2004

Characterization of Aligned Carbon Nanotube/Polymer Composites

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Characterization of Aligned Carbon Nanotube/Polymer Composites

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering at Virginia Commonwealth University.

by

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B.Tech., Mechanical Engineering (Mechatronics), Jawaharlal Nehru Technological University, Hyderabad, India, 2002

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Acknowledgement

I would like to acknowledge several people for their help in completing this thesis. I would like to thank my advisor Dr. Zoubeida Ounaies for the advice, guidance and support that she continuously provided to me throughout my graduate work. I would also extend my thanks to Dr. Karla Mossi and Dr. Gary Wnek for being on my thesis committee. My thanks to my colleagues at Electroactive Materials Characterization Laboratory for all the help they provided to me. This work was supported in part by the NASA University Research, Engineering and Technology Institute on Bio Inspired Materials (BIMat) under award No.NCC-1-02037.

I would like to thank my parents, my sister, my brother in-law, my grandparents and my friends for their encouragement and moral support. Special thanks to my uncle Ramesh Chamala for all the love, encouragement and moral support he provided during my masters study.
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List of Abbreviations & Symbols

\( \sigma_z \) Parallel conductivity, along \( z \) axis
\( \sigma_{x,y} \) Perpendicular conductivity, along \( x \) and \( y \) axis
\( \varepsilon_z \) Perpendicular dielectric constant, along \( z \) axis
\( \varepsilon_{x,y} \) Parallel dielectric constant, along \( x \) and \( y \) axis
\( \varepsilon_T \) Dielectric constant in transverse direction
\( \varepsilon_L \) Dielectric constant in longitudinal direction
\( \Delta \varepsilon \) Change in relative permittivity
\( \varepsilon_0 \) Dielectric constant in vacuum
\( \varepsilon' \) Dielectric constant
\( \nu_c \) Critical volume concentration
\( \pi \) bond Pie bond
\( \sigma \) bond Sigma bond
\( \delta \) Strain
\( \beta \) CN-APB 2,6 Bis (3-amino phenoxybenzo nitrile)
AIBN 2,2-azo bisisobutyronitrile
AC Alternating current
C\textsubscript{60} Carbon \textsubscript{60}
CNTs Carbon nanotubes
CVD Chemical vapor deposition
C\textsubscript{6} Chiral vector
C Capacitance
C\textsubscript{12}EO\textsubscript{8} Polyoxyethylene 8 lauryl
DMAC N,N dimethylacetamide
DMA Dynamic mechanical analysis
DC Direct current
DMF Dimethyl formamide
\( E_p \) Applied electric field
EDA Electron donor acceptor
\( E \) Electric field
\( e \) Eccentricity
H DMA 1,6-hexanediol dimethylacrylate
HCL Hydrochloric acid
Hipco High pressure carbon monoxide
\( L_{x,y,z} \) Depolarization factors along \( x \), \( y \) and \( z \) axis
MWNTs Multi wall carbon nanotubes
ODPA 4,4 oxydiphthalic anhydride
OM Optical microscopy
PDMA Poly(diallyldimethyl ammonium) chloride
PHAE __________________________ Polyhydroxyaminoether
PMMA __________________________ Poly(methyl) methacrylate
PANI ___________________________ Polyaniline
PS ______________________________ Polystyrene
P _______________________________ Polarization
PI ______________________________ Polyimide
P_r ______________________________ Remanent polarization
SiO_2 ___________________________ Silicon dioxide
SWNTs __________________________ Single wall carbon nanotubes
SEM ____________________________ Scanning electron microscopy
T_g ______________________________ Glass transition temperature
tan δ ____________________________ Loss tangent
TEM ____________________________ Transmission electron microscopy
THF ______________________________ Tetrahydrofuran
UV ______________________________ Ultra violet
UDMA ___________________________ Urethane dimethylacrylate
Y’______________________________ Complex shear modulus
Y’’______________________________ Loss modulus
Y’______________________________ Storage modulus
Y _______________________________ Shear modulus
Abstract

Characterization of Aligned Carbon Nanotube/Polymer Composites

By Sumanth Banda, B.Tech.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering at Virginia Commonwealth University.

Virginia Commonwealth University, 2004.

Major director: Dr. Zoubeida Ounaies, Assistant Professor, Mechanical Engineering.

The main objective of this thesis is to efficiently disperse and align SWNTs in two different polymer matrices to obtain an orthotropic composite whose strength, stiffness and electrical properties depend on the orientation of the SWNTs. The SWNTs are successfully dispersed and aligned in a polyimide matrix and a polymer blend of UDMA/HDDMA. In-situ polymerization under sonication is used to disperse the SWNTs in polyimide matrix and sonication is used to disperse SWNTs in the UDMA/HDDMA matrix. In both cases, an electric field is used to align the SWNTs in the polymer matrices. In the polyimide, the SWNTs are aligned by electrospinning technique, and in (UDMA/HDDMA) the SWNTs are aligned by applying an AC electric field, while the composite is cured.

The electrical and mechanical properties of randomly dispersed SWNT polyimide composites and SWNT/UDMA/HDDMA composite are measured. The dielectric
constant and storage modulus of SWNT polyimide composite increased with SWNT concentration. Low percolation (0.06 wt%) and an increase of 113% in storage modulus with 0.2 wt% SWNTs, both indicate good dispersion of SWNTs in the polyimide matrix. The dielectric constants, conductivity for the unaligned SWNT/UDMA/HDDMA composite are isotropic. The electrical and mechanical properties of the randomly dispersed SWNT polyimide composite and SWNT/UDMA/HDDMA composite are used as references when analyzing the aligned counterparts.

Different characterization methods are used to assess the alignment of the SWNTs in the polyimide and (UDMA/HDDMA) matrices. A variety of characterization techniques, i.e. microscopy, Raman spectroscopy, electrical conductivity, dynamic dielectric spectroscopy and dynamic mechanical analysis, indicate preferential alignment of SWNTs in two types of polymers: Polyimide and (UDMA/HDDMA). Optical microscope images showed alignment of the SWNTs in the UDMA/HDDMA composite. Inspection of the Raman spectra on aligned SWNT polyimide composite fibers and aligned SWNT/UDMA/HDDMA composite indicates a decrease in the intensity of the tangential peak of the SWNT with increase in the polarizer angle. The difference in the perpendicular and parallel Raman peaks indicate preferential alignment of SWNTs in both the polymer matrices. In the aligned polyimide composite, percolation transition is at 0.2 wt% SWNT concentrations when dielectric constant is measured parallel to the aligned SWNTs. But percolation transition is at 0.65 wt% SWNT concentrations when dielectric constant is measured perpendicular to the aligned SWNTs. Electrical
measurements on aligned SWNT polyimide and UDMA/HDDMA composite are highly anisotropic. In both cases, the dielectric constant values parallel to the direction of SWNT alignment are higher than the values perpendicular to the direction of SWNT alignment. To analyze the resulting anisotropy in the dielectric constant, Bruggeman’s effective medium approach is used. The effective medium theory predicts the effective dielectric constant of a composite with aligned anisotropic inclusions. The effective dielectric constant, perpendicular to the aligned inclusions and parallel to the aligned inclusions is estimated. The dielectric constant values of aligned SWNT polyimide and aligned SWNT/UDMA/HDDMA composites are compared to the experimental results. Both the values from the theory and experiment show anisotropy in dielectric constant. The theory indicated that the dielectric constant parallel to the aligned inclusions is highly influenced by the dielectric constant of the inclusion and the dielectric constant perpendicular to the aligned inclusions is highly influenced by the dielectric constant of the polymer matrix.

Results from the different characterizing techniques indicate that SWNTs are successfully aligned in the polyimide matrix and (UDMA/HDDMA) matrix by electrospinning technique and by an AC electric field respectively.
Chapter 1

Introduction

New avenues in the design of future aerospace vehicles can be enabled by taking advantage of multifunctionality in structures. Multifunctional polymer composites arise by merging structural functions with self sensing and actuation abilities. Multifunctional composites have the potential of enabling a revolution in air and space travel by increasing intelligence in aerospace systems and vehicles while reducing mass, size, power consumption and design complexity and improving performance. To meet this need it is envisioned that with their impressive suite of properties, carbon nanotubes (CNTs) can be embedded in polymers to produce composites that can provide both sensing, actuation and load bearing functionalities. CNTs have a very high aspect ratio, which makes them highly anisotropic; they can be aligned in polymers to obtain anisotropic electrical and mechanical responses in polymer composites. CNTs tend to agglomerate and form bundles because of the high van der Walls forces of attraction, which makes it a major challenge to disperse CNTs and have good adhesion between CNTs and the polymer matrix. It is also a major challenge to align CNTs in the polymer matrix. This chapter introduces the effect of CNT structure on its properties and addresses the existing methods used to disperse and align CNTs in polymers.
1.1 Background on carbon nanotubes:

The class of materials that is composed of the $C_{60}$ molecule is known as fullerene. The $C_{60}$ molecule exists in discrete molecular form and consists of a hollow spherical cluster of sixty carbon atoms. Each molecule is composed of groups of carbon atoms that are bonded to one another to form both hexagon and pentagon geometrical configurations. CNTs are long, slender fullerenes where the walls of the tubes are hexagonal carbon and are capped at both ends with $C_{60}$ fullerene hemispheres. CNT can be visualized as a graphene sheet that has been rolled into a tube. CNTs are either single walled nanotubes (SWNT) or multi walled nanotubes (MWNT), where SWNT is a tube with only one wall, and MWNT have many concentric tubes where the walls of the tubes are held together by weak van der Walls forces. Figures of SWNT and MWNT are shown in Figure 1.1(a) and Figure 1.1(b). The properties of CNTs depend on chirality, diameter and length of the tubes. Chirality is defined by the symmetry and the chiral angle formed between the tubes.

![Figure 1. (a) Image of SWNT with one tube [1], (b) image of MWNT with concentric tubes [2].](image)
carbon bonds. The graphene sheet can be rolled up with varying degrees of twist along its length resulting in CNTs having a variety of chiral structures. The atomic structure of CNTs is described in terms of the tube chirality, or helicity, which is defined by the chiral vector \( C_h \) and the chiral angle \( \theta \) which is shown in Figure 1.2. The chiral vector is \( C_h = na_1 + ma_2 \), where the integers \((n,m)\) are the number of steps along the zig-zag carbon bonds of the hexagonal lattice and \( a_1 \) and \( a_2 \) are unit vectors whose lengths are equal to \( \sqrt{3} \, d_{c-c} \) with \( d_{c-c} \) indicating the C-C bond length [3]. The different pairs of integers \((n,m)\) define a different way of rolling the graphene sheet to form a CNT. The diameter \( D \) of tube \((n,m)\) and the chiral angle \( \theta \) with equal \( d_{c-c} \) are given by

\[
D = \frac{\sqrt{3}d_{c-c}}{\Pi} \cdot \sqrt{n^2 + nm + m^2} \quad \text{and} \quad \theta = \arccos \frac{2n + m}{2\sqrt{n^2 + nm + m^2}}.
\]

Armchair CNTs are formed when \( n=m \) and the chiral angle is 30°. In zig-zag CNT, \( n \) or \( m = 0 \) and \( \theta = 0° \). All other chiral CNTs have chiral angles between 0° and 30° [4]. Depending on the tube

![Figure 1.2. Chiral vector and chiral angle explained on a graphene sheet [6].](image)
chirality the electrical properties of the CNTs differ; they can be metallic or semiconducting [5]. When n-m=3p, where p is an integer, the CNTs are metallic and when n-m≠3p, the CNTs are semiconducting.

Carbon based materials and molecules are unique in many ways. One distinction relates to the many possible configurations of the electronic states of a carbon atom, which is known as the hybridization of atomic orbitals. Each carbon atom has six electrons which occupy 1s², 2s², and 2p² atomic orbitals. The 1s² orbital contains two strongly bound electrons which are the core electrons. Four electrons occupy the 2s² 2p² orbitals which are weakly bound valence electrons. A crystalline phase is a collection of particles ionized with the same polarity that would have a crystalline configuration. In the crystalline phase the valence electrons give rise to 2s, 2px, 2py, and 2pz orbitals which are important to form covalent bonds in carbon materials. A schematic of s, px, py, and pz orbitals are shown in Figure 1.3. The energy difference between the upper 2p energy

![Figure 1.3. Schematic of s, px, py, and pz orbitals, which undergo hybridization in carbon.][7]
levels and the lower 2s level is small compared with the binding energy of the chemical bonds, the electronic wave functions for these four electrons can readily mix with each other which changes the occupation of the 2s and three 2p atomic orbitals so as to enhance the binding energy of the carbon atom with its neighboring atoms. This mixing of 2s and 2p atomic orbitals is called hybridization. The structures of carbon materials are related to the sp^n (n=1,2,3) hybridization which is a mixing of a single 2s electron with 2p electron. The fundamental atomic forces consist of strong $\sigma$ bonding and $\pi$ bonding forces between intralayer C=C and weak interlayer interactions. A $\sigma$ bond is a covalent bond in, which electrons are shared between atoms. In a $\sigma$ bond, the orbital overlap occurs directly between the nuclei of the atoms. The $\pi$ bond involves the electrons in the left over p orbital, which has orbital overlap off to the sides of the line joining the nuclei. In sp^n hybridization, (n+1) $\sigma$ bonds per carbon atom are formed. In sp^3 hybridization, four $\sigma$ bonds defining a regular tetrahedron are sufficient to form a three dimensional structure known as the diamond structure. Diamond is a metastable carbon polymorph at room temperature and atmospheric pressure. Each carbon bonds to four other carbons and these bonds are totally covalent. Due to its crystal structure and the strong interatomic covalent bonds it is very hard, has a very low electrical conductivity and has a very high thermal conductivity for a non metallic material. Another polymorph of carbon is graphite; it is a two dimensional planar structure formed by sp^2 hybridization. A schematic of sp^2 hybridization is shown in Figure 1.4. The graphite structure is composed of layers of hexagonally arranged carbon atoms and within the layers each carbon atom is bonded to three coplanar neighbor atoms by strong covalent bonds. The fourth bonding
electron participates in a weak van der Walls type of bond between the layers which makes it a good lubricant. CNT is another form of carbon that is made from the fullerene which is a planar closed polyhedra formed by $sp^2$ hybridization. Like graphite, CNTs are also $sp^2$ bonded; however, the curvature and cylindrical symmetry cause very important modifications compared with planar graphite. CNTs have exceptional material properties and these properties are a consequence of their symmetric structure, topology and highly
anisotropic nature; in contrast to planar graphite where the graphene sheets do not have a symmetric structure and are not anisotropic in nature. The chirality and the tube diameter, introduces significant changes in the electronic density of states and, hence provide unique electronic character for the CNTs [8, 9]. The other factor is topology, or the closed geometry of the individual layers in each tube [10, 11], which has a profound effect on the physical properties; in contrast to planar graphite where the individual graphene layers are stacked on top of each other with weak van der Walls forces of attraction. The combination of size, structure, and topology endows nanotubes with important and unique mechanical (stability, strength, stiffness, and elastic deformability), transport (coherent electron transport), and surface properties [12]. CNT is widely regarded as the ultimate fiber with regard to its strength in the direction of the nanotube axis as it is made of the strong covalent C=C bonds. The fundamental atomic forces consist of strong σ bonding and π bonding forces between intralayer C=C and weak interlayer interactions. A σ bond is a covalent bond in, which electrons are shared between atoms. In a σ bond, the orbital overlap occurs directly between the nuclei of the atoms, as shown in Figure 1.4. The π bond involves the electrons in the left over p orbital, which has orbital overlap off to the sides of the line joining the nuclei, as shown in Figure 1.4. By rolling a graphene sheet to form a CNT, the total energy of the nanotube is increased by the strain energy associated with the curvature of the nanotube, the strain energy increases with decreasing nanotube diameter. SWNTs have a tensile modulus that ranges from 270 GPa to 1 TPa and a tensile strength ranging from 11 to 200 GPa which is 10 to 100 times higher than the strongest steel at a fraction of the weight [13, 14].
SWNTs have a very low density of ~1.3 g/cm$^3$, this is because of the hollow structure of SWNTs. SWNTs also exhibit exceptional thermal and electrical properties. SWNTs are thermally stable up to 2800°C in vacuum, their thermal conductivity is about twice as high as that of diamond; these high values are due to the large phonon mean free paths present in SWNTs, the fact that their electric-current carrying capacity is 1000 times higher than that of copper wires [15].

Since the discovery of CNTs, there have been different techniques in producing them. The different methods to synthesize CNTs include arc-discharge [3, 16-19], laser ablation [20], chemical vapor deposition from hydrocarbons [21-23] and gas phase catalytic growth from carbon monoxide [24]. In 1991, Iijima [3] first observed MWNTs through the electric arc discharge method. Subsequently, in the year 1993 Iijima et al [8] and Bethune et al [25] reported the synthesis of SWNTs by the laser ablation technique. During the synthesis of the CNTs, impurities in the form of catalyst particles, amorphous carbon soot, and non tubular fullerenes are also produced such that the nanotubes have to be purified to eliminate them. The electric arc discharge technique generally involves the use of two high purity graphite rods as the anode and cathode, the rods are brought together under helium atmosphere and a voltage is applied until a stable arc is achieved. The material then deposits on the cathode to form a build up consisting of an outside shell of focused material and a softer fibrous core containing nanotubes and other carbon particles [16-19]. In laser ablation technique, a laser is used to vaporize a graphite target held in a controlled atmosphere oven at temperatures near 1200°C. The condensed
material is then collected on a water cooled target [20, 26, 27]. Both are discharge and laser ablation techniques produce small quantities of CNTs with a lot of impurities. Gas phase techniques are developed to overcome these limitations. Chemical vapor deposition from hydrocarbons is a gas phase technique that utilizes hydrocarbon gases as the carbon source for production of CNTs. The CNTs are formed by the decomposition of a carbon containing gas, the hydrocarbons pyrolyze readily on surfaces when they are heated above 600-700°C. This is a continuous process as the carbon source is continuously replaced by flowing gas [21-23]. High pressure carbon monoxide (Hipco) is another gas phase technique to produce exclusively SWNTs with carbon monoxide as the carbon source. SWNTs are produced by flowing carbon monoxide with a small amount of Fe(CO)\(_5\) through a heated reactor that is maintained between 800°C and 1200°C. The products of Fe(CO)\(_5\) thermal decomposition react to produce iron clusters in gas phase. These iron clusters act as nuclei upon which SWNTs nucleate and grow [24]. Hipco is an effective method to continuously produce high purity SWNTs. Besides the SWNTs, the raw Hipco material contains amorphous carbon and iron (Fe) particles coated by thin carbon layers. The unwanted products can be selectively removed by multistage procedure which is thermal oxidation in a wet Ar/O\(_2\) environment and washing with concentrated hydrochloric acid (HCL) [28].

Both SWNTs and MWNTs can be embedded in polymer matrices to improve the mechanical, electrical and dielectric properties of the polymers. SWNTs show exceptional mechanical, electrical, and thermal properties that can be exploited as
reinforcements for composite structures, but in the case of MWNTs very weak van der Walls forces exist to link the individual graphene shells together, allowing the inner shells to rotate and slide freely; therefore, using MWNTs as intrinsic reinforcements for composite structures may not allow the maximum strength to be achieved. For this reason, SWNTs are most desired for fundamental investigations of the structure/property relationships in CNT reinforced polymers. CNTs have a very low density, comparable to that of polymers. CNTs can be embedded into polymers to make light weight composites with exceptional properties for structural applications. The conductivity and dielectric properties of the polymers can be improved by the addition of CNTs in the polymers. Embeding SWNTs in the polymers increases the toughness of the polymer and at the same time does not change ductility [29].

1.2 Dispersion of CNTs:
The practical applications of CNT composites have so far been largely limited by their poor processibility. The intrinsic van der Walls attraction among the tubes in combination with their high surface area and high aspect ratio often leads to significant agglomeration of CNTs. The surface of CNTs is also non reactive which makes it difficult in achieving efficient dispersion, as they mix and blend with the host matrix. To effectively use CNTs as intrinsic reinforcements in composite structures and ensure a good stress transfer between CNTs and the polymer matrix, uniform dispersion within the polymer matrix and improved nanotube/matrix wetting and adhesion are critical. Different methods have been used to efficiently disperse the CNTs in polymer matrices. CNTs are ultra sonicated
in a solvent to disperse them before they are added to the polymer matrix or before another dispersion technique is applied [30-33]. Micro scale twin screw extruder [6, 34, 35] melt mixing [36, 37] and coagulation [32] are some mechanical methods that minimizes the aggregate formation by applying appropriate shear to CNT polymer composite. Dispersion of CNTs is also done by using dispersants as processing aids in CNT polymer composites [38, 39]. In another technique CNTs are chemically modified and functionalized to disperse them better in the polymer matrix [40-42]. The functionalization chemistry of the open ends, the exterior walls and the interior cavity of the CNTs play a vital role in tailoring the properties of CNTs. CNT sidewall surface is chemically modified by fluorinating and defluorinating them, CNTs then serve as a staging point for a wide variety of sidewall chemical functionalizations that results in better dispersion. Another method to disperse CNTs is by in situ polymerization in which CNTs are added while the polymerization is in process [33, 43]. Details on all methods follow below.

Ultrasonication is a very effective method used to disperse CNTs in a solvent before it is added to a polymer matrix. Safadi et al [30] dispersed MWNTs in toluene using an ultrasonic wand dismembrator at 300 W for 30 min. The MWNT suspensions are then admixed with toluene solutions of 30% Polystyrene (PS) to yield 1 wt%, 2 wt% and 5 wt% PS/MWNT solutions. These mixtures are further homogenized in an ultrasonic bath for 30 min. Approximately 20 mL of each solution was poured into a flat-bottomed glass dish, and the toluene was allowed to evaporate, to obtain thin uniform films. Conductivity
measurements showed good dispersion, as the composite samples exhibited percolation threshold at less than 0.5 vol% SWNTs. Composites up to 1 vol% MWNT loading exhibited an increase in tensile strength, but samples with higher MWNT loading showed a decrease in the tensile strength. This indicates that the MWNTs are not well dispersed at 1 vol% and higher concentrations. In another effort, Dufresne et al [31] performed centrifugation in addition to ultrasonication. Purified CNTs are suspended in a distilled water solution of 1 wt% sodium dodecyl sulfate surfactant, the solution is sonicated to break up and suspend the nanotube bulks. The sonication step is performed 5 times for 2 min with $20 \times 10^{-6}$ m$^3$ suspension volumes with a freezing step between each 2 min sonication. The resultant CNT suspension is concentrated by centrifugation at 14,000 rpm for 1h and the resultant residue is sonicated again 4 times for 2 min. A stable CNT aqueous suspension is then mixed with poly(styrene-co-butyl acrylate) matrix, which is obtained by the copolymerization of styrene and butyl acrylate containing acrylic acid and acrylamide. The MWNT poly(styrene-co-butyl acrylate) solutions were cast in a Teflon mold and films were obtained by storing the casting at 35°C to allow both water evaporation and polymer particle coalescence. Composite films with 0 to 15 wt% MWNTs were obtained. Scanning electron microscopy showed good dispersion of the filler for the samples with MWNT concentrations below 5 wt%. Scanning electron microscopy (SEM) images show MWNT clusters that are heterogeneously dispersed within the polymeric matrix for 5wt% and higher MWNT concentrations. The clustering of MWNTs is mostly by the evaporation of water after the composite is cast. For highly filled samples (5wt% and up), the evaporation step most probably induces translational
motion of the MWNTs leading to their sedimentation. Electrical conductivity results showed that a percolation threshold occurred below 3wt% MWNT concentration. Tensile tests showed a decrease in the elongation at break decreases with MWNT content greater than 3 wt%. Good dispersion is obtained up to 3wt% MWNT concentration, while results indicated bad dispersion of MWNTs at 3wt% and higher.

A micro scale twin screw extruder and micro compounding machine are used to obtain the high shear mixing necessary to disentangle and disperse MWNTs in polymers [6, 34, 35]. Thostenson et al [6] used a micro-scale twin screw extruder to disperse the MWNTs in polystyrene matrix. To obtain the correct weight fraction of MWNTs within the polymer and minimize exposure to nanotubes that become airborne, polystyrene is dissolved in tetrahydrofuran (THF) and mixed with MWNTs. The solution is cast in a petri dish and sonicated as the solvent evaporates. After drying, the mixture of MWNTs and polymer is fed into the twin screw extruder that is pre heated to 155°C, and the polymer is melted and subsequently mixed for 3 min at a screw speed of 100 rpm to disperse the MWNTs within the matrix. The high shear obtained from the micro-scale twin screw extruder disentangles the MWNTs and disperses them uniformly in a polystyrene thermoplastic matrix. Addition of the MWNTs increased the tensile modulus, yield strength and ultimate strengths of the polymer films. Increase in the mechanical properties of the composite indicate that the MWNTs were effectively dispersed in PS using a micro scale twin screw extruder. Sandler et al [34] also used a twin-screw extruder to disperse MWNTs in a polyamide matrix. Polyamide pellets and MWNTs were blended in a DSM
twin screw microextruder, operating at 220°C at 80 rpm. The extruder material is chopped and fed into a capillary rheometer also operating at 220°C. A single strand is spun from 1mm diameter die, and wound up at around 0.5 m/s to produce a final fiber. Nanocomposites with a range of loading fractions up to 15 wt% are produced. SEM images demonstrated a high level of dispersion for all the samples, although occasionally a few aggregates are shown in composites with high MWNT concentrations. This indicates that high concentrations of MWNTs were not perfectly dispersed in the polyamide matrix. Du et al [32] used a new and versatile fabrication method called coagulation method to achieve a better dispersion of SWNTs in PMMA matrix without changing the structure of the SWNTs. The SWNTs in DMF are sonicated at 45 kHz for 24 hours to disperse the SWNTs in DMF and then desired quantity of PMMA is dissolved in the SWNT and DMF mixture. The suspension is then dipped into a large amount of distilled water in a blender. PMMA precipitates immediately because of its insolubility in the DMF and water mixture. The precipitating PMMA chains entrap the SWNTs and prevent SWNTs from bundling again. The mixture is then filtered and vacuum dried at 120°C for 24 h to obtain SWNT/PMMA composite. Optical and SEM micrographs show good dispersion up to 7 wt% SWNT concentrations. Higher concentrations of SWNTs showed aggregation of SWNTs.

Gong et al [44] have reported the role of surfactants which function as a dispersing agent in processing of CNT epoxy composites. Polyoxyethylene 8 lauryl (C_{12}EO_8) is used as the surfactant, which is a nonionic surfactant containing an oxyethylenated hydrophilic
segment, a hydrocarbon which is a hydrophobic segment and a good dispersant for carbon. The mixture of $C_{12}EO_8$ and acetone is added to CNTs, which is stirred before it is added to epoxy. CNT epoxy samples with the surfactant and control epoxy samples with the surfactant are prepared. Results indicate that by the addition of only 1 wt% CNTs in the composite, the glass transition temperature increased from 63°C to 88°C. The increase in the glass transition temperature indicates good dispersion of CNTs in the epoxy matrix as the CNTs restrict the relaxation of the polymer matrix at 63°C, causing the relaxation to occur at a higher temperature. The epoxy samples with surfactant showed a decrease in the elastic modulus compared to the elastic modulus of the epoxy samples without the surfactant. The decrease in the elastic modulus indicates that the surfactant acts as a plasticizer. But when the surfactant is added along with the CNTs to the epoxy matrix, the elastic modulus increased by more than 30%. This indicates that the surfactant along with CNTs improves the properties of epoxy matrix. In a similar attempt poly(diallyldimethylammonium chloride) (PDMA) is used as a dispersing agent by Li et al [38] to disperse MWNTs in aqueous solutions. MWNT powder is added into a 1 wt% PDMA solution, sonicated for 20 min, centrifuged at 4500 rpm for 30 min and a suspension is obtained. Transmission electron microscopy (TEM) images indicate well-dispersed MWNTs in PDMA solutions. CNTs are usually neutrally charged, so the CNTs are attracted to each other by the van der Walls forces. It is assumed that the dispersing function of PDMA arises from the adsorption of PDMA on the surface of CNTs. It is found that cationic PDMA in aqueous solutions can be strongly absorbed onto the surfaces of many materials, thus it is likely that the polymer could be absorbed onto the
surface of the CNTs in solutions. As a result of adsorption, the tube surface is positively charged, which leads to the separation of the entangled tubes via electrostatic repulsion. This may be the origin of the dispersion of MWNTs in PDMA. However, due to the positive charge on the CNTs, the electrical properties and dielectric properties may be detrimentally affected.

Another method to disperse CNTs is by chemically modifying them. Mickelson et al [42] reported modifying SWNTs by fluorination. In fluorinating the SWNTs, elemental fluorine diluted with helium is passed through a temperature controlled flow reactor containing the SWNTs. The reactions are carried out at different temperatures 150°C to 600°C. After the fluorination is done, SWNTs are defluorinated with anhydrous hydrazine for 1 hour then washed with water. The fluorination and defluorination of CNTs makes the CNTs reactive and they serve as a staging point for a wide variety of sidewall chemical functionalizations. It is expected that due to the interaction between the polymer chains and the functionalized CNT, which is reactive, the CNTs will be dispersed in the polymer matrix. Raman spectroscopy and Infra red results indicate that fluorine is being covalently attached to the side wall of the SWNTs. The method of fluorination and defluorination tampers the structure of the CNTs, causing defects on the walls of the CNTs. Due to the defects on the walls of the CNTs the carbon bonds are affected, which in turn change the mechanical, electrical and thermal properties of the CNTs. Jia et al [41] reported efficient dispersion of CNTs in polymethyl methacrylate (PMMA) by opening their π bonds. CNT/PMMA composites are prepared by an in situ
process. PMMA is produced in a process of addition polymerization. In this process of addition polymerization AIBN (2,2’-azobisisobutyronitrile) is added into methyl methacrylate (MMA) to form long chain PMMA molecules. CNTs are ground in a high rate ball mill for 20 min, and then boiled for 0.5 h in concentrated nitric acid and were then washed. Appropriate amount of AIBN is put into the MMA and stirred for 75 min and then CNTs are put into the mixture. PMMA molecules grow and wrap around the CNTs and well dispersed CNT composite is obtained. In this process the CNTs are initiated by AIBN to open their $\pi$-bonds that can link each other and PMMA matrix. If the $\pi$ bonds are just at the curved points of CNTs, AIBN will break down the CNTs, which leads to CNTs becoming shorter and possessing opened ends. Because the $\pi$ bonds in CNTs are linked to the opened bonds in PMMA, the growth of PMMA molecules is obstructed by linking CNTs and may produce C-C bond between the CNT and the PMMA. With the bond, a strong interface between the CNTs and the PMMA is produced. In this method the $\pi$ bonds which contribute to the physical properties of the CNT are opened, which in turn changes the properties of the CNTs. Tensile strength, fracture toughness and hardness tests showed improved properties up to 7 wt% of CNTs. When the CNT content exceeds 7 wt% the mechanical properties of the composites decreases. The composites become very brittle when CNTs get to 10 wt%. The tensile strength of PMMA by the addition of 3 wt% functionalized CNTs increased by 21%, which was low compared to a 90% increase in the modulus of PMMA by the addition of 2 wt% non-functionalized SWNTs reported by Du et al [32].
Li et al [43] have reported the fabrication of SWNT/PANI composites by in situ polymerization of an aniline solution containing different SWNT contents. SWNT ranging from 1 wt% to 8 wt% is added to 5 ml of aniline. The mixture is heated at reflux for 3 hours in the dark. After reflux for a short time, the original colorless aniline solution first became brownish and then turned dark red indicating that SWNTs have been dissolved into aniline. SWNT solution is then obtained by filtration. Polymerization is started by adding a solution of HCL to aniline with dissolved SWNTs in various mixture ratios. This is then stirred at 0-5°C and then an equal volume of pre-cooled oxidant solution containing ammonium persulfate in HCL is slowly added drop wise to the well stirred solution. The mixture is then left for polymerization for 2 hours at 0-5°C under constant stirring. The color of the solution changes to green, indicating polymerization of aniline with dissolved SWNTs. SWNT/PANI composites are obtained by filtering and then drying under vacuum at 80°C for 24 hours. Electron microscopy and conductive analysis show uniform SWNT dispersion in the PANI matrix. In another attempt Park et al [33] used ultrasonication along with in situ polymerization to disperse SWNTs in polyimide composites. The polymer used as a matrix is a colorless polyimide (CP2). The diamine and dianhydride used to synthesize the CP2 are 1,3-bis(3-aminophenoxy) benzene (APB) and 2,2-bis(3,4-anhydridicarboxyphenyl) hexafluoropropane (6FDA), respectively. A dilute SWNT solution around 0.05 wt% in dimethylformamide (DMF) is prepared by homogenizing for 10 min and sonicating for one and a half hours in an ultrasonic bath (40 kHz). The diamine is then added to the SWNT solution and the mixture is stirred for 30 min before adding the dianhydride. The entire reaction is carried
out in an ultrasonic bath until the solution viscosity is increased and stabilized. Microscopy images show good dispersion of SWNTs, the composite exhibited significant conductivity enhancement at very low SWNT loading, mechanical properties as well as thermal stability increased by incorporating the CNTs. This method of in situ polymerization under sonication effectively dispersed SWNTs in a continuous polymer matrix.

**1.3 Alignment of CNTs:**

CNTs are highly anisotropic in nature because of their high aspect ratio. It is important to have aligned CNTs in the polymer matrix to take advantage of their anisotropic structure and to have improved properties in the direction of the alignment. By aligning the CNTs in the polymer matrix, the strength, stiffness, electrical and thermal properties of the composite can be controlled. Most of the proposed applications of CNTs like electrical field emitter for flat panel displays and artificial actuators require special synthesis routes so that the as grown tubes are aligned between two points in forming tube bundles [45-50]. These CNTs are aligned during fabrication. Depending on the application of CNTs, they can be aligned by arc discharge technique and CVD by applying an electric field while fabricating the CNTs [51-53] or they can be aligned after they are dispersed in a solvent [54]. The advantage of aligning CNTs while producing them by the CVD process is that it allowed assembling individual CNTs into desired architectures by placing them at specific locations with controlled orientations. The disadvantage with this method is that the CNTs are not perfectly aligned when they are embedded into composites as they
lose their alignment due to dispersion. An electric field can be applied to a CNT suspension to assemble, rearrange and orient the CNTs. Mechanical methods like microscale twin screw extruder, melt processing [55] and mechanical stretching of CNT composites [56] are also used to align the CNTs in polymer composites. Finally a strong magnetic field is applied to magnetically align CNTs in polymer composites [57, 58]. Aligning CNTs in polymer composites mechanically and by applying an electric field has rendered better alignment compared to aligning CNTs by a magnetic field. Using a magnetic field is not very effective, as conductivity results have showed only one order of magnitude increase in the direction of the aligned CNTs, for 1 wt% and 2 wt% CNTs in polyester matrix [57, 58]. CNTs are not easily influenced by magnetic fields; in addition, very high magnetic fields are usually required. Details on alignment methods are given below:

Haggenmueller et al [55] attained aligned SWNT polymer composites by a combination of solvent casting and melt mixing method. A solution of PMMA in DMF is prepared; it is combined with dispersed SWNTs and is sonicated. The solution is cast onto Teflon dishes. The cast composite films are folded and broken into pieces, then stacked between two polished metal plates. This stack is then hot pressed at 180°C and 300 lb for 3 min. The films are again broken and stacked between metal plates then hot pressed. This melt mixing procedure is repeated 25 times. The conductivity parallel to the aligned SWNTs was higher, compared to the conductivity perpendicular to the aligned SWNTs. The conductivity parallel and perpendicular to the aligned SWNTs was 0.118 S/m and 0.078 S/m respectively, for 1.3 wt% SWNTs in PMMA. Polarized Raman spectra on aligned
fibers showed a variation in the intensity of the tangential peak, for various polarizer angles. In another mechanical technique to align CNTs, Thostenson et al [6] aligned MWNTs in polystyrene matrix using the extrusion technique. The polymer melt is extruded through a rectangular die and drawn under tension before solidification. Micrographs taken with a transmission electron microscope (TEM) on samples sectioned to the drawing direction show overall alignment of MWNTs. As compared to the pristine polystyrene polymer, the storage modulus at 25°C of the aligned MWNT polystyrene composite increased 49% as compared to a 10% increase for the randomly oriented composites. Aligned MWNT polystyrene composites also showed an increase in the yield strength and ultimate strength as compared to the pristine polystyrene polymer. These results indicate that the process of extruding the nanocomposite through the die and subsequent drawing resulted in a continuous ribbon of aligned MWNT composite. In another technique Jin et al [56] aligned MWNTs in polyhydroxyaminoether (PHAE) by mechanical stretching. Thin films are made from the composite and the films are mechanically stretched at 100°C by applying a constant load. The sample is then cooled under the applied load and the load is released when the sample reaches room temperature. Micrographs taken with a TEM showed that the CNTs and the impurities are aligned in the direction of the stretch. X-ray diffraction patterns are collected from both the stretched and unstretched samples. The diffraction spectrum is dominated by a strong Bragg peak centered around 3.4 Å, which corresponds to the intershell spacing within the CNTs and nanoparticles. The slightly larger spacing is related to the stacking disorder in these nanostructures. When the CNTs are randomly oriented inside the polymer
matrix, a powder diffraction ring with a d spacing of ~3.4 Å is obtained. In the stretched sample due to the orientation of the CNTs, the Bragg peak intensity is concentrated at two spots. The change in the diffraction pattern from a uniform powder ring before stretching to two spots after stretching indicates that the nanotubes in the stretched composite film are aligned. Wood et al [59] used a flow orientation technique to align the SWNTs in the polymer matrix. SWNTs are dispersed in a UV curable urethane acrylate polymer and a curing agent is added to the mixture. The SWNT polymer composite is spread onto a glass slide and it is sheared twice with a doctor blade to induce flow orientation. The resulting thin films are immediately cured by exposing to a UV source. The flow orientation based on shearing the polymer encourages polymer molecular orientation and therefore nanotube alignment in the polymer matrix. X-ray diffraction and electron microscopy showed orientation of SWNTs in the polymer matrix. The advantage of melt mixing and extrusion techniques is that these methods disperse and align the CNTs in polymers. The disadvantage of melt mixing is that it is a very long procedure and time consuming, and the disadvantage of flow orientation technique used by Wood et al [59] is that it can be used only in UV curable polymers.

A high magnetic field is used by Kimura et al [57] to align the CNTs in a polymer matrix. The solution containing unsaturated polyester and styrene monomer is mixed with MWNTs. Under a constant magnetic field of 10 T, the monomer is polymerized by adding a radical indicator. Polymerizing this MWNT monomer dispersion under the magnetic field freezes the alignment of MWNTs in the polyester matrix. High resolution
TEM images, sliced in a parallel direction to the magnetic field had relatively long MWNTs, which were not seen in the images perpendicular to the magnetic field. The conductivity parallel to the magnetic field is one order of magnitude higher, than that measured perpendicular to the field at 1 wt% and 2 wt% MWNT concentrations. The elastic modulus measured in the parallel direction is greater than the perpendicular direction. Anisotropy in conductivity and elastic modulus show alignment of MWNTs in polyester composite. Smith et al [58, 60] used a higher magnetic field to make thick aligned SWNT films. A high magnetic field of 25 T is applied to align the SWNTs suspended in the magnetic fields. A magnetic field is applied across a syringe filter, in which suspended tubes deposit under axial flow onto a filter membrane normal to the syringe axis. Resistance is measured parallel and perpendicular to the direction of alignment. The resistance in the parallel and perpendicular directions showed anisotropy. The resistance value perpendicular to the aligned direction was greater than the resistance, parallel to the aligned direction. The parallel resistance value was 2.3 (mΩ cm) and perpendicular resistance was 0.095 (mΩ cm). The anisotropy in resistance indicates alignment of SWNTs. The major disadvantage in using these methods is that very high magnetic fields are required to align the SWNTs and a very small amount of anisotropy in conductivity is measured.

Ural et al[53] have studied the growth of aligned SWNTs on surface of substrates by electric field directed CVD growth. SiO$_2$ is used as a substrate and molybdenum metal electrodes are used to apply the electric field where the gap between the metal electrodes
is 10 µm. Aligned SWNTs across the gap are grown in a CVD system equipped with electrical feedthroughs. SWNTs are grown at 900°C for 2 min under 720 mL/min of methane, 500 ml/min of hydrogen, and 12 mL/min of ethylene flow. Pure hydrogen is passed during heating and cooling to prevent oxidation of the Mo electrodes by possible oxygen impurities. A voltage of (3-20) V is applied across the gap between the Mo electrodes. Control samples in the absence of electric fields show that the nanotubes grown from the catalyst regions bridge the electrodes in random orientations. A high degree of alignment is observed for nanotubes grown under applied electric fields between the Mo electrodes, where the nanotubes are clearly aligned perpendicular to the edges of the electrodes, in the direction of the electric field. Tanemura et al [52] synthesized well aligned CNTs on W wires covered with Co or Ni films using direct current plasma enhanced CVD. Mixtures of acetylene and ammonia in the ratio 1:2 are introduced into the CVD chamber and a negative dc potential (-500 V) is applied to the resistively heated W wire which induces a glow discharge growing CNTs on the W wire. SEM and TEM images showed well aligned CNTs perpendicular to the wire surface. The disadvantage of these electric field methods is that aligned CNT composites can not be obtained. Chen et al [54] aligned SWNTs by applying an AC electric field. SWNT solution is obtained by ultrasonically dispersing them in ethanol. Gold interdigitated electrodes are prepared on Si/SiO₂ substrates by the vacuum deposition method. The gap between two electrodes is 25 µm and the thickness of the electrodes is 50 nm. The substrates are immersed in the SWNT solution and an AC electric field applied to the gold interdigitated electrodes. SEM images show that there are aligned SWNTs when a
voltage of 10 V$_{pp}$ at a frequency of 5 MHz is applied. SEM image when voltage is 10 V$_{pp}$ at a frequency of 500 Hz, showed bundles of SWNTs between the interdigitated electrodes. It is observed that the alignment of the SWNTs is highly dependent on voltage magnitude and frequency, and as the frequency is decreased the alignment of the SWNTs decreased. Because of the anisotropy in the SWNTs, the dipole moment in the direction parallel to the tube axis is higher than the dipole moment in the direction perpendicular to the tube axis, resulting in alignment of tube axis with direction of electric field. In this work by Chen et al [54] the SWNTs were aligned in a solvent and not in a composite. This method of AC electric field alignment is used in this thesis to align SWNTs in UDMA/HDDMA polymer, to induce anisotropy in the polymer.
Chapter 2
Scope of thesis

2.1 Problem statement:

New avenues in the design of future aerospace vehicles can be enabled by taking advantage of multifunctionality in structures. Multifunctional polymer composites arise by merging structural functions with self-sensing and actuation abilities. Multifunctional composites have the potential of enabling a revolution in air and space travel by increasing intelligence in aerospace systems and vehicles while reducing mass, size, power consumption and design complexity and improving performance. They could be used as sensing and compensating systems for reliability and safety; and they could be adaptable and self-healing systems for extended space missions [61, 62]. Sensors and actuators for space applications need to be lightweight and flexible because of the limitation in weight and size for transportation, but at the same time they are expected to have a structural ability. To meet this need, multifunctional polymer composites could be designed as high strength smart materials for aerospace vehicles, large space structures and miniature space systems, which could be lightweight and have high energy conversion efficiency and low power consumption. State of the art lightweight aerospace structures are built from graphite fiber composites. It is envisioned that with their impressive suite of properties, SWNTs can be embedded in polymers to produce composites that have the potential to surpass the performance of conventional graphite fiber composites by providing both sensing, actuation and load bearing functionalities in
vehicle structures. SWNTs have a very high aspect ratio, which makes them highly anisotropic; they can be aligned to obtain anisotropic electrical and mechanical responses in polymer composites. For example, SWNTs, aligned perpendicular to the cracks in composites, slow down the crack propagation process by bridging up the crack faces [29, 63]. By aligning SWNTs in desired directions, composites used in space devices for electrostatic discharge and electromagnetic radio frequency interface could have micro-tailored properties. In addition to aerospace, these materials could have a tremendous impact in numerous industrial, civil, medical and electronics applications. Aligned SWNTs /polymers components are expected to be very promising as field electron sources for flat panel displays as they can be grown directly onto the desired locations of a large substrate [64, 65]. Vertically aligned MWNTs can be used in making thin film transistors, where electron transport is through the aligned MWNTs [66].

In this work, SWNTs are dispersed and embedded into two different polymer matrices to make composites with different SWNT volume fractions. It is a major challenge to disperse SWNTs in polymers, as they tend to agglomerate and form bundles due to their high van der Walls force of attraction. Bad dispersion of SWNTs in the polymer matrix results in poor electric, dielectric and mechanical properties. In situ polymerization in the presence of sonication in the polyimide matrix and sonication in UDMA/HDDMA matrix are accomplished to efficiently disperse the SWNTs in both polymer matrices. An electric field is used to align SWNTs in both the polymer matrices. In the polyimide matrix, electrospinning technique is used to align SWNTs, where it is believed that a
combination of DC electric field and mechanical stretching yields to alignment. In the UDMA/HDDMA polymer composites, AC electric field at different frequencies is used to align the SWNTs while the composite is being cured. These techniques have the potential to align SWNTs in the polymer matrices to produce an orthotropic material whose strength, stiffness, electrical and thermal properties depend on the orientation of SWNTs. Multifunctional composites with tailorable mechanical, electrical and dielectric properties can hence be designed.

The objectives of this study are: (1) to efficiently disperse SWNTs in the polymer matrices by using in situ polymerization under sonication, (2) to establish a benchmark for isotropic nanocomposites performance by determining the electric and mechanical properties of randomly dispersed SWNT polymer composites, (3) to effectively align SWNTs in the polymers, (3) to assess the alignment by optical spectroscopy, Raman spectroscopy, mechanical, dielectric and conductivity measurements, (4) to compare the performance of aligned and isotropically dispersed SWNT polymer composites and (5) to develop a theory for the anisotropy of dielectric permittivity in aligned SWNT polymer composites.

2.2 Thesis Organization:

The study on characterization of aligned carbon nanotube/polymer composites consists of five chapters. Chapter 1 offers a background on SWNT properties, their various processing methods, and dispersion and alignment techniques. Chapter 2 introduces the
problem statement of this study. Chapter 3 is the experimental section, consisting of processing of polyimide and UDMA/HDDMA composites with SWNT inclusions, aligning of SWNTs by electro spinning and AC electric field, and characterizing the resulting nanocomposites through optical microscopy, scanning electron microscopy, Raman spectroscopy, conductivity measurements, dielectric spectroscopy and mechanical properties of aligned and unaligned samples. Chapter 4 presents the results obtained from optical microscopy, Raman spectroscopy, conductivity measurements, dielectric spectroscopy, and mechanical testing of SWNT polyimide composites and SWNT/UDMA/HDDMA composites. It analyzes and discusses them, and validates findings using composite theory. Chapter 5 offers conclusions and recommendations for future work.
Chapter 3

Experimental

This section introduces processing of two different types of polymer composites: SWNT polyimide composites and SWNT/UDMA/HDDMA composites. The two techniques used to align SWNTs in polyimide and UDMA/HDDMA are described in detail. The experimental conditions and the description of different characterization tools like optical microscopy, scanning electron microscopy, Raman spectroscopy, conductivity, dielectric spectroscopy and dynamic mechanical analysis are described in this section.

3.1 Processing of randomly oriented SWNT polyimide composite:

A batch of purified, Hipco processed SWNTs is obtained from Carbon Nanotechnologies Inc. The polymer used as a matrix is a (βCN-APB/ODPA) polyimide. This particular polymer is chosen because of the presence of dipoles, namely, a nitrile aromatic moiety, added to make the polyimide electroactive. The diamine and dianhydride used to synthesize this polyimide are 2,6 Bis (3-amino phenoxybenzo nitrile) (βCN-APB) diamine and 4,4 Oxydiphthalic anhydride (ODPA) dianhydride respectively. The synthesis procedure of (βCN-APB)/ODPA is shown in Figure 3.1. N,N-dimethylacetamide (DMAC) is used as a solvent. A three neck round bottom flask equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube outlet is used. The diamine βCN(APB) is mixed along with DMAC in the three neck flask and is stirred for 15 min before the dianhydride (ODPA) is added. The entire solution is continuously stirred, until the viscosity of the solution increases. The increase in viscosity indicates
completion of polymerization and formation of polyamic acid. The polyamic acid solution is cast on a glass plate using a doctor's blade, and dried in a dry-box until it is tack-free. After drying, the cast film is thermally cured at 110°C, 170°C, 210°C and 250°C for 1 hr each in a nitrogen circulating oven to obtain solvent free polyimide films.

![Diagram of polyimide synthesis](image)

**Figure 3.1. The synthesis procedure of polyimide.**

To prepare a SWNT polyimide composite, the SWNTs are dispersed in polyimide matrix using in-situ polymerization under sonication, which is a technique developed by Park et al [33]. The processing technique of SWNT polyimide composite is shown in Figure 3.2. A dilute SWNT solution in DMAC is prepared in a three neck round bottom flask.
equipped with a mechanical stirrer, nitrogen gas inlet, and drying tube outlet. The solution is prepared by homogenizing for 10 min. Then the diamine βCN(APB) is added into the SWNT solution. The SWNT solution and diamine mixture is continuously stirred
for 15 min before adding the dianhydride (ODPA). The entire reaction is carried out in an ultrasonic bath (40 kHZ) until the solution viscosity increases and is stabilized indicating completion of polymerization. Additional stirring is continued overnight without sonication to obtain polyamic acid solution. Solid content for SWNT-polyamic acid is 15 wt% in DMF. A series of SWNT-polyamic acid solutions with SWNT concentrations ranging from 0.01wt% to 5wt% are prepared. The SWNT polyamic acid solution is cast on a glass plate using a doctor's blade, and dried in a dry-box until it is tack-free. After drying, the cast film is thermally cured at 110°C, 170°C, 210°C and 250°C for 1 hour each in a nitrogen circulating oven to obtain solvent free SWNT polyimide films. The method of film casting produces randomly oriented SWNT polyimide composite films.

3.2 Aligning of SWNT in polyimides by electrospinning:

SWNT-polyamic acid solution is prepared as mentioned in section 3.1, the solution is then chemically imidized. This is done to produce SWNT- polyimide solution, by adding acetic anhydride and pyridine to the SWNT-polyamic acid. Acetic anhydride and pyridine are added as catalysts to imidize the polyamic acid into polyimide solution. Polyimide solutions with 0 wt%, 0.1 wt%, 0.2 wt%, 0.65 wt% and 1 wt% SWNT concentrations are then processed for electrospining. Electrospinning is a technique where an electrode is connected to a high voltage power supply, which is inserted into a polymeric solution contained within a capillary tube or a syringe. A schematic of electrospinning set up is shown in Figure 3.3. A grounded collector screen is placed at a certain distance from the tip of the syringe. The polymer solution is placed in the syringe,
which is connected to a high voltage power supply and a metering pump is used at the end of the syringe to deliver the polymer solution. Initially, the polymer solution is held by its surface tension in the form of a droplet at the end of the syringe. As the voltage is increased, charge is induced on the fluid surface, and the droplet is distorted when the applied voltage overcomes the charge. Above a critical voltage, a single jet is ejected from the apex of the conical meniscus, which is referred to as a Taylor cone. Prior to the deposition on the collector, the jet may undergo a fluid instability that leads to accelerated solidification of the fluid jet and the collection of solid, in the form of charged fibers, on the collector, usually a non-woven fabric [67, 68]. The electrospinning apparatus used in this experiment is designed to eject polymer resins using a high DC electric field towards a collection device. A grounded stainless steel plate is used to collect the splaying polymer fibers. Attached to the collector is a motor, allowing the
plate to spin at a fast rotational velocity. The polymer resin is delivered using a 10ml plastic syringe with an 18-gauge needle tip. An electrode is attached to the needle with an alligator clip and the other end is attached to a Spellman CZE1000R high voltage power supply unit. Infusion from the syringe is controlled using a digitally controlled KD Scientific syringe pump (model number 100). The rate is set to deliver polymer resin at 5 ml/hr. Distance between the syringe tip and collection plate is held constant at 20 cm, at this distance the solvent evaporated and fibers were formed. Different voltages of 15 kV, 20 kV, and 25 kV are applied to determine the effects on resulting fiber properties.

3.3 Aligning SWNTs in the UDMA/HDDMA polymer matrix:

The polymer used in the preparation of the composite is a mixture of urethane dimethylacrylate (UDMA) and 1,6- hexandiol dimethylacrylate (HDDMA). The chemical structures of UDMA and HDDMA are shown in Figure 3.4(a) and Figure 3.4(b). The

![Chemical structures](a)

![Chemical structures](b)

Figure 3.4. Chemical structures of (a) urethane dimethylacrylate (UDMA) and (b) 1,6- hexandiol dimethylacrylate (HDDMA).
concentrations of UDMA and HDDMA are in the ratio of 9:1. A batch of purified Hipco processed SWNTs is obtained from Carbon Nanotechnologies Inc. Solutions of pure UDMA/HDDMA, which is a photocurable liquid, is mixed along with 0.03 vol% of SWNTs in UDMA/HDDMA. The SWNTs are first added to HDDMA and sonicated to break up the agglomerations of SWNTs and then UDMA is added to the solution. Camphorquinone a photo sensitive initiator, and N,N dimethylaminoethyl methacrylate, an accelerator are added to the solution. The initiator and accelerator are added, to help in the photo curing of the composite. The electrode assembly is hooked up to an HP 54601B oscilloscope, an HP 33120A function generator, and a Trek 50/750 high voltage amplifier. The schematic of the set up is shown in Figure 3.5. An AC electric field of 43.5 V/mm is applied for 10 min at room temperature. The electric field is applied at different frequencies between 0.1 Hz to 100 kHz to observe the effect of frequency on the

![Figure 3.5. Schematic of the AC electric field alignment set up of SWNTs in (UDMA/HDDMA).](image-url)
alignment of SWNTs. While the electric field is applied, SWNT-UDMA/HDDMA composite is cured with a blue light gun. Curing of the composite with applied electric field aligns the SWNTs in the UDMA/HDDMA composite, as shown in Figure 3.6.

Figure 3.6. Aligned SWNTs in the direction of the applied electric field.

3.4 Optical microscopy and scanning electron microscopy:

Optical images are obtained on an Olympus BH-2 optical microscope at 100x and 200x magnification. These images are utilized to compare and observe trends as a function of alignment parameters in aligned UDMA/HDDMA composites. Scanning electron microscopy images are obtained on a JEOL JSM 6400. These images are used to examine the aligned SWNT polyimide fibers.
3.5 Raman spectroscopy of SWNT aligned polymer composites:

A Nicolet Dispersive Raman Spectrometer with a polarizer is used to measure the degree of alignment of SWNTs in the electrospun polyimide fibers and in (UDMA/HDDMA). The spectrometer operates at a constant wavelength of 785 nm with a laser power of 10%, a 50x objective lens, and a 25µm aperture slit. The spectra are recorded at several angles between the SWNT axis and the incident polarization ranging from 0° to 180°. A polarizer consists of a laser beam polarization flipper and a polarization analyzer. The laser beam that reaches the sample has linear polarization and is oriented parallel to the entrance slit of the spectrograph. The response of the spectrograph is highly sensitive to the polarization orientation of the sample beam; the system scrambles the polarization of the signal just before it enters the spectrograph. With this, the polarization study on the sample is done without affecting the response of the spectrograph. Setting the polarization angle to 0° aligns the analyzer in the parallel orientation. This passes the signal component polarized in the parallel orientation and blocks the component polarized in the perpendicular orientation. Setting the polarization angle to 90° does the opposite. The polarization component of each angle is measured separately. Raman spectra are obtained by measuring the vibrational modes of a material. SWNTs consist of two vibrational modes that are sensitive to Raman spectroscopy: one is circumferential to the tube, referred to as transverse and the other is longitudinal to the tube, referred to as tangential. Figure 3.7 shows standard Raman spectra for a SWNT. The tangential peak of the SWNT is inspected to assess the degree of orientation, since the intensity of the tangential Raman band is sensitive to the polarizer angle. The tangential mode intensity
Figure 3.7. Raman spectra of a SWNT, indicating the tangential peak and transverse peak.

shows the maximum signal when the polarization of the incident light is parallel to the nanotube axis. The same tangential mode intensity is suppressed when the polarization of the incident light is perpendicular to the nanotube axis [69, 70]. By comparing the signal intensity of the tangential SWNT peak at 1590 cm\(^{-1}\) for each polarization angle, the degree of alignment of the SWNTs is qualitatively assessed.

**3.6 Conductivity measurements:**

AC electrical conductivity is measured on aligned SWNT/UDMA/HDDMA composites using a HP 4284A high precision LCR meter. The aligned SWNT/UDMA/HDDMA
samples are polished using Buehler Metadi diamond-polishing compound to obtain flat sides and to eliminate the surface effects. Silver paint is used to paint the electrodes on the surface of the UDMA/HDDMA composite and the samples are placed in a circular Teflon holder with top and bottom electrodes to measure the conductivity. Conductivity is measured in three different directions as shown in Figure 3.8. Conductivity is measured parallel and perpendicular to the aligned direction of the SWNTs. Figure 3.8(a) shows the parallel electrode configuration, and Figure 3.8(b) and Figure 3.8(c) shows the perpendicular electrode configurations. A labview® program is interfaced with the LCR meter to measure the conductivity. The conductivity is measured at applied frequencies of 20 Hz to 1 MHz at room temperature. The LCR meter measures the conductance of the sample, which is converted to conductivity using equation 3.1,

\[ \sigma = \frac{g^*t}{A} \]

Figure 3.8. Different electrode configurations (a) parallel (b), (c) perpendicular to aligned SWNTs.

where \( \sigma \) is the conductivity, \( g \) is the conductance, \( t \) is the thickness and \( A \) is the area.
3.7 Dielectric spectroscopy:

A HP 4284A high precision LCR meter is used to measure the dielectric constant of the randomly oriented polyimide composite films and oriented SWNT polyimide electrospun fibers. Silver is vapor deposited on the randomly oriented SWNT polyimide composite films as electrodes on the surface of the films. The dielectric constant is measured across the thickness of the sample. A labview program is interfaced with the LCR meter and an environmental chamber to measure the dielectric constant of the films. The dielectric constant is measured at frequency range of 20 Hz to 1 MHz at temperature range of 25°C to 300°C. Dielectric constant of the aligned SWNT polyimide fiber mats is measured parallel and perpendicular to the oriented fibers at room temperature at a frequency range of 20 Hz to 1 MHz. High purity silver paint is used to paint electrodes for measuring the dielectric constant in the parallel direction as shown in Figure 3.9(a). Aluminum foil electrodes are used to measure the dielectric constant in the perpendicular direction as shown in Figure 3.9(b). Aluminum electrodes are used for the perpendicular measurement as the electrodes get shorted when silver paint is used. The dielectric constant of aligned SWNT/UDMA/HDDMA composite is measured at room temperature at a frequency range of 20 Hz to 1 MHz. The measurements are done in two directions parallel to aligned SWNTs and perpendicular to aligned SWNTs. The electrode configuration for parallel measurement is shown in Figure 3.8(a) and perpendicular is shown in Figure 3.8(b). High purity silver paint is used to paint electrodes and the
samples are placed in a circular Teflon holder with top and bottom electrodes to measure the dielectric constant.

![Ag paint electrode](image1) ![Al foil electrode](image2)

(a) (b)

Figure 3.9 Different types of electrodes: (a) parallel silver electrodes on aligned SWNT polyimide fiber mats, and (b) perpendicular aluminum electrodes on aligned SWNT polyimide fiber mats.

Dielectric spectroscopy is a technique capable of probing the molecular motion and electrical properties of polymeric materials. It involves the measurement of the response of dipoles on polymeric main or side chains to a sinusoidally varying voltage. A dielectric material must contain a charge that can be displaced by applying an electric field and store a part of the applied field. The displacement of the charge by applying the electric field is called “polarization”. The dielectric properties of a material are defined by a complex dielectric permittivity, $\varepsilon^*$,

$$\varepsilon^* = \varepsilon' + i\varepsilon'' \quad 3.2$$

where $\varepsilon'$ is the relative dielectric permittivity also known as the dielectric constant of the material and $\varepsilon''$ is the imaginary part which is a measure of the heat related loss of the
material known as the dielectric loss. The dielectric constant ($\varepsilon'$) is used to define the ability of an insulator to store electrical charge,

$$
\varepsilon' = \frac{C \ast t}{\varepsilon_0 \ast A}
$$

where $C$ is the value of capacitance of a material when placed between parallel plates held in vacuum, $\varepsilon_0$ is the dielectric constant in vacuum ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m), $t$ is the thickness of the material and $A$ is the area of the parallel plates. The complex dielectric permittivity of the material depends on the polarizability of the molecules; the higher the polarizability of the molecules the higher is the permittivity of the material. Polarization within the polymer sample occurs as a response to an electric field, the relation between polarization and electric field is given by,

$$
P = (\varepsilon' - 1) \ast \varepsilon_0 \ast E
$$

where $P$ is the polarization, $\varepsilon'$ is the dielectric constant, $\varepsilon_0$ is the dielectric constant in vacuum and $E$ is the applied electric field, this is known as induced polarization. Orientation polarization is introduced in the material by applying a high electric field at temperatures above $T_g$, and the material is cooled with the electric field. In this case magnitude of the polarization depends on the applied field and it is known as remanent polarization ($P_r$),

$$
P_r = \Delta \varepsilon \ast \varepsilon' \ast E_p
$$

where $\Delta \varepsilon$ is the change in relative permittivity at $T_g$, $\varepsilon_0$ is the permittivity of vacuum and $E_p$ is the applied electric field. Polarization also arises from a range of mechanism, where each occurs with a different strength, response time and frequency. Understanding the
polarization mechanisms in the dielectric materials is very important, as they affect the
dielectric constant and the dielectric loss of the material. There are different types of
polarization mechanisms: electronic polarization, atomic polarization, orientation
polarization and interfacial polarization. In a given dielectric material, the total
polarization is a sum of all the polarizations resulting from each one of them. For the
polymers and composites studied here, orientation polarization and interfacial
polarization play a more dominant role. Although electronic polarization and atomic
polarization will be mentioned for completeness, emphasis of the discussion will be on
orientation polarization and interfacial polarization. Electronic polarization arises from a
shift of the center of mass of the negative electron charge cloud surrounding the positive
atomic nucleus when an electric field is applied, as shown in Figure 3.10. This charge
displacement acts to neutralize part of an applied field. This occurs in materials where the
structure is formed from the molecules of different atoms with different
electronnegativities. The formation of molecules of different types of atoms results in the
displacement of their electron clouds towards the stronger binding atom. The atoms

![Figure 3.10. Effect of electric field on electronic polarization.](image-url)
acquire charges of opposite polarity and applying an electric field on these charges can change the equilibrium positions of the atoms. Charge displacement occurs due to this displacement of positive and negative atoms. Atomic polarization occurs due to the relative motion of atoms instead of a shift of the charge cloud surrounding atoms like electronic polarization. A schematic of atomic polarization is shown in Figure 3.11.

![Figure 3.11. Effect of electric field on atomic polarization.](image)

Dipolar polarization occurs when an electric field is applied and the dipoles rotate and align parallel to the applied field by canceling a part of the applied field, as shown in Figure 3.12. When no electric field is applied the molecules are randomly oriented and no net charge exists in the material. Interfacial polarization arises for electrically

![Figure 3.12. Effect of electric field on dipolar polarization.](image)
heterogeneous materials such as a CNT polymer composite in which the conductivity of the polymer matrix and the conductivity of the inclusion are different. A schematic of interfacial polarization is shown in Figure 3.13. In these materials the motion of charge carriers may occur more easily through one phase and therefore are constricted at phase boundaries. Interfacial polarization results in an increase in the dielectric constant due to the motion of virtual charge which gets trapped at the interface of components of a multiphase material with different conductivity.

![Figure 3.13. Effect of electric field on interfacial polarization.](image)

The polarization mechanisms that occur in these dielectric materials are dependent on frequency, temperature and composition of the material. For Electronic and atomic polarizations due to the inertia of orbiting electrons, known as the inertia effect, the polarization will be very small for any frequency except for the resonant frequency [71]. Electronic polarization occurs at a characteristic frequency of about $10^{15}$ Hz and atomic polarization occurs at about $10^{13}$ Hz. The reorientation of dipoles in the field depends upon the viscosity of the medium, and therefore orientation polarization depends upon the frequency of measurement relative to the reorientation time. Lower frequencies of
measurement at a given temperature will allow dipoles to reorient and contribute to orientation polarization, whereas higher frequencies will not induce as large an orientation polarization. This occurs at about $10^7$ to $10^9$ Hz, depending on factors which affect mobility, such as temperature. Interfacial polarization occurs at frequencies below 10 Hz but, can occur at higher frequencies depending on the shape, size and orientation of the inclusions. Dielectric properties of a material are highly dependent on temperature as there is a major effect of temperature on polarization mechanisms. Electronic polarization is not dependent on temperature as the shift of mass of the negative electron charge cloud around the nucleus is not affected. Orientation polarization is highly dependent on temperature as the ability to rotate a dipole is temperature dependent. At a given temperature above the $T_g$, the dipoles start to reorient, which results in an increase in orientation polarization. Orientation polarization drops rapidly with further increase in temperature. The decrease with increasing temperature reflects the increasing energy associated with thermal motion ($kT$), which opposes the alignment of dipoles in the field. Interfacial polarization is temperature dependent because charge mobility is temperature dependent.

### 3.8 Mechanical properties of SWNT polyimide composites:

SWNTs are added to the polymer matrix to enhance the physical properties of the composite. The properties of the individual components and the interfaces between the components affect the properties of the composite. Factors that influence the mechanical properties of the composite include inclusion concentration, inclusion geometry and
packing, and the relative modulus of each component. Utilizing dynamic mechanical 
analysis (DMA), the relaxation in polymers under stress and temperature is studied. 
DMA can give information about the influence of inclusions on the relationships between 
structure and properties of a composite and hence, can reveal the modifications to 
mechanical properties of the polymer created by the inclusions. Dynamic mechanical 
results are generally given in terms of complex moduli or compliances. The notations 
illustrated in terms of shear modulus $Y$. The complex moduli are defined by,

$$Y^* = Y' + iY''$$  \hspace{1cm} 3.6

where $Y^*$ is the complex shear modulus, $Y'$ is the real part of the modulus, $Y''$ is the 
imaginary part of the modulus, and $i = \sqrt{-1}$. $Y'$ is the storage modulus, which is a 
measure of stiffness, and $Y''$ is loss modulus, which is a damping or energy dissipation 
factor. The angle that reflects the time lag between the applied stress and strain is $\delta$, and 
it is defined by a ratio called the loss tangent ($\tan \delta$).

$$\tan \delta = \frac{Y'}{Y''}$$  \hspace{1cm} 3.7

Tan $\delta$, a damping term, is a measure of the ratio of energy dissipated as heat to the 
maximum energy stored in the material during one cycle of oscillation. The storage($Y'$) 
modulus and the loss modulus ($Y''$) in terms of stress ($\sigma$) and strain ($\gamma$) are:

$$Y' = \frac{\sigma}{\gamma} \cos \delta ,$$   \hspace{1cm} 3.8

and

$$Y'' = \frac{\sigma}{\gamma} \sin \delta .$$   \hspace{1cm} 3.9
A TA instruments Q800 dynamic mechanical analyzer (DMA) is used to measure mechanical properties of the randomly oriented SWNT polyimide composite films. The storage modulus ($Y'$), loss modulus ($Y''$) and tan $\delta$ are measured on SWNT polyimide films for SWNT concentrations varying from 0.01 wt% to 2wt%. The measurements are done at 10 Hz frequency between 30°C and 280°C at a rate of 3°C/min in the tension mode with fixed displacement amplitude of 25 $\mu$m.
Chapter 4

Results and Discussion

This chapter presents the results and the related discussion. There are two different polymer composites in which the SWNTs are aligned: SWNT polyimide composites and SWNT/UDMA/HDDMA composites. Results from optical microscopy, SEM, and dielectric spectroscopy are used to prove good dispersion of SWNTs in both the polymer composites. Dielectric spectroscopy, Raman spectroscopy and dielectric spectroscopy are used to assess the alignment of SWNTs in polyimide and UDMA/HDDMA. A dielectric theory is used to validate the anisotropy in the experimental dielectric constants obtained from both the aligned SWNT polyimide and aligned SWNT/UDMA/HDDMA polymer composites.

4.1 SWNT polyimide composite:

4.1.1 Processing of SWNT polyimide composites:

A series of SWNT polyimide solutions with varying SWNT concentrations are prepared. The resulting composite solutions are cast and thermally cured, according to the process described in chapter 3, section 3.1. Randomly oriented SWNT polyimide composite films are obtained from this method. Different sample compositions, their curing cycles, film thickness, glass transition temperatures ($T_g$) and the electrode type are listed in Table 4.1. Collaborators at NASA LaRC have observed that the unimidized composite solutions exhibited excellent stability, remaining in solution for over two years in sealed bottles under refrigeration [72]. The transparent films containing SWNTs are deep green in color.
Table 4.1. List of randomly oriented SWNT polyimide films. Details of their composition, curing cycle, thickness, $T_g$ and electrode type are listed.

<table>
<thead>
<tr>
<th>Sample Composition</th>
<th>Curing cycle</th>
<th>Film thickness ($\mu$m)</th>
<th>Glass transition temperature ($T_g$) (°C)</th>
<th>Electrode type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyimide(PI)</td>
<td>Thermal curing</td>
<td>54</td>
<td>218.51</td>
<td>Evaporated silver (~100 Å)</td>
</tr>
<tr>
<td>0.02 wt% SWNT/PI</td>
<td>Thermal curing</td>
<td>55</td>
<td>212.66</td>
<td>Evaporated silver (~100 Å)</td>
</tr>
<tr>
<td>0.035 wt% SWNT/PI</td>
<td>Thermal curing</td>
<td>75</td>
<td>219.62</td>
<td>Evaporated silver (~100 Å)</td>
</tr>
<tr>
<td>0.05 wt% SWNT/PI</td>
<td>Thermal curing</td>
<td>63</td>
<td>219.13</td>
<td>Evaporated silver (~100 Å)</td>
</tr>
<tr>
<td>0.1 wt% SWNT/PI</td>
<td>Thermal curing</td>
<td>52</td>
<td>220.89</td>
<td>Evaporated silver (~100 Å)</td>
</tr>
<tr>
<td>0.2 wt% SWNT/PI</td>
<td>Thermal curing</td>
<td>28</td>
<td>221.36</td>
<td>Evaporated silver (~100 Å)</td>
</tr>
<tr>
<td>0.5 wt% SWNT/PI</td>
<td>Thermal curing</td>
<td>46</td>
<td>212.91</td>
<td>Evaporated silver (~100 Å)</td>
</tr>
<tr>
<td>1 wt% SWNT/PI</td>
<td>Thermal curing</td>
<td>62</td>
<td>220.38</td>
<td>Evaporated silver (~100 Å)</td>
</tr>
<tr>
<td>2 wt% SWNT/PI</td>
<td>Thermal curing</td>
<td>62</td>
<td>222.26</td>
<td>Evaporated silver (~100 Å)</td>
</tr>
<tr>
<td>5 wt% SWNT/PI</td>
<td>Thermal curing</td>
<td>48</td>
<td>212.65</td>
<td>Evaporated silver (~100 Å)</td>
</tr>
</tbody>
</table>

while, pristine films are pale yellow. The mechanism behind the long term stability and the observed color change is the formation of an electron donor-acceptor (EDA) complex between the nanotube filler and the polymer matrix. It is observed that SWNT polyimide composites synthesized from ODPA monomers and other diamines show no color change, but there is a color change observed when (β-CN)APB is used as a diamine along with ODPA as the monomer to prepare SWNT polyimide composites. It is believed that the (β-CN) dipole present in the diamine supports the EDA complex formation between
the SWNT and the diamine [72]. This results in a thermodynamically stable SWNT polyimide solution with good dispersion of SWNTs in the polyimide matrix. SEM images of 0.5 wt% SWNT polyimide films showed uniform dispersion of SWNTs in the polyimide matrix and there are no large bundles of SWNTs in the composite, as shown in Figure 4.1.

![SEM image of well dispersed 0.5 wt% SWNT polyimide film.](image)

**Figure 4.1.** SEM image of well dispersed 0.5 wt% SWNT polyimide film.

### 4.1.2 Aligning of SWNTs in polyimides by electrospinning:

Electrostatic fiber spinning or electrospinning, is a novel process for forming fibers with sub micron scale diameters through the action of electrostatic forces. The small fiber diameters and the porous structure of electrospun fabrics result in a high specific surface area, that is beneficial in a wide variety of applications such as wings for micro air vehicles, filters, membranes, wound dressings and vascular grafts [73, 74]. Chemically imidized SWNT polyimide solution with varying SWNT concentrations is prepared by in situ polymerization under sonication, according to the process described in chapter 3, section 3.2. Solutions with 0 wt%, 0.1 wt%, 0.2 wt%, 0.65 wt% and 1 wt% SWNT
content are spun according to the spinning conditions described in Table 4.2. After the fibers are collected, they are placed into a vacuum oven at 50°C for 18 hours to remove excess solvent and water. A digital image of electrospun SWNT polyimide fiber mat is shown in Figure 4.2. Details on various spinning conditions and sample compositions are listed in Table 4.2. The discussion in this thesis is limited to observations on different spinning conditions to produce electrospun fibers. A parametric study on different spinning conditions and their effect on the electrospun fibers is outside the scope of this thesis.

Table 4.2. Details on various spinning conditions for aligned SWNT polyimide fibers.

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>Spinning voltages (kV)</th>
<th>Rate of polymer delivery (ml/hr)</th>
<th>Distance of collector plate from tip of syringe (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% SWNT/PI</td>
<td>15 kV 20 kV 25 kV</td>
<td>5 ml/hr</td>
<td>20 cm</td>
</tr>
<tr>
<td>0.1 wt% SWNT/PI</td>
<td>15 kV 20 kV 25 kV</td>
<td>5 ml/hr</td>
<td>20 cm</td>
</tr>
<tr>
<td>0.2 wt% SWNT/PI</td>
<td>15 kV 20 kV 25 kV</td>
<td>5 ml/hr</td>
<td>20 cm</td>
</tr>
<tr>
<td>0.65 wt% SWNT/PI</td>
<td>15 kV 20 kV 25 kV</td>
<td>5 ml/hr</td>
<td>20 cm</td>
</tr>
<tr>
<td>1 wt% SWNT/PI</td>
<td>15 kV 20 kV 25 kV</td>
<td>5 ml/hr</td>
<td>20 cm</td>
</tr>
</tbody>
</table>

Figure 4.2. Digital image of a 0.65 wt% SWNT polyimide electrospun mat.
thesis. The goal is to have dry electrospun fibers that can be used to study alignment of SWNTs.

4.1.3 Scanning electron microscopy (SEM):

SEM images are obtained on 0.1 wt% SWNT polyimide fibers to observe the diameter size in the electrospun fiber mat. The 0.1 wt% SWNT polyimide fibers spun by applying 25 kV voltage, as shown in Figure 4.3(a), had an average diameter of 4.55 µm and a standard deviation of 0.95. The 0.1 wt% SWNT polyimide fibers spun by applying 15 kV voltage, as shown in Figure 4.3(b), had an average diameter of 4.19 µm and a standard deviation of 2.03. While the average diameter of the fibers formed by applying 15 kV and 25 kV was similar, the fibers spun at 25 kV had a larger variation in size.

![SEM images](image)

(a) (b)

Figure 4.3 (a) SEM image of an aligned SWNT polyimide fiber mat, spun at 15 kV, (b) SEM image of an aligned SWNT polyimide fiber mat, spun at 25 kV.
4.1.4 Raman spectroscopy of electrospun SWNTs in polyimide fibers:

Polarized Raman spectroscopy can be used to assess the orientation of SWNTs. The tangential peak of the SWNT in the Raman spectra is very sensitive to the polarizer, as described in chapter 3, section 3.5. Therefore, it is examined to detect alignment of SWNTs. Figure 4.4 illustrates the different polarizer angles with respect to perfectly aligned SWNTs. When the polarizer is parallel to the aligned SWNTs i.e. at an angle of 0°, maximum intensity in the tangential peak is obtained. When the polarizer is perpendicular to the aligned SWNTs i.e. at an angle of 90°, minimum intensity in the tangential peak is obtained. When the polarizer angle is further increased to 180°, maximum intensity of the tangential peak is obtained, as it is also again parallel to the aligned SWNTs.

Figure 4.4. Different polarizer angles with respect to perfectly aligned SWNTs.
Raman spectrum is obtained on SWNT polyimide electrospun mats. An SEM image of the electrospun mat is shown in Figure 4.3. The obtained polarized Raman spectra on the 0.1 wt% SWNT polyimide electrospun mat at various polarizer angles are shown in Figure 4.5. Highest Raman intensity of the tangential SWNT peak is obtained when the polarizer angle is at angle of 0° and then the peaks continuously decrease as the polarizer angle is increased up to 135°, as shown in Figure 4.5. The intensity of the tangential peak is supposed to increase when the polarizer angle is at 135° for aligned SWNTs, see Figure 4.4. However, in this case, a decrease is observed when the polarizer angle is at 135°. It is noted again that this sample is a mat. The Raman laser travels to a depth of 1-2
microns. It is believed that the spectrum is influenced by the SWNTs in more than one fiber, which results in an average value from all the different fibers. This happens because the fibers in the mat are not perfectly aligned in one direction as it is seen in Figure 4.3. When the polarizer angle is at 0° the polarizer is parallel to one fiber, but it is at a different angle to another fiber sitting below it. Therefore, the collected intensity is the response of SWNTs from more than the targeted fiber. To further investigate the alignment of SWNTs, single fibers are picked from the electrospun mat and placed on a substrate, as shown in Figure 4.6. Raman spectrum is obtained on the separated single fibers to confirm alignment of SWNTs inside each electrospun fiber.

![Single electrospun fiber](image)

Fig 4.6. SEM image of a single fiber separated from the electrospun mat.

Raman spectra on a 2.5 μm, 0.1wt% SWNT polyimide fiber spun at 25 kV, are shown in Figure 4.7. The Raman intensity of the tangential peak in the Raman spectrum is maximum when the polarizer is parallel to the nanotube axis i.e. \( \alpha_i = 0^\circ \) and the
tangential peak is suppressed when the polarizer is perpendicular to the nanotube axis i.e. $\alpha_i = 90^\circ$ as shown in Fig 4.7. The intensity of the tangential peak decreases as the angle of the polarizer increases from $\alpha_i = 0^\circ$ to $\alpha_i = 90^\circ$.

Raman spectrum obtained from the aligned SWNT polyimide fibers spun at different voltages of 15kV, 20kV, and 25kV showed a similar trend in the Raman intensities between the parallel and perpendicular peaks. The Raman spectrum from a 4 $\mu$m single fiber spun at 15 kV is shown in Figure 4.8. There is difference in the intensities of the parallel (0$^\circ$) and the perpendicular (90$^\circ$) peaks and also the parallel peak at 180$^\circ$ polarizer overlaps with the parallel peak at 0$^\circ$. The results shown in Figure 4.7 and Figure 4.8
Fig 4.8. Raman spectrum from a SWNT polyimide fiber spun at 15 kV. Difference in the tangential peak of SWNT at various polarizer angles.

indicate preferential alignment of the SWNTs in the fibers electrospun from the SWNT polyimide composite.

Raman spectra are successfully used to confirm alignment of SWNTs in the electrospun SWNT polyimide fibers. This method allows a qualitative assessment of alignment of SWNTs. Polarized Raman spectra proved that the SWNTs are aligned in fibers spun at 15 kV, 20 kV and 25 kV, but the difference in alignment at different voltages could not be assessed. It is believed that a combination of DC electric field and mechanical stretching aligns the SWNTs in the polyimide fibers. The electric field lines extend from the tip of
the syringe to a rectangular plate at a certain distance, as shown in Figure 4.9. The effect of electric field on alignment of SWNTs can be rationalized by considering the electronic polarization induced in SWNTs by the electric field. A dipole moment $P$ of a SWNT with length $L$ is defined as:

$$P = \alpha E$$

where $E$ is the applied electric field and $\alpha$ is the static polarizability tensor. The static polarizability tensor $\alpha$ of the SWNT is highly anisotropic, because of the structure of SWNT. The polarizability along the tube axis is much higher than that perpendicular to the tube axis\[51\]. A schematic of a SWNT in an electric field is shown in Figure 4.10. For a SWNT oriented at an angle $\theta$ with respect to $E$, the dipole moment of the SWNT is, along the tube axis, where

$$P = \alpha E \cos \theta.$$
The torque on the dipole moment $\tau$ is,

$$\tau = |P \times E| = \alpha E^2 \sin \theta \cos \theta. \quad 4.3$$

Correspondingly, the force applied on the dipole to rotate and align the SWNT with the electric field is,

$$F_r = (\alpha E^2 \sin \theta \cos \theta)/L \quad 4.4$$

![Figure 4.10. A schematic of a SWNT under the influence of an electric field (E).](image)

Because of the anisotropy of the SWNTs, the dipole moment created by the electric field in the direction parallel to the tube axis is stronger than in the perpendicular direction. Increase in the dipole moment results in an increase in the torque ($\tau$). The force applied on the dipole to rotate and align the SWNT with electric field is related to the static polarizability tensor ($\alpha$) and the length of the SWNT ($L$). The force, to align the SWNT in the direction of electric field is higher, as $\alpha$ is higher along the tube axis. Therefore
SWNTs could be aligned along the direction of the electric field [51, 54]. During electrospinning, the fiber also undergoes mechanical stretching before it reaches the collector. Variation in the amount of stretch, leads to different diameter size fibers. Instability in the whipping of jet causes it to travel through the different field lines shown in Figure 4.9. Because of the different travel distances there is a variation of stretch in different fibers before they are collected. It is believed that the combination of electric field and the mechanical stretching aligns the SWNTs by electrospinning. Previously, SWNTs were aligned in polymers by mechanical stretching [56] and SWNTs were also aligned by applying an electric field [51, 54].

As discussed in chapter 3, section 3.2, there are different parameters, such as the applied voltage, rate of spinning, distance between the collector and the syringe, and the diameter of the fiber, which could affect the alignment of the SWNTs in polyimide by electrospinning. Raman spectra on different diameter fibers can be used to compare the degree of alignment of SWNTs. Raman spectrum is obtained on SWNT polyimide fibers with different diameters, to observe the difference in the alignment of the SWNTs in polyimide matrix with varying diameter. The tangential peak Raman intensity when the polarizer angle is at 0° is represented by $P_{0}$, as shown in Figure 4.11. The tangential peak Raman intensity when the polarizer angle is at 90° is represented by $P_{90}$, as shown in Figure 4.11. The relative ratio ($P_{0}/ P_{90}$) is used to compare the degree of alignment of SWNT in the fibers with varying diameters to observe the effect of diameter size on alignment of SWNTs.
Figure 4.11. Parallel peak Raman intensity ($P_0$) and perpendicular peak Raman intensity ($P_{90}$), at polarizer angles of $0^\circ$ and $90^\circ$.

The relative ratio values for the different diameter fibers and different spinning conditions are shown in Table 4.3. When the SWNTs are aligned, the intensity value of the parallel peak is very high and the intensity value of the perpendicular peak is low, hence the higher the $P_0/P_{90}$ ratio, the better the alignment of SWNTs. For all the spinning conditions, the ratio of the Raman intensity peak decreases as the diameter of the fibers increases, as seen in Table 4.3. For example, 0.1 wt% SWNT polyimide fibers spun at 15 kV with 4 μm fiber diameter, the ratio is 4.411 and the ratio decreases to 2.732 for the 27 μm fiber. Similarly for the 0.1 wt% SWNT polyimide fibers spun at 25 kV with 2.5 μm fiber diameter, the ratio is 2.253 and the ratio decreases to 1.655 for the 90 μm diameter fiber. It is concluded that the higher $P_0/P_{90}$ ratio associated with the smaller fiber diameter for each spinning case is an indication of better alignment in the smaller
diameter fibers at a constant spinning condition. The better alignment of SWNTs in smaller diameter fibers is possibly due to the additional stretch the jet undergoes, which results in smaller diameter fibers and when the jet undergoes little stretching, it results in a fiber with larger diameter. It is also seen that the fiber with 4 mm diameter, spun at 15 kV has a higher intensity ratio compared to the fiber with 3.2 mm diameter, spun at 20 kV. This indicates that the SWNTs are better aligned when the SWNT polyimide composite is spun at 15 kV, because of the high Raman intensity ratio. Further work is needed to clarify the role of voltage magnitude on alignment.

Table 4.3. Raman intensity ratio’s of various diameter fibers electrospun at various voltages with increase in diameter.

<table>
<thead>
<tr>
<th>Spinning Conditions</th>
<th>Fiber Diameter (µ m)</th>
<th>Raman Intensity Ratio (P₀/ P₉₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spun at 15 kV, 20 cm distance</td>
<td>4</td>
<td>4.411</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>3.388</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>3.075</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>2.732</td>
</tr>
<tr>
<td>Spun at 20 kV, 20 cm distance</td>
<td>3.2</td>
<td>2.795</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>2.756</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>1.592</td>
</tr>
<tr>
<td>Spun at 25 kV, 20 cm distance</td>
<td>2.5</td>
<td>2.253</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td>2.405</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1.655</td>
</tr>
</tbody>
</table>
4.1.5 Dielectric spectroscopy on randomly oriented and aligned SWNT polyimide composites:

The dielectric properties of randomly dispersed SWNT polyimide composites are measured, to establish a benchmark on the performance of isotropic SWNT polyimide composites. The dielectric constant of the pristine polyimide is measured in the transverse direction ($\varepsilon_T$) and longitudinal direction ($\varepsilon_L$) at 25°C; the two directions of measurement are shown in Figure 3.9, in chapter 3. The dielectric constant in the transverse direction is 4 and the dielectric constant in the longitudinal direction is 7.5. The difference in the dielectric constant indicates anisotropy in the dielectric constant. It is believed that solution casting yields a planar structure and this preferential planar structure in the polyimide results in anisotropy [75, 76]. The planar structure formed can be explained by gel film collapse. The evaporation of solvent during the drying step leads to shrinkage of the film before thermal curing has occurred. If the film is constrained during solvent loss, shrinkage can result in the development of structure within the directions of constraint. This process is called the gel film collapse [77]. Russell et al [75, 76] have done an experiment in which a spin coated polyimide is constrained parallel to the coating surface by adhesion to the substrate. The shrinkage associated with solvent loss occurs primarily in the thickness direction. At the point at which the coating can sustain stress, further loss of solvent results in the alignment of the precursor chains parallel to the surface of the substrate (i.e. in the plane of the coating). The stresses that develop as a result of shrinkage induce further anisotropy [75, 76]. It is believed here that
a similar behavior results in a planar structure during solution casting of pristine polyimide, which results in anisotropy in the dielectric constant.

The transverse dielectric constant of randomly oriented SWNT polyimide films at 25°C is plotted as a function of frequency for various SWNT concentrations, as shown in Figure 4.12. There is a small increase in the dielectric constant of the polyimide at 20 Hz with 0.02 wt% and 0.035 wt% SWNT concentrations. The dielectric constant of the pristine polyimide is 3.726 and it increases to 4.016 and 4.406 by the addition of 0.02 wt% and 0.035 wt% SWNTs respectively. As the concentration of the SWNTs in the polyimide matrix is further increased to 0.1 wt% and above, there is a large increase in the dielectric constant at 20 Hz, as seen in Figure 4.12. The dielectric constant of the polyimide composite with 0.1 wt% SWNT concentration is 31 and the dielectric constant further increases to $10^5$ with 2 wt% SWNT concentration at 20 Hz. The increase in the dielectric constant with increase in SWNT concentration is due to the effect of interfacial polarization, as described in chapter 3, section 3.7. Interfacial polarization arises in an electrically heterogeneous material, in this case SWNT polyimide composite. The difference in the conductivity of the polyimide matrix and the conductivity of the SWNT inclusions causes interfacial polarization in SWNT polyimide composite. Interfacial polarization results in an increase in the dielectric constant due to the motion of the virtual charge which gets trapped at the interface of components of a multiphase material with different conductivity [78]. In the 0.02 wt% and 0.035 wt% SWNT polyimide
composites there is a very small increase in the dielectric constant, as there is less effect of interfacial polarization due to the low concentration of SWNTs. As the SWNT concentration in the polyimide matrix increases to 0.1 wt% and higher, the effect of interfacial polarization increases. The increase in the SWNT concentrations leads to more interactions between the SWNTs and the polyimide matrix, which increases the dielectric constant. The dielectric constant of polyimide with 0.1 wt% and higher SWNT concentration decreases at 100 Hz, as seen in Figure 4.12. The dielectric constant of 2 wt% SWNT polyimide drops from $10^5$ to 2351 and the dielectric constant of 0.1 wt% SWNT polyimide also drop from 31 to 11. The decrease in the dielectric constant is due
to the decreasing effect of interfacial polarization at 100 Hz. The effect of interfacial polarization is maximum and most prominent at a frequency of 10 Hz, as the frequency is increased or decreased the effect of interfacial polarization decreases [79], as described in chapter 3, section 3.7.

Referring back to Figure 4.12, the dielectric constant of the pristine polyimide, 0.02 wt% and 0.035 wt% SWNT polyimide composites is not dependent on frequency; the dielectric constant of the pristine polyimide is ~4 at all frequencies. Even with an increase in the SWNT concentration to 0.035 wt%, the dielectric constant remains ~4. These composites behave as insulators. As the concentration of the SWNTs in the polyimide matrix is further increased to 0.1 wt% and above, the dielectric constant becomes highly dependent on frequency as seen in Figure 4.12. The dielectric constant decreases with increase in frequency for the composites above percolation. The dielectric constant for the 0.1 wt% SWNT polyimide film is 31 at 20 Hz and it decreases to 11 at 1 kHz and remains constant at frequencies above 1 kHz. SWNT polyimide composites with SWNT concentrations above 0.1 wt% behave as conductors as they are dependent on frequency. The dependence of dielectric constant on frequency at 0.1 wt% SWNT polyimide composite is an indication of a percolation transition [35, 80]. Percolation theory predicts that at a critical volume concentration, there is a percolation transition at which the composite is converted from a capacitor to a conductor [80]. Below percolation the composite behaves as an insulator. Above percolation, because of the increase in the SWNT concentrations, a conductive network is formed by the SWNTs. The dielectric
constant of SWNT polyimide composite with 0.5 wt% and higher SWNT concentrations can not be measured at frequencies above 100 Hz, as seen in Figure 4.12 because of their high conductivity.

The dielectric constant of the randomly oriented SWNT polyimide films are plotted in Figure 4.13 as a function of SWNT concentration at 25°C at 20 Hz. The dielectric constant of the pristine polyimide is 4, as the SWNT concentration is increased to 0.02 wt% the dielectric constant remains at 4. Further increase of SWNT concentration to 0.1 wt% the dielectric constant increases to 32. The sharp increase in the dielectric constant
of the polyimide with 0.1 wt% SWNT is indicative of a percolation transition. The dielectric constant further increases to $10^5$ with 2 wt% SWNT concentration, as seen in Figure 4.13. The dielectric constant data can be fitted to a power law in terms of volume fraction of SWNT, to determine the critical volume concentration. The dielectric constant is linear with $(v-v_c)$ in a logarithmic scale and the relationship is described by \[80\]

$$\varepsilon' = A|v - v_c|^{-s} \quad 4.5$$

where $\varepsilon'$ is the dielectric constant of the composite, $v$ is the volume fraction of the SWNT in the composite, $v_c$ is the critical volume fraction, $A$ and $s$ are fitted constant. A critical volume fraction of 0.06 vol% is obtained for the SWNT polyimide composite [81]. This indicates that the composite behaves as a conductor above 0.06 vol% and behaves as an insulator below 0.06 vol% of SWNT concentrations. The low critical volume fraction of 0.06 vol% is indicative of very good dispersion of SWNTs in the polyimide matrix.

The effect of SWNT on the piezoelectric behavior of the polyimide is assessed for SWNT wt% below percolation. The dielectric constant for 0.1 wt% and lower SWNT polyimide composites as a function of temperature, at 20 Hz, is shown in Figure 4.14. The dielectric relaxation strength $\Delta \varepsilon$ is defined as the relative dielectric constant between the rubbery and the glassy state. The change in the dielectric constant between the rubbery and the glassy state is due to orientation polarization, as described in chapter 3, section 3.7. The dielectric relaxation strength influences the remanent polarization, which in turn affects the piezoelectric behavior of the polymer. The remanent polarization is given by

$$P_r = \Delta \varepsilon \varepsilon E_p \quad 4.6$$
where $\Delta \varepsilon$ is the change in relative permittivity at $T_g$, $\varepsilon_0$ is the permittivity of vacuum and $E_p$ is the applied electric field. It is observed that there is an effect of orientation polarization around $T_g$ region for the samples below percolation as shown in Figure 4.14. It is observed that the presence of the SWNTs increases the value of the dielectric relaxation strength $\Delta \varepsilon$. The dielectric relaxation strength of the pristine polyimide increases from 7 to 14 by the addition of 0.1 wt% SWNTs. The higher the $\Delta \varepsilon$, the higher the piezoelectric response of amorphous piezoelectric polyimide. The behavior indicates that the relaxation behavior is still due to orientation polarization of the dipoles in the

![Graph showing the increase in dielectric constant of SWNT composites below percolation as a function of temperature, at 20 Hz.](image)

Figure 4.14. Increase in the dielectric constant of SWNT composites below percolation as a function of temperature, at 20 Hz.
polyimide. The presence of the SWNT seems to increase the response of the dipoles, perhaps by stabilizing them further through some electrostatic interactions. The increase in $\Delta \varepsilon$ translates in an increase in the remanant polarization $P_r$, and subsequently an increase in the piezoelectric behavior [82]. The increase in the dielectric constant at 220°C disappears with SWNT concentrations higher than 0.1 wt%, as shown in Figure 4.15. Referring back to Figure 4.13, it is seen that the percolation starts at 0.06 wt% SWNT concentration and the composites starts to behave as a conductor. When the SWNT concentrations are at or above percolation, the conductive nature of the nanocomposite dominates and the sudden increase in dielectric constant at $T_g$ disappears.

Figure 4.15. Dielectric constant of different wt% SWNT polyimide films as a function of temperature at 20 Hz.
From the above results it is observed that for the randomly oriented SWNT polyimide composites that are below percolation, the remanent polarization of the composite increases with increase in SWNT content up to 0.1 wt%. The increase in remanent polarization indicates that the composite is piezoelectric, as remanent polarization is directly related to piezoelectricity. The composite also has a low dielectric constant up to 0.1 wt% SWNT content. The combination of low dielectric constant along with the piezoelectric nature indicates that the composites can be used as a piezoelectric sensor. Low dielectric constant results in a better sensor response, as the piezoelectric voltage coefficient (g) is inversely proportional to the dielectric constant. The piezoelectric voltage coefficient (g) is a measure of the sensor response in a piezoelectric material it gives the electric field generated in response to the applied stress or strain. The composites above 0.1 wt% SWNT concentration have a high dielectric constant and also behave as conductors, so they can be used as electrostatic actuators. The electrostatic actuator can be considered as an electrically conductive plate, which is placed between two parallel plates. This configuration forms an electrical capacitor, such that when a voltage is applied across the parallel plates, the actuator generates a force, which causes a displacement. In this case the composite shows a displacement when a potential difference is applied across the composite; this displacement is due to the electrostatic force that is generated. At SWNT concentrations of 2 wt% and above the conductivity reaches a plateau and this indicates that the composite is too conductive. There will be less electrostatic actuation in these composites as, applying an electric field leads to substantial current leakage, thus reducing the electric field on the sample. This indicates
that the randomly oriented SWNT polyimide composites below 0.1 wt% SWNT concentrations can be used as piezoelectric sensors and composites above 0.1 wt% SWNT concentration can be used as electrostatic actuators.

The characterization of dielectric constant as a function of frequency, SWNT concentration and temperature for randomly dispersed case, is a reference that will help us analyze the behavior and interaction of aligned SWNTs in polyimide matrix. The dielectric constant of the electrospun polyimide fibers is measured along the longitudinal direction and transverse direction as shown in Figure 3.9(b) and Figure 3.9(c) in chapter 3. The dielectric constant in the longitudinal direction is 8 and the dielectric constant in the transverse direction is 4. The anisotropy in the dielectric constant is due to the preferential alignment of polyimide chains in fiber direction due to stretching, during electrospinning. A similar anisotropy in the dielectric constant is also seen in solution cast polyimide films, as mentioned above. Similarly, dielectric constant is measured in the longitudinal direction (i.e. parallel to the aligned fibers) and in the transverse direction (i.e. perpendicular to the aligned fibers) for SWNT polyimide compositions up to 1 wt%, dielectric constant at 20 Hz is shown in Figure 4.16. Two significant findings are observed 1) the dielectric constant in both parallel and perpendicular directions increase with SWNT concentration and 2) the dielectric constant in the parallel direction is greater than the dielectric constant in the perpendicular direction for all SWNT concentrations. There is a very small increase in the perpendicular dielectric constant with increase in SWNT concentration, as seen in Figure 4.16. The dielectric constant of
the pristine polyimide, 0.1 wt% and 0.2 wt% SWNT polyimide composites is ~ 4. The
dielectric constant of the polyimide increases to 5.5 and 6.9 with 0.65 wt% and 1 wt%
SWNT concentrations respectively. The increase in the dielectric constant is due to the
effect of interfacial polarization on SWNT polyimide composite. The increase in the
dielectric constant at 0.65 wt% SWNT concentration is indicative of a percolation
transition. A very large increase in the parallel dielectric constant is observed with
increase in SWNT concentration, as seen in Figure 4.16. The parallel dielectric constant
of the pristine polyimide increases from 8.7 to 16.8 with 0.2 wt% SWNT loading and
further increases to 45 with 1 wt% SWNT concentration. The increase in the parallel

![Figure 4.16. Dielectric constant parallel and perpendicular to the aligned SWNT polyimide fibers at 20 Hz.](image)
dielectric constant is due to interfacial polarization. The sudden increase in the parallel dielectric constant of the polyimide with 0.2 wt% SWNT concentration is indicative of a percolation transition at 0.2 wt% SWNTs. According to percolation theory, there is a critical volume concentration of the inclusions at which the composite is converted from a capacitor to a conductor. Parallel to the aligned SWNT polyimide fibers this is observed at 0.2 wt% SWNT concentrations and perpendicular to the aligned SWNT polyimide fibers it is observed at 0.65 wt% SWNT concentration. This indicates that percolation in the composite is affected by the aligned SWNTs. The parallel dielectric constant is greater than the perpendicular dielectric constant for electrospun aligned SWNT fibers up to 1 wt% of SWNTs, as seen in Figure 4.16. The parallel dielectric constant for the 1 wt% SWNT electrospun mat is 45 and perpendicular dielectric constant is 6. The difference in the parallel and perpendicular dielectric constant indicates anisotropy in dielectric constant for the aligned SWNT polyimide fibers.

The dielectric constant measured parallel to the aligned SWNT polyimide fibers at various frequencies is shown in Figure 4.17. The parallel dielectric constant for the pristine polyimide fibers and 0.1 wt% SWNT polyimide fibers is less dependent on frequency. The parallel dielectric constant of the polyimide and 0.1 wt% SWNT polyimide fibers is ~8, which is not affected with frequency. When the SWNT concentration is increased to 0.2 wt% and above, the dielectric constant of the polyimide composite is frequency dependent, as seen in Figure 4.17. The dielectric constant drops with increase in frequency. The parallel dielectric constant for the 0.2 wt% SWNT
Figure 4.17. The dielectric constant parallel to the aligned SWNT polyimide fibers as a function of frequency

polyimide film is 16 at 20 Hz and it decreases to 10 at 1 kHz. The dependence of dielectric constant on frequency for the 0.2 wt% SWNT polyimide composite is an indication of a percolation transition. According to percolation theory, the polyimide composite is converted from a capacitor to a conductor at 0.2 wt% SWNT concentration, when the dielectric constant is measured parallel to the aligned SWNTs. Referring back to Figure 4.14 and Figure 4.15 the randomly oriented SWNT polyimide composites below percolation are piezoelectric and above percolation they are conductive. This indicates that in the parallel direction the pristine polyimide and 0.1 wt% SWNT polyimide composite are piezoelectric and SWNT polyimide composites with 0.2 wt%
and higher SWNT concentrations are conductive. It is seen in Figure 4.16 that the composites below percolation have a very low dielectric constant and above percolation they have a high dielectric constant. The composites below percolation can be used as piezoelectric sensors, because of the combination of their low dielectric constant and their piezoelectric nature. The composites above percolation can be used as electrostatic actuators, because they are conductive and have a high dielectric constant.

The dielectric constant measured, perpendicular to the aligned SWNT polyimide fibers at various frequencies is shown in Figure 4.18. The perpendicular dielectric constant for the pristine polyimide, 0.1 wt%, 0.2 wt%, and 0.65 wt% SWNT polyimide fibers is not
dependent on frequency and has a small dielectric constant. This indicates that these composites are below percolation and behave like insulators when measured perpendicular to the aligned SWNTs. As the SWNT concentration is increased to 1 wt% the composite is dependent on frequency. This indicates that there is a percolation transition in the polyimide composite at 1 wt% SWNT concentration, while possibly, the composites below percolation behave as piezoelectric sensors and composites above percolation behave as electrostatic actuators.

From the dielectric results of aligned SWNT polyimide composites it has been observed that, by aligning the SWNTs in the polyimide the composite can be used as a sensor and as an actuator at the same time. The 0.65 wt% aligned SWNT composite is piezoelectric as it is below percolation in the perpendicular direction, as shown in Figure 4.18. The 0.65 wt% aligned SWNT polyimide composite also has a low dielectric constant in the perpendicular direction, which results in a better sensor response, as the piezoelectric voltage coefficient (g) is inversely proportional to the dielectric constant. The combination of low dielectric constant and piezoelectric nature means that the 0.65 wt% aligned SWNT polyimide composite can possibly be used as a piezoelectric sensor in the perpendicular direction. The 0.65 wt% aligned SWNT polyimide composite has a high dielectric constant and also behaves as a conductor in the parallel direction as it is above percolation, as shown in Figure 4.17. The 0.65 wt% aligned SWNT polyimide composite can possibly be used as an electrostatic actuator in the parallel direction, because of its high dielectric constant and its conductive nature. When an electric field is applied across
the composite an electrostatic force is generated that results in displacement of the composite. This indicates that by aligning the SWNTs in the 0.65 wt% CNT polyimide composite by electrospinning, the composite may behave as an electrostatic actuator in the parallel direction and as a piezoelectric sensor in the perpendicular direction.

Dielectric equations, describing the anisotropy in aligned composites with cylindrical inclusions are developed using Bruggeman’s effective medium approach. With the cylindrical inclusions aligned along the z axis, the effective dielectric equations of the composite in x, y and z axes are obtained. In Bruggeman’s theory the composites composed of aligned inclusions dispersed in a dielectric host [83]. The major factors that affect the dielectric constant of the composite include size, shape, concentration and orientation of the inclusions in the host matrix. In this work, this theory is used to analyze the dielectric of composite containing aligned ellipsoidal inclusions and is extended for aligned cylindrical inclusions. An ellipsoidal particle with a dielectric constant of $\varepsilon_2$ is embedded in a homogenous medium with a dielectric constant of $\varepsilon_1$. It is assumed that the ellipsoids are aligned in the medium and thus they generate an overall anisotropic behavior in the composite medium. Let the axes of the ellipsoid be $a_x$, $a_y$ and $a_z$ aligned with axes x, y, z of the reference frame. Let a uniform electric field $E_0$ be applied to the composite structure. $E_{0x}$, $E_{0y}$ and $E_{0z}$ are the electric field in x, y and z axes respectively. The uniform electric field that appears inside the ellipsoid is defined as the function [84]

$$R(s) = \sqrt{(s + a_x^2)(s + a_y^2)(s + a_z^2)}$$
Depolarization factors for the aligned ellipsoids along each axis are:

\[
L_x = \frac{a_x a_y a_z}{2} \int_0^{+\infty} \frac{ds}{(s + a_x^2)R(s)},
\]

\[
L_y = \frac{a_x a_y a_z}{2} \int_0^{+\infty} \frac{ds}{(s + a_y^2)R(s)},
\]

\[
L_z = \frac{a_x a_y a_z}{2} \int_0^{+\infty} \frac{ds}{(s + a_z^2)R(s)}.
\]

It is observed that \(L_x + L_y + L_z = 1\). Therefore, the electric field inside the ellipsoid is given, in components by [84]

\[
E_{ix} = \frac{E_{0x}}{1 + L_x (\varepsilon_2 - \varepsilon_1) / \varepsilon_1},
\]

\[
E_{iy} = \frac{E_{0y}}{1 + L_y (\varepsilon_2 - \varepsilon_1) / \varepsilon_1},
\]

\[
E_{iz} = \frac{E_{0z}}{1 + L_z (\varepsilon_2 - \varepsilon_1) / \varepsilon_1}.
\]

where \(E_{ix}, E_{iy},\) and \(E_{iz}\) are the electric fields inside the ellipsoid in x, y and z directions.

Consider the volume fraction of ellipsoids as \(c\), here we consider a diluted dispersion where \(c \ll 1\). The average volume of the electric field over the mixture volume is evaluated by the following relationships:

\[
\langle E_x \rangle = cE_{ix} + (1-c)E_{0x},
\]

\[
\langle E_y \rangle = cE_{iy} + (1-c)E_{0y},
\]

\[
\langle E_z \rangle = cE_{iz} + (1-c)E_{0z}.
\]

The interactions between the inclusions are not considered, the assumption being that due to the low concentrations of the inclusions, each ellipsoid behaves as a single one in the whole space. To define the mixture, a greater ellipsoid is considered which contains all
the smaller ones. This ellipsoid represents the external surface of the composite materials. This ellipsoid has, by definition, the same shape of the inclusions where the axes are given by $\beta a_x, \beta a_y$ and $\beta a_z$, where $\beta$, a positive constant, is aligned to the embedded ellipsoids shown in Figure 4.19. It is observed that the depolarization factors of the greater ellipsoid are same as each inclusion contained in the mixture. The overall behavior of the composite will be anisotropic because of the alignment of the ellipsoidal particles. So the equivalent dielectric constant of the mixture along $x$, $y$, and $z$ directions are $\varepsilon_x$, $\varepsilon_y$, and $\varepsilon_z$ respectively. The average values of the electric field inside the whole mixture are:

![Figure 4.19. Structure of a dispersion of aligned ellipsoids. The external surface of the mixture is a greater ellipsoid with the same shape of the inclusions.](image-url)
Considering the whole mixture as a single inclusion in the whole space derives these expressions. By substituting equation (4.9) into equation (4.10) and comparing to equation (4.11) expressions for $\varepsilon_x$, $\varepsilon_y$, and $\varepsilon_z$ are evaluated which are equivalent permittivities for the whole composite material in x, y and z directions respectively.

\[
\langle E_x \rangle = \frac{E_{0x}}{1 + L_x (e_x - e_i) / e_i},
\]

\[
\langle E_y \rangle = \frac{E_{0y}}{1 + L_y (e_y - e_i) / e_i},
\]

\[
\langle E_z \rangle = \frac{E_{0z}}{1 + L_z (e_z - e_i) / e_i}
\]

The equivalent permittivity for the composite material in equation (4.12) are for aligned ellipsoidal inclusions. These equations are modified for long cylindrical inclusions. When the ellipsoids are converted to parallel elliptic cylinders where $a_z \to \infty$, the eccentricity of the elliptic base of these cylinders is $e = \frac{a_y}{a_x}$. The depolarization factors of aligned cylindrical inclusions are:
When the eccentricity $e$ becomes equal to 1 ($e=1$), the ellipsoid is converted to a sphere. In this case when $e=1$, the parallel elliptical cylinders are converted to cylindrical rods. Substituting $e=1$ in equation (4.13) the depolarization factors for cylindrical rods in $x$, $y$ and $z$ directions are:

$$L_x = \frac{1}{2}$$

$$L_y = \frac{1}{2}$$

$$L_z = 0$$

By substituting the depolarization factors of equation (4.14) in equation (4.12), the principal permittivities for cylindrical rods in $x$, $y$ and $z$ directions are:

$$\varepsilon_x = \varepsilon_1 + \frac{c(\varepsilon_2 - \varepsilon_1)2\varepsilon_1}{2\varepsilon_1 + (1-c)(\varepsilon_2 - \varepsilon_1)},$$

$$\varepsilon_y = \varepsilon_1 + \frac{c(\varepsilon_2 - \varepsilon_1)2\varepsilon_1}{2\varepsilon_1 + (1-c)(\varepsilon_2 - \varepsilon_1)},$$

$$\varepsilon_z = \varepsilon_1 + c(\varepsilon_2 - \varepsilon_1)$$
The dielectric equations for diluted anisotropic cylindrical inclusions, obtained in equation (4.15) can be applied to composites with diluted SWNT inclusions. The aligned SWNT polyimide composite can be considered as composites with aligned SWNTs as the anisotropic inclusions and polyimide matrix as the isotropic dielectric host. The effective dielectric constant parallel to the aligned SWNT polyimide composite is $\varepsilon_z$ and the dielectric constant perpendicular to the aligned SWNT polyimide composite is $\varepsilon_x$. Using the dielectric equations obtained from Equation (4.15), $\varepsilon_x$ and $\varepsilon_z$ are calculated. The polyimide matrix is considered as the dielectric host with a dielectric constant of $\varepsilon_1=4$, obtained from the experiment and the SWNTs are considered as the cylindrical inclusions with a dielectric constant of $\varepsilon_2$. The dielectric constant of the SWNT inclusions is a very high value, as it is a mixture of metallic and semiconducting tubes. A value of $5\times10^5$ is selected as the dielectric constant of the SWNTs; using this value reasonable dielectric constants for polyimide composite and (UDMA/HDDMA) composite are obtained. Table 4.4 lists the experimental and theoretical dielectric constants, parallel ($\varepsilon_z$) and perpendicular ($\varepsilon_x$) to the aligned SWNTs at various SWNT concentrations.
Table 4.4 Comparison of the parallel and perpendicular dielectric constants obtained from experimental and theoretical calculations.

<table>
<thead>
<tr>
<th>SWNT Concentration</th>
<th>Experimental dielectric constant</th>
<th>Theoretical dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon_x$</td>
<td>$\varepsilon_z$</td>
</tr>
<tr>
<td>0 wt %</td>
<td>4.286</td>
<td>8.78</td>
</tr>
<tr>
<td>0.1 wt%</td>
<td>4.645</td>
<td>9.52</td>
</tr>
<tr>
<td>0.2 wt%</td>
<td>4.491</td>
<td>16.9</td>
</tr>
<tr>
<td>0.65 wt%</td>
<td>5.56</td>
<td>30.0441</td>
</tr>
<tr>
<td>1 wt%</td>
<td>6.992</td>
<td>45.92673</td>
</tr>
</tbody>
</table>

The theoretical dielectric constant values using Equation (4.15) indicate anisotropy in the dielectric constant between parallel and perpendicular measurements. The dielectric constant perpendicular to the aligned SWNTs was lower than the dielectric constant parallel to the aligned SWNTs. It is observed that the perpendicular dielectric constant ($\varepsilon_x$) is more influenced by the dielectric constant of the polyimide matrix ($\varepsilon_1$) and the dielectric constant of SWNT does not affect $\varepsilon_x$. The parallel dielectric constant ($\varepsilon_z$) is highly influenced by the dielectric constant of SWNT, which results in a large increase in $\varepsilon_z$. Though the experimental and theoretical values did not match, a similar trend is seen in the dielectric constants obtained from both results.
4.1.6 Mechanical properties of randomly oriented SWNT polyimide composites:

Figure 4.20 shows the effect of temperature on the storage modulus of randomly oriented SWNT polyimide composite films, measured at 10 Hz. The storage modulus of the polyimide increases, as the concentration of SWNT is increased. This increase is shown in more detail in Figure 4.21 and Figure 4.22 at temperatures below and above $T_g$ respectively. The storage modulus drops moderately at temperatures below 220°C, as seen in Figure 4.20. Below $T_g$, the polymer is in the glassy state and the immobile polymer chains prevent the drop in the storage modulus. The storage modulus drops

![Figure 4.20. Storage modulus as a function of temperature for various SWNT polyimide films.](image-url)
rapidly around 230°C, which indicates the relaxation of the polymer at $T_g$, as seen in Figure 4.20. When the polymer reaches the $T_g$ region, the polymer chains become mobile as the polymer is in the rubbery state. The relaxation of the polymer chains in the rubbery state causes a drop in the storage modulus.

The storage modulus of the polymer is a measure of stiffness as described in chapter 3, section 3.8. The addition of SWNTs increases the stiffness in the polyimide matrix. The increase in storage modulus at 40°C, with increase in SWNT concentration is shown in Figure 4.21. The storage modulus of the pristine polyimide increases from 1427 MPa to

![Figure 4.21. Increase in the storage modulus at 40°C, as the SWNT concentration in the polyimide increases.](image-url)
2477 MPa by the addition of 0.035 wt% of SWNTs to the polyimide matrix. The interactions between the SWNT inclusions and the polymer chains prevent the movement of the polymer chains. With 0.2 wt% SWNT concentration the storage modulus of the composite increases to 3048 MPa, which remains almost constant with further increase in the SWNT concentration. The plateau in storage modulus at 0.2 wt% SWNT concentration is an indication of percolation threshold.

A similar increase in the storage modulus with increase in SWNT concentration is observed above $T_g$ at 230°C, as seen in Figure 4.22. The storage modulus of the pristine polyimide increases from 63 MPa to 542 MPa by the addition of 0.2 wt% SWNT

![Figure 4.22. Increase in the storage modulus at 230°C, as the SWNT concentration in the polyimide increases.](image-url)
concentration. The increase in the storage modulus of the polyimide from 63 MPa to 542 MPa by adding 0.2 wt% SWNTs, shows that the stiffness of the polyimide is increased at \( T_g \) by adding SWNTs. The SWNT inclusions interact with the polymer chains in polyimide; these SWNTs restrict the movement of the polymer chains in the rubbery state, which increases the stiffness in the polyimide matrix. As the concentration of SWNTs increases, there are more SWNTs that restrict the movement of the polymer chains which further increases the stiffness of the polyimide. This indicates that the stiffness of the composite at 230°C is increased by 760%. At 0.2 wt% SWNT concentration a threshold in the stiffness of the polyimide matrix is attained, further increase in SWNT concentration does not increase the storage modulus. A similar percolation threshold is observed in the dielectric constant of SWNT polyimide composite at 0.1 wt% SWNT concentration, as seen in Figure 4.13. The percolation obtained from the dielectric data is at a lower SWNT concentration compared to the percolation obtained from storage modulus data. It is believed that a physical contact is not necessary for percolation to occur in electrical data due to the electron hopping. In the mechanical measurements there is no hopping of electrons and the threshold is attained at a higher SWNT concentration.

Increasing the SWNT content in the polyimide films also changes the loss modulus. There is a rise in the peak height of the loss modulus around \( T_g \), as the SWNT concentration is increased in the polyimide matrix, as shown in Figure 4.23. The SWNTs
restrict the segmental motion of the polymer chains in the composites, which results in an increase in the peak of the loss modulus with SWNT loading [85].

![Figure 4.23. Loss modulus of various SWNT polyimide films as a function of temperature.](image)

The peak in tan $\delta$ is an indication of $T_g$ of the material, as described in section 3.8 in chapter 3. The $T_g$ of various SWNT polyimide composites, obtained from tan $\delta$ are listed in Table 4.5. The tan $\delta$ peak shifts to a higher temperature as the SWNT concentration is increased up to 0.2 wt%, as shown in Figure 4.24. The shift in the tan $\delta$ peak to a higher temperature indicates that the $T_g$ of the polyimide increases with SWNT concentration up to 0.2 wt%. The SWNTs in the polyimide matrix restrict the relaxation of the polymer chains, which causes an increase in the $T_g$. The tan $\delta$ peak for 1 wt% and 2 wt% SWNT concentrations shifts to a lower temperature. It is believed that the shift might be due to

- [85]
Figure 4.24. \( \tan \delta \) of various SWNT polyimide films as a function of temperature.

incomplete curing of the composite due to presence of SWNTs [86]. The \( T_g \) of various SWNT polyimide composites obtained from DSC is compared to the \( T_g \) from \( \tan \delta \) peaks in Table 4.5. As an aside, it has been reported that the analysis of \( T_g \) with DMA is more accurate than that using DSC [87]. The \( T_g \) obtained from DSC is at a lower temperature compared to \( T_g \) from \( \tan \delta \) as seen in Table 4.5. The \( T_g \) from \( \tan \delta \) for the pristine polyimide is 233°C and from DSC is 217°C. The \( T_g \) of the polyimide, obtained from both \( \tan \delta \) and DSC increases with the addition of SWNTs. The \( T_g \) of 0.2 wt% SWNT polyimide, obtained from \( \tan \delta \) is 241°C and from DSC is 221°C. There is a small decrease in \( T_g \) at 1 wt% SWNT concentration which may be an experimental error. The \( T_g \) obtained from \( \tan \delta \) and DSC are not the same, as they are two different types of
measuring techniques. The $T_g$ from DSC is measured by the heat loss from the sample and $T_g$ from tan $\delta$ is measured by loss of the mechanical structure of the sample. The trend obtained from DSC can be compared to the trend obtained from tan $\delta$. It can be concluded from both tan $\delta$ and DSC that there is an increase in $T_g$ of the pristine polyimide by the addition of SWNTs.

Table 4.5. Comparison of $T_g$, obtained from DSC and tan $\delta$ peaks for SWNT polyimide composites

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>$T_g$ from DSC</th>
<th>$T_g$ from DMA (tan$\delta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% SWNT + Polyimide</td>
<td>217</td>
<td>233</td>
</tr>
<tr>
<td>0.05% SWNT + Polyimide</td>
<td>219</td>
<td>235</td>
</tr>
<tr>
<td>0.1% SWNT + Polyimide</td>
<td>220</td>
<td>241</td>
</tr>
<tr>
<td>0.2% SWNT + Polyimide</td>
<td>221</td>
<td>241</td>
</tr>
<tr>
<td>1% SWNT + Polyimide</td>
<td>220</td>
<td>239</td>
</tr>
<tr>
<td>2% SWNT + Polyimide</td>
<td>221</td>
<td>239</td>
</tr>
</tbody>
</table>

The above results indicate that the mechanical properties of polyimide can be improved by the addition of SWNTs. The increase in the stiffness of the composite with increase in SWNT content indicates that there is good adhesion between the polyimide matrix and the SWNTs. The increase in the stiffness above $T_g$ indicates that the polyimide composite can be used even at very high temperatures of 230°C with good mechanical properties.
4.2 SWNT/UDMA/HDDMA polymer composite:

4.2.1. Aligning of SWNTs in UDMA/HDDMA composite:

The alignment of SWNTs in UDMA/HDDMA, can be rationalized by considering the electronic polarization induced in SWNTs by the electric field. A dipole moment \( P = \alpha E \) of a SWNT with length \( L \) is considered, where \( E \) is the applied electric field. The static polarizability tensor \( \alpha \) of the SWNT is highly anisotropic, because of the structure of SWNT. The polarizability along the tube axis is much higher than that perpendicular to the tube axis [51]. A schematic of a SWNT in an electric field is shown in Figure 4.10.

For a SWNT oriented at an angle \( \theta \) with respect to \( E \), the dipole moment of the SWNT is given in Equation 4.1. Referring back to Equation 4.2 and 4.3, because of the structure of anisotropy of the SWNTs, the dipole moment created by the electric field in the direction parallel to the tube axis is stronger than in the perpendicular direction. Increase in the dipole moment results in an increase in the torque \( \tau \). The force applied on the dipole to rotate and align the SWNT with electric field is related to the static polarizability tensor \( \alpha \) and the length of the SWNT \( L \). The force, to align the SWNT in the direction of electric field is higher, as \( \alpha \) is higher along the tube axis. Therefore SWNTs could be aligned along the direction of the electric field if its environment does not restrict the movement [51, 54].

In this case, an electric field is applied to the SWNT/UDMA/HDDMA composite before the composite is cured. The applied electric field influences the mobile SWNTs and aligns them in the direction of the electric field. The motion of the SWNTs is not
restricted, as the composite is not cured. Once the SWNTs are aligned by the electric field its movement is restricted by curing the composite while the electric field is still on. The composite is cured using a blue light gun, as the composite is photo curable.

4.2.2 Optical microscopy on aligned SWNT/UDMA/HDDMA composite:

Figure 4.25 shows the optical microscopy (OM) images for the control sample and for samples aligned at 1Hz, and 10Hz. Comparison of the first two OMs clearly shows alignment at 1Hz. Comparing the 1Hz sample to the 10Hz, a better alignment is visually observed for the 10Hz case. Above 10Hz, it is more difficult to conclude the best alignment simply based on optical microscopy.

![Optical micrographs of SWNT/UDMA/HDDMA samples:](image)

(a) control (unaligned), (b) aligned at 1Hz, (c) aligned at 10Hz.

4.2.3 Raman spectroscopy to measure the degree of alignment of SWNTs in UDMA/HDDMA composite:

A Raman spectrum is obtained for the 10 Hz samples and the 100 kHz samples. Inspection of the tangential peak (1590cm⁻¹) of Raman spectra for the 100 kHz sample,
shown in Figure 4.26, reveals that the maximum intensity is obtained when the polarization of incident radiation is parallel to the SWNT axis, i.e, $\alpha_i = 0^\circ$ and $\alpha_i = 180^\circ$ (only the range from $0^\circ$ to $90^\circ$ is shown here). The lowest Raman intensity is obtained when the polarization of incident radiation is perpendicular to the SWNT axis i.e $\alpha_i = 90^\circ$. The intensity of the tangential peak decreases when the polarizer angle is $\alpha_i = 15^\circ$ and the intensity continuously decreases as the polarizer angle is increased up to $\alpha_i = 90^\circ$. Similar results are obtained for the 10 Hz sample as shown in Figure 4.27. It is noted that the relative Raman intensity at $\alpha_i = 0^\circ$ coincides with that at $\alpha_i = 180^\circ$ shown in Figure 4.27, as both these intensities are parallel to the aligned SWNTs.

Figure 4.26. Raman spectra showing tangential peak of SWNTs aligned by AC electric field at 100 kHz.
The Raman intensity of the tangential peak varies with the polarizer angle for aligned SWNTs, as described in chapter 3, section 3.5. The decrease in the Raman intensity with increase in the polarizer angle up to $\alpha_i = 90^\circ$ and the difference in the intensity of tangential peaks when the polarizer is parallel and perpendicular to the aligned SWNTs, confirms a preferential alignment of SWNTs in UDMA/HDDMA matrix, as a result of the applied AC electric field at a frequency of 10 Hz and 100 kHz.

4.2.4 Conductivity measurements on aligned SWNT/UDMA/HDDMA composite:  
AC conductivity is measured parallel ($\sigma_z$) to the aligned SWNTs and perpendicular ($\sigma_x$, $\sigma_y$) to the aligned SWNTs. Figure 4.28 summarizes these results for all cases considered,
namely, the control and the aligned samples. Results demonstrate that for the control sample, $\sigma_x$, $\sigma_y$, and $\sigma_z$ have similar orders of magnitude, which indicates an isotropic behavior with respect to electrical properties when the SWNTs are randomly dispersed. For the aligned samples however, anisotropy in the conductivity increases as the frequency of alignment increases as seen in Figure 4.28. Comparing the parallel to the perpendicular direction in each case, the 10 Hz, 10 kHz and the 100 kHz samples show a greater conductivity parallel to the aligned SWNTs, as compared to the conductivity in the perpendicular directions. The parallel conductivity, $\sigma_z$, for the 10 kHz and 100 kHz samples is two orders of magnitude greater than $\sigma_x$ and one order of magnitude greater than $\sigma_y$. Conductivity for the control sample, 0.001 Hz and 0.1 Hz samples is of the same

Figure 4.28. Comparison of conductivity in directions parallel ($\sigma_y$) and perpendicular ($\sigma_x$, $\sigma_z$) to SWNTs at 10KHz.
order of magnitude in all directions of measurements. Furthermore, the conductivity in all three directions increases as the frequency of alignment increases, up to 10kHz, and seems to decrease slightly for the 100kHz samples. Referring back to Figure 4.28, parallel conductivity, $\sigma_z$, for the 10 kHz and 100 kHz samples is almost one order of magnitude higher than that of the 10 Hz sample. Similarly, $\sigma_z$ for the 10 Hz sample is almost two orders of magnitude higher than that of the 0.1 Hz sample and the control sample. We conclude that the increase in conductivity in the direction of alignment indicates a better alignment of the SWNTs in that direction (going from the control sample to 0.1Hz to 100kHz). The SWNTs form a conductive path when measured in the direction of alignment, which results in a high conductivity value, compared to the value obtained perpendicular to the aligned SWNTs, where there is no continuous conductive path. Perpendicular conductivity, $\sigma_x$, for the 10 Hz, 10 kHz and the 100 kHz samples is of the same order of magnitude and it is one order of magnitude higher than the control sample and the 0.1 Hz sample. The value of $\sigma_x$ increases from $2.1 \times 10^{-9}$ for the control sample to $6.5 \times 10^{-8}$ for the 100 kHz sample. Perpendicular conductivity ($\sigma_y$) for the 10 kHz and 100 kHz samples is one order of magnitude higher than the 10 Hz sample and similarly $\sigma_y$ for the 10 Hz sample is one order of magnitude higher than the control sample. The value of $\sigma_y$ increases from $2.6 \times 10^{-9}$ for the control sample to $2.6 \times 10^{-7}$ for the 100 kHz sample. The increase observed in $\sigma_x$ and $\sigma_y$ may be indicative of a network formation in the perpendicular directions under the influence of the electric field. As the SWNTs align in the direction of the electric field, their re-arrangement affects the path in the perpendicular directions in such a way that the conductivity values are improved.
Inspection of Figure 4.29 shows that the parallel conductivity, $\sigma_z$, for the 10 Hz, 10 kHz and the 100 kHz samples increases with frequency of measurement. A similar trend is

![Graph showing conductivity vs. frequency for 10 Hz, 10 kHz, and 100 kHz samples.](image)

**Figure 4.29.** Increase in Conductivity ($\sigma_z$) parallel to aligned SWNTs with frequency.

**Figure 4.30.** Increase in conductivity ($\sigma_x$) perpendicular to aligned SWNTs with frequency.
observed for the perpendicular conductivity ($\sigma_x$ or $\sigma_y$) for the 10 Hz, 10 kHz and the 100 kHz samples as shown in Figure 4.30. A closer inspection of the error bars in both Figure 4.29 and Figure 4.30 indicate that a plateau is reached somewhere around a 10 kHz frequency of alignment.

**4.2.5 Dielectric spectroscopy on aligned SWNT/UDMA/HDDMA composite:**

Dielectric constant is measured in two directions, parallel ($\epsilon_z$) and perpendicular ($\epsilon_x$) to the aligned SWNTs, as shown in Figure 3.8 in chapter 3. It is observed that the dielectric constant perpendicular to the aligned SWNTs does not increase when the frequency of alignment increases, as seen in Figure 4.31. The perpendicular dielectric constant remains at ~40 with increase in the frequency of alignment. The dielectric constant increases with frequency of alignment when measured parallel to the aligned SWNTs. The parallel dielectric constant of the control sample increases from 35 to 270 when the frequency of alignment is increased to 10 kHz. The dielectric constant in the direction of the aligned SWNTs is greater than, the dielectric constant measured perpendicular to the aligned SWNTs. This variation in dielectric constant increases as the frequency of the electric field to align increases, as seen in Figure 4.31. The dielectric constant for the control sample (unaligned) is ~ 30 in both the directions of measurement. The isotropy in dielectric constant is due to the randomly arranged SWNTs in the control sample. The dielectric constant of the 10 kHz sample, in the parallel direction and perpendicular direction is 240 and 40 respectively. The high dielectric constant in the parallel direction is due to the effect of aligned SWNTs. The anisotropy in dielectric constant increases as
the frequency of alignment increases from 0.001 Hz to 10 kHz; this indicates that the
alignment of SWNTs increases as the frequency of alignment increases.

Figure 4.31. Comparison of dielectric constant parallel ($\varepsilon_z$) and perpendicular ($\varepsilon_x$).

The anisotropy in the 10 kHz sample is due to the alignment of the SWNTs in
UDMA/HDDMA. The anisotropy in dielectric constant for the aligned
SWNT/UDMA/HDDMA composites is verified by using the effective dielectric
equations for diluted anisotropic cylindrical inclusions, obtained in equation (4.15). The
SWNT/UDMA/HDDMA composite is made up of aligned SWNTs as the anisotropic
inclusions and UDMA/HDDMA as the isotropic dielectric host. The effective dielectric
constant parallel to the aligned SWNT/UDMA/HDDMA composite is $\varepsilon_z$ and the
dielectric constant perpendicular to the aligned SWNT/UDMA/HDDMA composite is $\varepsilon_x$.

Using the dielectric equations obtained from Equation (4.15), $\varepsilon_x$ and $\varepsilon_z$ are calculated.
The UDMA/HDDMA matrix is considered as the dielectric host with a dielectric constant of $\varepsilon_1 = 40$, obtained from the experiment and the SWNTs are considered as the cylindrical inclusions with a dielectric constant of $\varepsilon_2$. The dielectric constant of the SWNT inclusions is considered to be a very high value, as it is a mixture of metallic and semiconducting SWNTs. On a trial and error basis a value of $5 \times 10^5$ is picked as the dielectric constant of the SWNTs, the concentration of the SWNTs is constant with $C = 0.03$ vol% using these value reasonable dielectric constants for UDMA/HDDMA composite are obtained. Table 4.6 lists the experimental and theoretical dielectric constants, parallel ($\varepsilon_x$) and perpendicular ($\varepsilon_z$) to the aligned SWNTs. The dielectric constant for the 10 kHz sample is taken as the experimental value, because it is seen that the SWNTs are well aligned at 10 kHz and 100 kHz.

<table>
<thead>
<tr>
<th>SWNT concentration</th>
<th>Experimental dielectric constant for 10 kHz sample</th>
<th>Theoretical dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon_x$</td>
<td>$\varepsilon_z$</td>
</tr>
<tr>
<td>0.03 vol %</td>
<td>31</td>
<td>240</td>
</tr>
</tbody>
</table>

The theoretical dielectric constant values using Equation 4.15 indicate anisotropy in the dielectric constant between parallel ($\varepsilon_z$) and perpendicular ($\varepsilon_x$) measurements. The dielectric constant perpendicular to the aligned SWNTs is lower than the dielectric constant parallel to the aligned SWNTs. It is seen that the perpendicular dielectric constant is influenced by the dielectric constant of UDMA/HDDMA matrix. The
dielectric constant of the SWNT does not play a major role on the effective dielectric constant perpendicular to the aligned SWNTs. The dielectric constant of the SWNTs influence the effective dielectric constant parallel to the aligned SWNTs. Similar anisotropy is also seen in the dielectric constants obtained from the experimental results.

The dielectric constant for the control sample, 10 Hz, 10 kHz and 100 kHz samples is measured as a function of frequency of measurement, parallel ($\varepsilon_z$) and perpendicular to the aligned SWNTs ($\varepsilon_x$) as shown in Figure 4.32 and Figure 4.33 respectively. The parallel dielectric constant ($\varepsilon_z$) of the control sample is not dependent on frequency. The value of $\varepsilon_z$ for the 10 Hz, 10 kHz and 100 kHz samples is largely dependent on frequency, $\varepsilon_z$ decreases with increase in frequency of measurement, as shown in Figure 4.32. The value of $\varepsilon_z$ for the control sample remains at around 40 at all frequencies, while
the value of $\varepsilon_z$ for the 10 kHz sample drops from 1208 to 52 as the frequency increases from 20 Hz to 100 kHz. This indicates that, parallel to the aligned SWNTs the control sample behaves as an insulator and the 10 Hz, 10 kHz and 100 kHz samples behave as conductors.

The dielectric constant in the perpendicular direction ($\varepsilon_x$) for the control and the 10 Hz sample is not dependent on frequency, as seen in Figure 4.33. This indicates that the control sample and the 10 Hz sample behave like insulators, when measured perpendicular to the aligned SWNTs. The dielectric constant of the 10 kHz and 100 kHz samples are dependent on frequency. The dielectric constant of 10 kHz sample decreases

![Figure 4.33. Dielectric constant as a function of frequency in the perpendicular direction ($\varepsilon_x$).](image)
from 240 to 25 as the frequency increases from 20 Hz to 100 kHz. The dependence on frequency for the 10 kHz and 100 kHz samples indicates that the composite starts to behave as a conductor in the direction parallel to the aligned SWNTs, when the SWNTs are aligned by applying an electric field at 10 kHz and 100 kHz.

It can be concluded that by applying an AC electric field of 43.5 V/mm at a frequency of 10 Hz, the SWNT/UDMA/HDDMA composite behaves as an insulator perpendicular to the aligned SWNTs and behaves as a conductor parallel to the aligned SWNTs.
Chapter 5

Conclusion and recommendations for future work

The main objective of this work was to efficiently disperse and align SWNTs in two different polymer matrices and characterize the resulting polymer composites. The SWNTs were aligned to obtain an orthotropic composite whose strength, stiffness and electrical properties depend on the orientation of the SWNTs, which ultimately would result in multifunctional materials. To fulfill this goal, SWNTs were effectively dispersed and aligned in polyimide and (UDMA/HDDMA) polymer matrices.

Polyimide was chosen because of its good mechanical properties and high glass transition temperature. In situ polymerization under sonication was used to disperse the SWNTs in polyimide matrix. In this method, the diamine was first added to the SWNT solution, then the dianhydride, while sonication was on. The dipole present in the diamine undergoes an electron donor acceptor interaction with the SWNT, which aids to disperse the SWNTs. In UDMA/HDDMA, the polymers were mixed along with SWNTs and the solution was sonicated to disperse the SWNTs. In both polymer composites, an electric field was used to align the SWNTs. In polyimide, the SWNTs were aligned by electrospinning technique, where it is believed that a combination of DC electric field and mechanical stretching of the fiber leads to alignment. In the (UDMA/HDDMA) blend, the SWNTs were aligned by applying an AC electric field, while the composite is cured. In this case, it is believed that simultaneous application of an electric field while curing locks the aligned SWNTs in the (UDMA/HDDMA) matrix.
The electrical and mechanical properties of randomly dispersed SWNT polyimide composites were measured. The dielectric constant of randomly oriented SWNT polyimide composites increased with SWNT concentrations. Percolation in the dielectric constant was achieved at a very low SWNT concentration of 0.06 wt%, which indicates very good dispersion of SWNTs in the polyimide matrix. The interactions between the dipoles present in the polyimide matrix and the SWNTs have been studied to assess the piezoelectricity in the SWNT polyimide composites. The dielectric constant was measured as a function of temperature for the randomly oriented SWNT polyimide composites. It was observed that at low SWNT concentrations up to 0.1 wt%, there was a sharp increase in the dielectric constant at 220 °C, which is the $T_g$. The sharp increase in the dielectric constant is known as dielectric relaxation strength. The dielectric relaxation strength is related to the remanent polarization, which is a direct measure of the piezoelectric behavior of the composite. Composites with SWNT concentrations greater than 0.1 wt% do not show the increase in the dielectric constant, as they are above percolation and they become conductive. This indicates that SWNT polyimide composites, which are below percolation can be used as sensors as they are piezoelectric and the composites above percolation are conductive. The storage modulus of the randomly oriented SWNT polyimide composite increased by 113% below $T_g$ and by 760% above $T_g$ with 0.2 wt% SWNT concentration in the polyimide. The increase in storage modulus further proved good dispersion and adhesion between the SWNTs and
the polyimide matrix. The increase in storage modulus of the SWNT polyimide composite indicates that SWNTs act as reinforcement in the polyimide.

SWNT polyimide composite was electrospun at 15 kV, 20 kV and 25 kV voltages, with a distance of 20 cm between the tip of the syringe and the collector. Electrospinning resulted in fibers of SWNT polyimide composite. Single fibers were picked from the bunch of electrospun fiber to obtain a Raman spectrum. A Raman spectrum of aligned SWNT polyimide composites at various polarizer angles was obtained to assess the orientation of SWNTs in the polyimide composite. It was observed that maximum intensity in the tangential peak of the SWNT in the Raman spectrum was obtained, when the polarizer was parallel to the nanotube axis. The tangential peak was totally suppressed when the polarizer was perpendicular to the nanotube axis. The difference in the intensities of the tangential peak indicates preferential alignment of SWNTs in the aligned SWNT polyimide composite. The dielectric constant of aligned SWNT polyimide composites was measured parallel and perpendicular to the aligned SWNTs. In the aligned SWNT polyimide composite the anisotropy in dielectric constant increases as the concentration of SWNTs is increased from 0 wt% to 1 wt%. The dielectric constant in the parallel direction increases as the SWNT concentration increases, but the dielectric constant in the perpendicular direction does not increase with SWNT concentration. This indicates that the dielectric constant parallel to the aligned SWNTs is influenced by the SWNTs and the dielectric constant perpendicular to the aligned SWNTs is influenced only by the polyimide matrix. The dielectric constant was measured as a function of
frequency in the parallel and perpendicular directions. The parallel dielectric constant for the pristine polyimide and 0.1 wt% aligned SWNT composite are not dependent on frequency, and remains fairly constant. The parallel dielectric constant of 0.2 wt%, 0.65 wt% and 1 wt% aligned SWNT polyimide composites is dependent on frequency and the dielectric constant decreases with increase in frequency. The perpendicular dielectric constant for the pristine polyimide, 0.1 wt%, 0.2 wt% and 0.65 wt% SWNT polyimide composites are not dependent on frequency while that of 1 wt% SWNT polyimide composite decreases with increase in frequency. These results indicate that percolation in the SWNT polyimide composite occurs at 0.2 wt% SWNT concentration when dielectric constant is measured parallel to the aligned SWNTs and percolation occurs at 0.65 wt% SWNT concentration, when measured perpendicular to the aligned SWNTs. The composites below percolation can be used as piezoelectric sensors, because of the combination of their low dielectric constant and their piezoelectric nature. The composites above percolation can be used as electrostatic actuators, because they are conductive and have a high dielectric constant. From the dielectric results of aligned SWNT polyimide composites it can be concluded that, by aligning the SWNTs in the polyimide the composite can be used as a sensor and as an actuator at the same time. The 0.65 wt% aligned SWNT composite is piezoelectric as it is below percolation in the perpendicular direction. The 0.65 wt% aligned SWNT polyimide composite also has a low dielectric constant in the perpendicular direction, which results in a better sensor response, as the piezoelectric voltage coefficient \((g)\) is inversely proportional to the dielectric constant. The combination of low dielectric constant and piezoelectric nature
means that the 0.65 wt% aligned SWNT polyimide composite can possibly be used as a piezoelectric sensor in the perpendicular direction. The 0.65 wt% aligned SWNT polyimide composite has a high dielectric constant and also behaves as a conductor in the parallel direction as it is above percolation. The 0.65 wt% aligned SWNT polyimide composite can possibly be used as an electrostatic actuator in the parallel direction, because of its high dielectric constant and its conductive nature. When an electric field is applied across the composite an electrostatic force is generated that results in displacement of the composite. This indicates that by aligning the SWNTs in the 0.65 wt% CNT polyimide composite by electrospinning, the composite may behave as an electrostatic actuator in the parallel direction and as a piezoelectric sensor in the perpendicular direction.

Different characterization methods were used to assess the alignment of the SWNTs in UDMA/HDDMA matrix by AC electric field while curing. Optical microscope images showed alignment of the SWNTs in the UDMA/HDDMA composite. Inspection of the Raman spectra on aligned SWNT/UDMA/HDDMA composite indicates a decrease in the intensity of the tangential peak of the SWNT with increase in the polarizer angle. The intensity of the tangential peak was maximum when the polarizer was parallel to the nanotube axis and the tangential peak was suppressed when the polarizer was perpendicular to the nanotube axis. The difference in the intensities of the tangential peaks indicates preferential alignment of SWNTs in UDMA/HDDMA. Conductivity and dielectric constant measurements on aligned SWNT/UDMA/HDDMA composites were
highly anisotropic. The conductivity increased with frequency of alignment and the conductivity parallel to the aligned SWNTs was greater than the conductivity perpendicular to the aligned SWNTs. The conductivity for the unaligned SWNT/UDMA/HDDMA composite was isotropic. The conductivity in the parallel and perpendicular directions was the same. The dielectric constant for the aligned SWNT/UDMA/HDDMA composites was highly anisotropic. The parallel dielectric constant increased with increase in frequency of alignment from 0.1 Hz to 100 kHz and the perpendicular dielectric constant remained fairly constant with increase in frequency of alignment. The greatest difference in dielectric constant was observed for the composites aligned at 10 kHz and 100 kHz frequency, indicating that the SWNTs were better aligned at these frequencies. The parallel dielectric constant for the unaligned SWNT/UDMA/HDDMA composite was not dependent on frequency while parallel dielectric constant for the 10 Hz, 10 kHz and 100 kHz samples was very dependent on frequency. The dielectric constant decreased with increase in frequency. The perpendicular dielectric constant for the unaligned and 10 Hz aligned SWNT/UDMA/HDDMA composite was not dependent on frequency while that of the 10 kHz and 100 kHz samples were highly dependent on frequency. The dielectric results indicate that the SWNT/UDMA/HDDMA composite aligned at 10 Hz frequency behaves as a conductor parallel to the aligned SWNTs and the same composite behaves as an insulator perpendicular to the aligned SWNTs.
To analyze the resulting anisotropy in the dielectric constant, a theory using Bruggeman’s approach was used. The effective medium theory predicts the effective dielectric constant of a composite with aligned anisotropic inclusions. The effective dielectric constant in both, perpendicular to the aligned inclusions and parallel to the aligned inclusions were estimated using this theory assuming cylindrical inclusions in a homogenous matrix. The dielectric constant values of aligned SWNT polyimide and aligned SWNT/UDMA/HDDMA composites obtained from the theory did not match with the experimental values, but anisotropy in dielectric constants was seen in both theoretical and experimental values. The value of the dielectric constant parallel to the aligned inclusions is greater than the dielectric constant value perpendicular to the aligned inclusion. The theory indicated that the dielectric constant parallel to the aligned inclusions is highly influenced by the dielectric constant of the inclusion and the dielectric constant perpendicular to the aligned inclusions is highly influenced by the dielectric constant of the polymer matrix.

A variety of characterization techniques, i.e. microscopy, Raman spectroscopy, electrical conductivity, dynamic dielectric spectroscopy and dynamic mechanical analysis, indicate preferential alignment of SWNTs in two types of polymers: Polyimide and (UDMA/HDDMA). It can be concluded that SWNTs can be successfully aligned in the polyimide matrix by electrospinning technique and SWNTs are aligned in (UDMA/HDDMA) matrix by an AC electric field.
The future work will focus on the following: 1) to investigate the mechanism responsible for the alignment of inclusions, by probing into the electrostatic forces acting on the conducting inclusions, 2) to investigate the nature of interaction between SWNT and various polymer matrices, 3) to observe the percolation in UDMA/HDDMA blends, 4) to measure the mechanical properties for both polyimide and (UDMA/HDDMA) polymers with aligned SWNT inclusions, 5) to obtain the optimum alignment parameters in SWNT/UDMA/HDDMA composites by varying the electric field and curing time.

References

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