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Dispersion of Carbon Nanotubes in Vinyl Ester Polymer Composites

by

Laura Peña-Parás

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APPROVED, THESIS COMMITTEE:

Enrique V. Barrera, Professor, Chair
Mechanical Engineering and
Materials Science

Boris I. Yakobson, Professor,
Mechanical Engineering and
Materials Science

Matteo Pasquali, Professor,
Chemical and Biomolecular
Engineering

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ABSTRACT

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This work focused on a parametric study of dispersions of different types of carbon nanotubes in a polymer resin. Single-walled (SWNTs), double-walled (DWNTs), multi-walled (MWNTs) and XD-grade carbon nanotubes (XD-CNTs) were dispersed in vinyl ester (VE) using an ultra-sonic probe at a fixed frequency. The power, amplitude, and mixing time parameters of sonication were correlated to the electrical and mechanical properties of the composite materials in order to optimize dispersion. The quality of dispersion was quantified by Raman spectroscopy and verified through optical and scanning electron microscopy. By Raman, the CNT distribution, unropeing, and damage was monitored and correlated with the composite properties for dispersion optimization. Increasing the ultrasonication energy was found to improve the distribution of all CNT materials and to decrease the size of nanotube ropes, enhancing the electrical conductivity and storage modulus. However, excessive amounts of energy were found to damage CNTs, which negatively affected the properties of the composite. Based on these results the optimum dispersion energy inputs were determined for the different composite materials. The electrical resistivity was lowered by as much as 14, 13, 13, and 11 orders of magnitude for SWNT/VE, DWNT/VE, MWNT/VE, and XD-CNT/VE respectively, compared to the neat resin. The storage modulus was also increased compared to the neat resin by 77%, 82%, 45%, 40% and 85% in SWNT, SAP-f-SWNT, DWNT, MWNT and
XD-CNT/VE composites, respectively. This study provides a detailed understanding of how the properties of nanocomposites are determined by the composite mixing parameters and the distribution, concentration, shape and size of the CNTs. Importantly, it indicates the importance of the need for dispersion metrics to correlate and understand these properties.
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# TABLE OF CONTENTS

## CHAPTER 1. Introduction

## CHAPTER 2. Background

2.1. Carbon Nanotubes

2.1.1. Properties of nanotubes

2.2. Properties of CNT/polymer thermosetting composites

2.3. Methods for dispersing CNTs

2.3.1. Chemical dispersion methods

2.3.1.1. Dispersion in acids

2.3.1.2. Surfactants

2.3.1.3. Solvents

2.3.1.4. Functionalization of CNTs

2.3.2. Mechanical dispersion methods

2.3.2.1. Ball milling

2.3.2.2. Ultrasonication

2.4. Characterization of dispersion

## CHAPTER 3. Dispersion of CNTs by ultrasonication
3.2.2. Effect of bulk liquid temperature .................................................. 26
3.2.3. Effect of viscosity ................................................................. 26

3.3. Effect of equipment properties......................................................... 29
3.3.1. Effect of intensity of irradiation .................................................. 29
3.3.2. Effect of frequency ................................................................. 31
3.3.3. Effect of sonication time ........................................................ 33

3.4. Conclusions .................................................................................. 35

CHAPTER 4. Materials and Composite Processing ..................................... 36
4.1. Materials ....................................................................................... 36
4.1.1. Carbon nanotubes ................................................................. 36
4.1.2. Vinyl Ester .............................................................................. 37

4.2. Material Characterization ............................................................... 39
4.2.1. Scanning Electron Microscopy .................................................. 39
4.2.2. Thermogravimetric Analysis ..................................................... 43
4.2.3. Raman Spectroscopy ............................................................... 47

4.3. Composite Preparation .................................................................. 53

CHAPTER 5. Dispersion Study of Carbon Nanotubes in Vinyl Ester .......... 59
5.1. Electrical resistivity testing .............................................................. 59
5.1.1. Evaluation of electrical properties of nanocomposites ................. 62

5.2. Dynamical Mechanical Analysis .................................................... 69
5.2.1. Results and Discussion ......................................................... 70
5.3. Morphological characterization ................................................................. 77
  5.3.1. Optical Microscopy ............................................................................. 77
  5.3.2. Scanning Electron Microscopy ......................................................... 83
5.4. Raman Spectroscopy of composites ............................................................. 90
  5.4.1. Distribution of CNTs ......................................................................... 91
  5.4.2. Unropeing of nanotubes ................................................................... 101
  5.4.3. Nanotube Damage ............................................................................. 110
5.5. Quantification of dispersion .................................................................... 116

CHAPTER 6. Conclusions .................................................................................. 123

REFERENCES .................................................................................................... 126

APPENDIX A. Study on surface coverage of carbon nanotubes on glass fiber..... 142
  A.1. Materials and experimental methods ..................................................... 143
  A.2. Results .................................................................................................. 145

Appendix B . Electrical properties of CNT polypropylene composites .............. 148
  B.1. Experimental ......................................................................................... 148
     B.1.1. Materials ...................................................................................... 148
     B.1.2. Composite Processing .................................................................... 149
  B.2. Results and discussion .......................................................................... 150
     B.2.1 Electrical Resistivity ....................................................................... 153
     B.2.2 Electromagnetic Shielding Effectiveness ....................................... 156
B.3. Conclusions

159
LIST OF FIGURES

Figure 1.1. Transmission Electron Micrograph of a SWNT rope [7].................................1

Figure 2.1. Shown are different types of CNTs: (a) SWNTs, (b) DWNTs, (c) MWNTs. (d) Shows a bundle of SWNTs [19]...............................5

Figure 2.2. Illustration of (a) poor distribution and poor dispersion, (b) poor distribution but good dispersion, (c) good distribution but poor dispersion and (d) good distribution and good dispersion [30].........................9

Figure 2.3. Schematic representations of the SWNTs dispersion mechanisms by surfactants. (a) SWNT encapsulated in a cylindrical surfactant micelle: right: cross section; left: side view. (b) Hemimicellar adsorption of surfactant molecules on a SWNT. (c) Random adsorption of surfactant molecules on a SWNT [67]..........................11

Figure 2.4. A series of nanotube chemistries depicting functionalization that couples SWNTs into polymeric systems. These various steps should lead toward a fully integrated nanotube composite for enhanced properties [68]...............................15

Figure 2.5. Change of the mean nanotube length as a function of milling time. Ball milling cuts CNTs into shorter segments as shown on the plot [70]...............................................................17

Figure 3.1. Proposed mechanism of nanotube isolation from bundles (i). Ultrasonic processing “frays” the bundle end (ii), which then becomes a site for additional surfactant adsorption. This latter process continues in an “unzippering” fashion (iii) that terminates with the release of an isolated, surfactant-coated nanotube in solution (iv) [61]. ..............................................................22

Figure 3.2. Schematic representation of ultrasonic cavitation and implosion. a) Formation of gaseous cavities in the liquid. b) Bubbles expand to a maximum size. c) The high pressure exerted on the expanded bubble compresses it, increasing the temperature of the gas contained. d) Bubble implodes releasing of impact energy [98]. ..................24
Figure 3.3. Simulation of ultrasonic intensity distribution for a tip sonicator [105]........................................................................................................................................27

Figure 3.4. Dependence of the attenuation coefficient on the viscosity of the liquid. Reduction in viscosity leads to a decrease on the attenuation coefficient [102]........................................................................................................................................28

Figure 3.5. The effect of ultrasonic amplitude on the electrical resistivity of XD-CNT/VE composites, sonicated for 5 min. The scanning electron micrographs can be correlated to the electrical resistivities....................................................................................................................................31

Figure 3.6. Cavitation Strength versus Frequency of Sonication [108].........................................................................................................................32

Figure 3.7. Effect of sonication on the dispersion of single-walled CNTs. Sonication breaks ropes of SWNTs but can also create defects [74]........................................................................................................................................34

Figure 3.8. Mean average MWNT length as a function of time in ultrasonic bath [60]........................................................................................................................................34

Figure 4.1. Side-wall carboxylic functionalization of SWNTs with succinic acid peroxide (SAP-f-SWNT). ........................................................................................................................................37

Figure 4.2. Chemical structures of (a) vinyl ester and (b) styrene. Vinyl esters contain ~40% styrene to reduce the viscosity.................................................................38

Figure 4.3. Raman spectra of Derakane 510A-40 vinyl ester...............................................................................................................................38

Figure 4.4. SEM micrographs of disentangled SWNTs at two different magnifications: (a) 20,000X and (b) 100,000X. SWNTs were disentangled by acid solvation and high shear mixing.........................................................................40

Figure 4.5. SEM micrographs of SAP-f-SWNTs at two different magnifications: (a) 15,000X and (b) 75,000X .................................................................41
Figure 4.6. SEM micrographs of XD-CNTs at two different magnifications: (a) 25,000X and (b) 35,000X. Micrographs show highly agglomerated nanotubes.

Figure 4.7. SEM micrographs of DWNTs at two different magnifications: (a) 30,000X and (b) 80,000X. The different diameters shown are due to the different nanomaterials in the mixture (SWNTs, DWNTs and MWNTs).

Figure 4.8. SEM micrographs of MWNTs at two different magnifications: (a) 30,000X and (b) 80,000X.

Figure 4.9. TGA mass loss of as received disentangled SWNTs under air. The average residue content is around 1.43%.

Figure 4.10. TGA mass loss of as received DWNTs under air. The average residue content is 2.63%.

Figure 4.11. TGA mass loss of as received disentangled MWNTs under air. The average residue content is 0.47%.

Figure 4.12. TGA mass loss of as received XD CNTs under air. The average residue content is 8%.

Figure 4.13. TGA mass loss of functionalized SWNT (SAP-f- SWNT) under argon. The residue content is 72.77%

Figure 4.14. Raman spectra of CNTs [119].

Figure 4.15. Normalized Raman spectra of SWNTs. (a) Radial Breathing Modes, (b) D and G bands range.

Figure 4.16. Normalized Raman spectra of SAP-f-SWNTs. (a) Radial Breathing Modes, (b) D and G bands range.

Figure 4.17. Normalized Raman spectra of XD-CNTs. (a) Radial Breathing Modes, (b) D and G bands range.
Figure 4.18. Normalized Raman spectra of DWNTs. (a) Radial Breathing Modes, (b) D and G bands range. ..........................................................52

Figure 4.19. Normalized Raman spectra of MWNT. (a) Radial Breathing Modes, (b) D and G bands range. ..........................................................53

Figure 4.20. Cole-Parmer 750 Watt Ultrasonic Processor, with a fixed frequency of 20 kHz. ..........................................................54

Figure 4.21. Uncured vinyl ester sonicated at different energies: a) 0 kJ, b) 22 kJ, c) 89 kJ, d) 178 kJ, e) 532 kJ ..........................................................55

Figure 4.22. TGA mass loss of uncured vinyl ester sonicated at 0, 22, 88, 178 and 532 kJ. a) Weight % vs. temperature (°C), b) Derivative weight % vs. temperature (°C) ..........................................................56

Figure 4.23. Nanocomposites created form incorporating CNTs in vinyl ester. ...............58

Figure 5.1. Schematic representation of an insulator polymer matrix with a conductive filler. At low concentrations the particles are surrounded by the polymer so there is little or no change on the conductivity of the composite. At the percolation threshold a network of fillers is formed and conductivity is achieved [131] ...............60

Figure 5.2. Effect of filler aspect ratio on the critical filler concentration needed to induce bulk conductivity in a filled polymer [133] ...............61

Figure 5.3. Bulk resistivity (Ω.cm) vs sonication energy (kJ) of 0.5 wt% SWNT/vinyl ester composites. ..........................................................65

Figure 5.4. Bulk resistivity vs sonication energy of 0.5 wt% XD-CNT/VE composites. ..........................................................65

Figure 5.5. Bulk resistivity vs sonication energy of 0.5 wt% DWNT/VE composites. ..........................................................66

Figure 5.6. Bulk resistivity vs sonication energy of 0.5 wt% MWNT/VE composites. ..........................................................66
Figure 5.7. Representation of nanotubes dispersed in a polymer matrix by sonication energy. Three stages are shown: (I) Poor dispersion, (II) Optimal dispersion, (III) Oversonication.

Figure 5.8. Storage Modulus (Pa) versus temperature (°C) for neat vinyl ester and 0.5 wt% SWNT/vinyl ester composites sonicated at different energies.

Figure 5.9. Storage Modulus (Pa) versus temperature (°C) for neat vinyl ester and 0.5 wt% SAP-f-SWNTs/vinyl ester composites sonicated at different energies.

Figure 5.10. Storage Modulus (Pa) versus temperature (°C) for neat vinyl ester and 0.5 wt% XD-CNT/vinyl ester composites sonicated at different energies.

Figure 5.11. Storage Modulus (Pa) versus temperature (°C) for neat vinyl ester and 0.5 wt% DWNT/vinyl ester composites sonicated at different energies.

Figure 5.12. Storage Modulus (Pa) versus temperature (°C) for neat vinyl ester and 0.5 wt% MWNT/vinyl ester composites sonicated at different energies.

Figure 5.13. Optical micrographs of 0.5 wt% SWNT/vinyl ester with varying sonication energies. (a) 22 kJ, (b) 89 kJ, (c) 178 kJ, (d) 266 kJ.

Figure 5.14. Optical micrographs of 0.5 wt% SAP-f-SWNT/vinyl ester with varying sonication energies. (a) 22 kJ, (b) 89 kJ, (c) 178 kJ, (d) 266 kJ.

Figure 5.15. Optical micrographs of 0.5 wt% XD-CNT/vinyl ester with varying input energies. (a) 4 kJ, (b) 44 kJ, (c) 115 kJ, (d) 266 kJ.

Figure 5.16. Optical micrographs of 0.5 wt% DWNT/vinyl ester with varying sonication energies. (a) 7 kJ, (b) 17 kJ, (c) 68 kJ, (d) 205 kJ.

Figure 5.17. Optical micrographs of 0.5 wt% MWNT/vinyl ester with varying sonication energies. (a) 9 kJ, (b) 89 kJ, (c) 17 kJ, (d) 266 kJ.
Figure 5.18. SEM micrographs of 0.5wt% SWNT/vinyl ester composites with varying sonication times. (a) 4 kJ, (b) 22 kJ, (c) 89 kJ, (d) 266 kJ. The magnification is 50,000x.

Figure 5.19. SEM micrographs of 0.5wt% SAP-f-SWNT/vinyl ester composites with varying sonication times. (a) 22 kJ, (b) 89 kJ, (c) 178 kJ, (d) 266 kJ. The magnification is 50,000x.

Figure 5.20. SEM micrographs of 0.5 wt% XD-CNT/vinyl ester composites with varying sonication times. (a) 4kJ (b) 44kJ, (c) 115kJ, (d) 266kJ. The magnification is 50,000x.

Figure 5.21. SEM micrographs of 0.5wt% DWNT/vinyl ester composites with varying sonication times. (a) 4 kJ (b) 10 kJ, (c) 89 kJ, (d) 230 kJ. The magnification is 50,000x.

Figure 5.22. SEM micrographs of 0.5wt% MWNT/vinyl ester composites with varying sonication times. (a) 7 kJ (b) 17 kJ, (c) 34 kJ, (d) 44 kJ. The magnification is 50,000x.

Figure 5.23. Example of an area selected for Raman mapping. The area measures 40μm x 40μm regions and the step size is 7 μm, giving a total of 49 scans.

Figure 5.24. Raman data accumulation of 5 wt% SWNT/VE composites sonicated at (a) 10 kJ and (b) 180 kJ. The composite sonicated at 180 kJ shows improved nanotube dispersion and more even Raman spectra intensities.

Figure 5.25. Raman mapping of G-peak intensities of SWNTs dispersed in vinyl ester with varying sonication energies: (a) 22 kJ, (b) 88 kJ, (c) 178 kJ, (d) 266 kJ.

Figure 5.26. Raman mapping of G-peak intensities of SAP-f-SWNTs dispersed in vinyl ester with varying sonication energies: (a) 22 kJ, (b) 89 kJ, (c) 178 kJ, (d) 266 kJ.

Figure 5.27. Raman mapping of G-peak intensities of XD-CNTs dispersed in vinyl ester with varying sonication energies: (a) 9 kJ, (b) 44 kJ, (c) 230 kJ, (d) 266 kJ.
Figure 5.28. Raman mapping of G-peak intensities of DWNTs dispersed in vinyl ester with varying sonication energies: (a) 38 kJ, (b) 44 kJ, (c) 115 kJ, (d) 266 kJ. ................................................................. 96

Figure 5.29. Raman mapping of G-peak intensities of MWNTs dispersed in vinyl ester with varying sonication energies: (a) 10 kJ, (b) 44 kJ, (c) 230 kJ, (d) 266 kJ. ................................................................. 97

Figure 5.30. Intensity of G-peak vs. sonication energy for SWNT/vinyl ester materials. The error bars correspond to the standard deviation of fifty different measurements in each sample. ........................................ 98

Figure 5.31. Intensity of G-peak vs. sonication energy for SAP-f-SWNT/vinyl ester composite materials .................................................................................................................................................. 99

Figure 5.32. Intensity of G-peak vs. sonication energy for XD-CNT filled vinyl ester composites .................................................................................................................................................. 99

Figure 5.33. Intensity of G-peak vs. sonication energy for DWNT/vinyl ester composites. .................................................................................................................................................. 100

Figure 5.34. Intensity of G-peak vs. sonication energy for MWNT/vinyl ester composite materials .................................................................................................................................................. 100

Figure 5.35. Radial Breathing Modes (RBM) of SWNTs indicating the roping peak at 266 cm$^{-1}$ .................................................................................................................................................. 102

Figure 5.36. Radial Breathing Modes of HiPco SWNTs. An increase in the roping peak at 266 cm$^{-1}$ from (a) to (d) is shown. Adapted from [160]. .................................................................................................................................................. 103

Figure 5.37. Raman mapping of I$_{235}$/I$_{268}$ ratios of SWNTs dispersed in vinyl ester with varying sonication energies. (a) 3.84 kJ, (b) 44 kJ, (c) 89 kJ, (d) 266 kJ. .................................................................................................................................................. 106

Figure 5.38. Raman mapping of I$_{235}$/I$_{268}$ ratios of SAP-f-SWNTs dispersed in vinyl ester with varying sonication energies: (a) 22 kJ, (b) 89 kJ, (c) 178 kJ, (d) 266 kJ. .................................................................................................................................................. 107
Figure 5.39. Raman mapping of I_{235}/I_{268} ratios of XD-CNTs dispersed in vinyl ester with varying sonication energies. (a) 6.84 kJ, (b) 44.4 kJ, (c) 68.4 kJ, (d) 266 kJ. ...............................108

Figure 5.40. Plot of the intensity ratio (I_{235}/I_{268}) vs. sonication energy of 0.5 wt% SWNT/VE composites. The error bars correspond to the standard deviation of fifty different measurements for each sample. .................................................................109

Figure 5.41. Plot of the intensity ratio (I_{235}/I_{268}) vs. sonication energy of 0.5 wt% SAP-f-SWNT/VE composites. .........................................................109

Figure 5.42. Plot of the intensity ratio (I_{235}/I_{268}) vs. sonication energy of 0.5 wt% XD-CNT/VE composites..............................................................110

Figure 5.43. Raman spectra of 0.5 wt% SWNT/VE composites with increasing sonication energy. Increasing sonication time generated defects as evidenced by the increase in the disordered induced peak (D-peak). .........................................................111

Figure 5.44. D/G ratio vs. sonication energy of 0.5 wt% SWNT/VE composites. .................................................................111

Figure 5.45. Raman spectra of 0.5 wt% SAP-f-SWNT/VE composites with increasing sonication energy.................................112

Figure 5.46. D/G ratio vs. sonication energy of 0.5 wt% SAP-f-SWNT/VE composites. .........................................................112

Figure 5.47. Raman spectra of 0.5 wt% XD-CNT/VE composites with increasing sonication energy.................................113

Figure 5.48. D/G ratio vs. sonication energy of 0.5 wt% XD-CNT/VE composites. .........................................................113

Figure 5.49. Raman spectra of 0.5 wt% DWNT/VE composites with increasing sonication energy.................................114
Figure 5.50. D/G ratio vs. sonication energy of 0.5 wt% DWNT/VE composites. ........................................................................................................114

Figure 5.51. Raman spectra of 0.5 wt% MWNT/VE composites with increasing sonication energy. ........................................................................................................115

Figure 5.52. D/G ratio vs. sonication energy of 0.5 wt% MWNT/VE composites. ........................................................................................................115

Figure 5.53. Plot of the G-peak RSD (%) versus Bulk Resistivity, Storage Modulus, D/G ratio, and I_{234}/I_{268} ratio of 0.5 wt% SWNT/vinyl ester composites. ........................................................................................................118

Figure 5.54. Plot of the G-peak RSD (%) versus Bulk Resistivity, Storage Modulus, D/G ratio, and I_{234}/I_{268} ratio of 0.5 wt% SAP-f-SWNT/vinyl ester composites. ........................................................................................................119

Figure 5.55. Plot of the G-peak RSD (%) versus Bulk Resistivity, Storage Modulus, D/G ratio, and I_{234}/I_{268} ratio of 0.5 wt% XD-CNT/vinyl ester composites. ........................................................................................................120

Figure 5.56. Plot of the G-peak RSD (%) versus Bulk Resistivity, Storage Modulus, D/G ratio, and I_{234}/I_{268} ratio of 0.5 wt% DWNT/vinyl ester composites. ........................................................................................................121

Figure 5.57. Plot of the G-peak RSD (%) versus Bulk Resistivity, Storage Modulus, D/G ratio, and I_{234}/I_{268} ratio of 0.5 wt% MWNT/vinyl ester composites. ........................................................................................................122
TABLE OF CONTENTS

Table 4.1. Typical Properties (1) of Post cured (2) Derakane 510 A-40 Resin
Clear Casting supplied by Derakane [115]...................................................39

Table 4.2. TGA results of SWNTs, DWNTs, MWNTs, XD-CNTs under air.
The iron content corresponds to 70% of the residue weight......................46

Table 4.3. D/G intensity ratios for all CNT materials.....................................53

Table 4.4. Sonication parameters studied for dispersing CNTs in vinyl ester.
Total energies in kJ at given time and amplitude are shown......................57

Table 5.1. Percolation Threshold and Resistivity Range of Nanocomposites..........62

Table 5.2. Surface and bulk resistivity of neat vinyl ester..................................63

Table 5.3. Experimental conditions for the dispersion of nanotubes in vinyl ester
.........................................................................................................................68

Table 5.4. Storage Modulus of different CNT reinforced polymer composites..........69

Table 5.5. Mechanical Properties of 0.5 wt% SWNT/vinyl ester composites...........74

Table 5.6. Mechanical Properties of 0.5 wt% SAP-f-SWNT/vinyl ester composites........74

Table 5.7. Mechanical Properties of 0.5 wt% XD-CNT/vinyl ester composites...........75

Table 5.8. Mechanical Properties of 0.5 wt% DWNT/vinyl ester composites............75

Table 5.9. Mechanical Properties of 0.5 wt% MWNT/vinyl ester composites............76

Table 5.10. Summary of electrical resistivity (Ω.cm) and storage modulus (GPa) of CNT/vinyl ester composites with optimized dispersion..............77
CHAPTER 1. Introduction

Dispersing individual CNTs has proven to be a difficult task [1-4]. For example SWNTs, a type of CNTs, align parallel to each other and pack into crystalline ropes, due to van der Waals attraction forces. Ropes of 10-100 nanotubes pack in a triangular lattice with a lattice constant of \( a = 1.7 \) nm [5], as shown in Figure 1.1. These ropes further aggregate into tangled networks. Aggregation is an obstacle to most applications, diminishing the special mechanical and electrical properties in composites, compared to dispersing individual nanotubes [6]. The reduction in properties combined with the difficulties in manipulating bundled nanotubes have motivated recent attempts to develop methods to enable solubilization, dispersion, and separation of SWNTs [1].

Figure 1.1. Transmission Electron Micrograph of a SWNT rope [7].

Several research groups have studied the effect of dispersion on the physical properties of nanocomposites [8-11]. However, how to effectively characterize nanotube
dispersion in the nanocomposites is still unclear. The objective of this thesis is to provide a dispersion metric that effectively correlates to the properties of nanocomposites through a parametric study of processing conditions.

Different types of CNTs were dispersed in a vinyl ester polymer resin with varying sonication parameters. The CNTs studied were SWNTs, DWNTs, MWNTs, and XD-grade CNTs, which are a mixture of SWNT, DWNT and few-wall nanotubes. The term CNT, as used in this thesis, will be a general term for all types of nanotubes including SWNTs, DWNTs and MWNTs.

Raman spectroscopy, electrical resistivity and dynamical mechanical analysis were used in addition to optical and scanning electron microscopy to quantitatively measure CNT dispersion. By combining all these techniques, a better understanding of the dispersion properties of CNTs was achieved.

The organization of this thesis is as follows: CHAPTER 2 shows a background section on CNTs, followed by a literature review on dispersion techniques, as well as some of the methods used to characterize dispersion. Since the method used in this project to disperse CNTs in polymers was ultrasonication energy, the phenomenon of ultrasonic cavitation is explained in CHAPTER 3. Then, the selection and properties of the materials and composite preparation is shown in CHAPTER 4. CHAPTER 5 shows the study of dispersion and damage of CNT materials done by electrical and mechanical testing, Optical Microscopy, Scanning Electron Microscopy, and Raman spectroscopy, and the correlation of the dispersion parameter to the composite properties. Finally, CHAPTER 6 shows the conclusions from this study and the basis for future work.
2.1. Carbon Nanotubes

Since their discovery in 1991 by Iijima and coworkers [12], CNTs have been studied by many researchers all over the world. A SWNT can be pictured as a sheet of graphite that has been rolled into a tube and capped by a mixture of hexagonal and pentagonal carbon. The end cap structure is derived from a smaller fullerene, such as C_{60}. A graphene sheet may be rolled up in many ways to form a SWNT. The rolling action breaks the symmetry of the planar system and imposes a distinct direction with respect to the hexagonal lattice, the axial direction. The atomic structure of nanotubes is described in terms of the nanotube chirality, or helicity, which is defined by the chiral vector, $C_h$, and the chiral angle $\theta$. The chiral vector, often known as the roll-up vector, can be described by the following equation:

$$C_h = na_1 + ma_2$$  \hspace{1cm} (1)

Where the integers $(n, m)$ are the number of steps along the ziz-zag carbon bonds of the hexagonal lattice and $a_1$ and $a_2$ are unit vectors [13].

SWNTs are classified into three groups according to their chirality: armchair, zigzag, and chiral nanotubes. Nanotubes with different chiral vectors have dissimilar properties such as optical activity, mechanical strength, and electrical conductivity. The chirality of the SWNTs has significant implications on the material properties. In particular, tube chirality is known to have a strong impact in the electronic properties of SWNTs. Graphite is considered to be a semi-metal, but it has been shown that nanotubes can be metallic to semi-conducting depending on tube chirality. Theoretical studies
indicate that all armchair nanotubes are metallic, as well as nanotubes exhibiting values of $m, n$ multiples of three [14].

SWNTs are composed of sp$^2$ carbon, like graphite. The carbon atoms in a graphene sheet are arranged in a planar hexagonal lattice structure, with each carbon covalently bonded to three neighboring atoms. This structure results from the sp$^2$ hybridization during which one s-orbital and two p-orbitals combine to form three hybrid sp$^2$ orbitals at 120 degrees to each other within a plane. Stronger than the sp$^3$ bonds found in diamond, this bonding structure provides them with their unique strength. The resulting covalent bond (σ bond) is a strong chemical bond and plays an important role in the mechanical properties of CNTs. The out of plane bond, also known as the π-bond contributes to the interaction between SWNTs in bundles.

CNTs exist as either SWNTs (Figure 2.1a) or MWNTs (Figure 2.1b). MWNTs (Figure 2.1c) are composed of concentric SWNTs separated by ~0.35 nm [12]. These concentric nanotubes are held together by secondary, van der Waals bonding. DWNTs are a special case of MWNTs consisting of only two, rather than many (~3–50), concentric seamless graphene cylinders [14]. SWNTs are most desired for fundamental investigations of the structure/property relationships, since the interactions between concentric tubes further complicate their properties.

Primary synthesis methods for SWNTs and MWNTs include: arc discharge [15], laser ablation [16], chemical vapor deposition (CVD) [17], and, more recently, gas-phase decomposition of CO (HiPco) [18].
2.1. Properties of nanotubes

The properties of nanotubes depend on atomic arrangement, the diameter and length of the tubes, and the morphology, or nanostructure. Generally, the diameter of a SWNT is about 1-2 nm and its length can be more than 1 μm [20], giving them a high aspect ratio. Rough estimates suggest that SWNT density could be as small as 1 g/cm³ [21]. Theoretical studies have shown that the surface area of SWNTs could be as high as 3000 m²/g [22]. However, the largest value of experimentally determined surface area is only 1587 m²/g, obtained for HiPco SWNTs [22].

The tensile strength of SWNT is 63 GPa [21] (in comparison, high-carbon steel has a tensile strength of approximately 1.2 GPa). The Young’s modulus of SWNT determined by analytical [23] and experimental observations is 1 TPa [20] [24], approximately five times higher than steel.

Nanotubes aggregate to form bundles or ropes held together by weak van der Waals forces (Figure 2.1d). These ropes, consisting of many nanotubes can have diameters of up to 200 nm [20]. Salvetat et al. [24] measured the properties of these
nanotube bundles with AFM. Results showed that as the diameter of the tube bundles increases, the axial and shear moduli decreased significantly, suggesting slipping of the nanotubes within the bundle.

Due to the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given \((n,m)\) nanotube, if \(2n + m=3q\) (where \(q\) is an integer), then the nanotube is metallic, otherwise the nanotube is a semiconductor. All armchair \((n=m)\) nanotubes are metallic, and nanotubes \((5,0)\), \((6,4)\), \((9,1)\), etc. are semi-conducting. An alternative (equivalent) representation of this condition is if \((n-m)/3= integer\), then the SWNT is metallic. In theory, metallic nanotubes can withstand an electrical current density more than 1,000 times higher than metals such as silver and copper. This property, combined with their high surface area and aspect ratio makes SWNTs an excellent candidate as conductive fillers. However, the presence of defects affects the nanotube properties. For electrical properties, a common result is the lowered conductivity through the defected region of the tube.

2.2. Properties of CNT/polymer thermosetting composites

Due to their wide range of industrial uses, thermosetting polymers have been widely studied as a potential matrix for CNT based composites. Generally, these are polymers that cure when mixed with a catalyzing agent or hardener. In most cases, the resin is in liquid form, facilitating CNT dispersion. Curing is then carried out to convert the liquid composite to the final solid state. However, studies have shown that the major factors affecting the reinforcing efficiency of CNTs are: a) strong interfacial bonding
between the CNTs and polymer, and b) good dispersion and distribution of CNTs in polymer matrices.

Bundling, aggregation and agglomeration are the major obstacles for realization of the technological potential of CNTs. Nanotubes must be uniformly dispersed to the level of isolated nanotubes individually coated with polymer in order to achieve efficient load transfer to the nanotubes network. This also results in a more uniform stress distribution and minimizes the presence of stress concentration centers. The effects of poor dispersion can be seen in a number of systems when the nanotube loading level is increased beyond the point where aggregation begins. This is generally accompanied by a decrease in strength and modulus.

Gryshchuk et al. [25] incorporated up to 2 wt% MWNT in vinyl ester. While fracture toughness showed an increase of 26% compared to the neat resin at 1 wt% reinforcement, the same property decreased by 7% at 2 wt%. Furthermore, Lau et al. [26] studied CNT/epoxy composites with a 2 wt% nanotube concentration. Poor interfacial strength as evidenced by nanotube pull-out resulted in a lower flexural strength compared to the neat resin.

Conductive filler particles in an insulating matrix lower the overall resistivity by several orders of magnitude when a network develops throughout the matrix. The transition from an insulating to a conducting composite as a function of filler concentration is known as percolation, and the critical concentration at which this drop occurs is called the percolation threshold. The electrical properties of nanocomposites are highly affected by the degree of dispersion. To obtain low electrical percolation thresholds the nanotubes have to be efficiently arranged in an electrically conductive
network within the matrix [27]. Moisala et al. [28] studied the electrical conductivities of epoxy composites containing 0.005–0.5 wt% of SWNTs or MWNTs. MWNTs were found to be dispersible in the resin via mechanical mixing since they were synthesized as aligned, non-entangled arrays. Chemically treated SWNTs were dispersed in ethanol by ultrasonication prior to mixing with the polymer resin. The chemical treatment debundled the tubes, while not apparently damaging their walls or shortening them. The ball-milling did break apart the SWNT aggregates, but also tended to shorten the tubes as indicated by electron microscopy. The MWNT composites had an electrical percolation threshold of <0.005 wt%, whereas in the case of the SWNT composites, the electrical percolation thresholds were higher (0.05–0.23 wt%). The higher percolation threshold for SWNT/epoxy was due to the shortening of the nanotubes that resulted in a much lower aspect ratio, compared to MWNTs.

A review article on the electrical properties of several carbon nanotube polymer composites by Bauhofer et al. [29] showed percolation thresholds ranging from .005 to 1 wt% for SWNTs/epoxy, and 0.002 to 5 wt% for MWNT/epoxy composites. It was concluded that the type of polymer and dispersion method, rather than the nanotube synthesis method and treatment, were the parameters that had the most influence in the maximum conductivities and percolation threshold.

2.3. Methods for dispersing CNTs

Optimal nanotube distribution and dispersion is critical to efficient reinforcement. Distribution describes the allocation of the reinforcement within the matrix, while dispersion refers to the breaking of the aggregates into small sizes. A good distribution
does not necessarily mean a good dispersion, as is illustrated in Figure 2.2. Figure 2.2a shows poor distribution and poor dispersion, in Figure 2.2b the particles are well dispersed but poorly distributed. Figure 2.2c shows good distribution but poor dispersion. Figure 2.2d shows a system where particles are well dispersed and distributed.

**Figure 2.2.** Illustration of (a) poor distribution and poor dispersion, (b) poor distribution but good dispersion, (c) good distribution but poor dispersion and (d) good distribution and good dispersion [30].

The dispersion of CNTs is affected by at least two competitive interactions: (1) van der Waals forces among CNTs, and (2) the interactions between CNT and dispersion medium. There are two different approaches to nanotube dispersion: mechanical and chemical methods. Commonly used mechanical methods are ball milling [31,32], high shear mixing [3,31,33,34], and ultrasonication [35-38]. These are convenient methods to achieve CNT dispersion; however, the dispersion quality is often unsatisfactory. Physical or mechanical methods can only break up agglomerates into
smaller parts or single-agglomerates. A stable suspension containing separated individual tubes is obtained only by chemical methods [3]. Chemical methods include acid treatments [39-44], functionalization [45-50, 39, 51-57], the use of surfactants [58-61], and dispersant systems [62, 63]. The covalent functionalization allows purification and solubilization of CNTs as well as enhancing the compatibility between filler and polymer matrices. However, some chemical treatments tend to disrupt the conjugated electronic structure, shorten the CNTs, and deteriorate the electrical and mechanical properties of CNTs.

2.3.1. Chemical dispersion methods

2.3.1.1. Dispersion in acids

When SWNTs are dispersed in superacids the protonation of the sidewalls eliminates wall–wall van der Waals interactions and promotes the dispersion process, as shown by Davis et al. [64] Pan et al. [65] prepared MWNT/PP composites by pre-dispersing the nanotubes in nitric acid. Acid treated MWNT/PP composites exhibited significantly lower electrical conductivity than the pristine MWNT/PP composites at the same loadings. While SEM micrographs showed an improved dispersion, the acid treatment created more defects, reducing the electrical conductivity of carbon nanotubes. This was verified by Raman spectroscopy observation in which the acid treated MWNTs showed a relatively higher D/G ratio. Also, the length of acid treated MWNTs might be reduced during chemical oxidation. With shorter lengths, it becomes more difficult for the nanotubes to form conductive networks.
2.3.1.2. Surfactants

The role of surfactants is to produce an efficient coating and induce electrostatic repulsions to counterbalance van der Waals attractions. The electrostatic repulsion provided by adsorbed surfactants stabilizes the nanotubes against the strong van der Waals interaction between the tubes preventing agglomeration. In covalently bonded nanotube-polymers, the polymer adsorbs onto the nanotube, and repulsive forces dominate over attractive van der Waals forces between the SWNTs. The balance of repulsive and attractive forces creates a stable dispersion, which may result in separation of SWNTs from the bundles into individual nanotubes [66].

![Figure 2.3](image)

**Figure 2.3.** Schematic representations of the SWNTs dispersion mechanisms by surfactants. (a) SWNT encapsulated in a cylindrical surfactant micelle: right: cross section; left: side view. (b) Hemimicellar adsorption of surfactant molecules on a SWNT. (c) Random adsorption of surfactant molecules on a SWNT [67].

Strano et al. studied [61] the ionic surfactant-assisted dispersion of SWNTs in aqueous solution during ultrasonic processing. The mechanism of dispersion consisted of
the formation of gaps or spaces at the bundle ends in the high-shear environment of the ultrasonicated solution. Surfactant adsorption and diffusion then propagated these spaces along the bundle length, separating the individual nanotubes. Yu et al. [58] dispersed MWNTs in aqueous SDS solutions aided by sonication. The dispersion was monitored by UV–vis spectroscopy and TEM. Time dependent sonication experiments revealed that the maximum achievable dispersion of MWNTs corresponds to the maximum UV–vis absorbance of the solution. With higher surfactant concentration the dispersion rate of MWNTs increased and less total sonication energy was required to achieve maximum dispersion.

2.3.1.3. Solvents

A common method for preparing polymer nanotube composites has been to disperse the nanotubes and polymer in a suitable solvent before evaporating the solvent to form a composite film. It should be pointed out that this method relies on the efficient dispersion of nanotubes in the solvent, and the feasibility to completely evaporate the solvent. Lau et al. [63] evaluated the role of solvent for nanotube dispersion on the mechanical and thermal properties of SWNT bundle reinforced epoxy composites. SWNTs dispersed with various solvents were incorporated into an epoxy matrix via sonication. Differential Scanning Calorimetry (DSC) results indicated that even small traces of residual solvent in the composite processing had a great impact on the cure reaction. The thermal and mechanical properties were also found to be related to the boiling point of the solvent used.
Vinyl ester and polyester resins contain 30-40 wt% of styrene. The major concern when processing these resins is styrene evaporation, which results in a dramatic increase in resin viscosity. This characteristic also restricts the use of solvents in combination with the CNT/vinyl ester system, as the subsequent solvent evaporation step would result in styrene loss. Seyhal et al. [36] found that styrene evaporation from the polyester resin system was a critical issue for nanocomposite processing. During toll-milling, styrene evaporation was accelerated due to the high temperature caused by the shear effect. This was evidenced by the increase in viscosity of the polyester resin. In the same study, a sonication method was employed with the same CNT/resin systems. Some problems with the sonication method similar to 3-roll-milling process were observed. Even though the sonication bath was cooled by water, the local heating due to energy created within the resin system, caused styrene evaporation from the polymer suspension, leading to a more viscous resin. In addition, it was observed that nanotubes were agglomerated in the volumes closer to the tip of the sonicator as van der Waals attractive forces between the CNT-surfaces are known to be sensitive to heat.

2.3.1.4. Functionalization of CNTs

As previously stated, the performance of a CNT reinforced composite depends on the interfacial properties. CNTs interact with the surrounding matrix mainly through van der Waals forces, which may not provide efficient load transfer across the CNT/matrix interface. Some researchers have chemically modified the nanotube surface to obtain better nanotubes dispersion and integration in polymer matrices. In addition the functional groups act to make the nanotubes more compatible both with polymer hosts
and solvents. This tends to dramatically improve the nanotube dispersion and hence further improve composite properties [52,53,55,56].

Composites based on functionalized nanotubes are expected to have better interfacial shear strengths. Figure 2.4 depicts a range of methods proposed for producing nanotube composites using functionalization of CNTs. Figure 2.4e shows how side-wall functionalization can be used to achieve cross-linking within a polymer. Figure 2.4f shows a fully integrated nanotube composite (FINC) obtained by end and side-wall functionalization, providing more sites for bonding with the polymer.
Figure 2.4. A series of nanotube chemistries depicting functionalization that couples SWNTs into polymeric systems. These various steps should lead toward a fully integrated nanotube composite for enhanced properties [68].

Functionalization of SWNTs is advantageous because functional groups can prevent the aggregation of nanotubes and in addition favor their solubilization in organic
solvents. The attached functional groups can be used as precursors for the subsequent attachment of a wide variety of other functional groups.

Zhu et al. [55] developed a FINC material through the use of functionalized SWNTs. The terminal amino groups covalently attached to the nanotubes acted as curing agents, resulting in heavily cross-linked composites with CNTs covalently bonded to the matrix. This resulted in an increase in the ultimate strength, modulus, and strain to failure of 30-70% by adding 1-4 wt% of functionalized tubes, compared to the neat epoxy. In another study by Zhu et al. [56] an improvement in the dispersion of purified SWNTs in an epoxy composite was obtained through an acid treatment prior to fluorination. The 30% increase in modulus, and 18% increase in tensile strength were attributed to the end-tip and sidewall functionalization, and the use of ultrasonication and high-shear mixing.

2.3.2. Mechanical dispersion methods

2.3.2.1. Ball milling

Ball milling can be used to break up nanotube agglomerates, or cut nanotubes at production scale quantities [69-71]. Figure 2.5 presents the mean nanotube length as a function of milling time obtained by Kukovecz et al. [70]. The length decreased from over 2 \( \mu \text{m} \) to approximately 950 nm in the first 2 h of the milling, then the rate of change became lower and quasi linear.

Kim et al. [72] investigated the effect of ball milling on the morphology of CNTs by means of high-resolution transmission electron microscopy (HRTEM). It was found that the application of a bending force on the sidewall of CNTs that is higher than the van der Waals forces results in the shortening of CNTs. To avoid nanotube damage Esawi et
al. [73] developed a technique to disperse the nanotubes within a soft Aluminum matrix which simultaneously protects the nanotubes from damage under the impact of the milling balls.

![Graph](image)

**Figure 2.5.** Change of the mean nanotube length as a function of milling time. Ball milling cuts CNTs into shorter segments as shown on the plot [70].

### 2.3.2.2. Ultrasonication

Ultrasonication is a common tool used to break up SWNTs aggregates during purification, mixing, and other type of solution processing techniques. Sonication of nanotubes in liquid resins involves the use of ultrasonic excitation of the mixtures to break up the nanotube bundles through acoustic cavitation. This action forms microscopic bubbles that expand during the negative pressure and causes a considerable amount of energy to be released at the point of implosion, generating a powerful shearing action. Although this phenomenon lasts microseconds, and the amount of energy released by
each individual bubble is minimal, the cumulative amount of energy generated can be extremely high.

The effects of nanotube sonication parameters including bath and tip sonication, sonication energy, frequency, time, and the effect of liquid properties have also been the subject of several investigations [37,61,74,60,39]. Ultrasonication was the chosen mixing and dispersion method for composite materials in this study. This method is further explained in CHAPTER 3.

2.4. Characterization of dispersion

There are two common methods for characterizing dispersion: direct microscopic observation and indirect estimative methods. Direct methods such as Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) are widely used to determine nanotube dispersion in the polymer matrix. SEM was used to assess the wetting and surface coverage on initial studies where functionalized and as-received XD-CNTs were sprayed on glass-fiber, as shown in APPENDIX A.

Direct methods should also be combined with image analysis techniques in order to obtain a dispersion parameter. TEM images of MWNT polymer composites were analyzed by Luo et al. [75] and the dispersion quantity, D, defined as the probability of inclusion particle free-path spacing falling into a certain range of the mean spacing, was calculated. A drawback of this method is that since the dispersion parameter is only related to filler free-path spacing distribution, it is independent of the filler shape, size, or content.
Indirect estimative methods consist in correlating the properties of the composite material to the state of nanotube dispersion. Examples of indirect methods include Raman spectroscopy, dynamic rheological measurements, and mechanical and electrical testing. According to the dispersion state of CNTs, different behaviors of storage modulus and complex viscosity are expected [76]. Higher electrical conductivity is obtained in the case of better CNT dispersion, based on the percolation theory [77] (explained in detail in CHAPTER 5).

Raman spectroscopy is a non-destructive method commonly used to investigate dispersion [61,79-89] and damage [74,90-93] of CNTs. By means of Raman spectroscopy Strano et al. [61] evaluated the dispersion by sonication of SWNTs in surfactants. Peaks at 233, and 266 cm$^{-1}$ (RBMs) underwent enhancement and diminishment, respectively, with increasing sonication time and as surfactant was added. It is explained that the dispersion of individual nanotubes from the bundles results in a significant increase in the 233 cm$^{-1}$ mode and a moderate decrease in this 266 cm$^{-1}$ mode for Raman scattering at 785 nm excitation. Du et al. [94] characterized nanotube dispersion in nanocomposites by Raman imaging. The G bands (1450-1650 cm$^{-1}$) were used to create the Raman maps. When the nanotube bundles are uniformly distributed and the surface is smooth, the Raman map is featureless.

Indirect methods can be combined with dispersion metrics and correlated quantitatively with the variation of basic nanocomposite properties. Kashiwagi et al. [78] determined the dispersion index for SWNT in PMMA through image analysis. For the nanocomposites containing the same amount of SWNTs, the relationships between the quantified dispersion levels and physical properties showed about 4 orders of magnitude
variation in storage modulus, almost 8 orders of magnitude variation in electric conductivity, and 70% reduction in peak mass loss rate at the highest dispersion level used in this study. These results indicate a great variation in the properties of the nanocomposites depending on nanotube dispersion, as well as the need for dispersion metrics.
Due to van der Waals attraction among nanotubes, and their large surface areas, CNTs tend to form agglomerates during processing, preventing efficient transfer of their superior properties to the nanocomposite [5,95]. Although ultrasonication of CNTs in organic solvents, aqueous surfactant solutions, or resin-like systems is widely used, the mechanism of this dispersion and the factors that optimize its efficiency are poorly understood.

As explained in Section 2.3.2.2., ultrasonication is a common tool for dispersing CNTs. Strano et al. [61] proposed a mechanism of ionic surfactant-assisted dispersion of single-walled CNTs in aqueous solution during ultrasonic processing, as illustrated in Figure 3.1. Ultrasonic processing provides high local shear, particularly to the nanotube bundle end (ii). Once “frayed” in this way, spaces between the bundle and individual nanotubes dangling in solution become sites for surfactant adsorption. In the absence of surfactant or an adsorbing polymer, the individual is unstable to complete reattachment through van der Waals attraction. The surfactant adsorbs and acts to keep the two connected entities partially separated. As the individuals moves relative to the bundle through Brownian motion, surfactant continues to progress along the nanotube length (iii) until separation (iv). Evidence for this “unzippering” type of mechanism has been captured by cryo-TEM by Bandyopadhyaya et al.[1].
Figure 3.1. Proposed mechanism of nanotube isolation from bundles (i). Ultrasonic processing “frays” the bundle end (ii), which then becomes a site for additional surfactant adsorption. This latter process continues in an “unzippering” fashion (iii) that terminates with the release of an isolated, surfactant-coated nanotube in solution (iv) [61].

There are two major methods to introduce ultrasonic energy into liquids, the ultrasonic bath, and the ultrasonic horn or wand. The ultrasonic wand oscillates at fixed frequency and creates a conical field of high energy. As only the fluid within the field is affected, repeated circulation through the conical zone is needed to treat all the particles. In bath sonicators, the water transfers the sonic energy from the transducer to the sample. Bath sonication is limited in the amount of energy transferred to the sample, since they dissipate a high fraction of the sonic energy. The ultrasonication bath does not produce a defined cavitation zone as does a horn, and the energy seems to be more uniformly dispersed through the liquid phase. Ultrasonicators with low frequencies (20–100 kHz) and high power (100–5000 W) are commonly used for nanotube dispersion [96].
3.1. Ultrasonic cavitation

Cavitation can be defined as the phenomena of the formation, growth and subsequent collapse of micro bubbles or cavities occurring in extremely small interval of time (milliseconds) releasing large magnitudes of energy. The local effects of the cavitation phenomena can be given as generation of very high temperatures, and pressures [97]. When water at room temperature is subjected to an intense ultrasonic field during the vacuum phase of cavitation (Figure 3.2a) numerous bubbles of gas are formed in the liquid that enlarge for the duration of this phase (negative pressure). The formation of microscopic bubbles of gas is the start of cavitation (i.e., the formation of gaseous cavities in the liquid). During the second phase of ultrasonic compression (Figure 3.2b), the high pressure exerted on the newly expanded bubble compresses the same, increasing the temperature of the gas contained in it (Figure 3.2c) until the bubble collapses on itself, imploding with a consequent release of impact energy (Figure 3.2d).
Figure 3.2. Schematic representation of ultrasonic cavitation and implosion. a) Formation of gaseous cavities in the liquid. b) Bubbles expand to a maximum size. c) The high pressure exerted on the expanded bubble compresses it, increasing the temperature of the gas contained. d) Bubble implodes releasing of impact energy [98].

As the bubble’s radius expands and contracts on the timescale of microseconds, convective flow patterns develop near the surface of an oscillating bubble. The collection of convective flow patterns produced by the oscillating bubble is termed “acoustic micro streaming” [99]. Such micro streaming exposes the attracted particles to extremely high shear rates near the bubble surface. Wu et al. [100] showed that these shear forces are strong enough to perforate cell membranes in the absence of any collapse cavitation.

When dispersing nanotubes in liquids, not all the bubbles may collapse immediately, particularly if the solvent does not wet the nanotubes well, or if a polymer
solution continuous phase of high viscosity reduces the rate of bubble coalescence. As Hilding et al. [60] explained, since suspensions of nanotubes are shear thinning, the flow field near the wand tip may be only a small volume and may have low recirculating velocities through the sonication zone, leading to low dispersion efficiencies. CNTs suspensions with polymer solutions as the continuous phase may also reduce fluid circulations near the wand tip. At high solids loadings, the nanotubes can trap gas bubbles and create a rigid network that prevents fluid flow.

3.2. Effect of liquid properties

Typically, the maximum viscosity at which a material can be processed effectively is 5,000 cps. With standard systems, the practical upper limit on temperature is approximately 100 °C [101]. The intensity of ultrasound is attenuated due to various properties of the liquid, such as viscosity, density, etc. [102]. The effect of liquid properties such as temperature, surface tension and viscosity are reviewed in Sections 3.2.1, 3.2.2, and 3.2.3.

3.2.1. Effect of surface tension

The collapse pressure has been found to increase with an increase in the surface tension of the liquid. Threshold pressure for cavitation is also a strong function of surface tension. Liquids with the highest values of surface tension, such as water, experience the maximum cavitation intensity.
3.2.2. Effect of bulk liquid temperature

The rate of the sonochemical reactions gets drastically reduced with the rise in the liquid temperature beyond a certain value. For water, the collapse pressure decreases linearly with an increase in the temperature [103]. The decrease in the collapse intensity in terms of temperature and pressure is mainly on account of increase in the vapor pressure. For reactants that are volatile in nature, the vapor content inside the cavity increases with the rise in the temperature. The temperature also affects the viscosity of liquids, which in turn determines how the energy is attenuated, as explained in Section 3.2.3.

3.2.3. Effect of viscosity

For cavitation to occur in a liquid, it has to overcome the natural cohesive forces present in the medium. Any increase in these forces will tend to increase the threshold pressure, and hence the energy required to generate cavitation. In highly viscous liquids, severe attenuation of the sound intensity occurs, and the active cavitating zone gets reduced substantially. As the viscosity of material increases, its ability to transmit vibrations decreases. Therefore, only a small fraction of the total volume of the liquid in the immediate vicinity of the ultrasound source experiences the effects of cavitation.

The intensity $I$ of the ultrasound at any distance $d$ from the source is given by:

$$I = I_o \exp(-\alpha d),$$  \hspace{1cm} (2)

Where $\alpha$ is the absorption or attenuation coefficient and $I_o$ is the ultrasound intensity at the tip of the ultrasound source. The relation between intensity $I$ and sonication power is as follows:
\[ I = \frac{E}{A_h}, \] (3)

Where \( E \) = the sonication power in Watts and \( A_h \) = the area of the sonicator probe in cm\(^2\).

The intensity of ultrasound reaching the interface through a given liquid drops exponentially with the distance it travels from the source \([104]\) as shown in Figure 3.3. The attenuation coefficient \( \alpha \) for a given liquid is dependent on the liquid-phase physicochemical properties, and on the characteristics of the ultrasound itself \([102]\).

\[ \alpha = \frac{8\mu \pi^2 f^2}{3\rho C^3}, \] (4)

Where \( \rho \) and \( \mu \) are the density and viscosity of the liquid, respectively, and \( C \) and \( f \) represent the speed of sound in the liquid and the ultrasound frequency, respectively. Knowledge of the attenuation coefficient can be used to determine the active volume in an ultrasonicator for a given ultrasound characteristic, and the properties of the liquid used in the system.

Figure 3.3. Simulation of ultrasonic intensity distribution for a tip sonicator \([105]\).
A study by Majumdar et al. [102] developed an experimental method for the quantification of the attenuation of ultrasound intensity, and the resulting cavitation activity due to sound propagation through various organic liquids. The experimental values of attenuation coefficient versus viscosity are plotted in Figure 3.4. These results showed that an increase in liquid viscosity results in a greater attenuation of sound intensity. The experimental value of the exponent (0.724), based on the study, was less than that predicted. Sonochemical degradation of higher viscous oils resulted in a drop in viscosity, which explains the lower dependence of the attenuation coefficient on viscosity.

When incorporating CNTs into polymer matrices a common problem is an increase in viscosity [10,94]. This effect should be taken into account when selecting the sonication parameters.

Figure 3.4. Dependence of the attenuation coefficient on the viscosity of the liquid. Reduction in viscosity leads to a decrease on the attenuation coefficient [102].
3.3. Effect of equipment properties

3.3.1. Effect of intensity of irradiation

The intensity of irradiation is defined as the power dissipation into the system per unit area of irradiation, and hence can be changed either by changing the power dissipation, or the area of irradiation. If the power dissipated into the system is increased, although the collapse pressure decreases with an increase in the intensity, the number of cavitation events also increases, thereby increasing the overall pressure pulse generated. The overall pressure pulse is defined as the product of the number of cavities in the system and the collapse pressure due to the single cavity. The cavitation yield increases initially, but usually the increase in number of cavities generated seizes after a particular limit of power dissipation beyond which the yield decreases [106].

The fraction of the total energy supplied to the system utilized for cavitation process can be determined from the concept of cavitation efficiency when considering the acoustic horn system the intensity is given by:

\[ I_0 = \frac{a^2 \rho C}{8\pi^2 f^2}, \]

(5)

Where \( \rho \) and \( C \) are the density and speed of sound in the liquid, respectively; and \( f \) and \( a \) are the ultrasound frequency and amplitude, respectively. The velocity of the horn is taken as the product of frequency and amplitude of the horn. The power dissipated into the liquid can be calculated from Eq. (2, 3, 4).

The cavitational efficiency \( \eta(\%) \) can be determined as follows:

\[ \eta(\%) = \frac{E}{E_0} NV_L, \]

(6)
Where $E$ is the energy dissipation rate at the end of bubble collapse in Watts and $E_0$ is the power input to the acoustic system. The number of cavities generated per unit volume of liquid ($N$) was determined experimentally by Naidu et al. [107] as $2.6445 \times 10^{13} \text{m}^{-3}$. The volume of liquid displaced by the cavities, $V_L$, can be determined as follows:

$$V_L = A_h \cdot \nu_h t_c,$$

(7)

where $\nu_h t_c$ = distance traveled by the cavity during its lifetime.

The ratio $(R_{\text{max}}/R_0)$, which indicates the maximum size, attained by the cavity during its growth phase increases with an increase in intensity. Simulations in the range of 1-300 W/cm$^2$ showed that the increase in the maximum size is large (about 30%) for an initial increase in the intensity, and after certain intensity the increase is not substantial (<10%). The bubble wall pressure at the collapse point of the cavity has been observed to decrease with an increase in the intensity of the ultrasound, keeping the initial size of the cavity ($R_0$) and frequency ($f$) constant (Gogate et al. [103]). This is due to the fact that even though there is an increase in the size of the bubble, the lifetime of the cavity was also observed to increase, while the energy associated with the bubble may be taken up by the compressible liquid medium.

Initial experiments done to determine the influence of ultrasonication parameters on the properties of nanocomposites show the influence of the amplitude (which is proportional to the intensity) on the electrical resistivity of XD-CNT/VE composites (Figure 3.5).
Figure 3.5. The effect of ultrasonic amplitude on the electrical resistivity of XD-CNT/VE composites, sonicated for 5 min. The scanning electron micrographs can be correlated to the electrical resistivities.

3.3.2. Effect of frequency

The frequency of the ultrasound determines the maximum bubble size in the fluid. Low frequencies (about 20 kHz) produce large bubbles and high energy forces occur as
they collapse. Increasing the frequency reduces bubble size and nucleation, so that cavitation is reduced, as seen in Figure 3.6.

![Cavitation Strength versus Frequency of Sonication](image)

**Figure 3.6.** Cavitation Strength versus Frequency of Sonication [108].

The frequency of the ultrasonic equipment is usually fixed and cannot be varied over a wide range, as the maximum transfer efficiency is obtained only when the transducer is driven at its resonating frequency. At constant intensity of irradiation and initial cavity size, maximum size attained by a cavity decreases with an increase in the frequency. At the same time the collapse of the cavity is very rapid, thereby leading to an increase in the magnitude of the collapse pressure generated. In addition, smaller bubbles produced at higher frequencies require fewer acoustic cycles before they reach the requisite resonant size [109]. Therefore, greater number of gas nuclei can reach the resonance size more quickly than at lower frequencies. At higher frequencies the threshold intensity required for the onset of cavitation also increases; then at the same operating intensity of irradiation, the number of cavitation events will be lower thereby lowering the cumulative effect of cavitation.
A study by Kojima et al. [110] showed the effect of ultrasonic frequency on polymerization of styrene under sonication at 50° at the frequencies of 23.4, 45.7, 92, 518 kHz and 1 MHz. The magnitude of the polymerization rate increased by the order of 92, 45.7 and 23.4 kHz. At the high frequencies of 518 kHz and 1 MHz, no polymerization was observed. These findings mean that there is an optimum frequency in the range from 92 to 518 kHz for effective polymerization. The optimal frequency depends on the type of reactants and the system geometry and hence this should be established using preliminary studies for the specific application.

3.3.3. Effect of sonication time

Yun et al. [11] investigated the sonication time effect in the preparation of MWNT/polyaniline composite. Results indicated an enhanced composite stiffness with increasing sonication times. However, long nanotubes can also be broken up into shorter segments or otherwise damaged by sonication [74, 111,112], and the amount of damage depends on the sonication power and time. Figure 3.7 shows how nanotubes can be dispersed and damaged by sonication. Mukhopadhyay et al. [112] reported the effect of sonication time on the structural features of CNTs. The graphene layers in the nanotubes are destroyed after prolonged sonication and the nanotubes are converted into amorphous carbon nanofibers. In MWNTs, excessive ultrasonication has also been found to “peel” graphene layers [111].
**Figure 3.7.** Effect of sonication on the dispersion of single-walled CNTs. Sonication breaks ropes of SWNTs but can also create defects [74].

Hilding et al. [60] showed the effect of ultrasonication time on the mean average length of MWNTs as shown in Figure 3.8. Most of the length reduction occurred during the first few minutes, then the rate of length reduction leveled out.

**Figure 3.8.** Mean average MWNT length as a function of time in ultrasonic bath [60].
Ultrasonication generates nanotube ends and cuts nanoropes facilitating nanorope assembly into “super-ropes”. SWNTs rearrange into super-ropes after the bundles are broken up and nanotubes are shortened [113,114]. These super-ropes have diameters of more than twenty times the initial bundle diameter. Ausman et al. [114] showed that shortened SWNTs, individually dispersed into a solvent, quickly self-assemble upon filtration into a spaghetti-like arrangement of long ropes of uniform diameter. It is explained that the smooth interaction surface along SWNTs allows a van der Waals binding energy that provides a significant thermodynamic driving force for such roping.

3.4. Conclusions

Ultrasonication is a commonly used method for breaking nanotube agglomerates and dispersing them in liquids through acoustic cavitation. Cavitation intensity and the efficacy of sonication processes depend strongly on the equipment as well as the liquid physical properties. Liquid viscosity, usually increased by the addition of CNTs, has a major impact on the cavitation intensity. The effect is mainly through the size of nuclei, cavity lifetime, threshold conditions and the extent of nucleation. Vapor pressure and operating temperature are important tools for the control and optimization of the sonication processes. As most of the liquid properties affect cavitation in more than one way, it is possible to evaluate the optimum conditions of power, frequency, amplitude, time and total energy at which the ultrasonication effect is maximum.
CHAPTER 4. Materials and Composite Processing

4.1. Materials

4.1.1. Carbon nanotubes

Different types CNTs were used in this study (SWNTs, DWNTs, MWNTs, and XD-CNTs) in order to understand the effect of the type of nanotube in the dispersion process. HiPco SWNTs from CNI (Carbon Nanotechnologies, Inc.) were disentangled through acid solvation and high shear mixing. DWNTs with a diameter and length of 2.33 nm and 3 μm, respectively, were provided by Litmus Nanotechnology. This material consisted of 50% DWNTs, 30% SWNTs and 20% MWNTs. MWNTs with diameters of 10-30 nm were provided by NTP (Shenzhen Nano-Technologies Port Co., Ltd). XD CNTs lot 3365A were provided by CNI. XD-CNTs consist of a mixture of few-wall, double-wall, and single-wall nanotubes, and are specifically made for electrical conductivity purposes. These nanotubes will be called XD-CNTs throughout this work.

The development of CNTs reinforced composites has been hindered by the difficulty of dispersing nanotubes into the polymer and the weak interfacial interaction between the components. Nanotube functionalization is an effective way to overcome these problems. SWNTs were functionalized following the procedure described by Peng et al. [54], as shown in Figure 4.1. These nanotubes will be referred to as SAP-f-SWNT. The level of functionalization achieved was 1 functional group per 20 Carbon atoms.
Figure 4.1. Side-wall carboxylic functionalization of SWNTs with succinic acid peroxide (SAP-f-SWNT).

4.1.2. Vinyl Ester

Vinyl ester is a common resin in the marine industry due to its increased corrosion resistance, and ability to withstand water absorption. This thermoset is a resin produced by the etherification of an epoxy resin with an unsaturated carboxylic acid, such as methacrylic or acrylic acid. The C=C double bonds occur only at the ends of a vinyl ester molecule, and therefore, cross-linking can only take place at the ends. Vinyl ester is dissolved in a reactive solvent, such as styrene, which reduces its viscosity (Figure 4.2). During polymerization, styrene also co-reacts with the vinyl ester resin to form cross-links between the un-saturation points in adjacent vinyl ester molecules. Vinyl ester resins can be used as an alternative to polyester and epoxy materials in matrices or composite material, where its characteristics and strengths are superior to that of polyester, however inferior to epoxy.
Figure 4.2. Chemical structures of (a) vinyl ester and (b) styrene. Vinyl esters contain ~40% styrene to reduce the viscosity.

Figure 4.3. Raman spectra of Derakane 510A-40 vinyl ester.

The matrix used for this study was a Derakane 510A-40 vinyl ester from Ashland. The resin is a brominated bisphenol-A based vinyl ester with a density of 1.23 g/ml, viscosity of 350 cps, and 38% styrene content. The bromination provides a fire resistant property to the resin. The typical properties of Derakane 510A-40 are shown in Table 4.1.
Table 4.1. Typical Properties (1) of Post cured (2) Derakane 510 A-40 Resin Clear Casting supplied by Derakane [115].

<table>
<thead>
<tr>
<th>Property</th>
<th>SI</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
<td>86 MPa</td>
<td>ASTM D-638/ISO 527</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>3.40 GPa</td>
<td>ASTM D-638/ISO 527</td>
</tr>
<tr>
<td>Tensile Elongation, Yield</td>
<td>4 – 5%</td>
<td>ASTM D-638/ISO 527</td>
</tr>
<tr>
<td>Flexural Strength</td>
<td>150 MPa</td>
<td>ASTM D-790/ISO 178</td>
</tr>
<tr>
<td>Flexural Modulus</td>
<td>3.6 GPa</td>
<td>ASTM D-790/ISO 178</td>
</tr>
<tr>
<td>Heat Distortion Temperature (3)</td>
<td>113°C</td>
<td>ASTM D-648 Method A/ISO 75</td>
</tr>
<tr>
<td>Barcol Hardness</td>
<td>40</td>
<td>ASTM D-2583/EN59</td>
</tr>
</tbody>
</table>

(1) Typical property values only, not to be construed as specifications. SI values reported to two significant figures; US standard values based on conversion.

(2) Cure schedule: 24 hours at room temperature; 2 hours at 120°C (250°F)

(3) Maximum stress: 1.8 MPa (264 psi)

4.2. Material Characterization

4.2.1. Scanning Electron Microscopy

Nanotube microstructures were observed using an Environmental SEM (FEI Quanta 400 ESEM FEG) in High Vacuum Mode with a 30 kV voltage. The uncoated samples were mounted on aluminum SEM holder pucks using double-sided carbon tape. Figure 4.4 to 4.8 show micrographs of the CNT types used in this study. A noticeable aspect is the difference in the sizes, and the level of agglomeration.
SWNTs were purified to remove amorphous carbon, and metal catalyst. Following purification nanotubes were disentangled by acid solvation, and high shear mixing. This led to the formation of highly roped structures shown in Figure 4.4. A similar SWNT disentangling method by Booker et al. [180] that included an extrusion and fiber spinning steps showed similar that nanotubes roped structures with improved alignment. Figure 4.5 shows that the functionalization of SWNTs was not strong enough to unrope the nanotubes sufficiently. XD-CNTs show the largest amount of agglomerates and entanglements. This is due to the lack of a purification step, which leaves large concentrations of metal catalyst as shown in Figure 4.6. DWNTs (Figure 4.7) show a different range of diameters, attributed to being a mixture material. The thicker tubes are most likely MWNTs, which make up 20% of this material. The MWNTs shown in Figure 4.8 presented a uniform diameter distribution, consistent with the supplier specifications.

![Figure 4.4. SEM micrographs of disentangled SWNTs at two different magnifications: (a) 20,000X and (b) 100,000X. SWNTs were disentangled by acid solvation and high shear mixing.](image-url)
Figure 4.5. SEM micrographs of SAP-f-SWNTs at two different magnifications: (a) 15,000X and (b) 75,000X.

Figure 4.6. SEM micrographs of XD-CNTs at two different magnifications: (a) 25,000X and (b) 35,000X. Micrographs show highly agglomerated nanotubes.
Figure 4.7. SEM micrographs of DWNTs at two different magnifications: (a) 30,000X and (b) 80,000X. The different diameters shown are due to the different nanomaterials in the mixture (SWNTs, DWNTs and MWNTs).

Figure 4.8. SEM micrographs of MWNTs at two different magnifications: (a) 30,000X and (b) 80,000X.
4.2.2. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material’s thermal stability, and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated [116]. In the particular case of CNTs, the weight change in an air atmosphere is due to the weight loss due to oxidation of carbon into gaseous carbon dioxide, and the weight gain due to oxidation of residual metal catalyst into solid oxides [117].

Samples weighting between 10-15µg were scanned in an air atmosphere (100 cc flow) from 25 to 700°C, at a heating rate of 10°C/min to determine the purity of nanomaterials. Figure 4.9 - 4.11 show the thermograms obtained for the SWNT, DWNT, MWNT, and XD-CNT. The residual material is assumed to be FeO. Therefore, the original iron content in the samples corresponds to 70% of the residual weight obtained after the TGA procedure. Table 4.2 summarizes the average residue and iron content of each as-received nanomaterial. The degree of functionalization was determined by TGA under an argon environment to prevent burning the CNTs (Figure 4.13). The weight loss for SAP-f-SWNT was 26%. The atomic weight of the functional group is 73gr/mol, yielding 1 functional group for every 20 Carbon atoms.
Figure 4.9. TGA mass loss of as received disentangled SWNTs under air. The average residue content is around 1.43 %.

Sample: DWNT

Figure 4.10. TGA mass loss of as received DWNTs under air. The average residue content is 2.63 %.
Figure 4.11. TGA mass loss of as received disentangled MWNTs under air. The average residue content is 0.47%.

Figure 4.12. TGA mass loss of as received XD CNTs under air. The average residue content is 8%.
Table 4.2. TGA results of SWNTs, DWNTs, MWNTs, XD-CNTs under air. The iron content corresponds to 70% of the residue weight.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Residue Content (wt%)</th>
<th>Average Iron Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNTs</td>
<td>1.55</td>
<td>1.09</td>
</tr>
<tr>
<td>DWNTs</td>
<td>2.63</td>
<td>1.84</td>
</tr>
<tr>
<td>MWNTs</td>
<td>0.47</td>
<td>0.33</td>
</tr>
<tr>
<td>XD-CNTs</td>
<td>8.10</td>
<td>5.80</td>
</tr>
</tbody>
</table>

Figure 4.13. TGA mass loss of functionalized SWNT (SAP-f- SWNT) under argon. The residue content is 72.77%.
4.2.3. Raman Spectroscopy

Raman spectroscopy provides an important characterization tool for carbon-based materials, showing different characteristic spectra for sp$^3$, sp$^2$, and sp carbons, as well as for disordered sp$^2$ carbons, fullerenes, and CNTs [118]. All carbon forms contribute to the Raman spectra in the range $1000–1700$ cm$^{-1}$, typically giving rise to a two-band feature with peaks at $\sim1300$ cm$^{-1}$ (D-band), and $\sim1600$ cm$^{-1}$ (G-band). The position, width and relative intensity of the peaks vary with carbon allotropes and can be used, with some limitations, for identification of non-CNT content.

![Raman Spectra of CNTs](image)

Figure 4.14. Raman spectra of CNTs [119].

In SWNTs, the G band spectrum, and the lower frequency radial breathing mode (RBM) are usually the strongest features in SWNT Raman spectra. The G band is also called the tangential stretching mode features indicative of sp$^2$ carbon bonding. The G-band frequency can be used for diameter characterization, and to distinguish between
metallic and semi-conducting SWNTs through strong differences in their Raman line shapes.

The radial breathing mode (RBM) corresponds to the coherent vibration of the C atoms in the radial direction. These features are unique to cylinder symmetry, and occur with frequencies between 120 and 350 cm\(^{-1}\) for SWNTs with diameters in the range 0.7 nm < \(d\) < 2 nm. The frequency of this feature is inversely proportional to the tube diameter. These RBM frequencies are therefore very useful for identifying whether a given carbon material contains SWNTs, through the presence of RBM modes. Various theoretical methods have been used to calculate the diameter dependence of the RBM frequency (\(\omega_{\text{RBM}}\)), and there is general agreement that the result does not depend significantly on the chirality, only the tube diameter \(d\). Furthermore, the functional form is found to be \(d_t = A/\omega_{\text{RBM}}\), where \(A\) is a constant, \(\omega_t\) the RBM frequency, and \(d\) is the tube diameter. Several values of the constant \(A\) have been reported: 223 cm\(^{-1}\)nm (zone folding method) [120], 218 cm\(^{-1}\)nm (force constant model) [121], 234 cm\(^{-1}\)nm (local density approximation) [122], 236 cm\(^{-1}\)nm (pseudopotential density functional theory) [123], and 227 cm\(^{-1}\)nm (elastic deformation model) [124]. When SWNTs are arranged on a triangular lattice to form a rope, their RBM frequencies increase 5–10% compared to the isolated one because of van der Waals interaction between SWNTs in the rope [93,125]. The effect of tube-tube interactions on the breathing mode have also been considered, and for a tube with diameter close to that of a (10,10) tube, the correction due to bundling is 14 cm\(^{-1}\) [125] or slightly higher 22 cm\(^{-1}\) [126].

The D and G' bands are usually the two strongest second-order features in nanotubes. Both the D-band, and the G' band are sensitive to the SWNT diameter and
chirality. Changes in the D-band and G’ band Raman spectra can be used for materials characterization, and to monitor structural modifications of the nanotube sidewalls that come from the introduction of defects (i.e. by sonication) or by the attachment of different chemical species, (i.e., via functionalization) [117,54,47,39,118].

Raman spectroscopy measurements of CNTs were obtained by a Renishaw MicroRaman spectrometer with a 785 nm diode laser with a 1800 l/m grating, and a resolution of 2cm$^{-1}$. The objective used is a 50X and the exposure time was 10 seconds. Figure 4.15 - Figure 4.19 show the normalized Raman spectra of as-received SWNT, SAP-SWNTs, DWNT, MWNT and XD-CNTs. The intermediate frequency range of 500 -1200 cm$^{-1}$ is omitted. Noticeable aspects between them are the D-peak intensities with respect to the G-peak, and the RBMs indicative of the different nanotube diameters present.

Using the $d = 234 \text{ cm}^{-1} \text{ nm/} \omega_{\text{RBM}}$ relation and the observed RBM frequencies of the SWNTs (Figure 4.15a), the calculated nanotube diameters range from 1.15 nm to 0.88 nm with an averaged value of 1.04 nm. This value is in close agreement with the specifications given for HiPco SWNT. Figure 4.16a shows that the functionalization of SWNTs (SAP-f-SWNTs) did not affect the diameter distribution of the nanotubes. XD-CNTs (Figure 4.17a) show peaks at 266, 232, 167 and 153 cm$^{-1}$. The first two peaks can be attributed to the SWNTs present while the peaks at 167 and 153 cm$^{-1}$ come from the DWNTs in the mixture. The spectra show the characteristic tangential mode band of SWNTs, however, a small intensity disruption in the increasing slope of the G-band peak typical in SWNTs, is absent.
In general, Raman bands detected in the frequency range between ~250 and ~400 cm$^{-1}$ for DWNTs (Figure 4.18a) are associated with the RBMs of the secondary or inner tubes. For this material, those peaks should be attributed to the SWNTs present in the mixture. Figure 4.18a shows the spectra collected in the 100-400 cm$^{-1}$ range for MWNTs. MWNTs consist of multiple coaxial SWNTs of ever-increasing diameter about a common axis. In the past decade, extensive Raman experiments have been performed on the MWNTs. However, due to their large diameters, the reported Raman spectra closely resemble that of graphite, and no RBMs have yet been found except by Jantoljak et al. [127].

For SWNTs, the D-band indicative of sp$^3$ carbon bonding in SWNTs is within the range 1285–1300 cm$^{-1}$ and has a line-width of 10–30 cm$^{-1}$. For other types of CNTs, such as MWNTs, the D-bands is found at 1305–1330 cm$^{-1}$, with line-widths of 10–30 cm$^{-1}$. The ratio of the D-peak with respect the G-peak is normally used as a proof of the disruption of the aromatic system of $\pi$-electrons on the nanotube sidewalls by attached functional groups, covalent bonding to the matrix, nanotube damage, or other type of defects [117]. MWNTs showed D-band intensities much higher than the G-band intensities. Similar MWNT spectra was also observed by Chae et al. [128], which was attributed to a partially defective graphitic structure. Table 4.3 shows the calculated D:G intensity ratios for all carbon nanomaterials. For SWNT, DWNT, MWNT and XD-CNTs the D:G ratio is attributed to concentration of defects. The higher ratio for SAP-f-SWNT compared to SWNTs is attributed to the sidewall attachment of functional groups.
Figure 4.15. Normalized Raman spectra of SWNTs. (a) Radial Breathing Modes, (b) D and G bands range.

Figure 4.16. Normalized Raman spectra of SAP-f-SWNTs. (a) Radial Breathing Modes, (b) D and G bands range.
Figure 4.17. Normalized Raman spectra of XD-CNTs. (a) Radial Breathing Modes, (b) D and G bands range.

Figure 4.18. Normalized Raman spectra of DWNTs. (a) Radial Breathing Modes, (b) D and G bands range.
Figure 4.19. Normalized Raman spectra of MWNT. (a) Radial Breathing Modes, (b) D and G bands range.

Table 4.3. D/G intensity ratios for all CNT materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D/G ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNTs</td>
<td>0.05</td>
</tr>
<tr>
<td>SAP-f-SWNTs</td>
<td>0.12</td>
</tr>
<tr>
<td>DWNTs</td>
<td>0.37</td>
</tr>
<tr>
<td>MWNTs</td>
<td>2.00</td>
</tr>
<tr>
<td>XD-CNTs</td>
<td>0.16</td>
</tr>
</tbody>
</table>

4.3. Composite Preparation

SWNTs, SAP-f-SWNTs, DWNTs, MWNTs and XD-CNTs were dispersed in vinyl ester by tip ultrasonication with varying energy rates and sonication times. The nanotube concentration was 0.5 wt% and the total weight of nanocomposites was 5g. A Cole-Parmer 750 Watt Ultrasonic Processor with a fixed frequency of 20 kHz was used, as shown in Figure 4.20. This instrument monitors both power (energy rate), and
total energy introduced to the system. The ultrasonic power delivered by the tip is
directly related to the amplitude. The amplitude control of the ultrasonic processor allows
the ultrasonic vibrations at the probe to be set at any level in the 10–100% range of the
nominal power. The sonication time at a given power or energy rate gives the total energy
introduced to the system.

Figure 4.20. Cole-Parmer 750 Watt Ultrasonic Processor, with a fixed frequency of
20 kHz.

Is a common practice to pre-disperse CNTs in a solvent prior to mixing with
polymer resins, such as in the case of epoxy resins [63,56,55,47,8,129,130]. Solvents are
then evaporated by placing the mixtures in an oven or heated bath. However, vinyl ester
resins contain up to 40% styrene. Therefore this approach was not practical since it would
also evaporate styrene causing an increase in the viscosity. To minimize loss of styrene
due to the heat generated by sonication, samples were placed in an ice bath.

The effect of sonication energy on neat vinyl ester was also studied. Uncured
vinyl ester was sonicated at 22, 88, 178 and 532 kJ. As shown in Figure 4.21, the resin
turns darker with increasing sonication energy. TGA tests were done to determine the materials’ thermal stability. Vinyl ester samples weighting between 45-50µg were scanned in an air atmosphere (100 cc flow) from 25 to 400°C, at a heating rate of 10°C/min. The oxidation temperature for neat vinyl ester was 358.03°C, and 362.55°C and 365.56°C for 22 kJ and 88 kJ, respectively. This indicates that initially increasing energy promotes cross-linking of vinyl ester. However, at 178 kJ and 532 kJ the oxidation temperature decreased to 361.79°C and 358.69°C, suggesting polymer degradation.

Figure 4.21. Uncured vinyl ester sonicated at different energies: a) 0 kJ, b) 22 kJ, c) 89 kJ, d) 178 kJ, e) 532 kJ.
Figure 4.22. TGA mass loss of uncured vinyl ester sonicated at 0, 22, 88, 178 and 532 kJ. a) Weight % vs. temperature (°C), b) Derivative weight % vs. temperature (°C).
CNT/vinyl ester samples were sonicated for 0.5, 2, 5, 10, 20, 40, 60 and 120 minutes at varying energy rates to determine the optimal sonication parameters. The sonication times and amplitudes studied, and their correspondent total energies are shown in Table 4.4. Figure 4.23 shows all the nanocomposites made with varying type of nanotube, dispersion method, power, and sonication energy. Following sonication, nanotube/vinyl ester blends were cured at room temperature. The curing system consisted of 1.25% ratio per weight of MEKP (Methyllethylketone peroxide) as the initiator, 0.20% CoNap (Cobalt Naphthenate) to promote cross-linking, and 0.05% 2, 4-P (2, 4-pentanedione) as a retarder. The blends were degassed for 5 min, and cast into an aluminum mold.

**Table 4.4.** Sonication parameters studied for dispersing CNTs in vinyl ester. Total energies in kJ at given time and amplitude are shown.

<table>
<thead>
<tr>
<th>Sonication time (min)</th>
<th>Amplitude (Power)</th>
<th>Total Sonication Energy (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35 % (32 W)</td>
<td>65 % (57 W)</td>
</tr>
<tr>
<td>0.5</td>
<td>0.96</td>
<td>1.71</td>
</tr>
<tr>
<td>2</td>
<td>3.84</td>
<td>6.84</td>
</tr>
<tr>
<td>5</td>
<td>9.60</td>
<td>17.10</td>
</tr>
<tr>
<td>10</td>
<td>19.20</td>
<td>34.20</td>
</tr>
<tr>
<td>20</td>
<td>38.40</td>
<td>68.40</td>
</tr>
<tr>
<td>40</td>
<td>76.80</td>
<td>136.80</td>
</tr>
<tr>
<td>60</td>
<td>115.20</td>
<td>205.20</td>
</tr>
<tr>
<td>120</td>
<td>230.40</td>
<td>410.40</td>
</tr>
</tbody>
</table>
Figure 4.23. Nanocomposites created from incorporating CNTs in vinyl ester.
CHAPTER 5. Dispersion Study of Carbon Nanotubes in Vinyl Ester

5.1. Electrical resistivity testing

The electrical conductivity for intrinsic polymer composite materials depends on the filler's conductivity, concentration, distribution and morphology. The effect of filler loading on the composite resistivity follows a nearly universal pattern regardless of which fillers are chosen. At low filler loadings, the composite properties remain almost undisturbed. There is little or no change in resistance because the electrons moving through the composite still encounter the insulating polymer. As the filler loading reaches a critical point, the resistivity precipitously drops. This point is called the percolation threshold (Figure 5.1), i.e., the filler concentration that marks this insulator-conductor transition. This behavior is described by the following relationship, as proposed by Stauffer and Aharony [77]:

\[ \sigma = C |f - f_c|^t \]  \hspace{1cm} (8)

Where \( \sigma \) is the composite conductivity, \( f \) the weight percent of the reinforcement, \( C \) is a constant, and \( t \) the critical exponent.
Figure 5.1. Schematic representation of an insulator polymer matrix with a conductive filler. At low concentrations the particles are surrounded by the polymer so there is little or no change on the conductivity of the composite. At the percolation threshold a network of fillers is formed and conductivity is achieved [131].

Network formation occurs with a small increase in filler volume and yet results in a tremendous change in resistivity. The formation of the conductive network does not necessarily imply physical contact between the fibers. Increasing the filler concentration reduces the distance between the fibers and favors electron hopping or tunneling.

The shape of the particle plays a critical role in where percolation occurs. The more structured or elaborately shaped the particle, the more likely it is to contact a nearest neighbor and form a continuous network. Copper particles, with a conductivity of \( \rho \sim 1E-06 \ \Omega \cdot \text{cm} \), require 15wt% to reach percolation due to their low aspect ratio (closer to 1) [132]. Carbon-black particles are more irregularly shaped and often have long branches reaching out from the main body of the particle, and may require anywhere from 5 to 35% loading to reach the percolation threshold. High aspect ratio fibers, such as CNTs, may be present in very low volumes in order to achieve low resistance. The influence of the fiber aspect ratio with respect to the volume fraction of the filler required
to conduct electricity is represented in Figure 5.2. It can be observed that as the aspect ratio increases the volume fraction of the filler decreases. Ruoff and Lorents [77] showed that the SWNTs aspect ratio could exceed 1000, making these fibers attractive as conductive fillers. Aggregates of nanotube bundles reduce the aspect ratio (length/diameter) of the reinforcement, which represents a significant increase in the percolation threshold.

![Figure 5.2](image)

**Figure 5.2.** Effect of filler aspect ratio on the critical filler concentration needed to induce bulk conductivity in a filled polymer [133].

A wide range of values has been reported for percolation thresholds and conductivity of CNT composites, depending on the processing method, polymer matrix and nanotube type [25,28,10,134-140]. The percolation threshold of different types of
nanotubes dispersed in thermosetting matrices ranging between 0.0025 and 0.5 wt% are shown in Table 5.1. As a comparison, some typical percolation thresholds for other fillers are: 9-18 wt% for VGCFs in polypropylene [141], 15 wt % for Cu powder [132], 35 wt% for Al-powder [133], and 20- 40 wt% for carbon black in epoxy [134]. Appendix B shows a study on the electrical properties of as received and functionalized CNTs dispersed in a thermoplastic polymer. The percolation threshold was found to be 1.7 wt% for CNTs/polypropylene and 4 wt% for BP-f-CNT/polypropylene.

**Table 5.1.** Percolation Threshold and Resistivity Range of Nanocomposites.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Matrix</th>
<th>Percolation Threshold</th>
<th>Resistivity (Ω.cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT</td>
<td>Epoxy</td>
<td>0.025%</td>
<td>$10^8$</td>
<td>[142]</td>
</tr>
<tr>
<td>MWNT</td>
<td>Vinyl ester</td>
<td>0.1 wt%</td>
<td>$10^6$</td>
<td>[143]</td>
</tr>
<tr>
<td>Oxidized MWNT</td>
<td>Epoxy</td>
<td>0.017-0.077 vol%</td>
<td>$10^2 - 10^4$</td>
<td>[135]</td>
</tr>
<tr>
<td>MWNT</td>
<td>Epoxy</td>
<td>0.5 wt%</td>
<td>$10^1$</td>
<td>[10]</td>
</tr>
<tr>
<td>MWNT</td>
<td>Epoxy</td>
<td>0.0025 wt%</td>
<td>$10^4 - 10^5$</td>
<td>[136]</td>
</tr>
<tr>
<td>SWNT</td>
<td>Epoxy</td>
<td>0.1 wt%</td>
<td>$10^4 - 10^5$</td>
<td></td>
</tr>
<tr>
<td>MWNT</td>
<td>Epoxy</td>
<td>0.1 wt%</td>
<td>$10^5 - 10^5$</td>
<td></td>
</tr>
<tr>
<td>DWNT</td>
<td>Epoxy</td>
<td>0.25 wt%</td>
<td>$10^5 - 10^5$</td>
<td></td>
</tr>
<tr>
<td>DWNT-NH$_2$</td>
<td>Epoxy</td>
<td>0.1-0.3 wt%</td>
<td>$10^8 - 10^{10}$</td>
<td></td>
</tr>
<tr>
<td>MWNT-NH$_2$</td>
<td>Epoxy</td>
<td>~0.3-0.5 wt%</td>
<td>$10^8 - 10^{10}$</td>
<td>[144]</td>
</tr>
</tbody>
</table>

### 5.1.1. Evaluation of electrical properties of nanocomposites

The surface and bulk resistivities of the composites were measured by the four-point probe method, according to the ASTM D-257 standard, the most widely accepted method to determine the conductivity of plastics and plastic compounds. Surface resistivity can be defined as the ratio of DC voltage drop per unit length to the surface current per unit width. The physical unit of surface resistivity is Ohms (Ω). Surface
resistivity is expressed in Ohms per square (Ω/sq), and is traditionally used to evaluate insulative materials for electrical applications. Bulk (or volume) resistivity, expressed in Ω.cm, is defined as the ratio of the DC voltage drop per unit thickness to the amount of current per unit area passing through the material. This property indicates how readily a material conducts electricity through the bulk of the material.

Neat vinyl ester samples were tested with a Keithley Model 6517A Electrometer/High Resistance Meter, adapted with a Keithley 8009 resistivity test fixture. The surface and bulk resistivities of vinyl ester are shown in Table 5.2.

**Table 5.2.** Surface and bulk resistivity of neat vinyl ester.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Resistivity [Ω/sq.]</th>
<th>Bulk Resistivity [Ω.cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat vinyl ester</td>
<td>3.12x10^{16}</td>
<td>8.16x10^{14}</td>
</tr>
</tbody>
</table>

Nanotube filled vinyl ester composites were tested by a Jandel Multi Height Microposition four-point probe with a current of 5 microamperes. This setup measures resistivity up to 10^6 Ω/sq, or 10^5 Ω.cm. Figure 5.3- Figure 5.6 show the bulk resistivity of CNT/vinyl ester composites as a function of total energy input, and energy rate (power). Interestingly, the energy input rate had no effect in the selected range, with all points laying on the same trend for all composite materials. This behavior has been explained by Lucas et al [179]. It was shown that the scission kinetics of CNTs by sonication is governed by the acoustic energy supplied to the system, which suggests that the efficiency of sonication does not depend on the sonication power as long as the acoustic
pressure is above the cavitation threshold. Above this threshold, the sonication energy controls the nucleation rate of cavitation bubbles.

Figure 5.3 shows that the electrical resistivity of SWNT/vinyl ester decreases exponentially with increasing input energy up to around 90 kJ; hits a plateau from 90 kJ to 230 kJ, with resistivities of 1 - 1.4 Ω.cm; and increases linearly with greater energy inputs. The standard deviation in the 90 kJ – 230 kJ range is ~ 0.2 Ω.cm. DWNT/vinyl ester and XD-CNT/vinyl ester composites show a very similar behavior. The optimal sonication range for XD-CNT/vinyl ester composites (Figure 5.4) is obtained for energies lying in the range of 40 kJ – 230 kJ. The resistivity in this region was 4 – 6 Ω.cm with a standard deviation of 0.5 – 1.2 Ω.cm. DWNT/vinyl ester materials (Figure 5.5) show resistivities of 5 – 7 Ω.cm, with a standard deviation of 1 - 1.7 Ω.cm. These values were shown for the range of 10 kJ – 210 kJ. Further sonication also resulted on an increase in resistivity. DWNTs and XD-CNTs are both a mixture of multi-, double- and single-walled nanotubes. This explains the lower energy needed to achieve the optimal dispersion, as both DWNTs and MWNTs are higher aspect ratio and surface area materials and are easier to disperse compared to roped SWNTs. The increase in resistivity at the highest input energy (530 kJ) is more pronounced for DWNTs and XD-CNTs, compared to SWNTs composites. This is consistent with the Raman data presented in Section 4.2.3 that showed that DWNTs and XD-CNTs were more defective materials, and therefore more prone to propagate defects as a result of sonication that ultimately affected the electrical properties. MWNT/vinyl ester composites (Figure 5.6) showed the least stable results as composites reached their minimum resistivity of 83 Ω.cm at ~17 kJ.
Composites with MWNTs sonicated at energies larger than 35 kJ had resistivities higher than the instrument precision, and therefore could not be plotted.

**Figure 5.3.** Bulk resistivity (Ω·cm) vs sonication energy (kJ) of 0.5 wt% SWNT/vinyl ester composites.

**Figure 5.4.** Bulk resistivity vs sonication energy of 0.5 wt% XD-CNT/VE composites.
Dispersion energy was found to be a factor that affected net electrical conductivity, which indicates that electrical conductivity measurements may be used as a
quick method for assessing the degree of dispersion. In general, three different dispersion stages were observed for SWNT, DWNT, MWNT and XD-CNT filled vinyl ester (Figure 5.3 - Figure 5.6). Low input energies were not strong enough to break and distribute nanotube bundles resulting in areas with high resin content. This explains the larger variation on surface resistivities on the lower energy region, as represented by the error bars. When the optimal input energy range is reached thinner nanotube ropes are well dispersed and distributed throughout the matrix, giving rise to resistivities with small standard deviations. The optimal sonication conditions for each material according to the electrical testing are summarized in Table 5.3. As vinyl ester has a bulk resistivity of $\sim 10^{14} \ \Omega \cdot \text{cm}$, these results represent a drop of $\sim 14$ orders of magnitude by incorporating SWNT; $\sim 13$ orders of magnitude with DWNT and XD-CNTs; and $\sim 11$ by adding MWNTs.

Over-sonication has several detrimental effects such as damaging, re-agglomerating and cutting of nanotubes [111,114,145,60,112,113]. Nanotube damage affects the electron flow, and shorter and thicker ropes of nanotubes have a smaller aspect ratio increasing the percolation threshold. Sections 5.3.1, 5.3.2, and 5.4. show the morphological and Raman spectroscopy analysis of the nanocomposites, which provide a better understanding on dispersion and damage of CNTs by sonication, and their effect on the composite properties.

Similar results were obtained by Garg et al.[146] when correlating the ultrasonic dispersion time to the viscosity properties of MWNT in aqueous suspensions. Ultrasonication was found to have a twofold effect on the MWNT nanofluids, as in with this studies. Viscosity of the nanofluids increased with sonication time until a maximum
value was reached, and decreased thereafter. The initial increase was associated with declustering bundles, resulting in a better dispersion. The later decrease in viscosity can be explained by increased breakage rate of MWNTs, resulting in shorter nanotubes and affecting networking of MWNTs in the matrix.

Figure 5.7. Representation of nanotubes dispersed in a polymer matrix by sonication energy. Three stages are shown: (I) Poor dispersion, (II) Optimal dispersion, (III) Oversonication.

Table 5.3. Experimental conditions for the dispersion of nanotubes in vinyl ester.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Studied Interval</th>
<th>Optimum Sonication Conditions</th>
<th>Surface Resistivity [Ω/sq.]</th>
<th>Bulk Resistivity [Ω.cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT</td>
<td>1-535 kJ</td>
<td>90 – 230 kJ</td>
<td>9 – 12</td>
<td>1 – 1.4</td>
</tr>
<tr>
<td>XD-CNT</td>
<td></td>
<td>40 – 230 kJ</td>
<td>32 – 50</td>
<td>4 – 6</td>
</tr>
<tr>
<td>DWNT</td>
<td></td>
<td>10 kJ – 210 kJ</td>
<td>40 – 61</td>
<td>5 – 7</td>
</tr>
<tr>
<td>MWNT</td>
<td></td>
<td>10 kJ – 25 kJ</td>
<td>110</td>
<td>85</td>
</tr>
</tbody>
</table>
5.2. Dynamical Mechanical Analysis

Dynamical Mechanical Analysis (DMA) is a nondestructive test technique that makes use of the fact that polymer systems display viscoelastic properties; this is to say that they are capable of exhibiting both the properties of an elastic solid and that of a viscous fluid depending on the environment. DMA measures the temperature dependent properties of materials, such as the storage modulus $E'$, the loss modulus $E''$, and the loss tangent $\tan \delta$. These properties reflect the amount of energy stored in the composites as elastic energy, and the amount of energy dissipated during mechanical strain, which are highly affected by the existence of fillers, their geometrical characteristics, volume fractions, dispersion in the matrix, and adhesion between filler and the matrix. The ratio of $E'/E''$ equals to $\tan \delta$, and is known as the loss tangent; $\tan \delta$ represents the glass transition temperature in a polymer [147].

Table 5.4. Storage Modulus of different CNT reinforced polymer composites.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Filler</th>
<th>Matrix</th>
<th>Increase in Storage Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shofner et al.[148]</td>
<td>5 wt% SWNT</td>
<td>ABS</td>
<td>61%</td>
</tr>
<tr>
<td>Diez-Pascual et al.[149]</td>
<td>0.1 wt% SWNT</td>
<td>PEEK</td>
<td>16%</td>
</tr>
<tr>
<td></td>
<td>0.5 wt% SWNT</td>
<td></td>
<td>23%</td>
</tr>
<tr>
<td></td>
<td>1 wt% SWNT</td>
<td></td>
<td>27%</td>
</tr>
<tr>
<td>Camponeschi et al.[150]</td>
<td>3 wt% SWNT</td>
<td>Epoxy</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>3 wt% MWNT</td>
<td></td>
<td>35%</td>
</tr>
<tr>
<td>Liu et al.[151]</td>
<td>1 wt% f-MWNT</td>
<td>PA6</td>
<td>27%</td>
</tr>
<tr>
<td>Jin et al.[152]</td>
<td>4 wt% MWNT</td>
<td>PMMA</td>
<td>60%</td>
</tr>
<tr>
<td></td>
<td>26 wt% MWNT</td>
<td></td>
<td>100%</td>
</tr>
<tr>
<td>Zhou et al.[153]</td>
<td>0.4 wt% MWNT</td>
<td>Epoxy</td>
<td>93%</td>
</tr>
</tbody>
</table>
5.2.1. Results and Discussion

DMA testing was done by a Perkin-Elmer Pyris Diamond DMA instrument in bending mode at a frequency of 1 Hz. Rectangular shaped samples with cross-sectional dimensions of 50x10x1.5 mm were cut and heated from 25 to 160 °C at a rate of 5 °C per minute. Figure 5.8 - Figure 5.12 show the storage modulus of CNT/VE composites. Samples from each of the dispersion regions, as defined by the electrical resistivity results, were tested. The storage modulus results are summarized in Table 5.5 – 5.9 show the %increase with respect to vinyl ester. The letters in parenthesis I, II, III denote the sample belongs to the poor dispersion, optimal sonication, and oversonation region, respectively. All composite materials showed a similar trend in storage modulus, but this property proved to be more susceptible to sonication energy, compared to the electrical properties, where the resistivity remain stable for a range of energies. This is mainly due to the high volume fraction of nanotubes in the sample that aided the formation of a conductive network. For a lower concentration of CNTs, a behavior similar to the mechanical properties should be expected for the electrical resistivity. Dispersion proved to be essential on achieving the maximum reinforcement effect. SWNT reinforced vinyl ester composites sonicated at 17 kJ (poor dispersion) showed an increase of 10.67% in the storage modulus, compared to the neat resin. However, the same material dispersed with an energy of 88 kJ showed an increase of 77.29%. SAP-f-SWNTs showed only a small improvement on the mechanical properties, compared to the SWNTs, with an increase of about 81.81%. This was due to the functionalization not being aggressive enough to unrope the SWNTs completely, evidenced by the SEM micrographs. XD-CNT/vinyl ester materials showed the highest increase in the storage modulus at 68 kJ
(optimal dispersion), with an improvement of 84.63%. Interestingly, samples dispersed with energies lying in the oversonication range showed a small increase or even a decrease in the storage modulus, compared to unreinforced vinyl ester that can be attributed to damage and reagglomeration of the nanotubes.

Figure 5.8. Storage Modulus (Pa) versus temperature (°C) for neat vinyl ester and 0.5 wt% SWNT/vinyl ester composites sonicated at different energies.
Figure 5.9. Storage Modulus (Pa) versus temperature (°C) for neat vinyl ester and 0.5 wt% SAP-f-SWNTs/vinyl ester composites sonicated at different energies.

Figure 5.10. Storage Modulus (Pa) versus temperature (°C) for neat vinyl ester and 0.5 wt% XD-CNT/vinyl ester composites sonicated at different energies.
Figure 5.11. Storage Modulus (Pa) versus temperature (°C) for neat vinyl ester and 0.5 wt% DWNT/vinyl ester composites sonicated at different energies.

Figure 5.12. Storage Modulus (Pa) versus temperature (°C) for neat vinyl ester and 0.5 wt% MWNT/vinyl ester composites sonicated at different energies.
Table 5.5. Mechanical Properties of 0.5 wt% SWNT/vinyl ester composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersion Region</th>
<th>Storage Modulus (Pa)</th>
<th>Standard Deviation</th>
<th>Increase in Storage Modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat vinyl ester</td>
<td>-</td>
<td>2.95E+09</td>
<td>8.97E+07</td>
<td>-</td>
</tr>
<tr>
<td>0.5 wt% SWNT/VE, 17 kJ</td>
<td>I</td>
<td>3.27E+09</td>
<td>4.04E+08</td>
<td>10.67%</td>
</tr>
<tr>
<td>0.5 wt% SWNT/VE, 44 kJ</td>
<td>I</td>
<td>4.52E+09</td>
<td>3.12E+08</td>
<td>52.96%</td>
</tr>
<tr>
<td>0.5 wt% SWNT/VE, 88 kJ</td>
<td>II</td>
<td>5.23E+09</td>
<td>2.52E+07</td>
<td>77.29%</td>
</tr>
<tr>
<td>0.5 wt% SWNT/VE, 178 kJ</td>
<td>II</td>
<td>5.01E+09</td>
<td>2.66E+08</td>
<td>69.61%</td>
</tr>
<tr>
<td>0.5 wt% SWNT/VE, 266 kJ</td>
<td>III</td>
<td>3.21E+09</td>
<td>2.01E+08</td>
<td>8.86%</td>
</tr>
</tbody>
</table>

Table 5.6. Mechanical Properties of 0.5 wt% SAP-f-SWNT/vinyl ester composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersion Region</th>
<th>Storage Modulus (Pa)</th>
<th>STD Deviation</th>
<th>Increase in Storage Modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat vinyl ester</td>
<td>-</td>
<td>2.95E+09</td>
<td>8.97E+07</td>
<td>-</td>
</tr>
<tr>
<td>0.5 wt% SAP-SWNT/VE, 22 kJ</td>
<td>I</td>
<td>3.99E+09</td>
<td>7.21E+07</td>
<td>35.17%</td>
</tr>
<tr>
<td>0.5 wt% SAP-SWNT/VE, 88 kJ</td>
<td>II</td>
<td>5.17E+09</td>
<td>6.11E+07</td>
<td>75.03%</td>
</tr>
<tr>
<td>0.5 wt% SAP-SWNT/VE, 178 kJ</td>
<td>II</td>
<td>5.37E+09</td>
<td>5.77E+07</td>
<td>81.81%</td>
</tr>
<tr>
<td>0.5 wt% SAP-SWNT/VE, 266 kJ</td>
<td>III</td>
<td>4.67E+09</td>
<td>1.53E+08</td>
<td>58.10%</td>
</tr>
</tbody>
</table>
### Table 5.7. Mechanical Properties of 0.5 wt% XD-CNT/vinyl ester composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersion Region</th>
<th>Storage Modulus (Pa)</th>
<th>Standard Deviation</th>
<th>Increase in Storage Modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat vinyl ester</td>
<td>-</td>
<td>2.95E+09</td>
<td>8.97E+07</td>
<td>-</td>
</tr>
<tr>
<td>0.5 wt% XD-CNT/VE, 22 kJ</td>
<td>I</td>
<td>4.47E+09</td>
<td>2.25E+08</td>
<td>51.28%</td>
</tr>
<tr>
<td>0.5 wt% XD-CNT/VE, 44 kJ</td>
<td>II</td>
<td>4.77E+09</td>
<td>4.30E+08</td>
<td>61.54%</td>
</tr>
<tr>
<td>0.5 wt% XD-CNT/VE, 68 kJ</td>
<td>II</td>
<td>5.45E+09</td>
<td>2.12E+08</td>
<td>84.63%</td>
</tr>
<tr>
<td>0.5 wt% XD-CNT/VE, 266 kJ</td>
<td>III</td>
<td>3.58E+09</td>
<td>1.99E+08</td>
<td>21.25%</td>
</tr>
<tr>
<td>0.5 wt% XD-CNT/VE, 410 kJ</td>
<td>III</td>
<td>2.72E+09</td>
<td>4.45E+08</td>
<td>-8.02%</td>
</tr>
</tbody>
</table>

### Table 5.8. Mechanical Properties of 0.5 wt% DWNT/vinyl ester composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersion Region</th>
<th>Storage Modulus (Pa)</th>
<th>Standard Deviation</th>
<th>Increase in Storage Modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat vinyl ester</td>
<td>-</td>
<td>2.95E+09</td>
<td>8.97E+07</td>
<td>-</td>
</tr>
<tr>
<td>0.5 wt% DWNT/VE, 2 kJ</td>
<td>I</td>
<td>3.15E+09</td>
<td>4.80E+08</td>
<td>6.60%</td>
</tr>
<tr>
<td>0.5 wt% DWNT/VE, 34 kJ</td>
<td>II</td>
<td>4.29E+09</td>
<td>1.87E+08</td>
<td>45.45%</td>
</tr>
<tr>
<td>0.5 wt% DWNT/VE, 115 kJ</td>
<td>II</td>
<td>3.84E+09</td>
<td>1.19E+08</td>
<td>29.98%</td>
</tr>
<tr>
<td>0.5 wt% DWNT/VE, 532 kJ</td>
<td>III</td>
<td>2.59E+09</td>
<td>1.94E+09</td>
<td>-12.17%</td>
</tr>
</tbody>
</table>
Table 5.9. Mechanical Properties of 0.5 wt% MWNT/vinyl ester composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersion Region</th>
<th>Storage Modulus (Pa)</th>
<th>Standard Deviation</th>
<th>Increase in storage modulus (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat vinyl ester</td>
<td>-</td>
<td>2.95E+09</td>
<td>8.97E+07</td>
<td>-</td>
</tr>
<tr>
<td>0.5 wt% MWNT/VE, 4 kJ</td>
<td>I</td>
<td>3.15E+09</td>
<td>1.65E+08</td>
<td>6.71%</td>
</tr>
<tr>
<td>0.5 wt% MWNT/VE, 22 kJ</td>
<td>II</td>
<td>4.12E+09</td>
<td>3.58E+07</td>
<td>39.45%</td>
</tr>
<tr>
<td>0.5 wt% MWNT/VE, 44 kJ</td>
<td>III</td>
<td>3.07E+09</td>
<td>2.08E+08</td>
<td>6.79%</td>
</tr>
<tr>
<td>0.5 wt% MWNT/VE, 88 kJ</td>
<td>III</td>
<td>3.05E+09</td>
<td>2.07E+08</td>
<td>3.18%</td>
</tr>
<tr>
<td>0.5 wt% MWNT/VE, 178 kJ</td>
<td>III</td>
<td>2.28E+09</td>
<td>1.66E+08</td>
<td>-22.66%</td>
</tr>
</tbody>
</table>

DMA testing demonstrated that optimized nanotube dispersion is critical to achieving the reinforcing effect of CNTs. Storage modulus of composites dispersed with energies in region II (optimal dispersion) showed the highest improvement in properties, which was consistent with the electrical resistivities shown in Section 5.1. Table 5.10 shows the optimal sonication parameters that provided the highest improvement of both the electrical and mechanical properties of nanotube/vinyl ester composites.
Table 5.10. Summary of electrical resistivity (Ω.cm) and storage modulus (GPa) of CNT/vinyl ester composites with optimized dispersion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sonication Energy (kJ)</th>
<th>Storage Modulus (GPa)</th>
<th>Increase %</th>
<th>Electrical Resistivity (Ω.cm)</th>
<th>Increase %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl Ester</td>
<td>-</td>
<td>3.00</td>
<td>-</td>
<td>1x10^{14}</td>
<td>~10^{14}</td>
</tr>
<tr>
<td>0.5 wt% SWNT/vinyl ester</td>
<td>88</td>
<td>5.20</td>
<td>77</td>
<td>1</td>
<td>~10^{14}</td>
</tr>
<tr>
<td>0.5 wt% SAP-f-SWNT/vinyl ester</td>
<td>178</td>
<td>5.37</td>
<td>82</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>0.5 wt% XD-CNT/vinyl ester</td>
<td>68</td>
<td>5.45</td>
<td>85</td>
<td>5</td>
<td>~10^{13}</td>
</tr>
<tr>
<td>0.5 wt% DWNT/vinyl ester</td>
<td>45</td>
<td>4.29</td>
<td>45</td>
<td>6</td>
<td>~10^{13}</td>
</tr>
<tr>
<td>0.5 wt% MWNT/vinyl ester</td>
<td>22</td>
<td>4.12</td>
<td>40</td>
<td>300</td>
<td>~10^{11}</td>
</tr>
</tbody>
</table>

5.3. Morphological characterization

5.3.1. Optical Microscopy

Nanotube dispersions in vinyl ester were observed using a ZEISS Polarizing OM. The distribution of nanotubes in the epoxy matrix was photographed using a digital camera at a low magnification of 50x. Optical micrographs of SWNTs, SAP-f-SWNTs, XD-CNTs, DWNTs, and MWNTs dispersed in vinyl ester with varying sonication energies are shown in Figure 5.13- Figure 5.17. In general, increase in sonication energy resulted in a reduced amount of large agglomerates. Evidence of reagglomeration is apparent for sonication energies over 266 kJ for SWNT/VE (Figure 5.13), and XD-CNT/VE composites (Figure 5.15), and 205 kJ for DWNT/VE (Figure 5.16). Interestingly, these are the energies at which the composites showed an increase of resistivity and a decrease in the storage modulus. SAP-f-SWNT/VE composites showed a
smaller degree of reagglomeration. This was most likely due to the breaking of large functionalized nanotube ropes into smaller ones, which in turn freed some unfunctionalized nanotubes that re-roped with increasing energies. MWNT/VE exhibited better dispersion at high energies (Figure 5.17(b) and (c)), but the improved dispersion was apparently outweighed by the damaged caused by sonication with respect to the composite properties shown in Section 5.1.1 and 5.2.1.
Figure 5.13. Optical micrographs of 0.5wt% SWNT/vinyl ester with varying sonication energies. (a) 22 kJ, (b) 89 kJ, (c) 178 kJ, (d) 266 kJ.
Figure 5.14. Optical micrographs of 0.5wt% SAP-f-SWNT/vinyl ester with varying sonication energies. (a) 22 kJ, (b) 89 kJ, (c) 178 kJ, (d) 266 kJ.
Figure 5.15. Optical micrographs of 0.5wt% XD-CNT/vinyl ester with varying input energies. (a) 4 kJ, (b) 44 kJ, (c) 115 kJ, (d) 266 kJ.
Figure 5.16. Optical micrographs of 0.5wt% DWNT/vinyl ester with varying sonication energies. (a) 7 kJ, (b) 17 kJ, (c) 68 kJ, (d) 205 kJ.
5.3.2. Scanning Electron Microscopy

The morphology of nanotubes/vinyl ester composites was observed using an Environmental SEM (FEI Quanta 400 ESEM FEG) in High Vacuum Mode with a 30 kV
voltage. Samples were fractured to study the degree of dispersion in vinyl ester. The materials were broken in liquid nitrogen to cause a brittle fracture, and coated with gold for 45 seconds in an Ar plasma sputter coater to prevent charging. While at a different scale, SEM micrographs showed a similar trend than the optical micrographs (Figure 5.18 - 5.22). For SWNT, DWNT and XD-CNT vinyl ester composites increasing energy resulted in breaking of bundles and agglomerates, which provided better distributed nanotubes. SWNT/VE, SAP-f-SWNT/VE and XD-CNT/VE also show thinner nanotubes which suggests un-roping.
Figure 5.18. SEM micrographs of 0.5wt% SWNT/vinyl ester composites with varying sonication times. (a) 4 kJ, (b) 22 kJ, (c) 89 kJ, (d) 266 kJ. The magnification is 50,000x.
Figure 5.19. SEM micrographs of 0.5wt% SAP-f-SWNT/vinyl ester composites with varying sonication times. (a) 22 kJ, (b) 89 kJ, (c) 178 kJ, (d) 266 kJ. The magnification is 50,000x.
Figure 5.20. SEM micrographs of 0.5 wt% XD-CNT/vinyl ester composites with varying sonication times. (a) 4kJ, (b) 44kJ, (c) 115kJ, (d) 266kJ. The magnification is 50,000x.
Figure 5.21. SEM micrographs of 0.5wt% DWNT/vinyl ester composites with varying sonication times. (a) 4 kJ (b) 10 kJ, (c) 89 kJ, (d) 230 kJ. The magnification is 50,000x.
Figure 5.22. SEM micrographs of 0.5wt% MWNT/vinyl ester composites with varying sonication times. (a) 7 kJ (b) 17 kJ, (c) 34 kJ, (d) 44 kJ. The magnification is 50,000x.
5.4. **Raman Spectroscopy of composites**

Raman spectroscopy is a powerful tool for studying dispersion of CNTs in composites. Some of its advantages are that it is a non-destructive method, it measures bulk samples, and does not require special sample preparation. The Raman spectrum of CNTs consists of the three prominent bands that are assigned to the radial breathing mode, the disordered band, and the tangential mode [118,154], previously discussed in Section 4.2.3.

Raman mapping analysis can be used to characterize the homogeneity of the sample, compare the different Raman features in the select area, get information of CNT dispersions, as well as their interaction with the matrix [94,155,156]. Raman spectra were collected using a 785nm laser excitation with a spot size of 2μm to scan 40μm x 40μm regions at 7μm intervals in x and y. Three areas were scanned per sample to provide statistically significant data.

![Figure 5.23](image.png)

**Figure 5.23.** Example of an area selected for Raman mapping. The area measures 40μm x 40μm regions and the step size is 7 μm, giving a total of 49 scans.
Figure 5.24. Raman data accumulation of 5 wt% SWNT/VE composites sonicated at (a) 10 kJ and (b) 180 kJ. The composite sonicated at 180 kJ shows improved nanotube dispersion and more even Raman spectra intensities.

5.4.1. Distribution of CNTs

The G-band is an intrinsic feature of CNTs that is closely related to vibrations in all sp$^2$ carbon materials [157]. Given that the G band intensity in the composites is exclusively from CNTs the Raman intensity is to a very good approximation proportional to the number of CNTs in a volume of 1 x 1 x $t$ mm$^3$, where $t$ is the thickness. The Raman intensity map represents the state of nanotube distribution in vinyl ester on a scale of tens of microns, or “micro-dispersion”. When the nanotube bundles or ropes are uniformly distributed and the surface is smooth, the Raman map should be featureless.

Figure 5.25 – 5.29 show the 3-D contour plots of the G-peak Raman intensity for SWNT/VE, SAP-f-SWNT/VE, XD-CNT/VE, DWNT/VE, and MWNT/VE composites. Four different maps with energies corresponding with the three different dispersion stages (poor dispersion, optimal dispersion, and oversonication) are presented. Map a
corresponds to poor dispersion, \( b \) and \( c \) are maps collected in the optimal dispersion energy region, and map \( d \) was taken from an oversonicated sample. OM and SEM micrographs were consistent with Raman mapping data from the same samples. The G-peak Raman map of SWNT/vinyl ester composites sonicated at 178 kJ is relatively flat (Figure 5.30d), and shows the smallest standard deviation; this indicates that the nanotube bundles are well distributed in the polymer matrix. In contrast, there are several big peaks in the Raman map of the composite sonicated at 22 kJ, and 266 kJ (Figure 5.25c and e), providing evidence of poor dispersion and reagglomeration respectively.
Figure 5.25. Raman mapping of G-peak intensities of SWNTs dispersed in vinyl ester with varying sonication energies: (a) 22 kJ, (b) 88 kJ, (c) 178 kJ, (d) 266 kJ.
Figure 5.26. Raman mapping of G-peak intensities of SAP-f-SWNTs dispersed in vinyl ester with varying sonication energies: (a) 22 kJ, (b) 89 kJ, (c) 178 kJ, (d) 266 kJ.
Figure 5.27. Raman mapping of G-peak intensities of XD-CNTs dispersed in vinyl ester with varying sonication energies: (a) 9 kJ, (b) 44 kJ, (c) 230 kJ, (d) 266 kJ.
Figure 5.28. Raman mapping of G-peak intensities of DWNTs dispersed in vinyl ester with varying sonication energies: (a) 38 kJ, (b) 44 kJ, (c) 115 kJ, (d) 266 kJ.
Figure 5.29. Raman mapping of G-peak intensities of MWNTs dispersed in vinyl ester with varying sonication energies: (a) 10 kJ, (b) 44 kJ, (c) 230 kJ, (d) 266 kJ.
The average intensities and standard deviations for the different type of composites were plotted and are shown in Figure 5.30 – 5.34. In general, the average G-peak intensities were very similar within the same material. Since all composites contain the same nanotube concentration, the average intensities should be similar for each type of composite. The larger standard deviations are the result of the uneven distribution of nanotubes in the composite (evidenced also by the Raman maps); therefore information can be used as a parameter for dispersion metrics.

![Graph showing the intensity of G-peak vs. sonication energy for 0.5 wt% SWNT/vinyl ester materials.](image)

**Figure 5.30.** Intensity of G-peak vs. sonication energy for SWNT/vinyl ester materials. The error bars correspond to the standard deviation of fifty different measurements in each sample.
Figure 5.31. Intensity of G-peak vs. sonication energy for SAP-f-SWNT/vinyl ester composite materials.

Figure 5.32. Intensity of G-peak vs. sonication energy for XD-CNT filled vinyl ester composites.
Figure 5.33. Intensity of G-peak vs. sonication energy for DWNT/vinyl ester composites.

Figure 5.34. Intensity of G-peak vs. sonication energy for MWNT/vinyl ester composite materials.
5.4.2. Unroping of nanotubes

The RBM mode is the real signature of the presence of SWNTs in a sample, since it is not present in graphite [158]. The dispersion of SWNTs in polymer matrices can be characterized by analyzing the changes in intensity of Raman bands corresponding to RBMs associated with isolated and bundled nanotubes. This is the region of the Raman spectrum between 100 and 400 cm$^{-1}$, which is sensitive to differences in nanotube chirality and/or nanotube diameters. It has been shown that a single excitation at 785 nm can be used to show the differences between bundled and isolated nanotubes [159]. The major difference at this excitation is the absence of the (10,2) RBM at 266 cm$^{-1}$, the so-called "roping peak", in the spectra of isolated tubes. Changes in the intensity of this peak relative to other RBMs present in both isolated and bundled nanotubes give a qualitative estimation of the state of nanotube aggregation, or un-roping. This technique was used for SWNT/VE and SAP-f-SWNT/VE composites, as well as for XD-CNT/VE materials, since XD-CNTs contain a high amount of SWNTs. RBMs of DWNT/VE were not strong and therefore this approach was not applied to assess the un-roping of the SWNTs present in the mixture.
Figure 5.35. Radial Breathing Modes (RBM) of SWNTs indicating the roping peak at 266 cm\(^{-1}\).
Figure 5.36. Radial Breathing Modes of HiPco SWNTs. An increase in the roping peak at 266 cm\(^{-1}\) from (a) to (d) is shown. Adapted from [160].

For both SWNT/VE and XD-CNT/VE composites, Raman spectra showed a shift to higher frequencies of the ~266 and ~232 cm\(^{-1}\) modes, corresponding to the
nanocomposites compared to the “as-received” nanotubes. These peaks shift 3 and 4 cm$^{-1}$, respectively. Doorn et al. [159], and Strano et al. [160] showed no differences in RBM frequencies for individual and bundled nanotubes, therefore the observed shift could not be associated with inter-tube interactions due to a different state of bundling. This suggests that the shift is related to specific interactions of the nanotubes with the vinyl ester matrix. In reference to the as-received SWNTs, the shift of the 232 cm$^{-1}$ peak to higher values reflects reduced SWNT diameters. In this case, it is possible that the matrix exerts some compressive effect on the nanotubes, and that this effect is more pronounced in the modes associated with isolated SWNT (the 100-250 cm$^{-1}$ region). Modes associated with isolated nanotubes are subjected to a larger shift than for modes associated with bundles (the 266 RBM).

For the nanocomposites prepared for this study, the bundle size is a characteristic of the state of aggregation, and correlates proportionally to the intensity of the “roping” peak, shifted to 268 cm$^{-1}$ [159-161]. It has been shown that as bundle size decreases, a steady loss in the intensity of the 268 cm$^{-1}$ mode occurs relative to the 235 cm$^{-1}$ mode. For polymer nanocomposites, the ratio of these two bands is clearly a very good indicator of bundle size and, thus, of the dispersion of the filler. The ratios of these peaks were calculated for each scan made into 3-D maps, as shown in Figure 5.37 – 6.27.

As shown in Figure 5.40 and Figure 5.42, the integrated intensity ratio ($I_{235}/I_{268}$) increases with increasing sonication energy until reaching a maximum of 0.67 at 89 kJ for SWNT/VE, and of 0.63 at 44 kJ for XD-CNT/VE composites. This indicates nanotube de-bundling. Above this energy the ratio decreases, showing evidence of re-bundling. Another noticeable aspect is the high standard deviation obtained for all
materials. SAP-f-SWNT/VE (Figure 5.41) composites showed a stable average unropeing ratio for all sonication energies, with a value of 0.88. This is evidence of the enormous difficulty to completely suppress all aggregation of SWNT in polymer resins by sonication without surface functionalization, or the use of surfactants.
Figure 5.37. Raman mapping of I$_{235}$/I$_{268}$ ratios of SWNTs dispersed in vinyl ester with varying sonication energies. (a) 3.84 kJ, (b) 44 kJ, (c) 89 kJ, (d) 266 kJ.
Figure 5.38. Raman mapping of $I_{235}/I_{268}$ ratios of SAP-f-SWNTs dispersed in vinyl ester with varying sonication energies: (a) 22 kJ, (b) 89 kJ, (c) 178 kJ, (d) 266 kJ.
Figure 5.39. Raman mapping of I\textsubscript{235}/I\textsubscript{268} ratios of XD-CNTs dispersed in vinyl ester with varying sonication energies. (a) 6.84 kJ, (b) 44.4 kJ, (c) 68.4 kJ, (d) 266 kJ.
0.5 wt% SWNT/vinyl ester

Figure 5.40. Plot of the intensity ratio (I_{235}/I_{268}) vs. sonication energy of 0.5 wt% SWNT/VE composites. The error bars correspond to the standard deviation of fifty different measurements for each sample.

0.5 wt% SAP-f-SWNT/vinyl ester

Figure 5.41. Plot of the intensity ratio (I_{235}/I_{268}) vs. sonication energy of 0.5 wt% SAP-f-SWNT/VE composites.
0.5 wt% XD-CNT/vinyl ester

![Graph showing the intensity ratio (I_235/I_268) vs. sonication energy of 0.5 wt% XD-CNT/VE composites.]

**Figure 5.42.** Plot of the intensity ratio (I_235/I_268) vs. sonication energy of 0.5 wt% XD-CNT/VE composites.

### 5.4.3 Nanotube Damage

The ratio between the D-band and G-band in the Raman spectra of CNTs is a good indicator of the quality of bulk samples. It is known that the D-band is present in the form of disordered Carbon containing vacancies, impurities, or other symmetry breaking defects [118]. In this case the ratio of D/G can quantitatively represent the rate of defect generation during sonication [74]. Lu et al. [111] evaluated damage caused by sonication time by monitoring the increase in intensity in the D-band. The observation of the increase in defect concentration during sonication by the TEM work matched with the increase in D-band intensity of the Raman spectra.
**Figure 5.43.** Raman spectra of 0.5 wt% SWNT/VE composites with increasing sonication energy. Increasing sonication time generated defects as evidenced by the increase in the disordered induced peak (D-peak).

**Figure 5.44.** D/G ratio vs. sonication energy of 0.5 wt% SWNT/VE composites.
Figure 5.45. Raman spectra of 0.5 wt% SAP-f-SWNT/VE composites with increasing sonication energy.

Figure 5.46. D/G ratio vs. sonication energy of 0.5 wt% SAP-f-SWNT/VE composites.
Figure 5.47. Raman spectra of 0.5 wt% XD-CNT/VE composites with increasing sonication energy.

Figure 5.48. D/G ratio vs. sonication energy of 0.5 wt% XD-CNT/VE composites.
Figure 5.49. Raman spectra of 0.5 wt% DWNT/VE composites with increasing sonication energy.

![Raman spectra of 0.5 wt% DWNT/VE composites with increasing sonication energy.](image)

Figure 5.50. D/G ratio vs. sonication energy of 0.5 wt% DWNT/VE composites.

![D/G ratio vs. sonication energy of 0.5 wt% DWNT/VE composites.](image)
Figure 5.51. Raman spectra of 0.5 wt% MWNT/VE composites with increasing sonication energy.

Figure 5.52. D/G ratio vs. sonication energy of 0.5 wt% MWNT/VE composites.
5.5. Quantification of dispersion

Common methods used to characterize dispersion rely on a qualitative approach, such as the use of microscopy to observe dispersion, and methods based on assessing dispersion through measuring the properties for different dispersion states [10, 94]. Quantitative methods are usually based on image analysis to obtain a dispersion or distribution index, and its correlation to the composite properties [78]. The relative standard deviation (RSD) of the G-peak, the standard deviation divided by the G-peak mean value, was used to quantitatively characterize dispersion of CNTs in vinyl ester composites. As explained in Section 5.4.1, for a given sample, the G-peak intensities of the Raman spectra taken at different spots should be the same for evenly dispersed nanotubes (zero standard deviation). Therefore, the G-peak RSD can give us an idea on how well are the nanotubes distributed in a composite, and so it was used as the “dispersion indicator”.

Figure 5.53 to 5.57 show the plot of % standard deviation of the G-peak intensities versus Bulk Resistivity, Storage Modulus, D/G ratio, and I_{234}/I_{268} ratio of 0.5 wt% SWNT, SAP-f-SWNT, XD-CNT, DWNT, and MWNT/vinyl ester composites. These plots show the influence of nanotube dispersion, un-roping, and damage on the electrical and mechanical properties of composites. In general, the G-peak RSD decreased with increasing energy, following an increase when the oversonication energy range was reached. The decrease on the modulus and increase in resistivity was attributed to the combination of reagglomeration, re-roping, and damage. Figure 5.53 shows that the G-peak RSD of SWNT/VE correlated well with the electrical properties, where the mechanical properties were more dependant on both the distribution and level of
unrooping. SAP-f-SWNT/VE materials (Figure 5.54) showed no significant variation in the I_{234}/I_{268}, and damage ratios; the mechanical properties depended mainly on the distribution of SAP-f-SWNTs in the matrix. For XD-CNT/VE composites, the electrical resistivity was related to the distribution of nanotubes, whereas the storage modulus was highly dependent on the level of unrooping, as both plots show a very similar trend (Figure 5.55). Both distribution and damage had a strong effect on the DWNT/VE composite properties (Figure 5.56). Figure 5.57 shows that improved dispersion resulted in a higher storage modulus. In the case of the electrical properties, the effect of the improved dispersion was overshadowed by the increase in damage, which resulted in an increase in resistivity for energies higher than 22 kJ. As-received MWNTs (Figure 5.57) had a high D/G ratio, and increasing sonication energy further damaged the material. A similar behavior was observed by Zaragoza-Contreras et al.[162] in MWNT/polystyrene composites prepared by ultrasonication. Evidence of significant length reduction was found by SEM; the cause of such fragmentation was attributed to the induction of strong cavitation due to the application of ultrasound during the synthesis. The decrease in length of MWNT would account for the decrease in the electrical properties of the composite, due to the lower aspect ratio, as well as the propagation of defects.
Figure 5.53. Plot of the G-peak RSD (%) versus Bulk Resistivity, Storage Modulus, D/G ratio, and $I_{234}/I_{268}$ ratio of 0.5wt% SWNT/vinyl ester composites.
Figure 5.54. Plot of the G-peak RSD (%) versus Bulk Resistivity, Storage Modulus, D/G ratio, and $I_{234}/I_{268}$ ratio of 0.5wt% SAP-f-SWNT/vinyl ester composites.
Figure 5.55. Plot of the G-peak RSD (%) versus Bulk Resistivity, Storage Modulus, D/G ratio, and I_{234}/I_{268} ratio of 0.5wt% XD-CNT/vinyl ester composites.
Figure 5.56. Plot of the G-peak RSD (%) versus Bulk Resistivity, Storage Modulus, D/G ratio, and l_{234}/l_{268} ratio of 0.5wt% DWNT/vinyl ester composites.
Figure 5.57. Plot of the G-peak RSD (%) versus Bulk Resistivity, Storage Modulus, D/G ratio, and I_{234}/I_{268} ratio of 0.5wt% MWNT/vinyl ester composites.
CHAPTER 6. Conclusions

An ideal nanotube/composite material can take advantage of the extraordinary properties of CNTs while maintaining the thermosetting flexibility of the polymer. The full achievement of the reinforcing potential of CNTs requires good dispersion and spatial distribution of nanotubes in the polymer, and efficient interfacial stress transfer between the CNTs and the matrix.

This research focused on understanding the nature of ultrasonic dispersion of CNTs through a parametric study. Quantitative relationships between dispersion levels and the physical properties of CNT nanocomposites at a fixed concentration were determined. The ultrasonication parameters (i.e., time, power, energy) that provided the maximum increase in electrical and mechanical properties of CNT vinyl ester dispersions were optimized, and correlated to the nanotube distribution, unroping and damage, obtained by Raman spectroscopy. Different materials were studied to obtain a better understanding on how the type and quality (i.e., level of defects, impurities) of CNT may affect the dispersion behavior. The measurements of nanocomposite properties over a broad range of dispersion levels achieved by ultrasonication indicated a high variation, and hence the evident need to quantify dispersion to allow some control of these properties.

It is proposed that sonication of CNT in polymer composites leads to three distinct dispersion regions with: poor dispersion, optimal sonication conditions, and
oversonication. With increasing energies, improved dispersion and distribution occurs and the mechanical and electrical properties increase. Over-sonication leads to a decrease in properties and is a result of the combination of reagglomeration and/or nanotube damage, as evidenced by optical micrographs, and the increasing Raman D/G ratios.

Composite properties are strongly dependent on the dispersion of the CNTs. For the 0.5wt% concentration, mechanical strength was more sensitive to dispersion than the electrical conductivity. It was also found that increasing nanotube damage had a stronger effect on the conductivity of composites, as defects interrupt the electron flow. By Raman mapping, a 'dispersion index' was developed to quantitatively characterize dispersion. The advantage of this 'dispersion index' is that it was obtained by a simple, non-destructive method, compared to other methods that involve image analysis and are destructive in natures. The 'dispersion index' correlated well with the testing results and helped understand the factors that affect the overall composite properties. Functionalized nanotubes had the highest dispersion index, with a G-peak RSD as low as 10%. This shows the need to combine sonication, with chemical dispersion methods in order to achieve maximum dispersion. The 'dispersion index' obtained by this study should enable the translation of these results to other systems by simple scaling techniques.

After determining the optimal ultrasonic dispersion parameters for CNTs in vinyl ester, future work should focus on nanotube alignment, dispersing nanotubes in different liquid media, the optimization of sonication parameters for different concentrations, and issues with scale up. Previous experiments on alignment of CNTs dispersed in liquid
media have shown promising results; therefore an optimized dispersion combined with alignment should result in a higher increase in the physical properties of polymer nanocomposites.
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APPENDIX A. Study on surface coverage of carbon nanotubes on glass fiber

Fiber reinforced polymer (FRP) composite materials consist of fibers of high strength and modulus embedded in or bonded to a polymer matrix with distinct interfaces between them [22]. Delamination - the separation of two adjacent plies in composite laminates - represents the weakest failure mode in laminated composites [166]. Some of the solutions are: proper lay-up sequence to minimize the interlaminar stresses [167]; improved structural configuration [168]; stitching [169,170]; resin toughening [171], amongst others. The incorporation of filler particles in the mid-plane has shown to enhance the interface properties of fiber reinforced polymer composites [172-174,137,175]. Zhu et al. [172] showed a 45% increase in the interlaminar shear strength by spraying 0.015wt% CNTs on glass fiber prior to the resin infusion. Using a similar spray method, Rojas et al. [173] introduced CNTs and Vapor Grown Carbon Fibers (VGCFs) into the interlaminar region of a carbon fiber/epoxy composite to enhance the resistance to delamination. A maximum toughness increase of 51% with respect to the un-reinforced material was obtained when 0.025 wt% VGCF and 0.025 wt% CNT were combined, a result attributed to synergism occurring between the filler materials.

The objective of this study was to improve the bonding of CNTs to glass fiber through a sidewall carboxylic acid functionalization with good dispersion and surface coverage. XD-CNTs were solvent sprayed into glass fiber plies following the studies by Zhu et al.[172], and Rojas et al.[173]. Dispersion and surface coverage was studied SEM.
A.1. Materials and experimental methods

*Glass fiber:* An E-glass woven roving fabric with a unit aerial weight 800 g/m² and fiber density of 2.6 g/cm³ was obtained from Saint-Gobain Vetrotex. Glass fiber plies were also surface modified by heating and etching to remove the original sizing and then aminated by submerging the plies into a 1% solution of 3-aminopropyltriethoxysilane (APTES) in ethanol for five minutes (Figure A.1). Subsequently, the glass fibers are dried in a furnace for 4 h. The purpose of this amination is to promote coupling to functionalized nanotubes.

![Figure A.1. Aminated glass fiber.](image)

*Carbon nanotubes:* XD-CNTs lot 3365A, with 6 wt% metal content, were obtained from Carbon Nanotechnology, Inc (CNI). XD-grade CNTs are a mixture of few-wall, double-wall, and single wall material. Nanotubes were sidewall functionalized with succinic acid peroxide following the procedure described by Peng et al.[54], as shown in Figure B.1. Carboxylic groups provide sites for covalent integration of XD-CNTs to polymer materials.
As-received and functionalized XD-CNTs were dispersed in Dimethylformaldehyde (DMF) by bath sonication for 1 hr, and with 30 seconds of ultrasonication prior to spraying them on the glass fiber. A 1,3-dicyclohexylcarbodiimide (DCC) coupling agent was also added to the solution to enhance bonding to glass fiber (Figure A.4). Aminated and untreated glass fiber plies were sprayed with XD-CNT/DMF and SAP-f-XD-CNT/DMF solutions, as shown in Figure A.3. The fiber plies were then placed in an oven at 140°C for 24 h to evaporate any remaining solvent.

Figure A.3. Schematic representation of nanotubes dispersed in a solvent sprayed on glass fiber using the aerosol spraying method [176].
Figure A.4. Coupling of SAP-f-CNTs to GF and NH-s-GF by spray-up process: Figure shows the reactive treatment of APTES-sized fiberglass surface with the DMF dispersion of SAP-f-CNTs in the presence of DCC as coupling agent.

A.2. Results

Figures A.5 – A.6 show the SEM micrographs of as-received and aminated glass fiber sprayed with XD-CNT/DMF and SAP-f-XD-CNT/DMF solutions. As-received glass fiber did not show a difference in XD-CNT wetting when adding the coupling agent (Figure A.5). SAP-f-XD-CNTs showed improved dispersion, evidenced by smaller size of agglomerates compared to the as-received material (Figure A.7 – A.8). The wetting effect of the DCC coupling agent is also enhanced with spraying SAP-f-CNTs. The best wetting is seen when spraying SAP-f-XD-CNTs on NH-s-glass fiber, as the functionalization was tailored for that glass fiber sizing (Figure A.8).
Figure A.5. 0.01wt% CNTs/DMF sprayed on as-received glass fiber A) With coupling agent. B) No coupling agent.

Figure A.6. 0.01wt% CNTs/DMF sprayed on NH-s-glass fiber A) With coupling agent. B) No coupling agent.
Figure A.7. 0.01wt% SAP-f-CNTs/DMF sprayed on as-received glass fiber. A) With coupling agent. B) No coupling agent.

Figure A.8. 0.01wt% SAP-f-CNTs/DMF sprayed of NH-s-glass fiber A) With coupling agent. B) No coupling agent.
Appendix B. Electrical properties of CNT polypropylene composites

Nanotube reinforced polypropylene composites were prepared for electrically conductive applications. As-received and benzoyl peroxide in situ functionalized CNTs were used. The materials were prepared by high shear mixing and molded into sheets. SEM and Raman Spectroscopy were used for nanotube and composite characterization. The mechanical and electrical properties of the bulk materials were studied. Nanotube sidewall functionalization is known to diminish the electrical properties of the composite; however BP functionalization did not show a significant decrease in the electrical conductivity. The percolation threshold of polypropylene composites was modeled to be 1.7wt% for CNTs and 4wt% for BP-f-CNTs, showing strong agreement with experimental results. The electromagnetic interference shielding was evaluated at room temperature, in accordance to ASTM D4935-99. The maximum shielding effectiveness obtained was 28 dB with a 15wt% CNT/PP.

B.1. Experimental

B.1.1. Materials

CNTs lot XD 3365A with a 6wt% metal content were obtained by Carbon Nanotechnology Inc. XD-grade CNTs are a mixture of few-wall, double-wall, and single wall CNTs. Isotactic polypropylene with a melt flow index of 12g/10min was purchased from Sigma Aldrich in pellet form. Benzoyl peroxide (reagent grade, 97%) was purchased from Fluka (Sigma-Aldrich).
B.1.2. Composite Processing

Two different sets of samples were prepared. The first one consisted of polypropylene matrix reinforced with CNTs. The second one, termed BP-f-CNTs/PP included one part by mass of benzoyl peroxide per part of CNTs. A sample consisting only of polypropylene was mixed under the same conditions for comparison purposes.

CNTs were first dispersed in chloroform using a Cole Parmer bath sonicator for one hour. Polypropylene pellets were added to the nanotube dispersion and the slurry was put in an oil bath at a temperature of 60-70°C to evaporate the solvent. Polypropylene swells in chloroform so that when the solvent evaporates the pellets go back to their original size trapping some nanotubes on the surface. This is called incipient wetting and it is done to provide initial dispersion of the nanotubes on the polymer [148]. The mixtures were put in an oven at 100°C for 5-6 hours to completely evaporate any remaining solvent. This was done for every concentration of CNTs in batches of 16-20 g. Composites were prepared with conventional Banbury mixing. A HAAKE Polylab Rheomix 600 internal batch mixer, with roller type rotor blades and a 30 cm³ mixing bowl was used. This mixing process provided a strong high shear mixing torque for the reinforcement to disperse better in the polymer. For samples containing CNTs, batches of 16-20 grams were mixed at 75 rpm and 165°C for a residence time of 13 minutes. In the case of BP-f-CNT/PP samples, the chamber was preheated to 40°C and the temperature was increased 10°C/min until it reached 175°C. Figure B.1 represents the functionalization reaction initiated during the high shear mixing, shown by McIntosh et al. [44]. At high temperatures carbon dioxide is generated leaving the phenyl free radical, which in turn scavenges a proton from the polypropylene chain. This causes the
formation of radical sites on polypropylene chain that bond directly to the nanotubes promoting the cross-linking of the polypropylene and the CNTs.

![Chemical structure diagram]

**Figure B.1.** Schematic of the benzoyl peroxide CNT functionalization initiated during high shear mixing [44].

Composite materials were molded into sheets using a Carver laboratory heated press at 150°C with pressure of 6-7 metric tons for 5 min. Aluminum molds were used to make 130 mm by 130 mm sheets with a 1 mm thickness.

### B.2. Results and discussion

Raman spectroscopy measurements were obtained by a Renishaw MicroRaman spectrometer with a 780.6 nm diode laser, 1200 l/m grating, and a resolution of 2cm⁻¹. The objective used was 50X, and exposure time was 10 seconds. The Raman spectra of CNT/PP and BP-f-CNT/PP composites are shown in Figure B.2. For both composites the intensity of the peaks increased with the nanotube content. The increase in intensity of the D-peak, the disorder peak, of BP-f-CNT/PP compared to the CNT/PP composites indicates that functionalization of SWNTs was achieved.
Figure B.2. Raman spectra of CNT/PP and BP-f-CNT/PP composites containing 5wt% CNTs.

Table B.1. Raman G/D ratios for CNT and BP-f-CNT polypropylene composites

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The degree of dispersion of CNTs was observed by the means of Scanning Electron Microscopy. The micrographs of the composite were obtained using an Environmental SEM (FEI Electro Scan, XL-30 ESEM-FEG) in high vacuum mode using a voltage of 30 kV. Samples made from each of the CNTs concentrations were fractured to examine the degree of dispersion in the PP matrix. The materials were broken in liquid nitrogen to cause a brittle fracture, and coated with gold for 30 seconds to prevent charging under the electron beam. The fracture surfaces of the CNT/PP and BP-f-CNT/PP composites were observed under the SEM to verify dispersion. Figure B.3 shows the SEM micrographs of 5wt% CNT/PP composite with different magnifications. The micrographs show the dispersion of the reinforcement in the matrix. The nanotubes are distributed uniformly, with some agglomerates present. Figure B.4 shows a 2.5 BP-f-CNT/PP composite with improved distribution of nanotubes compared to the CNT/PP composite at the same nanotube concentration.

Figure B.3. SEM micrographs of a 2.5wt% CNT/PP composite at 8000x and 25000x.
Figure B.4. SEM micrographs of a 2.5wt% BP-f- CNT/PP composite at 8000x and 20000x.

B.2.1 Electrical Resistivity

The surface and volume resistivity of the composites was measured with a JANDEL resistivity apparatus Model RM2, incorporated with a four-point cylindrical probe, and a Monroe Electronics Model 272A Portable Surface Resistivity/Resistance. This was done according to the ASTM D-257 standard, the most widely accepted method to determine the conductivity of plastics and plastic compounds. Measurements higher than $2 \times 10^{14} \Omega$/square could not be obtained due to equipment limitation.

The electrical resistivity measurements of the CNTs and BP-f-CNTs reinforced PP composites are shown in Table B.3 for comparison purposes. It can be noted that the CNT/PP composites show a drop of 12 orders of magnitude in resistivity with only 2.5 wt% filler, while BP-f-CNT/PP composites show a drop of 6 orders of magnitude with the same concentration. High conductivity is desirable for better EMI shielding effectiveness. Nanotube functionalization was done to promote bonding to the matrix that may result in enhanced mechanical properties. A decrease in the conductivity of benzoyl
peroxide functionalized CNT composites is expected due to the introduction of functional
groups that lower the electric flow on the nanotube.

Table B.2. Surface resistivity of the CNT/PP and BP-f-CNT/PP composites in Ω/square.

<table>
<thead>
<tr>
<th>wt%</th>
<th>Electrical Resistivity of CNT/PP composites (Ω/square)</th>
<th>Electrical Resistivity of BP-f-CNT/PP composites (Ω/square)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.00E+17 [70]</td>
<td>1.00E+17 [70]</td>
</tr>
<tr>
<td>1.0</td>
<td>&gt;2E14</td>
<td>&gt;2E14</td>
</tr>
<tr>
<td>1.5</td>
<td>9.23E+13</td>
<td>&gt;2E14</td>
</tr>
<tr>
<td>2.0</td>
<td>2.01E+09</td>
<td>&gt;2E14</td>
</tr>
<tr>
<td>2.5</td>
<td>1.90E+05</td>
<td>1.32E+11</td>
</tr>
<tr>
<td>5.0</td>
<td>1.09E+04</td>
<td>3.68E+03</td>
</tr>
<tr>
<td>7.5</td>
<td>1.81E+03</td>
<td>1.07E+03</td>
</tr>
<tr>
<td>10.0</td>
<td>1.36E+02</td>
<td>6.47E+02</td>
</tr>
<tr>
<td>15.0</td>
<td>2.72E+01</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure B.4 and B.5 show the conductivity (i.e., the inverse of the volume resistivity) versus nanotube concentration for the composite materials. The experimental data was fitted by the relationship: \( \sigma = C f - f_c^t \) (Eq.1), where \( \sigma \) is the composite conductivity, \( f \) the weight percent of the reinforcement, \( C \) is a constant, and \( t \) the critical exponent. The percolation threshold and the critical exponent were found to be \( f_c = 1.7 \text{wt%} \) and \( t = 4.57 \) for CNTs/PP composites, and \( f_c = 4 \text{wt%} \) and \( t = 0.91 \) for BP-f-CNT/PP composites.
Figure B.5. Electrical conductivity versus weight fraction of CNTs in polypropylene. The percolation threshold is found to be equal to 1.7wt%. Inset is the percolation equation fitting.
Figure B.6. Electrical conductivity versus weight fraction of CNTs in polypropylene. The percolation threshold is found to be equal to 4wt%. Inset is the percolation equation fitting.

B.2.2 Electromagnetic Shielding Effectiveness

The Shielding Effectiveness (SE) is a measure of the reduction of EMI at a specific frequency achieved by a shielding material and is defined as:

\[ SE = 10 \times \log \left( \frac{P_t}{P_i} \right) \text{ (decibels, dB)} \]  \hspace{1cm} (Eq. 2)

Where \( P_t \) is the received signal when the test sample is present, \( P_i \) is the received signal when the test sample is absent.

A shielding effectiveness of 10 dB means 90% of the signal is blocked, and a SE of 20 dB means 99% of the signal is blocked. For most business electronic equipment...
with 30-1000 MHz frequencies, 18-23dB attenuation is adequate [177]. For Automotive and computer industries a reduction of signal strength by 30 dB would be adequate in 50% of the cases and 40 dB would fulfill 95% of their requirements [178].

The SE of the composites was analyzed using a Hewlett Packard 8752C network analyzer in accordance with ASTM D4935-99. The set-up consisted of a sample holder with its input and output connected to the network analyzer. The thickness of the sample was 1 mm, and the frequency range evaluated was from 30 MHz to 1.3 GHz. The Shielding Effectiveness is defined as the ratio of power received with the load specimen in place (P_t), with the reference specimen in place (P_r), eq.(2).

The SE of the composite materials is shown in Figures B.7 - B.8. BP-f-CNTs/PP composites, with lower electrical conductivities, had much lower SE compared to CNTs/PP composites for all concentrations. The EMI shielding effects of electrically conductive composites as a function of the composite resistivity can be estimated by the Simon’s equation [49]:

$$SE(\text{dB}) = 50 + 10 \log_{10}(1/pf) + 1.7 \ t(f/p)^{1/2}$$  \hspace{1cm} (Eq. 3)

Where $\rho$ is the volume resistivity in $\Omega$.cm, $f$ is the frequency MHz, and $t$ is the thickness in cm. Simon’s equation considers the shielding effectiveness due to reflection and absorption mechanisms.

The performance of shielding materials can be evaluated by comparing the SE measurements with those predicted by the Simon’s equation. The comparison between this equation and the experimental results are shown on Table B.3.
The experimental shielding effectiveness was 3–7dB larger than the empirical value calculated from Eq. (3). The difference between these values is most likely due to skin effect, which states that high frequency electromagnetic radiation only interacts with the surface region of a conductor. Thus, high surface conductors like nanotubes provide better shielding.

**Figure B.7.** Electromagnetic Interference Shielding Effectiveness of the CNT/PP composites shows increasing SE with nanotube content.
Figure B.8. Electromagnetic Interference Shielding Effectiveness of the BP-f-CNT/PP composites.

Table B.3. The comparison of SE from Simon's equation and experimental results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frequency (MHz)</th>
<th>Bulk Resistivity $\Omega\cdot$cm</th>
<th>SE, emp (dB)</th>
<th>SE, exp (dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5 wt% P-SWNT/PP</td>
<td>650</td>
<td>146</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td></td>
<td>-2</td>
<td>1</td>
</tr>
<tr>
<td>10 wt% P-SWNT/PP</td>
<td>650</td>
<td>13.3</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td></td>
<td>9</td>
<td>12</td>
</tr>
<tr>
<td>15 wt% P-SWNT/PP</td>
<td>650</td>
<td>2.37</td>
<td>21</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>1300</td>
<td></td>
<td>19</td>
<td>25</td>
</tr>
</tbody>
</table>

B.3. Conclusions

The electrical resistivity of polypropylene was lowered by 15 orders of magnitude by incorporating 10wt% CNTs. The percolation threshold for CNT/PP and BP-f-CNT/PP
composites was 1.7 and 4wt% respectively. BP-f-CNTs composites showed up to 7.5dB of shielding at 650MHZ with 10wt% reinforcements while CNTs/PP composites showed a SE of 15dB at the same nanotube concentration and Megahertz. The maximum shielding effectiveness was 28 dB with a CNT concentration of 15wt%.