHz.
Figure 5.17 DC resistivity of Z-MWCNT/continuous glass fiber/epoxy composite manufactured using orifice size 0.038 in. Electric field of 1000 V/cm was applied at 100 Hz.

The in-plane transverse resistivity of the composites made using 0.031-in. orifice size did not change on using electric fields applied at 100 and 1 kHz (Figures 5.14 & 5.15). However, the transverse resistivity of composites made using the 0.038-in. orifice increased on using electric field in comparison to random CNT composites (Figures 5.16 & 5.17). Increase in resistivity indicates reduction in electrical connections in that direction. The reassembly of CNTs to form chains in the field direction reduces the connections in the transverse direction to increase the resistivity. As seen in Figures 5.7 and 5.8, the CNTs drift outwards from region ABCD in the transverse direction. As a result of fewer connections in the transverse direction, the transverse resistivity increased, as observed for composites made with 0.031-in. orifice size. However, the trend of increasing transverse resistivity due to field application was observed only in composites made using orifice size 0.038-in. A possible reason could be the reduced resistance offered to CNT translation by farther spaced fibers in a lower fiber volume fraction composite. The higher fiber volume fraction composites made with 0.031-in. orifice size suppressed the translation of CNTs resulting in similar in-plane transverse resistivity for composites made with and without electric field.
The resistivities along the fiber direction obtained with and without electric field are plotted in Figures 5.14-5.17. For composites made with both the orifice sizes, only the use of 100 Hz resulted in composites with the fiber direction resistivities higher than random CNT composite resistivities. The use of 1 kHz did not change the resistivities as expected. The increase in resistivity on using 100 Hz in the fiber direction indicates preferential alignment of CNT chains in the through thickness direction.

5.6 Conclusions
The use of electric field is demonstrated for chaining CNTs in unidirectional glass fiber composites. The effect of continuous fibers on the spatial distribution of electric field and dielectrophoretic forces on CNTs is investigated using FEA models. Continuous fiber composites with chains of CNTs are manufactured using electric fields applied at 100 Hz and 1 kHz. The conclusions of this investigation are broken down into subsections on FEA results, effect of orifice size or fiber volume fraction, and the effect of electric field frequency. This style has the disadvantage of repeating the conclusions but makes it easier to read, understand, and follow the recommendations of this investigation.

5.6.1 Spatial distribution of electric field using FEA
The electric field was found to be nonuniform due to the presence of continuous fibers. The magnitude and direction of electric field varied due to the presence of continuous fibers. This variation in electric field resulted in DEP forces on polarized CNTs. The variation in electric field magnitude and direction was observed to be higher for higher volume fraction of fibers. Also, the FEA results indicate that the use of release film lowers the overall magnitude of electric field in the uncured composite part. It is recommended that electrodes should be placed in contact with the composite part to avoid any loss of electric field strength.

5.6.2 Effect of orifice size on DC resistivity of composites
In comparison to DC resistivity of random CNT composite, the use of 1000 V/cm (calculated by dividing the applied voltage with the distance between the electrodes) across the through-thickness direction decreased though-thickness DC resistivity for composites made with 0.031-in. and 0.038-in. orifice sizes. The resistivity in the through-thickness direction for both the orifice sizes decreased on using 100 Hz and 1 kHz fields.
The in-plane transverse to fibers DC resistivities did not change on using electric fields for manufacturing composites with orifice size of 0.031-in, however in-plane transverse DC resistivities marginally increased over randomly oriented CNT composite resistivity for composites made with 0.038-in orifice size. A possible reason for no increase in the in-plane transverse DC resistivity for 0.031-in orifice size was the high fiber volume fraction that suppressed the CNT translation under the influence of electric field. The resistivities in fiber direction could only be changed using 100 Hz.

5.6.3 Effect of electric field frequency
The use of 100 Hz reduced the DC resistivity in the through-thickness direction and increased the resistivity along the fiber direction. No change in resistivity could be obtained using 100 Hz in the in-plane transverse to fiber direction. The use of 1 kHz reduced the DC resistivity in the through-thickness direction, but was not effective in changing the in-plane resistivities.

5.6.4 Summary
Overall, the presence of continuous fibers causes non-uniform electric field in the composite part. CNT chains assemble in the direction of electric field lines. Since the electric field lines go around glass fibers and are not straight in between the electrodes, the CNTs in the chains are not all oriented in the same direction. The variation in electric field lines increases with increasing fiber volume fraction in the composite. Also, it is recommended that the electrodes be kept in contact with the composite part to maximize the strength of electric field in the composite to effectively orient CNTs in the field direction. In the end, to generate anisotropy in resistivity, 100 Hz was found to be better than 1 kHz. However, 1 kHz can still be used to align and chain CNTs in continuous fiber composites.
5.7 References
6 Manufacturing Carbon Nanotube and Nanofiber Buckypaper

6.1 Introduction
CNTs and CNFs due to their small size and exceptional properties are considered suitable for reinforcing matrices of continuous fiber composites. The weakest link in continuous fiber composites is the resin rich area between the fibers. Introducing CNTs in between fibers offers a solution to reinforce the resin rich areas. In the past decade, efforts have been made to improve the transverse direction properties of continuous fiber composites by using CNT reinforced resins. The less-than-expected improvement in transverse direction properties was obtained in all the studies. As shown in Chapter 2, the improvement due to CNTs and CNFs can be diminished by low values of aspect ratio of nanoparticles resulting from the dispersion process. A marginal improvement of 30% in elastic modulus was reported in Chapter 2 with the residual lengths of CNTs and CNFs obtained after dispersion. In addition, the amount of CNTs that can be used has an upper limit that is governed by the increase in viscosity of the resin due to the CNTs. High viscosity renders nanoreinforced resins unsuitable for infusing continuous fiber preforms. As a result, the vast majority of research involving the infusion of resins into continuous fiber composites has been focused on CNT and CNF epoxy composites with weight fractions in the resin ranging up to 1 or 2 wt%. Realizing the limitation on the weight fractions of CNTs that can be used to make continuous fiber composites, alternate ways of reinforcing continuous fiber composites using high weight fractions of CNTs and CNFs are desired.

The literature review presented below focuses on the techniques used to incorporate high weight fractions of CNFs and CNTs into regions of continuous fiber composites. After discussing the current methods available for incorporating high weight fractions of CNFs and CNTs, the aim of this investigation is stated. Subsequently, experiments designed in this investigation to incorporate high weight fractions of CNFs and CNTs in continuous fiber composites are discussed, followed by the experimental results, discussion, conclusions, and recommendations for making composites are made.

6.2 Literature review
There are currently two well-documented methods for incorporating regions of high weight fractions of CNTs in continuous fiber composites: the chemical vapor deposition (CVD) process
to grow CNTs directly on fibers, and to use ‘buckypapers’ of CNTs and CNFs as interleaves between the plies of continuous fiber composites. CNTs have been grown on carbon fiber perfoems using the CVD process [1-3]. Typically to deposit CNTs, the carbon fiber preforms were first dip-coated with a CNT growth catalyst. Later, these preforms were subjected to CVD to grow forests of CNTs on the fibers. The CVD technique grows CNTs uniformly over the surfaces of carbon fibers and provides high fraction of CNTs in the fiber preforms. This carbon fiber preform with CNTs can be infused with resin to make composites. However, the high temperature and aggressive chemicals used for growing CNTs in the CVD process can degrade the fibers and the fiber/matrix interface properties [2-3].

The second well-known method of reinforcing regions of composites with high weight fraction of CNFs and CNTs is to use buckypaper at the interface between plies. Using buckypaper is relatively simple and preserves the properties of the fibers. However, reinforcing the interface between plies is not the same as uniformly reinforcing the composite. Despite this limitation, exceptional interlaminar properties have been obtained using buckypapers [4]. The most popular method of manufacturing buckypaper is based on the filtration of a solution of CNTs and CNFs on a microporous membrane. CNTs and CNFs are dispersed in water with the aid of a surfactant and ultrasonic agitation at very low concentrations (≈40 mg in 1 L of water). The suspension is then filtered on a porous membrane using vacuum. Free standing, large sized, buckypapers have been successfully made using filtration process [5]. Buckypapers also find use in electromagnetic interference shielding (EMI) on account of their high electric conductivity [6], as a fire retardant [7], and as structural materials for micro-scale applications. Buckypapers with aligned CNTs have also been prepared using magnetic fields during the filtration process. Aligning the nanoparticles increases the elastic modulus, thermal conductivity, and electrical conductivity in the direction of alignment. However, extremely high strength magnetic fields are required for aligning CNTs in water (≈7-15 Tesla). To generate such high strength magnetic fields, sophisticated equipment is required—usually with a severe size limitation. As a result, processing of buckypapers using magnetic fields is not suitable for large scale composite manufacturing.
A relatively simpler technique was presented by Wang et al. [8] for making aligned buckypapers. The technique is called ‘domino-pushing.’ In domino-pushing technique, CNTs in a forest of vertically aligned CNTs are pushed form one side by applying force on the CNTs. As a result of this push, CNTs fall on the substrate aligned in the direction of the push. The steps of domino-pushing involve, covering the forest of CNTs with a micro porous membrane and then applying pressure on the CNT array using a roller placed on top of the membrane. The CNTs align in the direction of roller movement and stick to the porous membrane. The aligned buckypaper can then be peeled of the membrane using ethanol. Wetting the buckypaper membrane with ethanol promoted easy removal of buckypaper. A free-standing buckypaper of aligned CNTs is obtained by this process. However, domino-pushing can be used only with unfunctionalized CNTs. To author’s knowledge, a process of growing functionalized CNTs on a substrate has not been reported to-date in the literature.

The usefulness of buckypapers as interleaves in continuous fiber composites primarily depends on the complete infusion of buckypapers with resin. Since the reported permeability of buckypapers is 8-10 orders of magnitude lower than a regular glass fiber or carbon fiber preforms, the time taken to infuse buckypapers is much longer in comparison to fiber preforms. The reported permeability of SWCNT buckypaper is around $2 \times 10^{-19}$ m$^2$ [5], in comparison the permeability of compressed glass fiber performs ($V_f \sim 60\%$) under atmospheric pressure is $10^{-12}$-$10^{-13}$ m$^2$ [9]. According to 1D Darcy’s law, the infusion time is directly proportional to the ratio of thickness squared divided by permeability of the medium. Since the infusion time should be less than the gel time of resin, it is critical to use buckypapers of appropriate thicknesses and permeability to insure complete wetting of buckypapers by resin. A poorly wetted buckypaper would reduce rather than increase the interlaminar properties of fiber composites. Typically a free standing buckypaper has a minimum thickness of 25 µm, and would require 50 min. under vacuum pressure to completely wet by resin of viscosity 100 cP [5]. Typically the viscosity of b-staged epoxies in a continuous fiber epoxy prepregs is of the order of 500 to 1000 cP at elevated temperatures. Since the viscosity of epoxy resin rapidly changes at elevated temperature, thinner buckypapers are required to achieve quicker infusion to avoid problems in infusion due to increase in viscosity.
Another way of manufacturing sheets of randomly oriented CNTs is by the process of electrophoretic deposition (EPD). EPD is considered as a promising technique to make ceramics, coatings and composite materials [10-11]. The interest in EPD is driven not only by its applicability to great variety of materials, but also because of its simplicity. The basic idea is to use the surface charge of the particles suspended in a solvent to manipulate the particles using a DC electric field. EPD is a cost-effective technique that requires simple equipment and can be scaled-up to large dimensions if necessary.

EPD is achieved by the motion of charged particles towards an electrode, followed by subsequent deposition on the electrode, in a suitable solvent under the influence of DC electric field. By controlling the charge, electric field strength, and the time of deposition, films of controlled thickness and microstructural homogeneity can be deposited on complex shaped substrates. However, the particles can be deposited only on conducting surfaces. Various organic solvents used for EPD of CNTs are ethanol, mixtures of ethanol and acetone, dimethylformamide (DMF), isopropyl alcohol (IPA), and ethanol with bisphenol-A epoxy and aliphatic amine as the curing agent [12]. The most relevant work to discuss in detail considering the nature of present investigation was done by Du et al. [13-14]. Thin carbon nanotube composite sheets were prepared by EPD. The resin system used was EPI-Rez, a bis-A epoxy, and aliphatic amine curing agent EPI-CURE. The epoxy and curing agent were mixed with ethanol and the CNTs were dispersed in this mixture using sonication. Aluminum electrodes placed 50 mm apart were used to carry out EPD. A constant deposition voltage of 45 V was used to produce a homogeneous CNT-reinforced composite polymer coating on aluminum electrodes. The final concentration of CNTs in the polymer films was 45-55 wt%. The 55 wt% film showed a resistance of 7k Ohms measured by placing the leads of a multimeter 10 mm apart; however the 45 wt% film was not conducting. A possible reason for 45 wt% film to turn out insulating could be the way resistance was measured. Usually, a resin rich layer forms on top of CNT deposit after evaporating the solvent. For same amount of resin, the thickness of resin layer would be more in 45 wt% than 55 wt% film. Since the multimeter leads were placed on the outer surface of the film, measurement of resistance would depend on the penetration of electrons through the resin rich layer to reach the underlying conducting network of deposited CNTs to complete the circuit between the leads. A thicker layer would provide more resistance to current...
flow than a thinner layer, and thus a film with thicker layer or less concentration of particles would appear less conducting.

EPD has also been used to deposit CNTs directly on a conducting carbon fiber fabric. Bekyarova et al. [15] deposited CNTs on carbon fiber woven fabrics using EPD. These fabrics were impregnated with epoxy resin using vacuum assisted resin transfer molding (VARTM). The carbon nanotube/carbon fabric/epoxy composites showed an increase of 30% in the interlaminar shear strength as compared to without nanotubes, and demonstrated significant electrical conductivity through the thickness of the composites.

Driven by the usefulness of buckypaper and improvement observed due to alignment of CNTs in the buckypaper, there is a need to develop a technique that does not require magnetic field or domino-push for manufacturing buckypapers of aligned CNTs and CNFs. The usefulness of electric field to align CNFs and CNTs in a dielectric medium, such as liquid epoxide, has been demonstrated in Chapters 2, 3 and 4. Also, there is a need to manufacture buckypapers with thicknesses less than 25 µm that can be completely infused in a short time such that interlaminar fracture toughness of b-staged prepregs can benefit. Building on the understanding and knowledge gained from these previous chapters, the objective of the research described in the current chapter is to develop methods for manufacturing thin buckypapers with random and aligned CNTs and CNFs. AC electric fields are used in combination with electrophoretic filtration and deposition process to create buckypapers with aligned CNFs and CNTs. The buckypapers are used as interleaves in carbon fiber/epoxy laminates to determine the effect of buckypapers on Mode II interlaminar fracture toughness of the laminates.

6.3 1D Darcy's law
The minimum time to infuse the buckypaper in the through-thickness direction can be calculated by the following equation given in reference [5]

$$t = \frac{\eta T_b^2}{K_z P}$$

(6.1)

where, \(t\) is the time, \(T_b\) is the thickness, \(K_z\) is the permeability in through-thickness direction, and \(P\) is the pressure.

6.4 Approach
To achieve the objectives, EPD, filtration on porous media, and deposition on non-porous media are evaluated for making buckypapers of randomly oriented and aligned CNFs and CNTs. The
usefulness of buckypaper manufacturing methods is characterized by the effective transfer of buckypapers to the prepregs. The methods that successfully transferred buckypapers to prepregs were further modified to make buckypapers with aligned CNFs and CNTs using electric field.

6.5 Materials
The nanoparticles investigated were e-MWCNTs purchased from Cheaptubes (Cheaptubes Inc., Brattleboro, VA), and u-CNFs purchased from Applied Sciences (Applied Sciences Inc., Cedarville, OH). The e-MWCNTs have a purity of >95 wt%, diameters in the range of 10-20 nm and lengths of 10-20 μm. The u-CNFs are a commercial product designated Pyrograf®-III PR-24 HHT, with diameters in the range of 60–150 nm and as-received lengths of 30–100 μm, according to the manufacturer. The concentration of e-MWCNTs and u-CNFs used varied between 0.05 and 1 wt%. Unidirectional carbon fiber/epoxy prepreg was selected for this investigation to manufacture composites with one buckypaper interlayer.

6.6 Experiments
The methods for making buckypapers are first investigated using CNTs, if a method is found suitable for making buckypapers that can be transferred to a prepreg, that method is then also developed for making CNF buckypapers. Procedures for manufacturing carbon fiber/epoxy composites with a single buckypaper interlayer are described next. The Mode II interlaminar fracture strength testing of composites with one buckypaper interlayer is described after the manufacturing procedures.

6.6.1 Methods of manufacturing buckypapers
Three different methods were explored for making CNT/CNF buckypapers. In the following paragraphs, first the method of using electric field assisted deposition is described to make CNT buckypapers which is followed by the method of using filtration to deposit CNTs on a porous membrane, and finally a method to deposit CNTs and CNFs on a non-porous PTFE-coated glass cloth is described.

6.6.1.1 Electrophoretic deposition (EPD)
EPD is a direct current (DC) electric field driven process (Figure 6.1). CNTs suspended in an appropriate solvent acquire surface charge due to various chemical processes. Based on the polarity of the surface charge, CNTs move towards the electrode of opposite polarity due to the action of electric field on their surface charge. On reaching the electrode, CNTs stick to the
electrode due to image charge and van der Waals forces. The planned method using EPD is to deposit a uniform layer of CNTs onto an electrode, remove the electrode from the solvent and dry it in air, place the prepreg to top of the CNT-side of the electrode, press the prepreg against the CNTs using a roller so that the CNTs adhere to the prepreg, and then peel the prepreg and CNTs off of the electrode. Water and acetone were evaluated as solvents for EPD of CNTs. Aluminum foil was used as the electrode material.

6.6.1.1 Water as a solvent
CNTs were dispersed at 0.05 wt% in distilled water using ultrasonic agitation and a non-ionic surfactant commercially known as Triton-X 100. Sonication was carried out in an ultrasonic bath operating at 45-W and 38.5-kHz (Crest Ultrasonic, Trenton, NJ) for an hour. Appropriate amount of CNTs were added to 200 ml of water in a 250 ml glass beaker. The glass beaker was immersed in the water bath for ultrasonic agitation. Tap water was used as the fluid for ultrasonic bath.

6.6.1.2 Acetone as a solvent
CNTs were dispersed in acetone at 0.05 wt% using ultrasonic agitation and a non-ionic surfactant, Triton-X 100. Sonication was done for one hour in the same ultrasonic bath as that used for the water solution.

![Figure 6.1 EPD setup for bucky paper manufacture.](image)
6.6.1.2 Filtration of CNTs onto a porous membrane

Since the plan for buckypapers in this investigation is to use them as interleaves between commercially available prepreg plies, a thick buckypaper (> 30 µm) could create potential problems in resin infusion as discussed in section on literature review. Also, a thicker buckypaper would require a lot of resin to fully infiltrate. Especially in zero-bleed prepreg systems, a thick buckypaper might not get wet entirely due to the lack of sacrificial resin in zero-bleed systems. If the resin does migrate from the prepreg layers into the buckypapers, the fiber or void volume fraction in the prepreg plies would necessarily increase. Therefore, thinner buckypapers are of interest for zero-bleed prepreg systems and in general as interleaves. Since a thin buckypaper would be difficult to handle by itself, a support or backing would be required to improve buckypaper handling. A possible way to improve handling of buckypapers could be to leave the buckypapers deposit on the filter membranes, and then transfer buckypapers to the prepregs by taking the advantage of prepreg’s tackiness.

Two different types of PTFE membranes, laminated and unlaminated, were evaluated for transferring CNTs to the prepregs. The laminated membranes had a highly porous glass fabric attached to one side of the membrane. The PTFE membranes were glued to the glass fabric for support and strength. The laminated membranes should provide needed strength to peel the membranes off the prepreg after CNT transfer. The pore size was 1 µm and 10 µm for laminated and unlaminated membranes, respectively. Both types were purchased from Sterlitech (Sterlitech Corp., Kent, WA). CNTs dispersed in acetone at a concentration of 0.1 wt% were filtered through the membranes using vacuum to increase the flow rate of acetone through the membranes. Dispersion of CNTs was carried out using ultrasonic horn operating at 900W and 20k Hz for 30 min. No surfactant was used to disperse CNTs in acetone. CNTs were mixed in a 2.5 oz steel container. After sufficient amount of CNTs were collected on the membranes, the membranes were dried in air for 10 min. to evaporate the acetone. The dried membranes were placed onto the prepreg and a roller was used to press the membranes against the prepreg. The membranes were pulled off the prepreg surface slowly to prevent the membranes from ripping apart.
6.6.1.3 Depositing CNTs and CNFs onto a non-porous PTFE-coated glass cloth

A very simple technique using a mixture consisting of 1 wt% CNT/CNF in acetone was developed for making thin buckypapers. The mixture was directly poured on nonporous PTFE-coated glass cloth placed on a hot plate preheated to 160°F. The CNFs and CNTs were dispersed in acetone using ultrasonic bath. No surfactant was used to disperse CNFs and CNTs in acetone. The sonication was performed for 30 min. to achieve dispersion of CNFs and CNTs in the acetone. The vat of ultrasonic bath was filled with mixture of acetone and nanoparticles. This way the mixture was directly exposed to the vibrating walls of the ultrasonic bath. The reason for using the ultrasonic bath’s vat was the large amount of CNFs and CNTs that need to be mixed for making large sized buckypapers. After sonication, the mixture was immediately transferred to a 250 ml glass beaker and poured over a non-porous PTFE-coated glass cloth placed on a hot plate at 70-80°C. Since surfactant was not used, the dispersion of CNFs and CNTs was not stable in the suspension. The CNFs and CNTs would settle out in the beaker that was used to pour the suspension on non-porous PTFE-coated glass cloth. As a result, the suspension was vigorously shaken in the beaker after every 30 sec. to maintain the suspension of CNFs and CNTs. After pouring the suspension, the buckypaper was left on the hot plate for 10 min. and then dried additionally for a day at room temperature.

The non-porous cloth is placed onto the prepreg with the CNT-side facing the prepreg kept at 80-90°C. A roller is used to press the cloth against the prepreg. After making few passes with the roller, the prepreg with the cloth is removed from the hot plate and cooled to room temperature by placing it on a heavy steel plate. The prepreg cooled to room temperature in less than a minute. The prepreg was exposed to high temperature for less than 5 min. in this entire operation. To get a uniform coat of CNTs on the prepreg, the cloth is gently moved in a circular motion to spread the CNTs uniformly over the prepreg surface. The circular motion produces shear forces that smear a visually uniform layer of CNTs and CNFs onto the prepreg. CNTs and CNFs were transferred to one side of each of the two plies nearest to the plane of the starter crack. The prepregs with buckypaper were then exposed to elevated temperature and through-thickness pressure for a short duration of time in a hot press.
The prepregs were placed in a hot press with buckypaper side facing down. The hot press was at 80°C and the prepreg in that orientation was left there for 2 min. After two minutes, the press was closed to apply a pressure of roughly 100k Pa for 30 sec. This exercise ensured buckypaper stuck to the prepreg well.

6.6.2 Manufacturing interlaminar fracture specimens
The composites were manufactured using 26 plies of unidirectional carbon fiber/epoxy prepreg. The buckypapers were transferred on one surface of only to two plies. The two plies with buckypapers were placed in the center of the laminate where a PTFE insert film was placed to initiate a starter crack. A 12.7-μm-thick Teflon film was used at the mid-plane to serve as a starter crack. The plies were placed with their respective buckypaper sides facing each other. This placement results in the insert film sandwiched between the buckypapers, as shown in Figure 6.2. The prepreg used for this investigation was a carbon fiber/epoxy prepreg.

Figure 6.2 Schematic of the longitudinal section view close to the tip of the insert film, showing the CNT/CNF bucky paper placement during manufacturing of the laminates.

Unidirectional carbon/epoxy laminates were made in a closed steel mold in a computer-controlled hot press. The mold dimensions were 55×10.5×1.9 cm³. Laminates were made with and without buckypaper. One laminate for each CNT buckypaper and CNF buckypaper was manufactured. The laminates were cured at 122°C for 2 hours. The laminate was cured under
483k Pa pressure. The temperature was ramped at a rate of 3°C/min. from the room temperature to the maximum temperature of 122°C. The dwell time at 122°C was 2 hours. After curing for two hours at 122°C, the temperature was ramped down at a rate of 3°C/min. The pressure was released after cooling down to 60°C. After curing, specimens of dimensions 15.4×2.54×0.35 cm$^3$ were cut from the laminate with a water cooled diamond saw. The specimens were pat dried using a paper towel and then placed on a hot plate at 60°C for 2 hours. After drying the specimens were stored in a desiccator until they were taken out for testing. The length of the starter crack was around 30 mm. For comparison purposes, control specimens without buckypaper were also manufactured. The control specimens were prepared similarly to specimens with buckypapers.

6.6.3 Optical micrographs of buckypaper interlayers in composites
To determine the thickness of buckypaper embedded in the carbon fiber/epoxy composite specimens, the edges of specimens prepared for Mode II testing were observed under optical microscope. To get a clearer image of buckypaper, one untested specimen each containing CNF and CNT buckypaper was split open to expose the buckypaper on the edges of the specimens. The edges of the split open specimens were observed under microscope to determine the thickness of buckypapers.

6.6.4 ENF quasi-static test method
The testing was done by graduate student Ye Zhu for this section. Three specimens of each type were tested in quasi-static Mode II end-notch-flexure loading. The Mode II interlaminar fracture toughness test was conducted in two steps: 1) compliance calibration; 2) crack initiation. For compliance calibration and crack initiation, the ENF specimen was placed in a three point bending fixture and loaded by a servo-hydraulic MTS 810 machine. Load was measured by a 13.5 kN MTS load cell using the 2.2 kN (500 lb) range. Loading point displacement was measured directly from the MTS machine by the built-in LVDT. The test was conducted under displacement control with a constant displacement rate of 0.5 mm/min for loading and 1 mm/min for unloading. To obtain the compliance versus crack length relationship, compliance calibration procedures were conducted before the crack initiation test at crack lengths of $a_0 + 12$, $a_0 + 9$, $a_0 + 6$, $a_0 + 3$, $a_0$ and $a_0 - 3$ mm. A schematic of the specimen and loading arrangement is shown in Figure 6.3.
Compliance calibration
Compliance values of each ENF specimen were measured at 6 different crack lengths. The specimen was loaded to a loading point displacement, $\delta$, of about 50% of the estimated critical displacement ($\delta_{IIc}$) at each crack length. Load versus displacement relationships were obtained for loading at these six crack lengths. The compliance value at each crack length of compliance calibration was obtained by taking the inverse of the best-fit slopes of linear portion of loading curves.

Two third order polynomials are typically used to relate compliance to crack length. One is a complete third order polynomial with four parameters in the form of equation (6.2).

$$C = C_0 + C_1a + C_2a^2 + C_3a^3$$

(6.2)

The other polynomial is derived from classical plate theory (equation (6.3)) with only two parameters in the form of $A$ and $B$ in equation (6.4).

$$C = \frac{2L^3 + 3a^3}{8Ebh^3}$$

(6.3)

$$C(8bh^3) = A + Ba^3$$

(6.4)
To find the parameters for various specimens using equation (6.2), the compliance ($C$) versus crack length ($a$) data are plotted and a third order polynomial is fitted using the least squares method. To use equation (6.4), normalized compliance ($C(8bh^3)$) was plotted against the cube of crack length ($a^3$) and a straight line is fitted to the data using least squares.

**Mode II critical strain energy release rate (SERR) ($G_{IIc}$) onset value**

a) Classical Plate Theory (CPT) method

According to JIS standard K7086, the Mode II interlaminar fracture toughness according to the Classical Plate Theory (CPT) method is given by equation (6.5),

$$G_{IIc} = \frac{9a_0^2P^2C_1}{2b(2L^3 + 3a_0)}$$

(6.5)

where

- $G_{IIc} =$ mode II interlaminar fracture toughness,
- $a_0 =$ initial crack length of the precracked specimen;
- $P_c =$ initial critical load;
- $L =$ distance between support point and loading point (see Figure 6.3);
- $b =$ width of test specimen,
- $C_1 =$ load point compliance for the initial critical load.

b) Compliance Calibration (CC) method

The mode II SERR can be calculated by equation (6.6), if a relationship between the compliance and crack length is available.

$$G_{IIc} = \frac{P^2}{2b} \frac{dC}{da}$$

(6.6)

*Compliance Calibration (CC) method 1*

On substituting the compliance-crack length relation given by equation (6.2) into equation (6.6), mode II SERR can be obtained as shown in equation (6.7).
Another way of obtaining mode II SERR is by substituting the compliance-crack length relation given by equation (6.4) into equation (6.6). The resulting expression for mode II SERR is then given by equation (6.8).

\[
G_{IIc} = \frac{p^2}{2b} (c_1 + 2c_2a + 3c_3a^2) 
\]

\[
G_{IIc} = \frac{3p^2}{2b} \frac{B}{8bh^3} a^2 
\]

6.7 Results

6.7.1 Deposition using EPD

No EPD of CNTs was observed using 50-200 V/cm. CNTs dispersed in water did not acquire surface charge as expected, preventing the electric field from migrating CNTs towards an electrode. To accomplish EPD of CNTs, the pH of the water needs to be altered by adding chemicals like sodium hydroxide (NaOH). However, the use of NaOH or any other chemical compound will contaminate prepregs and could hinder the curing process in an unknown way. No further attempts were made to use water as a solvent for EPD, and it is concluded that dispersion of CNTs in water is not suitable for a process using EPD.

The CNTs dispersed in acetone deposited on the anode (positive electrode) on applying 100 V/cm electric field, indicating a negative charge on the CNTs in acetone. The electric field was applied for 30 min. After removing the electrode with CNTs, the CNT deposit was dried in air at room temperature for a couple of hours. Afterwards, the prepreg was placed on the CNT-side of the electrode at room temperature and was gently pressed onto the CNTs using several passes of a roller while the material was at room temperature. The CNTs did not lift off from the electrode. The means of transfer of CNTs to the prepreg is expected to be epoxy wetting of the CNTs and lifting of the CNTs by surface tension as the prepreg is peeled off the electrode. To improve the prospects of lifting the CNTs, transfer was attempted with the prepreg pre-heated to 121°C to reduce the viscosity of the epoxy and potentially improve wetting of the CNTs. The prepreg and electrode were heated for 5 min. before using the roller on the prepreg. After rolling the material a few times, the electrode and prepreg were cooled to room temperature. After peeling the
 prepreg from the electrode at room temperature, no CNTs were removed from the electrode. Instead, it was observed that a considerable amount of epoxy stuck to the electrode. It is therefore concluded that EPD of CNT onto a metallic electrode is not a good method for transferring CNTs to the prepreg.

In a yet another attempt to remove CNTs from the electrode, the CNT deposit was scratched with a sharp knife edge. Use of a knife edge resulted in broken pieces of CNT buckypaper. Therefore, no further investigation was done on making CNT or CNF buckypaper involving EPD.

6.7.2 Deposition using a porous filter membrane
The CNTs transferred well onto the prepreg surface when using the porous membrane approach, as shown in Figures 6.4 and 6.5. The distribution of CNTs on the prepreg surface appears to be of adequate uniformity across the entire transfer area. However, the unlaminated membrane broke while peeling off the prepreg surface as shown in Figure 6.4. The unlaminated membranes are weak in tension and could not withstand the peeling force. To resolve the problem of weak membrane, laminated membranes were evaluated. Laminated membranes have a backing of glass fiber film to give it structural strength. The laminated membranes on the other hand peeled of relatively easily but left very small amount of PTFE membrane on the prepreg which debonded from the glass substrate. Since it is desired to prevent contamination of the prepreg surface while transferring the CNTs, use of PTFE membranes was not evaluated any further. Moreover, the cost of large size PTFE membranes prohibits their use as potential transfer membranes.

![Figure 6.4](image)

**Figure 6.4** CNTs transferred onto prepreg from unlaminated PTFE membrane.
6.7.3 Deposition on a non-porous PTFE-coated glass cloth

Figure 6.6 shows uniform deposit of u-CNFs on PTFE-coated glass cloth obtained with a 1 wt% CNF/acetone mixture. The CNFs are randomly oriented in this deposit. The disadvantage of this technique is that buckypapers with aligned CNFs cannot be manufactured. The use of high temperature to facilitate the quick removal of acetone and high weight fraction of CNFs is the key to obtaining a deposit of uniform thickness on the glass cloth. The suspension of CNFs in acetone is highly unstable. Once the suspension is poured onto the cloth and the fluid comes to a rest, the CNFs agglomerate quickly and settle onto the cloth. The quick agglomeration of CNFs assists in forming a uniform deposit of CNFs. The formation of agglomerates prevents the CNFs from being washed away from the spot where the solution is poured.

Since agglomerates of CNFs form quickly, application of electric field can only orient the agglomerates and not individual CNFs. Moreover, application of high strength electric field would draw high currents due to the formation of chains of agglomerates in between electrodes. Due to high currents, there is a possibility that the deposited CNFs or CNTs might burn due to joule heating.
Based on visual observation of the PTFE release cloth after transfer, it was found that nearly all of the CNFs transferred to the prepreg (Figure 6.7) in a layer of good uniformity. A uniform transfer of CNFs onto the prepreg surface was obtained. Complete transfer is advantageous because it simplifies the determination of the amount of CNFs actually deposited onto the prepreg. That is, knowing the amount of CNTs in the acetone suspension, the areal weight of CNFs transferred to the prepreg can be easily determined.

Figure 6.6 u-CNFs transferred onto nonporous PTFE-coated glass cloth.

Figure 6.7 PTFE-coated glass cloth after u-CNF buckypaper transfer.
6.7.4 Micrographs of u-CNF and e-MWCNT buckypapers placed between plies

One specimen each from the carbon fiber/epoxy laminates with u-CNF and e-MWCNT buckypapers was prepared for optical observations as described in Section 6.6.3. The specimens were fractured in Mode I type of loading by pulling the two halves of the specimen apart, using hands. The crack was observed to propagate at the interface between one of the plies and buckypaper layer on fracturing the specimens (Figure 6.8). The thickness of u-CNF buckypaper is measured to be in the range 15-18 µm (Figure 6.8), and the thickness of e-MWCNT buckypaper is around 24 µm (Figure 6.9).

Knowing the thickness of u-CNF and e-MWCNT buckypapers in the carbon fiber/epoxy laminates, the time taken by the resin to infuse the buckypapers in the through-thickness direction can be estimated using equation (6.1). The pressure applied during the manufacturing of carbon fiber/epoxy laminates with u-CNF and e-MWCNT buckypapers was 483k Pa. Assuming the resin viscosity at 122°C to be around 500 cP, and permeability of 2×10^{-19} m² for both CNF and CNT buckypapers, the time taken for the resin to infuse u-CNF and e-MWCNT buckypapers are estimated to be 25 and 50 min., respectively. The predictions of time are assuming constant viscosity throughout the duration of infusion. However, the resin viscosity continuously changes with time at elevated temperature due to the progression of curing. Therefore, it is anticipated that it will take longer than 25 and 50 min. for the resin to infuse through the u-CNF and e-MWCNT buckypapers, respectively.
Figure 6.8 Micrograph depicting u-CNF buckypapers sandwiched between plies of interlaminar fracture toughness specimen of carbon fiber/epoxy composite. (Thickness of CNF buckypapers = 15-18 µm)

Figure 6.9 Micrograph depicting e-MWCNT buckypapers sandwiched between plies of unidirectional carbon fiber/epoxy composite prepared for Mode II testing. (Thickness of e-MWCNT buckypapers = 24 µm)
6.7.5 ENF quasi-static test results

To evaluate the usefulness of buckypapers manufactured using non-porous PTFE glass cloth and the transfer technique, unidirectional carbon fiber/epoxy composites were manufactured and tested for determining the Mode II interlaminar fracture toughness. Figure 6.10 compares Mode II quasi-static fracture toughness values for carbon/epoxy composites manufactured in a hot press with u-CNF and e-MWCNT buckypapers. Using u-CNF buckypaper provided higher fracture toughness values than e-MWCNT buckypaper. For ENF specimens made in the hot press, the fracture toughness increased by 170% in comparison to the control made by a similar process. In comparison, a e-MWCNT buckypaper resulted in only 28% improvement.

Figure 6.10 Comparison of Mode II interlaminar fracture toughness of unidirectional carbon/epoxy material made using e-MWCNT and u-CNF buckypapers. Bars show range of scatter among three test repetitions per material.

On evaluating the edges of broken Mode II specimens under microscope, it was observed that crack propagated only at the interfaces between u-CNF buckypaper layer and plies (Figure 6.11), and at some places along the interfaces between e-MWCNT buckypaper layer and plies and at others through the mid section of e-MWCNT buckypaper (Figure 6.12).
Figure 6.11 Longitudinal cross-sectional views along the length of a Mode II specimen, showing propagation of crack at the interface between u-CNf buckypaper layer and a carbon fiber/epoxy ply.

Figure 6.12 Longitudinal cross-sectional views along the length of a Mode II specimen showing propagation of crack. a) at the interface between e-MWCNT buckypaper layer and a carbon fiber/epoxy ply; b) through the mid section of e-MWCNT buckypaper layer.

The lower improvement in fracture toughness using e-MWCNT buckypaper in comparison to u-CNf buckypaper can be explained based on the occurrence of crack at the interface of buckypaper and plies or through the midsection of buckypaper layer. Since the e-MWCNT buckypaper was thicker than u-CNf buckypaper, the chances of incomplete impregnation of e-MWCNT buckypaper layer were higher than u-CNf buckypaper layer. In case of incomplete
impregnation through the thickness of the buckypaper layer, the likelihood of crack appearing midway through the buckypaper layer is higher than at the interface between buckypaper layer and plies. The resin impregnated regions of buckypaper are stronger and stiffer than regions devoid of resin because, in the absence of resin the strength and stiffness of buckypaper is due to the weak van der Waals forces holding the particles together. The crack is known to take the path of least resistance. The observation of crack propagation through the e-MWCNT buckypaper layer (Figure 6.12 (b)) indicates regions in that layer that are weaker than the interfaces between the buckypaper layer and plies (Figure 6.12 (a)). The location of the crack midway through the thickness is consistent with the argument of resin not being able to permeate through the entire thickness of the buckypaper layer. Ideally, the resin should permeate the buckypaper layer from both sides and meet midway through the thickness of buckypaper layer. Since the crack in some regions is observed midway through the thickness of e-MWCNT buckypaper layer (Figure 6.12 (b)), it can be concluded that these regions were not completely impregnated by the resin and were more susceptible to crack propagation. The lack of complete impregnation resulted in weaker interlayer and lower increase for e-MWCNT buckypaper composites.

6.8 Discussion and conclusions

6.8.1 EPD as a technique for manufacturing buckypaper
The technique of EPD is limited to using conducting substrates. A uniform deposit of CNFs or CNTs can be achieved using EPD, but the subsequent removal of deposit for further use is not possible due to strong adherence of CNFs and CNTs to the conducting substrate. The conducting substrate cannot be coated with a release agent for facilitating the removal of CNT deposit because the reduced conductivity of the substrate prevents CNTs from depositing on the electrode.

6.8.2 Filtration assisted manufacturing of buckypaper
Filtration of CNFs and CNTs on a porous membrane resulted in formation of thin buckypapers, but the subsequent removal of buckypapers from the porous membrane could not achieved without contaminating the prepregs. The technique of directly transferring buckypaper onto the prepreg by taking advantage of prepreg’s tackiness resulted in the breakage of unreinforced filter membrane and left small amount of PTFE membrane sticking to the prepreg in case of laminated PTFE membrane. Use of PTFE membranes showed potential, but was not investigated further on
account of the high cost of PTFE filter membranes. To give an idea of the cost, one filter membrane of 21×21 cm dimensions costs around $500. Since the membranes cannot be re-used for making more than one buckypaper, the cost of manufacturing composites by this method would be prohibitive.

6.8.3 Deposition of CNFs and CNTs on non-porous PTFE coated glass cloth for making buckypapers

The technique of directly depositing CNFs and CNTs on glass cloth using acetone with high weight fractions of CNFs and CNTs resulted in a fairly uniform deposit. The bucky papers were completely transferred to the prepregs. The advantage of this technique is an easy setup, ease of scale-up, and the reuse of PTFE glass cloth for making buckypapers to keep the overall cost of composite manufacturing low. The limitation of this process is that buckypapers with aligned CNFs and CNTs cannot be manufactured.

CNF and CNT buckypapers increased the interlaminar fracture toughness of carbon fiber/epoxy laminates. CNF buckypapers were found to be better than CNT buckypapers in improving the Mode II interlaminar fracture toughness of a carbon/epoxy prepreg laminate. The lower increase in Mode II interlaminar fracture toughness for e-MWCNT buckypaper in comparison to u-CNF buckypaper was due to the lack of complete impregnation of e-MWCNT buckypaper by resin. Overall, an increase in fracture toughness indicates that this method of manufacturing thin buckypapers of randomly oriented CNFs and CNTs is promising for manufacturing large scale composites. Special care should be given to the thickness of buckypapers to ensure successful infusion by the resin.
6.9 References


7 Conclusions

The overall conclusions of this thesis can be divided into two parts, the effective dispersion of CNFs and CNTs and the manipulation of orientations of effectively dispersed CNFs and CNTs using electric field in a low viscosity epoxy resin to tailor the elastic modulus and electrical conductivity of epoxy-based composites. More specifically, the two-part approach developed in this thesis tailored the elastic modulus and electrical conductivity of epoxy-based composites by controlling the dispersion, lengths, functionalization, and orientation of carbon nanotubes and nanofibers suspended in the epoxy resin. In the following paragraphs, conclusions are drawn separately for each of the four areas of focus: a) dispersion of CNFs and CNTs, b) controlling lengths of dispersed CNFs and CNTs, c) functionalization of CNFs and CNTs, and d) controlling the orientations of CNFs and CNTs in epoxy based composites.

7.1 Dispersion of CNFs and CNTs

The dispersion of CNFs and CNTs depends on the type of nanoparticles used, viscosity of liquid epoxide, time of sonication, and the type of functionalization used for enhancing the interface bond between particles and epoxy matrix.

Entangled nanoparticles vs. untangled nanoparticles

The entanglement state of nanoparticles in the as-received dry powders of u-CNFs and MWCNTs affects the dispersion of u-CNFs and MWCNTs. More work was needed to disperse entangled than untangled CNFs and CNTs. The amount of work needed to disperse nanoparticles was defined as the product of sonication power and time. a-MWCNTs are better than e-MWCNTs for dispersion in mixture of liquid epoxide and acetone.

Viscosity of the suspension

Use of diluted epoxide was found to be better than plain epoxide in dispersing nanoparticles. The amount of work done to disperse particles reduces considerably on reducing the viscosity of the suspension. The effect of suspension viscosity on particle dispersion can be adequately described by the theory of cavitation. A physical explanation based on the decaying strain rate around a
cavitation bubble captures the effects of suspension viscosity on particle dispersion. The rate of dispersion of particles decreases with an increase in suspension viscosity.

**Time of sonication**
With increase in sonication time, the lengths of CNFs progressively decreased to a critical length, beneath which, no scission of CNFs was observed with increasing time. Extended periods (15-60 min) of sonication considerably reduced the lengths of suspended CNFs. However, the degree of dispersion improved with increasing sonication time. It appears that to achieve good dispersion, lengths of nanoparticles will have to be sacrificed. It was determined in this investigation that the strain rate generated by ultrasonication in mixture of epoxide and acetone is $10^8$ s$^{-1}$. For a mix ratio of 20 ml:10 ml, epoxide to curative, 5 min. of sonication was adequate to disperse CNTs and CNFs. An aspect ratio close to 60 was obtained after 5 min. sonication for both CNFs and CNTs.

**Functionalization of CNFs and CNTs**
Among covalent functionalized MWCNTs, Amine1- and COOH-MWCNTs should be used for preparing stable dispersions of MWCNTs in curative or liquid epoxide (as the case may be depending on the functionalization of MWCNT) and acetone. Amine2- and PEI-MWCNTs cannot be used with the mixture of curative and acetone because the dispersed MWCNTs reagglomerated during the process of acetone evaporation. The non-covalently functionalized Z-MWCNTs dispersed well in the composites.

**Surfactant Triton-X 100 vs. BYK 9076**
Triton-X 100 resulted in good dispersion of CNFs in the mixture of liquid epoxide and acetone, but could not maintain the stability of the dispersion in liquid epoxide after acetone removal. BYK 9076 successfully maintained the dispersion of a-MWCNTs in liquid epoxide after acetone removal.

**Elastic modulus of random CNF and CNT epoxy composites**
Use of Triton-X 100 resulted in negligible improvement in elastic modulus of 1 wt% u-CNf/epoxy composites over the baseline epoxy modulus. Though PEI functionalized CNFs did
not disperse uniformly in the composite, the expected increase in elastic modulus and good wetting of PEI-CNFs by epoxy matrix indicated a good bond between PEI-CNFs and matrix.

Elastic modulus improved as expected for all the types of MWCNTs used, except for COOH-MWCNTs. The increase in modulus agreed fairly well with the predictions made using measured length distribution of a-MWCNTs after 5 min.

7.2 Aligning and chaining CNFs and CNTs in epoxy resin
The effect of AC field frequency on CNF and CNT chain assembly in liquid epoxide/curative system was studied by developing a 2-D FEA model for a single chain attached to an electrode. Experiments were performed using u-CNFs to corroborate the predictions of the model. Two forces, electrostatic and electro-hydrodynamic, are included in the FEA model. The assembly of chains close to the electrode is frequency dependent. The spacing between the chains decreases with increasing AC frequency. Closely spaced chains have more cross-links between them in comparison to chains farther apart. The number of cross-links between chains governs the resistivity transverse to chain direction. Higher electrical anisotropy is achieved for lower frequencies. Composites with non-covalently functionalized Z-MWCNTs exhibited DC resistivity anisotropy ratios ranging from 700 to 10. The anisotropy in DC resistivity was found to decrease with increase in electric field frequency used for assembling chains.

The growth of chains is maximized for an intermediate frequency of 1 kHz. Chains were assembled over large distances (~25 mm) using 1 kHz. The rate of chain growth is adequately explained by the FEA model. Considering chain growth to be a function of chain stretching and particle addition explained the occurrence of maximum chain growth rate at an intermediate frequency. The stretching of chain is affected by the hydrodynamic forces generated by the fluid flow due to AC electroosmosis, demonstrating the importance of considering hydrodynamic forces in assembling CNF chains in liquid epoxide.

A new method of assembling chains in liquid epoxide was discovered following the predictions of the FEA modeling. Chains were assembled in regions with CNFs and extended into regions where there were no CNFs. The observed stretching of chains into regions of no CNFs revealed
a new mechanism of chain growth that is different from the well-known assembly of polarized particles at the tip of the growing chain in a nonpolar medium.

The non-covalent functionalized Z-MWCNTs were found to be most useful to generate anisotropic resistivity in 0.5 wt% composites. For all the other 0.5 wt% MWCNTs composites, no anisotropy in DC resistivity could be generated using AC electric fields. The polymer wrapped around non-covalently functionalized MWCNTs assists in polarizing MWCNTs, eventually leading to alignment and chaining of MWCNTs in a 0.5 wt% composite. The pre-existing conducting pathways in a- and Amin1-MWCNT/liquid resin mixtures prevented polarization of CNTs, thereby leading to no preferential alignment of CNTs in these composites.

Alignment of 1 wt% CNFs and 0.5 wt% CNTs in epoxy composites resulting from the dispersion method used in this part of the investigation did not increase the elastic modulus appreciably. The shortened lengths of CNFs and CNTs resulted in insignificant improvement in elastic modulus due to alignment of CNFs and CNTs in the composites. The improvement due to alignment over random CNF/CNT composite modulus was expected to be 10% based on modified Halpin-Tsai model. It appears, to achieve good dispersion of CNFs and CNTs for effective alignment and chaining, the resulting shorter CNFs and CNTs will only improve electrical conductivity and not elastic modulus due to alignment.

7.3 CNT alignment in continuous fiber composites

AC electric field of 1000 V/cm at 100 and 1k Hz was found suitable to chain CNTs in the through-thickness direction of continuous glass fiber/epoxy composite. Electric field operating at 100 Hz resulted in increased anisotropy transverse to field direction, indicating preferential alignment of chains in the field direction. Use of 1k Hz was not effective in changing the resistivities transverse to the field directions, though a decreased resistivity in the direction of electric field indicated chains of aligned CNTs in the field direction. The chains in glass fiber/epoxy composites are not all uniformly oriented in one direction according to finite element analysis.
7.4 Manufacturing buckypapers of u-CNFs and e-MWCNTs

EPD was found to be unsuitable for making buckypapers. Filtration on a porous membrane resulted in buckypaper, but the buckypaper could not be transferred to the prepregs from the porous membrane without contaminating the surface of the prepregs with pieces of porous membranes. The direct deposition of CNFs and CNTs from a 1 wt% CNF and CNT/acetone suspensions on a non-porous PTFE-coated glass cloth was a useful way for making buckypapers. The buckypaper transferred well onto the surfaces of carbon fiber/epoxy prepregs. The thickness of bucky paper obtained from this process varied between 15-24 µm. Use of buckypapers as interlayers between plies increased the Mode II interlaminar fracture toughness of unidirectional carbon fiber/epoxy composites. The effective wetting of buckypaper was shown to be dependent on the thickness of buckypaper.
Appendix A: Procedure for Solving the Single Chain FEA Model

The finite element software COMSOL was used for modeling a chain of CNFs attached to an electrode. The following paragraphs show the step-by-step procedure for developing the model geometry, using the in-built modules for coupling the electrostatic and electrohydrodynamic problems, setting the domain properties, applying the boundary conditions, and then analyzing the results using the post-processing feature of COMSOL. The example shown here corresponds to the case of electric field strength of 100 V/cm applied at 100 Hz shown in Figure 3.10 in Section 3.6.2.

Step 1: Building the model geometry.

Figure A.1 shows schematic of a single chain attached to an electrode. Due to the symmetry in domain around the chain, only half of the domain shown in Figure A.1 was modeled using COMSOL. Figure A.2 shows the domain analyzed using finite elements.

Figure A. 1 Schematic of a CNF chain attached to an electrode.
Figure A. 2 Model geometry used in COMSOL for analyzing a chain attached to an electrode (right column). Numbers close to the lines in the model represent names of the boundaries. The in-built COMSOL modules used are shown at the top in the left column. The dependent variables and the type of elements used by each module appear in the second and third blocks of the left column.
**Step 2**: Defining governing equations for the domain.

After constructing the domain, the equations governing the electrostatic (PDE module) and hydrodynamic (Incompressible Navier-Stokes module) behavior were defined as shown in Figure A.3.
Step 3: Defining boundary conditions.

The boundary conditions for electrostatic problem were defined as shown in Figure A.4. Figure A.5 shows the boundary conditions for the hydrodynamic problem. Type is set to “Neumann” for the PDE module.

![Image of boundary conditions for PDE, Coefficient Form module.](image-url)

**Figure A. 4** Boundary conditions for PDE, Coefficient Form module.
Figure A. 5 Boundary conditions for Incompressible Navier-Stokes module.
**Step 4:** Defining constants and expressions.

The constants used in evaluating the boundary conditions were assigned as shown in Figure A.6.

![Figure A.6 Constants and expressions used for calculating FEA results.](image)

**Figure A.6** Constants and expressions used for calculating FEA results.

**Step 5:** Mesh and solve the model.

The model is meshed using the automatic-mesh-generation feature of COMSOL. The domain was meshed using unstructured triangular elements. After meshing, the model is solved in two steps. The first step solves the model for electrostatic problem using the PDE module. The results of PDE module are stored and used to solve the fluid problem using the Incompressible Navier-Stokes module. Figure A.7 shows the solver options used for obtaining the results.

![Figure A.7 Solver options used for obtaining the results.](image)
Step 6: Analyze the results using Postprocessing feature of COMSOL.
Appendix B: Non-technical Abstract

To meet the many demands that are being placed on the structures and components in aerospace applications, considerable efforts are being aimed at developing ways to provide additional functionality to commonly used aerospace materials and take them beyond their structural role. The ubiquitous use of epoxy-based composite materials in aerospace applications makes them prime candidate for conducting research to engender functionalities in such composite materials to meet the demands of aerospace industry. One such way to provide functionality to epoxy composites is to incorporate multi-functional fillers in the composites. Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) show great promise as multi-functional nanofillers for epoxy-based composites due to their small size, exceptional mechanical and electrical properties, and high aspect ratio (length/diameter ratio ~1000). CNTs and CNFs can be used for tailoring epoxy properties such as the stiffness, strength, thermal and electrical properties, particularly if well aligned. Well aligned and connected networks of CNTs and CNFs can render epoxy composites sufficiently electrically conducting to be used in various electrical applications, as well.

The effective reinforcement of epoxy composites by CNTs/CNFs is hindered mainly by the difficult dispersion of CNTs/CNFs in the epoxy resin and the poor interfacial adhesion between the CNTs/CNFs and the epoxy matrix. Due to CNT/CNF processing procedures, CNTs/CNFs tend to form tight bundles or ropes which, in turn, agglomerate into entangled networks or webs. Ropes and webs do not exhibit the same outstanding mechanical properties as individual CNTs and CNFs because of CNTs/CNFs slipping within the ropes and webs. To realize the full potential of dispersed CNTs and CNFs as reinforcement, it is also necessary to ensure good transference of load from the matrix to dispersed CNTs and CNFs. Due to the lack of affinity between CNTs/CNFs and epoxy matrices, there is insufficient transfer of mechanical loads between the CNTs/CNFs and the matrix.

Part of the results presented in this work is on controlling the dispersion of CNFs and CNTs to obtain well dispersed CNTs and CNFs with controlled lengths. The process of ultrasonic agitation was used to disperse CNTs and CNFs in epoxy resin. To improve the interfacial bond between dispersed CNTs and CNFs, the outer surface of CNTs and CNFs was functionalized with amine polymers. The use of amine polymer covalently integrated CNTs and CNFs with epoxy matrix and facilitated the load transfer between CNTs/CNFs and the matrix.

In another part of this effort, alternating current (AC) electric field was used to manipulate the orientations of dispersed and functionalized CNTs and CNFs to further enhance the elastic properties and electrical conductivity of epoxy-based composites. Aligning CNTs and CNFs in load bearing direction improves the load bearing capacity of the composite material. A theoretical frame work is proposed to understand the interaction of CNTs and CNFs with the applied AC field. Building on the theoretical understanding, manufacturing efforts were guided to align and assemble CNTs and CNFs in epoxy-based composites to engender nano-scale morphological textures. CNTs and CNFs were successfully aligned and assembled to improve the elastic and electrical properties of epoxy-based composites. It is envisioned that the efforts of this investigation will provide techniques to manufacture epoxy-based composites with additional functionalities by incorporating CNTs and CNFs in epoxy composites.
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RESEARCH INTEREST: Interested in the manufacturing, performance, evaluation, and mechanics of fiber reinforced composites. Research focus is on using carbon nanotubes and nanofibers for enhancing the multi-functionality of epoxy based composites. This multi-functionality is achieved by developing nano-scale morphological textures using AC and DC electric fields. Application areas include composites for aerospace structures, civil structures, and industrial machinery.

- Carbon Nanotube Enhancement of Interlaminar Fracture Toughness of Carbon and Glass Fiber Prepreg Laminates
- High Performance Damping with Carbon Nanotube-Polymer Composites
- Fabrication of Flexible Matrix Composite Skins for Structure Actuation
- Thermomechanical Characterization of Carbon Nanoreinforced Composites
- Investigation of Zentron and E-Glass Composite Strength for AGY’s Composites
- Material testing of Carbon/Epoxy Composites for Boeing Flywheel Rotor Rim
- Radial Tensile Strength of Carbon/Epoxy Rings by C-ring Test Method

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