Characterization of Chemical and Mechanical Properties of Polymer Based Nanocomposites

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SCHOOL OF MATERIALS
List of contents

List of contents ................................................................. 2
List of tables ............................................................... 8
List of figures .............................................................. 10
List of symbols ............................................................. 20
List of abbreviations ...................................................... 23
Abstract ........................................................................... 25
Declaration .......................................................................... 26
Copyright statement ......................................................... 27
Acknowledgement ............................................................. 28

1 CHAPTER ONE: LITERATURE REVIEW .................................. 29

1.1 Introduction ........................................................................ 29

1.2 Nanocarbons synthesis ................................................. 29
  1.2.1 Single-walled carbon nanotubes (SWCNTs) .................. 30
  1.2.2 Double-walled carbon nanotubes (DWCNTs) ............... 31
  1.2.3 Multiwall carbon nanotubes (MWCNTs) ...................... 31

1.3 Carbon nanotube properties ........................................... 33
  1.3.1 Mechanical properties ............................................. 33
  1.3.2 Thermal stability .................................................... 33

1.4 Nanocarbon / epoxy composites ..................................... 34
  1.4.1 Epoxy resins ........................................................ 34
  1.4.2 Dispersion methods .............................................. 35
  1.4.3 Mechanical properties ........................................... 35
  1.4.4 Fracture surface studies ......................................... 38

1.5 Raman spectroscopy ....................................................... 38
  1.5.1 The classical approach ......................................... 39
  1.5.2 The quantum mechanical approach ......................... 40
  1.5.3 Raman spectroscopy instrumentation ....................... 41

1.6 Raman studies of nanocarbons ....................................... 42
  1.6.1 Introduction ........................................................ 42
  1.6.2 Radial breathing modes (RBM) ............................... 42
  1.6.3 D-band ............................................................... 45
  1.6.4 G-band (tangential modes) .................................... 46
  1.6.5 G′-Band (2D-band) ............................................. 47
## Contents

1.7 Stress transfer Raman studies in nanocarbon/epoxy composites .................................. 49

1.8 Conclusions ................................................................................................................. 51

2 CHAPTER TWO: RESEARCH METHODOLOGY .......................................................... 53

2.1 General ....................................................................................................................... 53

2.2 Materials .................................................................................................................... 53

2.3 Preparation of multiwall carbon nanotubes (MWCNTs) and their epoxy composites 54

2.3.1 Preparation of multiwall nanotubes (MWCNTs) .................................................. 54

2.3.2 Preparation of nanocarbon/epoxy composites ...................................................... 54

2.3.2.1 Description of the process .............................................................................. 54

2.4 Characterization of nanocarbon and nanocarbon/epoxy composites .......... 56

2.4.1 Raman spectroscopy ............................................................................................ 56

2.4.1.1 Raman Scattering of Nanocarbons and their epoxy nanocomposites ............. 56

2.4.1.2 A Raman spectroscopic investigation of deformation behaviour ................. 57

2.4.2 Bulk density determination .................................................................................... 59

2.4.3 Thermogravimetric analysis .................................................................................. 59

2.4.4 Scanning electron microscopy (SEM) .................................................................. 59

2.4.4.1 Basics of scanning electron microscopy ......................................................... 59

2.4.4.2 Nanocarbon morphologies ............................................................................. 60

2.4.4.3 Fracture surface of carbon nanotubes/epoxy composites ................................ 60

2.4.5 Transmission electron microscopy (TEM) ............................................................ 60

2.4.5.1 Basics of transmission electron microscopy (TEM) ...................................... 60

2.4.5.2 TEM observation of nanocarbons ................................................................. 61

2.4.6 DMA of carbon nanotube/epoxy composites ....................................................... 61

2.4.7 Tensile testing of carbon nanotube/epoxy composites ......................................... 61

3 CHAPTER THREE: SYNTHESIS AND CHARACTERIZATION OF
MULTIWALL CARBON NANOTUBES (MWCNTS) ............................................. 63

3.1 Introduction ................................................................................................................. 63

3.2 Effect of injection duration on MWCNTs yield and catalyst yield ....................... 63

3.3 The change in MWCNTs morphology along the quartz tube .................................... 64

3.3.1 Effect of the injection duration along the reactor tube location ......................... 64

3.3.1.1 The length of MWCNTs arrays ($L_{MWCNTs}$) ............................................. 64
3.3.1.2 The outer diameter of MWCNTs ................................................................. 65
3.3.2 Raman spectroscopy of the MWCNTs produced .............................................. 69
  3.3.2.1 Selection of the most appropriate Raman laser ............................................ 69
  3.3.2.2 Dispersive effects of the D-band, G-band and G’-band ............................... 70
  3.3.2.3 Band intensity ratios and linewidths ......................................................... 72
3.4 Standard material for composite studies .............................................................. 75
  3.4.1 Scanning electron microscopy (SEM) analysis ................................................. 75
  3.4.2 Energy Dispersive X-ray Analyses (EDX) ...................................................... 76
  3.4.3 Transmission electron microscopy (TEM) analysis ......................................... 76
  3.4.4 Thermogravimetric analysis (TGA) .............................................................. 78
  3.4.5 Visual appearance .......................................................................................... 79
  3.4.6 The true density ............................................................................................. 80
  3.4.7 The surface area ........................................................................................... 80
3.5 Comparison with commercial MWCNTs ............................................................... 81
  3.5.1 The bulk density ............................................................................................ 81
  3.5.2 Raman spectroscopy characterization .............................................................. 82
  3.5.2.1 Raman spectra dependence on MWCNTs quality ....................................... 82
3.6 Conclusions ........................................................................................................... 84
4 CHAPTER FOUR: SINGLE-WALLED CARBON NANOTUBES (SWCNTS) AND THEIR EPOXY COMPOSITES ................................................................. 85
  4.1 Introduction ........................................................................................................ 85
  4.2 Raman spectra data analysis of SWCNTs (HiPco) .............................................. 85
  4.3 Raman spectra data analysis of the LY5052/HY5052 epoxy resin system .......... 89
  4.4 Scanning electron microscopy analysis (SEM) ................................................... 91
  4.4.1 The microstructure ....................................................................................... 91
  4.4.2 Energy dispersive x-ray analysis (EDX) ....................................................... 91
  4.5 Transmission electron microscopy analysis (TEM) .......................................... 92
  4.6 Thermogravimetric analysis (TGA) .................................................................. 92
  4.7 Deformation of the SWNT/epoxy composites .................................................... 94
    4.7.1 Raman spectra of SWCNTs in epoxy composites ...................................... 94
    4.7.2 Analysis of deformation using Raman spectroscopy .................................. 95
    4.7.2.1 Tensile loading up to 1.5 % strain .......................................................... 95
4.7.2.2 Loading and unloading to the same maximum strain ............................................. 97
4.7.2.3 Estimation of the interfacial energy dissipated during the cyclic deformation ... 99
4.7.2.4 Cyclic deformation with increasing maximum strains ...................................... 100
4.7.2.5 Effect on the intensity of the RBM Raman bands ............................................. 101

4.8 Conclusions .............................................................................................................. 104

5 CHAPTER FIVE: DOUBLE-WALLED CARBON NANOTUBES (DWCNTS) AND THEIR EPOXY COMPOSITES ................................................................. 106

5.1 Introduction .............................................................................................................. 106

5.2 Raman spectra data analysis of DWCNTs ............................................................... 106

5.3 The true density .................................................................................................... 110

5.4 The surface area .................................................................................................... 110

5.5 Scanning electron microscopy analysis (SEM) ........................................................ 110
  5.5.1 The microstructure ............................................................................................... 110
  5.5.2 Energy dispersive X-ray analyses (EDX) ............................................................ 110

5.6 Transmission electron microscopy analysis (TEM) .................................................. 111

5.7 Thermogravimetric analysis (TGA) ....................................................................... 112

5.8 Deformation of DWCNTs /epoxy composites ......................................................... 113
  5.8.1 Raman spectra of DWCNTs in epoxy composites ............................................. 113
  5.8.2 Analysis of deformation using Raman spectroscopy .......................................... 115
    5.8.2.1 Tensile loading up to 1.5 % strain ................................................................. 115
    5.8.2.2 Loading and unloading to the same maximum strain ................................... 117
    5.8.2.3 Cyclic deformation up to increasing maximum strains .............................. 118
    5.8.2.4 Effect on the intensity of the RBM Raman bands ....................................... 119

5.9 Conclusions .............................................................................................................. 124

6 CHAPTER SIX: MULTIWALL CARBON NANOTUBES (MWCNTS) AND THEIR EPOXY COMPOSITES .................................................................................. 126

6.1 Introduction .............................................................................................................. 126

6.2 Deformation of the MWCNTs /epoxy composites .................................................... 126
  6.2.1 Raman spectra of the MWCNTs and the MWCNTs /epoxy composites .......... 126
6.2.2 Analysis of deformation using Raman spectroscopy .......................................................... 126
  6.2.2.1 Tensile Loading up to 1.5% tensile strain ................................................................. 126
  6.2.2.2 Loading and unloading to the same maximum strain for 0.1 wt% MWCNTs /epoxy composites ........................................................................................................... 128
  6.2.2.3 Cyclic deformation with increasing maximum strain .................................................. 130

6.3 Dynamic mechanical properties ............................................................................................ 131
  6.3.1 The storage modulus \( (E') \) .......................................................................................... 132
  6.3.2 The loss modulus \( (E'') \) ............................................................................................ 133
  6.3.3 The loss factor (\( \tan \delta \)) ......................................................................................... 134

6.4 Mechanical properties ............................................................................................................ 135
  6.4.1 Stress-strain curves ........................................................................................................ 135
  6.4.2 Tensile fracture surface analysis by SEM ......................................................................... 138

6.5 Discussion ............................................................................................................................. 141
  6.5.1 Young’s moduli of the MWCNTs comparison ................................................................. 141
  6.5.2 Effect of wt% MWCNTs on the mechanical properties ................................................... 143

6.6 Conclusions ........................................................................................................................... 144

7 CHAPTER SEVEN: EFFECT OF DEFORMATION UPON THE RAMAN SPECTRA OF CARBON NANOTUBE / EPOXY COMPOSITES ........................................ 145

7.1 Relations between the G'-band frequency and tensile strain .............................................. 145
  7.1.1 Introduction ................................................................................................................ 145
  7.1.2 SWNT/epoxy composites ............................................................................................. 146
  7.1.3 DWCNTs/epoxy composites ........................................................................................ 147
  7.1.4 MWCNTs/epoxy composites ......................................................................................... 148

7.2 Relations between the RBM-band intensities and tensile strain ......................................... 154
  7.2.1 Introduction ................................................................................................................ 154
  7.2.2 SWNT/epoxy composites ............................................................................................. 155
  7.2.3 DWCNTs/epoxy composites ........................................................................................ 155

7.3 Conclusions ........................................................................................................................... 156

8 CHAPTER EIGHT: CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK ......................................................................................................................... 158

8.1 Conclusions ........................................................................................................................... 158
  8.1.1 Carbon nanotubes ........................................................................................................ 158
8.1.1.1 MWCNTs manufacture ................................................................. 158
8.1.1.2 Morphology .............................................................................. 158
8.1.1.3 Size, surface area and true density ................................................. 158
8.1.1.4 Thermal stability ...................................................................... 159
8.1.2 Carbon nanotube / epoxy composites .............................................. 159

8.2 Suggestions for further work ................................................................ 159
8.2.1 Mechanical properties of SWCNTs and DWCNTs epoxy composites ... 159
8.2.2 Improving the processing methods ...................................................... 159
8.2.3 Surface modification for all nanotubes ................................................ 160
8.2.4 Using other polymer matrices ........................................................... 160
8.2.5 Using different Raman laser wavelengths .......................................... 160
8.2.6 Other nano-reinforcements ............................................................... 160
8.2.7 Preliminary data analysis of graphene composites ................................ 160
  8.2.7.1 Introduction ........................................................................... 160
  8.2.7.2 Raman spectra data analysis of as-produced graphene powders ........ 161
  8.2.7.3 Scanning electron microscopy (SEM) analysis ............................. 162
  8.2.7.4 Transmission electron microscopy (TEM) analysis ....................... 162
  8.2.7.5 Raman spectra of graphene powder in epoxy composites ............... 163
  8.2.7.6 Performance of the graphene / epoxy composites .......................... 164
  8.2.7.7 Performance comparison between the graphene and MWCNTS / epoxy composites ........................................................................ 164
  8.2.7.8 Young’s moduli comparison of the MWCNTs and graphene .............. 165

9 REFERENCES ................................................................................. 168

The word count is 53,031
List of tables

Table 1.1 Young's modulus and tensile strength comparison of SWCNTs, DWCNTs, and MWCNTs by experimental observation and theoretical prediction ................................................. 33
Table 2.1 The main characteristics of used raw materials.......................................................... 53
Table 2.2 The average acquisition times and the accumulations of the Raman spectra were used for the epoxy nanocomposites and the nanocarbon powders using 632.8 nm (1.96 eV) laser excitation lines. ................................................................. 57
Table 3.1 The yield and the catalyst yield for the different injection times ...................................... 64
Table 3.2 The temperature characteristics of the quartz tube regions. ............................................. 65
Table 3.3 The typical values of the outer diameters and the array lengths for the MWCNTs produced from injection times of 30 and 240 minutes ......................................................... 69
Table 3.4 Raman spectroscopy characteristic bands of MWCNTS using an Ar+ ion laser, 514.5 nm ; a He–Ne laser, 633 nm; a NIR, 785 nm laser and 830 nm laser ......................... 71
Table 3.5 The dispersive effect parameters of the Raman band features in MWCNTs ..................... 71
Table 3.6 EDX analysis of pristine MWCNTs powder ................................................................. 76
Table 3.7 Raman spectroscopy characteristic bands of MWCNTs produced using an injection time of 30 and 240 minutes in the 3rd region compared with the commercial MWCNTs Nanocyl NC7000 and 724769 Aldrich ......................................................... 83
Table 4.1 The band assignments for the Raman spectra of the LY5052/HY5052 epoxy resin system [182-184] .............................................................................................................. 90
Table 4.2 The elements weight % content of SWNT bundles (HiPco) as derived from EDAX spectra ....................................................................................................................... 92
Table 4.3 The energy dissipation in the composites and at the interface and the predicted extent of the interface damage in the hot-cured SWCNTs/epoxy composites during the cyclic deformation up to 1% maximum loading strain ................................................. 100
Table 5.1 The G'-band doublet parameters from DWCNTs bundles excited using four different laser wavelengths (fitted to the Lorentzian peaks) .................................................. 109
Table 6.1 The average storage modulus ($E'$) of the of neat epoxy and hot-cured neat epoxy and MWCNTs/ epoxy composites at 25 °C for different weight contents of MWCNTs. 133
Table 6.2 The Young's modulus ($E$), tensile strength ($\sigma_{\text{max}}$) and the fracture strain (%) of the hot-cured neat epoxy and MWCNTs/ epoxy composites with different weight contents of MWCNTs.................................................................................................................. 136
Table 6.3 Calculation the effective elastic modulus of MWCNTs based on the G'-band shift rate using Raman spectroscopy ................................................................................. 142
List of tables

Table 6.4 Calculated effective Young’s modulus of MWCNTs powders based on the experimental tensile testing, Dynamic mechanical analysis (DMA) and Raman spectroscopy results for the nanotube reinforced composites ........................................ 142

Table 7.1 Calculation the effective Young’s modulus of 0.1 wt% CNTs / epoxy composites based on the G’-band shift rate using Raman spectroscopy ........................................ 146

Table 7.2 List of Raman radial breathing modes for SWCNTs, predicted indices which define the nanotube structure \((n, m)\) and their diameters observed in SWCNTs/epoxy composites excited using a 633 nm (He-Ne) laser and their intensity behaviour during deformation ........................................................................................................ 155

Table 7.3 List of Raman radial breathing modes for DWCNTs, predicted indices which define the nanotube structure \((n, m)\), and their diameters observed in DWCNTs/epoxy composites excited using a 633 nm (He-Ne) laser and their intensity behaviour during deformation ........................................................................................................ 156

Table 7.4 Raman peak positions and the calculated diameters for the DWCNTs .................. 156

Table 8.2 Calculation the effective elastic modulus of graphene and MWCNTs based on the G’-band shift rate using Raman spectroscopy ........................................ 165
List of figures

Figure 1.1 Two typical examples of SWCNTs: armchair and zigzag types ........................................ 30
Figure 1.2. Schematic mechanism of MWCNTs growth on a quartz surface, (A) root growth and (B) tip growth [43]. ........................................................................................................................................... 32
Figure 1.3 General amine–epoxy curing reaction [70] ............................................................................. 35
Figure 1.4 (A) Stress–strain curve of cured pure epoxy and nanocomposites with different weight fraction of unthreaded MWCNTs [91] and (B) with different surface modification MWCNTs [92] .............................................................................................................................................. 36
Figure 1.5 (A) Young’s modulus of and (B) ultimate tensile strength of epoxy-based composites containing non-functionalized nanoparticles [96] ........................................................................................................................................ 37
Figure 1.6 SEM images of the fracture surface of (A) 1 wt% of untreated MWCNTs/epoxy, (B) magnification (60,000X) of agglomerate shown in (A); (C) 3 wt% of untreated MWCNTs/epoxy, and (D) magnification (15,000X) of pull-out on fracture surface of 3 wt% untreated MWCNTs/epoxy [94, 98] ..................................................................................................................................... 38
Figure 1.7 Mechanisms of various light-scattering processes, Rayleigh and non-resonance Raman (Stokes scattering, anti-Stokes scattering) where $\omega$ is the scattering photon frequency [99] ................................................................................................................................. 40
Figure 1.8 The schematic illustration of a Raman optical system main assemblies [103] ................. 41
Figure 1.9 Raman spectra of CNTs in the range 1000–3000 cm$^{-1}$ using 633 nm (1.96 eV) laser excitation; (A) HiPco SWCNTs [105], (B) DWCNTs (CVD) [106, 107] and MWCNTs [109] ................................................................................................................................................. 43
Figure 1.10 The schematic representation of the radial breathing mode (RBM) mode for a zigzag SWNT (14, 0). All ball colours represent the C atoms according to the carbon-depth distribution in a carbon nanotube. Blue arrows represent the radial vibrations of the C atoms ............................................................................................................................... 43
Figure 1.11 The RBM of (A) the SWCNTs – HiPco bundle at excitation wavelength of 1.96 eV (633 nm) and (B) the DWCNTs bundle made from CVD and the DWCNTs bundle made from peapods at excitation wavelength of 2.31 eV (520 nm), S and M symbolizes to semiconducting and metallic respectively [10, 114] ......................................................... 44
Figure 1.12 RBM wavenumber and chirality dependence of the interband energy $E_{ia}$ between the $l^{th}$ van Hove singularities for SWCNTs based on the extended tight binding model. The horizontal lines mark the $E_{laser}$ regions where Raman spectra were acquired in 5 nm intervals. In the contour Raman maps the red (blue) colour corresponds to regions of maximum (minimum) Raman intensity in arbitrary units [115, 116] ................. 45
Figure 1.13 Schematic representations of the G-band mode for a zigzag SWCNTs (14,0). All colours represent the C atoms according to the carbon-depth distribution in a carbon nanotube. The carbon atom vibrations along the nanotube axis and vibrations of
carbon atoms along the circumferential direction of the SWNT represented by black and blue arrows respectively. .......................................................... 47

Figure 1.14 Raman scattering spectra for the tangential mode region and D-band using a 633 nm excitation wavelength for (A) DWCNTs and (B) SWCNTs [129]......................... 48

Figure 1.15 Comparison of Raman scattering spectra for the G’- mode region for SWNT, C60 (peapods) and DWCNTs made from peapods using a 488 nm (2.540 eV) excitation wavelength [136]................................................................. 48

Figure 1.16 Shift of the Raman G’ bands shifts with tension and compression strain for SWCNTs/ epoxy composites [146].................................................................................. 50

Figure 2.1 View of the laboratory production of multiwalled carbon nanotubes by the ferrocene catalyzed pyrolysis of toluene............................................................................ 55

Figure 2.2 The stainless steel square mould filled with 0.1 wt% MWCNTs/epoxy composites.. 56

Figure 2.3 Two specimen polytetrafluoroethylene plastic (Teflon, PTFE) mould filled with 0.1 wt% MWCNTs/epoxy composites ............................................................................. 56

Figure 2.4 The typical prepared composite specimens for Raman spectroscopy investigation of specimens for 0.1, 0.2, 0.5 and 1.0 wt% MWCNTs/epoxy composites respectively 58

Figure 2.5 Specimen setting in the four point bending rig showing tensile loading on the top surface .................................................................................................................. 58

Figure 2.6 The Raman microscope stage upon four-point bending rig loaded by 0.1wt%
MWCNTs/epoxy composite specimen ......................................................................... 59

Figure 2.7 The 0.1wt % MWCNTs/epoxy composite specimen mounted on the large 3-point bending clamp of dynamic mechanical analysis Q8000 system ......................... 62

Figure 2.8 Instron model 5569 mechanical testing instrument .................................................. 62

Figure 3.1 The temperature profile along the quartz tube ........................................................ 65

Figure 3.2 SEM images of arrays of MWCNTs in all regions at scale bar 1mm produced using injection times of 30 min and 240 min . The red arrows indicate MWCNTs arrays .. 66

Figure 3.3 SEM images of diameters of MWCNTs in all regions at scale bar 1µm produced using injection times of 30 min and 240 min ................................................................. 67

Figure 3.4 (A) The temperature profile along the quartz tube; (B) and (C) the array lengths (Figure 3.2) and the diameters (Figure 3.3) of the MWCNTs for injection times of 30 and 240 minutes respectively. ................................................................. 68

Figure 3.5 Fitted Raman spectra of MWCNTs; (A) 1000 to 1800 cm⁻¹ (B) 2000 to 3000 cm⁻¹. The original spectrum is solid black line; the fitting peaks are dashed green lines and the total fitting curve is presented as a dashed red line. .................................................. 69

Figure 3.6 (A) Normalized Raman spectra of MWCNTs to the G’-band intensity and, (B) Lorentzian fits of normalized G’ band line shape of the MWCNTs using an Ar⁺ ion
laser, 514.5 nm; a He–Ne laser, 633 nm; a NIR, 785 nm laser and a 830 nm laser taken with a laser power of about 1.2 mW.

Figure 3.7 Shift of (A) the G-band (B) the D-band and (C) the G’-band for MWCNTs as a function of the energy of the exciting laser.

Figure 3.8 Typical normalized offset Raman spectroscopy lines of the MWCNTs using a laser excitation of 633 nm (1.96 eV) in the range 100-3000 cm\(^{-1}\) for injection times of: (A) 30 minutes and (B) 240 minutes in the 5 regions.

Figure 3.9 (A) The ratio of the intensity of D-Raman peak and G-Raman peak \(I_D/I_G\) (B) ratio of the intensity of G-Raman peak and G’-Raman peak \(I_G/I_{G'}\) and (C) FWHM of the G’-bands for MWCNTs obtained using laser excitation of 633 nm (1.96 eV) in the range 100-3000 cm\(^{-1}\) for injection times of 30 minutes and 240 minutes.

Figure 3.10 Typical SEM images of the standard MWCNTs material at different magnifications with scale bars (A) 1 mm, (B) 50 \(\mu\)m, (C) 10 \(\mu\)m, (D) 5 \(\mu\)m, (E) 2 \(\mu\)m, (F) 500 nm (the outer diameter of MWCNTs represented by solid green lines).

Figure 3.11 (A) Array lengths distribution of the standard MWCNTs material; (B) outer diameters distribution of the standard MWCNTs material.

Figure 3.12 EDX spectrum of pristine MWCNTs powder.

Figure 3.13 TEM image of the standard MWCNTs material at different magnifications with scale bars (A) 2 \(\mu\)m, (B) 500 nm, (C) 200 nm, (D) 100 nm, (E) 50 nm, (F) 5 nm (inset with scale bar 1 nm).

Figure 3.14 (A) The TEM image of as-grown MWCNTs with the inner and outer diameters measurements, (B) outer diameters distribution of the standard MWCNTs material and (C) inner diameters distribution of the standard MWCNTs material.

Figure 3.15 The thermogravimetric analysis of as-produced MWCNTs in air. The original TGA line and their corresponding derivatives DTGA are solid blue and black lines respectively. The Gaussian fitting peak is represented by the dashed green line.

Figure 3.16 Photograph of MWCNTs grown for 4 hours at 760 °C, 100 ml/min Argon flow rate using a feed rate of 0.04 ml/h with 5.0 wt% ferrocene concentrations in toluene solution.

Figure 3.17 The true density of the MWCNTs as a function of their outer and inner diameters.

Figure 3.18 The variation in the surface area with the outer diameters of MWCNTs.

Figure 3.19 The bulk density of the as-produced, Nanocyl NC7000, and Aldrich 724769 MWCNTs powders.

Figure 3.20 The typical normalized offset Raman spectroscopy lines of the MWCNTs using 633 nm (1.96 eV) laser excitation in the range 100-3000 cm\(^{-1}\) from an injection time of 30 and 240 minutes compared with the commercial MWCNTs Nanocyl NC7000 and Aldrich 724769 materials (* technical data sheet values).
Figure 3.21 The Raman peak intensity ratio of G` band over G band measured using a 633 nm excitation laser for the MWCNTs produced along the tube reactor for injection time of 30 and 240 minutes compared with the commercial MWCNTs Nanocyl NC7000 and 724769 Aldrich materials ......................................................... 83

Figure 4.1 The Raman spectra for the SWCNTs (HiPco) in the range between 100 and 3000 cm\(^{-1}\) excited with 633 nm (He-Ne) laser ......................................................................................................................... 85

Figure 4.2 Raman spectra for the SWCNTs (HiPco) in the range between 100 and 3000 cm\(^{-1}\) excited at four different laser frequencies .................................................................................................................. 86

Figure 4.3 Raman spectra for the SWCNTs (HiPco) in the range between 2100 and 2800 cm\(^{-1}\) excited at four different laser frequencies, frequency (cm\(^{-1}\)), FWHM (cm\(^{-1}\)) ...... 87

Figure 4.4 Typical examples of RBMs-band ‘radial breathing modes’ of the SWCNTs (HiPco) in the range 100 - 500 cm\(^{-1}\) excited with (A) 514 nm (Ar\(^+\)), (C) 633 nm (He-Ne), (E) 785 nm and (G) 830 nm lasers and the corresponding Estimated diameter distribution of the SWCNTs (HiPco) obtained by Raman spectroscopy; (B), (D), (F), and (H), respectively ......................................................................................................................... 88

Figure 4.5 Estimated diameter distribution of the SWCNTs (HiPco) obtained by Raman spectroscopy ................................................................................................................................................... 89

Figure 4.6 Raman spectrum of the hot cured epoxy resin system 5052 in the region 1000-3000 cm\(^{-1}\) and inset 1200-1350 cm\(^{-1}\) excited by a 632 nm (1.96 eV) laser. The original spectrum is solid violet line; the fitting peaks are dashed green line and the total fitting curve represented by a solid red line .......................................................................................................................... 90

Figure 4.7 SEM images of the SWNT bundles (HiPco) at different magnifications with scale bars (A) 10 µm, (B) 5 µm, (C) 2 µm, (D) 500 nm ........................................................................................................................................................................ 91

Figure 4.8 Energy dispersive X-ray (EDX) spectrum for SWNT bundles (HiPco) ............................................................................................................................... 92

Figure 4.9 TEM image of SWCNTs HiPco powders at different magnifications with scale bars (A) 1 µm, (B) 200 nm, (C) 100 nm, (D) 50 nm, (E) 20 nm, (F) 10 nm ........................................................................................................................................ 93

Figure 4.10 Thermogravimetric analysis of the SWCNTs (HiPco) in air. the original TGA line and the corresponding derivatives DTGA are solid blue and black lines respectively. The Gaussian fitting peak is dashed red line .................................................................................................................................................. 94

Figure 4.11 (A) Raman spectra of the epoxy resin, the SWCNTs (HiPco) and hot-cured SWNT / epoxy nanocomposites in the range 1000-3000 cm\(^{-1}\) excited using 633 nm (He-Ne) laser. (B) G’-Raman spectra of SWNT powder and hot-cured SWCNTs / epoxy nanocomposites in the range 2500-2800 cm\(^{-1}\) excited using 633 nm (He-Ne) laser. .................................................................................................................................................................................. 95

Figure 4.12 A typical G’-Raman spectra of hot-cured SWNT (HiPco) / epoxy nanocomposites in the range 2500-2800 cm\(^{-1}\), excited using a 633 nm (He-Ne) laser, in the undeformed state and at 1.5 % tensile strain ......................................................................................................................... 96
Figure 4.13 The typical examples of; (A) the shift of G'-band positions of the SWCNTs HiPco versus tensile strain of hot-cured SWCNTs HiPco / epoxy nanocomposites. The overall fitting is represented by a solid green line, the 0 - 0.7 % strain region liner fitting is a dashed red line, the 0.7 – 1.1 % strain region polynomial fitting is a dashed blue line and the 1.1 – 1.5 % strain region liner fitting is a dashed purple line (B). The G'-band FWHM of the SWCNTs HiPco versus tensile strain tensile strain of hot-cured SWNT (HiPco) / epoxy nanocomposites. The overall polynomial fitting is presented by a solid red line................................................................. 97

Figure 4.14 Variation of the G'-band of the hot-cured SWNT / epoxy nanocomposites for three cycles of loading and unloading up to 1.0 % maximum strain (A) band positions and (B) band FWHM............................................................................................................................................................................ 98

Figure 4.15 The derived stress-strain curve for the loading and unloading cycle to demonstrate the determination of the energy dissipated in the hot-cured SWCNTs/epoxy composites............................................................................................................................................................................ 99

Figure 4.16 The features of G'-band of the hot-cured SWCNTs / epoxy nanocomposites for cyclic deformation up to 0.5, 1.0 and 1.5 % maximum loading strains (A) band positions and (B) band FWHM ........................................................................................................................................... 101

Figure 4.17 The RBM positions as a function of strain upon the SWNT/ epoxy composites for the 333 (solid squares), 299 (solid circles), 283 (down solid triangles), 255 (up solid triangles), 219 (solid pentagon) and 197 (star) cm$^{-1}$ peaks................................................................. 101

Figure 4.18 (A) Typical RBM-band Raman spectra comparing SWCNTs bundles powder with the SWCNTs in undeformed and 1.5 % loaded strain SWNT/ epoxy composites. (B) RBM-band Raman spectra of SWCNTs in undeformed SWNT/ epoxy composites ........................................................................................................................................... 102

Figure 4.19 The Kataura plot [191] used to determine the metallic or semiconducting nature of the SWCNTs in resonance with the 633 nm laser excitation energy. The green line indicates the excitation energy of the 633 nm laser and the area between the two solid green lines represents the resonance window. The violet open circle is used to mark a Raman frequency where the RBM intensity should be strong. .................. 103

Figure 4.20 Examples of typical changes of the intensities of the RBM-band as a function of strain ........................................................................................................................................................................... 104

Figure 5.1 The Raman spectrum for DWCNTs in the range between 100 and 3000 cm$^{-1}$ excited using a 633 nm (He-Ne) laser ........................................................................................................................................................................... 106

Figure 5.2 Lorentzian fits of the Raman spectrum of DWCNTs for the G'-bands near 2650 cm$^{-1}$ excited at 633 nm (He-Ne) laser. The original spectrum line is shown as solid black line, the overall fitting peak is solid red line and the fitted two peaks are dashed green lines, (frequency (cm$^{-1}$) (FWHM, cm$^{-1}$). .................................................................................................................................................. 107
Figure 5.3 Raman spectra for DWCNTs excited using four different laser frequencies in the range between 100 and 3000 cm\(^{-1}\) ................................................................. 108

Figure 5.4 Raman spectra for DWCNTs in the range between 2500 and 2800 cm\(^{-1}\) excited at four different laser wavelengths ................................................................. 108

Figure 5.5 RBMs-band 'radial breathing modes' of DWCNTs in the range 100 - 500 cm\(^{-1}\) excited using 830 nm, 785 nm, 633 nm (He-Ne), and 514 nm (Ar\(^+\)) lasers. ......................... 109

Figure 5.6 Estimated diameter distribution of isolated DWCNTs obtained using Raman spectroscopy and Equation 4.1, (A) outer diameters and (B) inner diameters. ...... 110

Figure 5.7 SEM images of the DWCNTs bundles at different magnifications with scale bars (A) 10 \(\mu\)m, (B) 5 \(\mu\)m, (C) 2 \(\mu\)m and (D) 500 nm. ....................................................... 111

Figure 5.8 The energy dispersive X-ray (EDX) spectrum for the DWCNTs bundles. ............. 111

Figure 5.9 TEM images of DWCNTs bundles at different magnifications with scale bars (A) 1 \(\mu\)m, (B) 200 nm, (C) 100 nm, (D) 20 nm, (E) 10 nm, (F) 2 nm. ......................... 112

Figure 5.10 The thermogravimetric analysis of the DWCNTs bundles in air. The original TGA line and the corresponding derivative DTGA are shown by solid blue and black lines respectively. The Gaussian fitting peak presented as a dashed red line ......... 113

Figure 5.11 (A) Raman spectra of epoxy, DWCNTs and hot-cured DWCNTs / epoxy nanocomposites in the range 100-3000 cm\(^{-1}\) excited using 633 nm (He-Ne) laser. (B) G\(^{'}\)-Raman spectra of epoxy, DWCNTs bundles and hot-cured DWCNTs / epoxy nanocomposites in the range 2500-2800 cm\(^{-1}\) excited using a 633 nm (He-Ne) laser. (Frequency (cm\(^{-1}\)) / (FWHM, cm\(^{-1}\)). ................................................................. 114

Figure 5.12 Lorentzian fits of the Raman spectrum of the DWCNTs G\(^{'}\)-bands near 2650 cm\(^{-1}\)excited using a 633 nm (He-Ne) laser. The original spectrum line represented by solid black lines, the overall fitting peak as a solid red line and the fitted two peaks are dashed green lines, (frequency (cm\(^{-1}\)) / (FWHM, cm\(^{-1}\)). ......................... 115

Figure 5.13 Typical G\(^{'}\)-Raman spectra of hot-cured DWCNTs / epoxy nanocomposites in the range 2500-2800 cm\(^{-1}\) excited using a 633 nm (He-Ne) laser in the undeformed state and at 1.5 % axial strain. ........................................................................ 116

Figure 5.14 Shift of the G\(^{'}\)-band position during tensile deformation for the hot-cured DWCNTs /epoxy nanocomposites excited using a 633 nm (He-Ne) laser, (A) fitted to one Lorentzian peak (C) for the higher frequency G\(^{'}\)-band (outer tubes) (E) for the lower one G\(^{'}\)-2 band (inner tubes) and (B) (D) and (F) the corresponding changes of the widths of G\(^{'}\)-band (FWHM) respectively. ................................................................. 117

Figure 5.15 (A) Variation of G\(^{'}\)-band of the overall G\(^{'}\)-band for the hot-cured DWCNTs / epoxy nanocomposites for three cycles of loading and unloading up to 1.0 % maximum strain fitted as a one Lorentzian fitted peak and (B) the corresponding changes of the width of G\(^{'}\)-band (FWHM) for three cycles of loading and unloading up to 1.0 % maximum strain ........................................................................ 118
Figure 5.16 (A) Variation of G’-band of the overall G’-band for the hot-cured DWCNTs / epoxy nanocomposites for cyclic deformation for 0.5, 1.0 and 1.5 % maximum loading strain fitted as a one Lorentizan fitted peak and (B) the corresponding changes of the width of G’-band (FWHM) ................................................................. 119

Figure 5.17 The RBM positions for the DWCNTs/ epoxy composites as a function of strain for the 338 (solid squares), 307 (solid circles), 289 (up solid triangles), 284 (down solid triangles), 253 (solid diamond), 218 (lift solid triangles), 176 (right solid triangles), 167 (solid hexagon), 154 (star) and 125 (solid pentagon) cm⁻¹ peaks. .................. 121

Figure 5.18 (A) Typical RBM-band Raman spectra of DWCNT powder compared with the DWCNTs in undeformed and 1.5 % strain loaded DWCNTs/ epoxy composites. (B) RBM-band Raman spectra of DWCNTs in an undeformed DWCNTs/ epoxy composites ....................................................................................................................................................................................... 121

Figure 5.19 The Kataura plot [191] used to determine the metallic or semiconducting nature of DWCNTs in resonance with excitation energy of the 633 nm laser for (A) the inner tubes and (B) the outer tubes. The green line indicates the excitation energy of the 633 nm laser and the area between the two solid green lines represents the resonance window. The open circle is used to mark a Raman frequency where the RBM intensity is strong. ......................................................................................................................................................................................... 122

Figure 5.20 Shift of the intensities of the RBM-band of strain upon the DWCNTs/ epoxy composites for the 338 (solid squares), 307 (solid circles), 289 (up solid triangles), 284 (down solid triangles), 253 (solid diamond) and 218 (lift solid triangles) cm⁻¹ peaks for the inner tubes. ......................................................................................................................................................................................... 123

Figure 5.21 Shift of the intensities of the RBM-band of strain upon the DWCNTs/ epoxy composites for the 176 (right solid triangles), 167 (solid hexagon), the 154 (star) and 125 (solid pentagon) cm⁻¹ peaks for the outer tubes. ......................................................................................................................................................................................... 124

Figure 6.1 (A) Raman spectra of the epoxy, as-produced MWCNTs and hot-cured MWCNTs / epoxy nanocomposites in the range 100-3000 cm⁻¹ excited using a 633 nm (He-Ne) laser (B) G’- band of the MWCNTs powders and hot-cured MWCNTs / epoxy nanocomposites in the range 2500-2800 cm⁻¹ excited using a 633 nm (He-Ne) laser. (Frequency (cm⁻¹) / (FWHM, cm⁻¹)) ......................................................................................................................................................................................... 127

Figure 6.2 A typical G’-Raman spectra of hot-cured (0.1 wt %) MWCNTs / epoxy nanocomposites in the range 2500-2800 cm⁻¹ excited using a 633 nm (He-Ne) laser in the undeformed state and at 1.5 % axial strain ......................................................................................................................................................................................... 128

Figure 6.3 Typical examples of the shift of G’-band positions versus tensile strain up to 1.5 % strain for the hot-cured MWCNTs / epoxy nanocomposites excited using a 633 nm (He-Ne) laser for different wt% MWCNTs; (A) 0.1 % (C) 0.2 % (E) 0.5 % and (G) 1.0 % and the corresponding change of G’-band width (FWHM); (B), (D), (F), and (H), respectively. ........................................................................................................................................................................................................................................................................................................ 129
Figure 6.4 (A) Variation of the position of the G'-band for three cycles of loading and unloading up to 1.0% maximum strain fitted as a one Lorentizan peak and (B) the corresponding change of G'-band FWHM for the 0.1 wt% MWCNTs/epoxy composite in tension. ................................................................. 130

Figure 6.5 The shift of the G'-band for cyclic deformation for 0.5, 1.0 and 1.5% maximum loading strain for MWCNTs/epoxy nanocomposites excited with a 633 nm (He-Ne) laser at different wt%; (A) 0.1%, (C) 0.2%, (E) 0.5% and (G) 1.0% and the corresponding the change of the G'-band FWHM for the 0.1 wt% MWCNTs/epoxy composite in tension. ................................................................. 131

Figure 6.6 Typical DMA data for the hot-cured epoxy resin where the black, red and blue arrows referring to the $T_g$ values from the onset of the drop in the storage modulus ($E'$), from the maximum peaks of the loss modulus ($E''$) curve and of tan delta ($\delta$) curve in the high temperature region ................................................................. 132

Figure 6.7 (A) Storage modulus ($E'$) of hot-cured MWCNTs/epoxy composites at different weight contents of MWCNTs over a range of temperatures from (-100 °C to 200 °C). (B) The storage modulus as a function of weight fraction of MWCNTs at 25 °C. (C) The onset of the drop in the storage modulus ($E'$) curve as a function of weight fraction of MWCNTs in the rubbery region. ................................................................. 133

Figure 6.8 The loss modulus ($E''$) of the hot-cured MWCNTs/epoxy composites at different weight contents of MWCNTs over a range of temperatures. (A) Full range from (-100 °C to 200 °C), (B) the $\alpha$-transition from 75 °C to 150 °C, and the corresponding maxima loss modulus peaks shifting in $\alpha$-regions in (C) ................................................................. 134

Figure 6.9 Tan $\delta$ of the hot-cured MWCNTs/epoxy composites with different weight contents of MWCNTs over a range of temperatures. (A) The $\alpha$-relaxation from (75 °C to 200 °C), and (B) the corresponding maxima the loss factor (tan $\delta$) peaks shifting in $\alpha$-regions. ................................................................. 135

Figure 6.10 Stress-strain curves of the hot-cured neat epoxy and MWCNTs/epoxy composites with different weight contents of MWCNTs ................................................................. 136

Figure 6.11 (A) The Young's modulus (B) tensile strength and (C) fracture strain of the hot-cured neat epoxy and MWCNTs/epoxy composites for different weight contents of MWCNTs ................................................................. 137

Figure 6.12 SEM fracture surface of the hot-cured neat epoxy at different magnifications with scale bars (A) 1 mm, (B) 100 µm, (C) 5 µm and (D) 1 µm. ................................................................. 138

Figure 6.13 SEM fracture surface of the hot-cured 0.1 wt% MWCNTs/epoxy composite at different magnifications with scale bars (A) 100 µm and (B) 1 µm. Pulled out MWCNTs are marked with solid red arrows ................................................................. 139

Figure 6.14 SEM fracture surface of the hot-cured 0.2 wt% MWCNTs/epoxy composite at different magnifications with scale bars (A) 100 µm, and (B) 1 µm. Pulled out
MWCNTs and cavities are marked with the solid red and green arrows respectively

Figure 6.15 SEM fracture surface of the hot-cured 0.5 wt% MWCNTs/ epoxy composite at different magnifications with scale bars (A) 1 mm (agglomerated area represented by yellow round dots and the well dispersed area by red round dots), (B) 100 µm, (C) 1 µm (higher magnifications of agglomerated area) with dashed yellow arrows and (D) 1 µm (higher magnifications of dispersed area) with dashed red arrows. Pulled out MWCNTs indicated by solid red arrows

Figure 6.16 SEM fracture surface of the hot-cured 1.0 wt% MWCNTs/ epoxy composite at different magnifications with scale bars (A) 1 mm (agglomerated areas represented by yellow round dots and the well dispersed area by red round dots), (B) 100 µm, (C) 1 µm (higher magnifications of agglomerated area) with dashed yellow arrows and (D) 1 µm (higher magnifications of dispersed area) with dashed red arrows. Pulled out MWCNTs indicated by solid red arrows

Figure 6.17 The effective Young’s modulus of MWCNTs determined from DMA, tensile test and Raman spectroscopy.

Figure 7.1 (A) The shift of the G’-band position and (B) the change of widths of the G’-band (FWHM) for hot cured SWCNTs, DWCNTs and MWCNTs/ epoxy composites up to 1.5 % maximum loading strain fitted to one Lorentizan peak (excited using a 633 nm (He-Ne) laser)

Figure 7.2 (A) The shift of the G1’-band (outer walls) and G2’-band position (inner walls) for the hot-cured DWCNTs/ epoxy nanocomposites excited using 633 nm (He-Ne) laser and (B) the corresponding changes of the of the G1’-band and G2’-band widths (FWHM)

Figure 7.3 (A) Experimental shift of the Raman G’ bands positions and their corresponding model simulation and (B) Experimental shift of the Raman G’ bands widths (FWHM) and their corresponding model simulation as a function of strain from 0 to 1.5 % for a hot cured 0.1 wt % SWNT/ epoxy nanocomposite.

Figure 7.4 The depicted geometry for MWCNTs where n=10. The outermost wall (50, 50) is in contact directly with the polymer epoxy matrix.

Figure 7.5 A schematic diagram representing the scattered light from the layers of MWCNTs

Figure 7.6 The simulated Raman spectrum for G’ bands for MWCNTs in MWCNTs/ epoxy nanocomposites at 0 % strain

Figure 7.7 The Experimental shift of the Raman G’ bands positions (solid navy hexagons) and their corresponding model simulation (solid green downtringles) as a function of strain from 0 to 1.5 % for hot cured 0.1 wt % MWCNTS/ epoxy nanocomposites and the different values of the stress transfer efficiency parameters, ki as a function of strain from 0 to 1.5 % for hot-cured 0.1 wt % MWCNTS/ epoxy nanocomposites.
Figure 7.8 (A) Experimental shift of the Raman G' bands positions and their corresponding model simulation and (B) Experimental shift of the Raman G' bands widths (FWHM) and their corresponding model simulation as a function of strain from 0 to 1.5 % for the hot cured 0.1wt % MWCNTs /epoxy nanocomposite, where (k ≈ 0.7) for the simulated data. .......................................................... 154

Figure 8.1 (A) Raman spectrum of epoxy, as-produced graphene powders and (B) comparison between Raman spectra of MWCNTs and as-produced graphene powders excited at 633 nm (He-Ne) laser in the range 1000-3000 cm⁻¹ .......................................................... 161

Figure 8.2 SEM images of the graphene powder at different magnifications with scale bars (A) 50µm, and (B) 2µm ........................................................................................................... 162

Figure 8.3 TEM images of as-produced graphene powders at different magnifications with scale bars 0.5 µm and 0.1 µm........................................................................................................... 162

Figure 8.4 (A) Raman spectra of the epoxy, graphene powder and hot-cured graphene (1wt%) / epoxy nanocomposites excited using a 633 nm (He-Ne) laser in the range 100-3000 cm⁻¹. (B) G'-Raman spectra of epoxy, graphene powder and hot-cured graphene (1 wt%)/ epoxy nanocomposites excited using a 633 nm (He-Ne) laser in the range 2500-2800 cm⁻¹ ........................................................................................................... 163

Figure 8.5 The shifting of the G'-band positions with tensile deformation up to 0.4 % strain of hot-cured graphene (1 wt%) / epoxy nanocomposites excited using a 633 nm (He-Ne) laser and (B) the corresponding change of the G' -band widths (FWHM) .... 164

Figure 8.6 Experimental frequencies of the Raman G' bands as a function of strain from 0 to 0.4 % for hot cured 1.0 wt % graphene and for hot cured 1.0 wt % MWCNTs/ epoxy nanocomposites........................................................................................................... 165
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>Percentage</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$\beta$-relaxation, the region monitored by dynamic mechanical analysis (DMA) for the epoxy and their composites in low temperature region</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$\alpha$-transition, the region monitored by dynamic mechanical analysis (DMA) for the epoxy and their composites in high temperature region</td>
</tr>
<tr>
<td>$^\circ\text{C min}^{-1}$</td>
<td>Heating rate of carbon nanotubes</td>
</tr>
<tr>
<td>$(n, m)$</td>
<td>The chiral indices for carbon nanotubes</td>
</tr>
<tr>
<td>$\Gamma_\alpha$</td>
<td>The half width at half maximum (HWHM), cm$^{-1}$</td>
</tr>
<tr>
<td>$I_0$</td>
<td>The maximum intensity of the G'-band, a.u</td>
</tr>
<tr>
<td>$\omega$</td>
<td>The values of the G'-band (position) in the range 2500-2800 cm$^{-1}$</td>
</tr>
<tr>
<td>$\omega_{G'_0}$</td>
<td>The laser dependent centre of the G'-band (position) of monolayer graphene, cm$^{-1}$</td>
</tr>
<tr>
<td>$\omega_{G'_1}$</td>
<td>The centre of the G'-band (position) of the inner walls of DWCNTs, cm$^{-1}$</td>
</tr>
<tr>
<td>$\omega_{G'_2}$</td>
<td>The centre of the G'-band (position) of the outer walls of DWCNTs, cm$^{-1}$</td>
</tr>
<tr>
<td>$\omega_{G'_\text{CNTs}}$</td>
<td>The centre of the G'-band (position) of CNTs, cm$^{-1}$</td>
</tr>
<tr>
<td>$E_{11}^M$</td>
<td>Energy transition between the first pair of van Hove singularities for metallic nanotubes</td>
</tr>
<tr>
<td>$E_{11}^S$</td>
<td>Energy transition between the first pair of van Hove singularities for semiconducting nanotubes</td>
</tr>
<tr>
<td>$E_{22}^S$</td>
<td>Energy transition between the second pair of van Hove singularities for semiconducting nanotubes</td>
</tr>
<tr>
<td>$E_{33}^S$</td>
<td>Energy transition between the third pair of van Hove singularities for semiconducting nanotubes</td>
</tr>
<tr>
<td>$E_{44}^S$</td>
<td>Energy transition between the fourth pair of van Hove singularities for semiconducting nanotubes</td>
</tr>
<tr>
<td>$E_0^0$</td>
<td>The maximum amplitude of the electric field</td>
</tr>
<tr>
<td>$E_C$</td>
<td>The predicted effective Young’s modulus of the composites, GPa</td>
</tr>
<tr>
<td>$E_{\text{eff (CNT)}}$</td>
<td>The predicted effective Young’s modulus of carbon nanotubes, GPa</td>
</tr>
<tr>
<td>$E_{ln}$</td>
<td>Transition energy between the $i^{th}$ pair of van Hove singularities for nanotubes</td>
</tr>
<tr>
<td>$E_{\text{laser}}$</td>
<td>The excitation laser energy</td>
</tr>
<tr>
<td>$E_m$</td>
<td>The effective Young’s modulus of the epoxy matrix, GPa</td>
</tr>
<tr>
<td>$E_{\text{vib}}$</td>
<td>The vibration energy</td>
</tr>
<tr>
<td>$E_{\text{vib}}(t)$</td>
<td>The amplitude of the electric field at any time</td>
</tr>
<tr>
<td>$K_e$</td>
<td>The factor accounts the effect of misorientation of CNTs in composites</td>
</tr>
<tr>
<td>$SA_{\text{MWNTs}}$</td>
<td>The theoretical surface area of MWCNTs or DWCNTs, m$^2$/g</td>
</tr>
<tr>
<td>$d_{in}$</td>
<td>The inner diameter of MWCNTs or DWCNTs, nm</td>
</tr>
<tr>
<td>$d_{out}$</td>
<td>The outer diameter of MWCNTs or DWCNTs, nm</td>
</tr>
<tr>
<td>$m_C$</td>
<td>The mass of carbon atoms in the feedstock</td>
</tr>
<tr>
<td>$m_{Fe}$</td>
<td>The mass of iron atoms in the feedstock</td>
</tr>
<tr>
<td>$m_{\text{MWNTs}}$</td>
<td>The mass of MWCNTs synthesised</td>
</tr>
<tr>
<td>$q_{\text{vib}}$</td>
<td>The natural vibration vector</td>
</tr>
<tr>
<td>$q_{\text{vib}}^0$</td>
<td>The maximum vibration of a diatomic molecule</td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>The polarizability tensor of the molecule at equilibrium position</td>
</tr>
<tr>
<td>$\rho_{\text{MWNTs}}$</td>
<td>The theoretical true density of MWCNTs, g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_{\text{graphite}}$</td>
<td>The density of graphite, g/cm$^3$</td>
</tr>
<tr>
<td>$\nu_0$</td>
<td>The frequency of incident monochromic light on classical theory of Raman spectroscopy</td>
</tr>
<tr>
<td>$\nu_{\text{vib}}$</td>
<td>The natural vibration frequency</td>
</tr>
<tr>
<td>$\partial \omega_r$</td>
<td>The slop of the laser excitation energy dependence the Raman band frequency</td>
</tr>
<tr>
<td>$\partial E_{\text{laser}}$</td>
<td>The volume fraction of CNTs</td>
</tr>
<tr>
<td>$\sim$</td>
<td>The tilde means approximately</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>±</td>
<td>Represented the standard deviation</td>
</tr>
<tr>
<td>ΔE</td>
<td>The energy spacing between the n levels</td>
</tr>
<tr>
<td>°C</td>
<td>Celsius</td>
</tr>
<tr>
<td>μm</td>
<td>Micrometre</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminium oxide</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon gas</td>
</tr>
<tr>
<td>Ar⁺ ion laser</td>
<td>Argon-ion laser emits green light at 514 nm</td>
</tr>
<tr>
<td>atm</td>
<td>Atmospheric pressure</td>
</tr>
<tr>
<td>C</td>
<td>The chemical carbon element</td>
</tr>
<tr>
<td>C=C</td>
<td>The double bond of carbon</td>
</tr>
<tr>
<td>C₆₀</td>
<td>Buckminsterfullerene (or buckyball)</td>
</tr>
<tr>
<td>Cl</td>
<td>The chemical chlorine element</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetre</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td>The wavenumber</td>
</tr>
<tr>
<td>cm⁻³/min, (ml/min)</td>
<td>The flow rate of gases</td>
</tr>
<tr>
<td>Co</td>
<td>The chemical Cobalt element</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide gas</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide gas</td>
</tr>
<tr>
<td>D(5,5)</td>
<td>Tube diameter of (n,m)=(5,5) metallic SWCNTs, nm</td>
</tr>
<tr>
<td>D_{ropes(SWCNTs)}, D_{ropes(DWCNTs)}</td>
<td>The diameter of the SWCNTs and DWCNTs bundles, nm</td>
</tr>
<tr>
<td>E'(G)</td>
<td>Storage modulus, MPa</td>
</tr>
<tr>
<td>E''(G'')</td>
<td>Loss modulus, MPa</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>Fe(CO)₅</td>
<td>Iron pentacarbonyl</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Iron oxide</td>
</tr>
<tr>
<td>CₙHₙ</td>
<td>Hydrocarbon components</td>
</tr>
<tr>
<td>GPa</td>
<td>Gigapascal</td>
</tr>
<tr>
<td>h</td>
<td>Plank’s constant</td>
</tr>
<tr>
<td>He-Ne laser</td>
<td>A helium–neon laser emits red light at 633 nm</td>
</tr>
<tr>
<td>i</td>
<td>Integer</td>
</tr>
<tr>
<td>I(ω)</td>
<td>The resulting intensity of a forced damped oscillator model of the phonon excitation, a.u</td>
</tr>
<tr>
<td>ID</td>
<td>The inner diameter of the quartz tubular reactor for synthesis carbon nanotubes</td>
</tr>
<tr>
<td>I₉/I₉</td>
<td>The band intensity ratios between the Raman D-band and the Raman G-band of the carbon nanotubes</td>
</tr>
<tr>
<td>I₉/I₉</td>
<td>The band intensity ratios between the Raman G'-band and the Raman G-band of the carbon nanotubes</td>
</tr>
<tr>
<td>J/m²</td>
<td>The units of energy dissipation at the interface over the loading deformation of the composites</td>
</tr>
<tr>
<td>k</td>
<td>The stress transfer efficiency parameter in CNTs composites</td>
</tr>
<tr>
<td>kV</td>
<td>Kilovolt</td>
</tr>
<tr>
<td>L_{reactor}</td>
<td>The length of the quartz tubular reactor for synthesis carbon nanotubes, mm</td>
</tr>
<tr>
<td>L_{MWNTs}</td>
<td>The array length of the MWCNTs, μm</td>
</tr>
<tr>
<td>mg/h</td>
<td>Rate of production of carbon nanotubes, milligram per hour</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesium Oxide</td>
</tr>
<tr>
<td>MJ/m³</td>
<td>The units of the energy dissipated in the composites over the loading deformation of the composites</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>MJ</td>
<td>Megajoule</td>
</tr>
<tr>
<td>ml</td>
<td>Millimetre</td>
</tr>
<tr>
<td>Mo</td>
<td>Molybdenum</td>
</tr>
<tr>
<td>MPa</td>
<td>Migapascal</td>
</tr>
<tr>
<td>(n,m)</td>
<td>Indices defining the nanotube structure</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>N</td>
<td>Newton</td>
</tr>
<tr>
<td>(n)</td>
<td>Number of tube layers, for SWNT = 1 and MWCNTs = 10</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>O</td>
<td>The chemical oxygen element</td>
</tr>
<tr>
<td>(O_2)</td>
<td>The molecular formula of oxygen at standard temperature and pressure</td>
</tr>
<tr>
<td>OD</td>
<td>The inner diameter of the quartz tubular reactor for synthesis carbon nanotubes</td>
</tr>
<tr>
<td>Si</td>
<td>The chemical Silicon element</td>
</tr>
<tr>
<td>(SiO_2)</td>
<td>Silica</td>
</tr>
<tr>
<td>(sp^2)</td>
<td>One type of hybridisation of carbon element</td>
</tr>
<tr>
<td>T</td>
<td>The absorption fraction of the light for monolayer graphene</td>
</tr>
<tr>
<td>(\tan \delta)</td>
<td>Tan delta</td>
</tr>
<tr>
<td>(T_g)</td>
<td>The glass-liquid transition or glass transition temperature for polymers and their composites, °C</td>
</tr>
<tr>
<td>(T_{ox})</td>
<td>The oxidation temperature of carbon nanotubes, °C</td>
</tr>
<tr>
<td>TPa</td>
<td>Terapascal</td>
</tr>
<tr>
<td>W</td>
<td>Tungsten element</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percent (weight component/weight total mixture) multiply by one hundred</td>
</tr>
<tr>
<td>(x) and (y)-direction</td>
<td>A Cartesian coordinate system</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>The applied strain on the CNTs composites, %</td>
</tr>
<tr>
<td>(\mu(t))</td>
<td>The amplitude of the dipole moment at any time</td>
</tr>
<tr>
<td>(\pi)</td>
<td>The mathematical constant number and is approximately equal to 3.14159</td>
</tr>
<tr>
<td>(S(0))</td>
<td>Raman band shift rate for the sample parallel to the strain direction, (cm^{-1}/%)</td>
</tr>
<tr>
<td>(d)</td>
<td>The diameter of SWCNTs, nm</td>
</tr>
<tr>
<td>(t)</td>
<td>Time</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>The polarizability tensor of the molecule</td>
</tr>
<tr>
<td>(\theta)</td>
<td>The chiral angle of the carbon nanotubes</td>
</tr>
<tr>
<td>(\nu)</td>
<td>The wavenumber of the Raman peaks, (cm^{-1})</td>
</tr>
<tr>
<td>(\omega)</td>
<td>The scattering photon frequency</td>
</tr>
<tr>
<td>(k_i)</td>
<td>The stress transfer efficiency parameter</td>
</tr>
</tbody>
</table>
# List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.u.</td>
<td>Arbitrary units</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>Aradur</td>
<td>A registered trademark of Huntsman Advanced Materials for commercial hardeners</td>
</tr>
<tr>
<td>Araldite</td>
<td>A registered trademark of Huntsman Advanced Materials for commercial resins</td>
</tr>
<tr>
<td>BSE</td>
<td>Back-scattered electrons</td>
</tr>
<tr>
<td>ca.</td>
<td>Latin and non-english abbreviations means around</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon black</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device for Raman applications</td>
</tr>
<tr>
<td>CCVD</td>
<td>Catalytic chemical vapour deposition process</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>CNFs</td>
<td>Carbon nanofibers (CNFs)</td>
</tr>
<tr>
<td>Co.,</td>
<td>Company</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition process</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DOS</td>
<td>The density of states of carbon nanotubes</td>
</tr>
<tr>
<td>DTGA</td>
<td>The derivative thermogravimetric curve</td>
</tr>
<tr>
<td>DWCNTs</td>
<td>Double-walled carbon nanotubes</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy on the SEM (sometimes referred to as EDX)</td>
</tr>
<tr>
<td>et al.</td>
<td>And others.</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum of a Raman peak</td>
</tr>
<tr>
<td>HiPco</td>
<td>High-pressure carbon monoxide synthesis</td>
</tr>
<tr>
<td>HNF</td>
<td>Holographic notch filter for Raman applications</td>
</tr>
<tr>
<td>HTEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>Inc.</td>
<td>Incorporated company</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared spectroscopy</td>
</tr>
<tr>
<td>Lot</td>
<td>A set of goods for supplier identification between material batches</td>
</tr>
<tr>
<td>Ltd</td>
<td>A business incorporated under the laws of England</td>
</tr>
<tr>
<td>M</td>
<td>Metallic carbon nanotubes</td>
</tr>
<tr>
<td>MTS</td>
<td>Systems corporation global supplier of high-performance test systems and position sensors</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>Multiwall carbon nanotubes</td>
</tr>
<tr>
<td>Nanocyl NC7000</td>
<td>Multwall carbon nanotubes from Nanocyl company</td>
</tr>
<tr>
<td>NIR laser</td>
<td>Near-infrared laser</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile polymer used to produce carbon fibers</td>
</tr>
<tr>
<td>Philips XL30 FEG</td>
<td>The XL series of a field emission high resolution scanning electron microscope</td>
</tr>
<tr>
<td>PhilipsCM200 TEM</td>
<td>The CM series of a transmission electron microscope</td>
</tr>
<tr>
<td>ρ-sub</td>
<td>Electrophilic para aromatic substitution</td>
</tr>
<tr>
<td>PTFE, (Teflon)</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RBM</td>
<td>Raman radial breathing modes for carbon nanotubes</td>
</tr>
<tr>
<td>S</td>
<td>Semiconducting carbon nanotubes</td>
</tr>
<tr>
<td>SE</td>
<td>Second electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SGE</td>
<td>Scientific glass engineering analytical science company</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>Single-walled carbon nanotubes</td>
</tr>
<tr>
<td>Sym.</td>
<td>Symmetric</td>
</tr>
<tr>
<td>TB1</td>
<td>Tight-binding model for assignment of CNTs structure</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>UK</td>
<td>The United Kingdom</td>
</tr>
<tr>
<td>USA</td>
<td>The United States of America</td>
</tr>
<tr>
<td>VHS</td>
<td>A van Hove singularity is a singularity (non-smooth point) in the density</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
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</tr>
<tr>
<td>VWR</td>
<td>Georges Van Waters &amp; Nat Stuart Rogers global laboratory supply and distribution company</td>
</tr>
</tbody>
</table>

List of abbreviations
Abstract

Characterization of Chemical and Mechanical Properties of Polymer Based Nanocomposites
The University of Manchester
Tamer Wafy
Doctor of Philosophy
17 January, 2013

One of the most significant issues in nanocomposite performance is improving the dispersion of carbon nanotubes (CNTs) in thermosetting or thermoplastic polymers in order to gain good mechanical properties. Several studies have investigated the fabrication of nanocomposites based on carbon nanotubes and analysed properties, but there is still insufficient data on their structure-property relationships.

This thesis has investigated the central importance of stress transfer Raman studies in epoxy composites reinforced with single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multiwall carbon nanotubes (MWCNTs) to elucidate the reinforcing ability of the CNTs in an epoxy matrix. This project was undertaken to synthesize and characterize MWCNTs and determine the effect of different weight fractions of untreated MWCNTs on the stress transfer efficiency at the MWCNTs / epoxy interface and on the stiffness of the thermomechanical properties of the MWCNTs / epoxy composites. It was undertaken to assess the stress transfer efficiency at the CNT / epoxy interface and at the inter-walls of the CNTs with tensile deformation and with cyclic loading.

Optimized conditions of the injection chemical vapour deposition method (CVD), such as long injection times were applied to produce MWCNTs with a high yield, high aspect ratio and well-defined G’ Raman peak. The morphology and size of CNTs were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) while their thermal stability was examined by Thermogravimetric analysis (TGA).

Both Raman spectroscopy and mechanical testing (static and dynamic) were utilized in this study. The Raman spectroscopy research consisted of following the G’-band frequency and linewidth as well as the intensity of radial breathing modes (RBM) during tensile deformation. The stress-induced Raman shifts in the nanocomposites have been shown to be controlled by the number of carbon nanolayers. A theory has been developed to determine and simulate the stress transfer efficiency parameter, (k_i) for MWCNTs. Tensile tests and dynamic mechanical testing were used to assess the mechanical properties of the nanocomposites.

The most obvious finding to be drawn from the present study is that the reinforcement of the epoxy resin with different loadings of MWCNTs is useful, but the best reinforcement was at low loadings of MWCNTs. One of the more significant findings to emerge from this study is that (k_i) between the inner walls of the DWCNTs and MWCNTs are quite similar (~0.7), which suggest that (k_i) may be similar for all CVD MWCNTs and DWCNTs. The second major finding was that there were RBM intensity variations for the SWCNTs and DWCNTs in the hot-cured epoxy composites and that for the DWCNTs both the inner and outer nanotube walls are stressed during deformation.
Declaration

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Acknowledgement

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Special thanks also to all graduate friends of Raman group and nanostructure group / School of Materials / Manchester University especially group members; Dr. Libo Deng, Mr. Khaled Rashed, Dr. Lei Gong, Dr Lucy Bosworth and Mr Basheer Alshammari for sharing the literature and invaluable assistance. Also I would like to thank to Mr. Andrij Zadoroshnyj who boosted me morally and provided me technical support for Raman spectroscopy. I thank Mr. Michael Faulkner (senior experimental officer in Manchester Materials Science Centre) for his help with scanning electron microscopy. I wish to express my deepest thanks to Dr Alan Harvey who was abundantly helpful and offered invaluable assistance in transmission electron microscopy (TEM) usage.

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My deepest sense of gratitude to all current and former members of the chemical engineering department of Military Technical College/ Egypt, in particular I would like to acknowledge the help of Col Dr. Hosam Mostafa (member of the follow-up committee of UK Ph.D. students) for his support. I also wish to thank the Egyptian Armed Forces on the material and moral support throughout the study period represented in the Egyptian Defence Attaché in London.

I especially wish to express my deepest sense of gratitude to all members of my family, my parents, for their patience and loving support throughout the course of this work. Finally, I can't say thank you enough for the tremendous understanding and support from my wife and my daughter in completing this project.
1 Chapter One: Literature review

1.1 Introduction

The distinguished road to carbon nanotechnology was launched with the discovery of fullerenes $C_{60}$, which have carbon atoms linked through a series of pentagons and hexagons in a structure shaped like a soccer ball and were discovered by Kroto et al [1]. Thereafter, Iijima [2] highlighted the scientific revolution of allotropes of carbon by publishing a paper in which he imaged multiwall carbon nanotubes (MWCNTs). Two years later, Iijima et al [3] observed single walled carbon nanotubes (SWCNTs). Thereafter extensive research has been carried out on carbon nanotube polymer two-phase nanocomposite systems to understand the potential of carbon nanotubes as reinforcement in a polymer matrix. When Novoselov et al. [4] reported a new and convenient procedure to obtain graphene films, international research started racing to discover more of its unprecedented mechanical and electrical properties. Professor Andre Geim and Professor Konstantin Novoselov who are scientists at The University of Manchester were awarded the Nobel Prize in Physics in 2010 for their research into graphene.

Carbon nanotubes (CNTs) possess extremely high tensile modulus (~1 TPa) and strength (~120 GPa), which have prompted many scientists to use them as reinforcements in composite materials. On the other hand, epoxy resins are known for their high tensile strength, modulus and adhesion, and their ability to withstand high temperature, complete with corrosion and chemical resistance. Due to the exceptional mechanical, thermal, and electrical properties of composites made from CNTs and epoxy resins, there is a wide range of potential applications which focus on their use as reinforcements in structural materials, coatings, or integrated constituents in multifunctional materials.

The surface and interface play an important role in controlling the properties of a broad range of composite materials including CNTs/epoxy nanocomposites. The development of improved high performance composites based on polymers can only be achieved by simultaneously optimizing the CNT aspect ratio, uniform CNT dispersion, CNT packing, bonding between the epoxy and CNTs at the interface, interwall sliding within CNTs under tension and reduced polymer shrinkage during processing [5-7]. Raman spectroscopy can be used to characterise the deformation behaviour of carbon nanotubes in composites. Evidence of stress transfer between the matrix and the carbon nanotubes can be observed from the stress induced shifts of the Raman bands.

1.2 Nanocarbons synthesis

There is a large number of published studies describing the synthetic procedures to obtain CNTs. This section provides a survey of the procedures to synthesize SWCNTs, DWCNTs and MWCNTs. It has been considered that the presence of impurities depends on the how the CNTs were synthesized. Yet in any kind of synthesis the most common impurities already defined as
various types of carbon such as graphitic nanoparticles, amorphous carbon, fullerenes, or polyaromatic hydrocarbons and nanometre-size catalyst particles (typically iron particles (Fe), cobalt particles (Co) and/or nickel particles (Ni)) coated with carbon [8-10]. The mechanisms of growth of carbon nanotubes (CNTs) will subsequently be discussed.

1.2.1 Single-walled carbon nanotubes (SWCNTs)

The structure of single wall nanotubes (SWCNTs) is a molecular-scale hollow cylinder formed by rolling up single graphene sheets. Depending on the axis of “graphene sheet folding”, its structure can be uniquely characterized by the two integers $n, m$. The nanotubes are called zigzag nanotubes if $m = 0$ and termed armchair nanotubes if $n = m$, otherwise, they are called chiral. Figure 1.1 illustrates examples of nanotube models as either armchair or zigzag. Armchair tubes are metallic; whereas zigzag and chiral nanotubes, will be also be metallic if $n - m = 3i$, or a semiconductor if $n - m \neq 3i$ (where $i$ is an integer).

![Figure 1.1 Two typical examples of SWCNTs: armchair and zigzag types](image)

In their review, Govindaraj et al. [6] listed the preparation strategies of single-walled carbon nanotubes (SWCNTs), which include the methods of arc discharge, laser ablation, chemical vapour deposition (CVD) and high-pressure carbon monoxide (HiPco).

The well-known “floating catalyst” method developed at Rice University also known as the HiPco (high-pressure CO) method. This involves a catalytic production process in a continuous-flow gas-phase using CO as the carbon feedstock and Fe(CO)$_5$ as the iron-containing catalyst precursor [11-14]. Researchers have drawn attention to the effect of different reaction pressures, temperatures and CO gas flow rates on the yield and the diameter distribution of the grown SWCNTs. The optimal conditions used a pressure of 10 atm and a temperature between 900 and 1200 °C in order to produce highly pure SWCNTs with 0.6-1.3 nm diameters or larger (3.0 nm) at a rate of 1.24 - 3.3 mg/h [11-13]. It is a continuous-flow process rather than a batch process, which would allow scaling to produce SWCNTs in much larger quantities.

Several attempts have been made to understand the growth mechanism of single walled nanotubes and concluded that in the HiPco process, the iron carbonyl molecules decompose at high temperature in the gas phase to release their Fe atoms, which cluster together to form small catalytic particles from which SWCNTs nucleate and grow. Hence the SWNT growth rate increases by increasing the CO concentration or decreasing the CO$_2$ concentration [15, 16]. The diameter of the nanotubes is controlled by the size of the catalytic particles, with nanometre size particles yielding SWCNTs.
1.2.2 Double-walled carbon nanotubes (DWCNTs)

The structure of double wall nanotubes (DWCNTs) is of two concentric hollow cylinders formed by rolling up double graphene sheets. Double wall carbon nanotubes are one of the forms of carbon nanotubes that have concentric intertubes. Both direct growth and indirect techniques have been used to synthesise DWCNTs.

Both the arc-discharge process and CCVD (catalytic chemical vapour deposition) process are direct synthesis methods, while the “peapod” route using SWCNTs filled with C_{60} or higher fullerenes, as well as ferrocene or anthracene precursors is used as an indirect growth method [17-20]. The production of DWCNTs by catalytic decomposition of hydrocarbons using stationary nanometre-size catalytic metals (CCVD) is one of the most important processes due to it leading to easy mass production at low cost. Gaseous and liquid hydrocarbon such as acetylene, propanol, ethanol and methane are the main carbon sources used to grow DWCNTs combined with transition metal particles catalysts, such as Fe/Co, Fe/Mo, Fe, and Mo which are attached to porous catalyst support materials, such as Al_{2}O_{3}, MgO, SiO_{2}, zeolites, etc. that are essential for nanotube growth and strongly influence the structure and quality of the DWCNTs [21-24].

Previous studies of the production of DWCNTs by CCVD have underlined the link between the reaction temperature, pore size, and thermal stability of the support material and the diameter distribution and selectivity of the DWCNTs. They found the outer diameter of DWCNTs to be in the range of 1.5-6 nm and the yield is as high as 80 % at 900 °C [18, 25]. Numerous studies have attempted to explain the DWCNTs growth during the high temperature annealing of C_{60}-peapods. It was hypothesized that the mechanism of DWCNTS (CVD) growth is also similar to formation mechanism of peapod-derived double-walled carbon nanotubes. It suggested that an outer tube acts as a template for the inner tube formation where it nucleates, although growth is simultaneous during the CVD growth [26-28].

1.2.3 Multiwall carbon nanotubes (MWCNTs)

The structure of multiwall nanotubes (MWCNTs) consists of concentric hollow cylinders formed by rolling up graphite or graphene nanoplatelets. MWCNTs are currently synthesized by different methods which differ largely by the achievable yield and carbon purity. As well as the conventional arc-evaporation technique, MWCNTs are produced by a variety of CVD processes such as thermal CVD, aerosol-supported CVD, water-assisted CVD and injection CVD methods [23, 29-32].

Several studies [23, 29-32] have revealed that the MWCNTs’ diameter, length, alignment and yield produced by the injection CVD method should be affected by the growth temperature, the size of the catalyst particle (catalyst concentration), the duration of injection, gas mixtures concentration (from pure argon to pure hydrogen), and carrier gas flow rate. Injection chemical vapour deposition (CVD) was used to grow high aspect-ratio MWCNTs. The correlation between the positive impact of mechanical properties of nanocomposites and the aspect ratio of MWCNTs has been investigated by many researchers [33-36].
In general, the aspect ratio of MWCNTs ranges between 20 and 5000 [33, 34, 36-38]. However, in the case of carbon nanofibers (CNFs) they have diameters ranging from 200 to 500 nm, the outermost tube diameter having a broad distribution ranging from 10 nm up to 100 nm depending on the number of layers. The smallest innermost tubes of the MWCNTs are ranging from 0.6 nm to 3.7 nm [39-41].

The predicted MWCNTs-growth mechanism of the injection CVD method used in this present study has been proposed based on SEM and TEM images of the synthesized MWCNTs as shown in Figure 1.2. Some analysts suggest that the nanotubes were growing via the root, tip and/or combined root-tip growth mechanism [42, 43]. There are strong interactions between the catalyst and the quartz tube walls in the root growth mechanism, whereas in tip growth the catalyst particle starts to lift-off due to the weak interaction with the quartz tube walls.

First, toluene and ferrocene are vaporized at 110 °C and 175 °C respectively, and then ferrocene is thermally decomposed above 400 °C to form iron and carbon atoms in the gas phase which catalyze the toluene pyrolysis (chemically stable up to about 650 °C [44]). Subsequently, the iron catalyst particles are deposited and form upon the walls of the quartz furnace tube and then the carbon atoms diffuse rapidly to the exposed catalyst surface. Hydrogen from the hydrocarbon helps to keep the exposed catalyst surface clear of encapsulating carbon that would deactivate it [42].

![Figure 1.2. Schematic mechanism of MWCNTs growth on a quartz surface, (A) root growth and (B) tip growth [43].](image)

As the reaction progresses, an $sp^2$ graphene sheet precipitate with its edge atom surface covalently bonded in the catalyst surface. Thereafter the graphene sheet is exposed to high strain which compels it to grow normal to the substrate surface on the continuous filamentous surface form of the carbon nanotubes. In the same manner, nested MWCNTs with several concentric cylinder structures are formed which trap the catalyst inside the core of the
MWCNTs. The catalytic activity of the catalyst finally ceases due to its surface becoming fully covered with carbon atoms.

1.3 Carbon nanotube properties

1.3.1 Mechanical properties

Since the discovery of carbon nanotubes, theoretical and experimental investigations have been undertaken to determine their unprecedented mechanical properties. Several studies have revealed that the nanocarbons (graphene and CNTs) are strong and are elastic. In this section the mechanical responses (elastic and plastic) are discussed focusing on the Young’s moduli of CNTs and their tensile strengths.

Due to their small size and the difficulty of manipulating carbon nanotubes during the measurement of their mechanical properties by conventional methods (tensile test and DMA), new methods have been developed such as measuring the amplitude of the intrinsic vibrations of the nanotubes in the transmission electron microscope [45], following the Raman band position upon strain by Raman spectroscopy [46] and atomic force microscopy (AFM) [47].

The Young’s modulus and tensile strength of SWCNTs, DWCNTs, and MWCNTs obtained by experimental observation and theoretical prediction from several sources are compared in Table 1.1. This demonstrates the varied range of the experimental approaches and of the Young’s modulus and tensile strength values. The variations in modulus are associated with the intratube interactions, the directions of the applied forces with respect to the nanocarbon structure, the amount of disorder in the nanocarbon walls and the different test methods. However the most reliable values are Young’s modulus of ~1.0 TPa [48] and ultimate tensile strength of 120 GPa [49], which are similar to the value of monolayer graphene which is the mother of all $sp^2$ carbons [50].

<table>
<thead>
<tr>
<th>Property</th>
<th>Approaches</th>
<th>CNTs type</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>SWCNTs</td>
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<tr>
<td></td>
<td></td>
<td>DWCNTs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MWCNTs</td>
</tr>
<tr>
<td>Young’s modulus, TPa</td>
<td>Experimental observation</td>
<td>0.320-1.470</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[51, 52]</td>
</tr>
<tr>
<td></td>
<td>Theoretical prediction</td>
<td>0.73–1.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[53, 54]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.270-0.950</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[55]</td>
</tr>
<tr>
<td>Tensile strength, GPa</td>
<td>Experimental observation</td>
<td>~1000 [51]</td>
</tr>
<tr>
<td></td>
<td>Theoretical prediction</td>
<td>13 – 46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[53, 54]</td>
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<td></td>
<td></td>
<td>11– 63</td>
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<td></td>
<td></td>
<td>[55]</td>
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<tr>
<td></td>
<td></td>
<td>94.5-126.2</td>
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<td></td>
<td></td>
<td>[59]</td>
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<td></td>
<td>43 [59]</td>
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<tr>
<td></td>
<td></td>
<td>150 [60]</td>
</tr>
</tbody>
</table>

1.3.2 Thermal stability

Thermogravimetric analysis (TGA) is an effective method to evaluate the thermal stability (oxidation temperature) of carbon nanotube populations in air. It has been observed that the
oxidation temperatures for amorphous carbon contaminants, SWCNTs, and MWCNTs are typically in the range of 200 – 300 °C, 350 – 500 °C and 400–650 °C respectively. However the DWCNTs bundles and bucky papers (a thin sheet made from DWCNTs) can be stable in air in the range 500–800 °C [61-65].

In their review of thermogravimetric analysis and purity of MWCNTs, Lehman et al [66] identified five effects on thermal stability; the number of walls (diameter), the length of the tubes, the presence and composition of catalyst, the defects within the tubes, and the presence of other materials within the sample (i.e. amorphous carbon, graphitic particles).

1.4 Nanocarbon / epoxy composites

The number of applications for CNT/epoxy composites in both civilian and military applications is expanding rapidly. Since their introduction in military applications, Schrand et al [67, 68] concluded that the structural composite materials developed have included: lighter weight personnel armour; transparent armour for windows and windshields, visors, blast shields, lookdown windows, lenses, goggles, face shields; and canopies for aircraft.

Due to the outstanding physical and mechanical properties of carbon nanotubes, many scientists have endeavoured to fabricate advanced CNT composite materials that exhibit these properties. In this section, the field of carbon nanotube reinforced epoxy composites has been reviewed.

1.4.1 Epoxy resins

For thermosetting materials, epoxy resins are one of the most commercially important. Hodgkin et al [69] defined thermosetting materials as materials made by the reaction of low molecular weight monomer combinations which, with or without the application of heat, form cross-linked, extended-network structures. The chemical polymerization mechanism of epoxies is known as a step-growth mechanism whereby network formation steps occur by individual chemical reactions. Epoxy resins can be ambient-cured systems where cross-linking is achieved by the addition of a curing agent (hardener). Stoichiometric ratios are necessary for epoxy curing agents [70]. The most important commercial epoxy resins are bisphenol A based resins which are produced by the reaction of bisphenol A (diphenylolpropane) and epichlorohydrin under basic conditions [69, 70].

The curing or cross-linking of epoxy resins can be carried out by the reaction with chemically active compounds containing other active chemical groups in the molecule called curing agents or hardeners. Polyaddition can be achieved without the formation of any by-product. The curing agents or hardeners are usually multifunctional amines. The most commonly used are the aliphatic amines. The reaction sequence of these amine hardeners with the epoxy resins is often quite complex [69, 70]. The generalized reaction sequence is shown in Figure 1.3.

The tensile strength and Young’s modulus of cast epoxy resins lie in the range of 40–130 MPa and 2.0–4.1 GPa, respectively. The elongation to break lies in the 2–9 % range. Cure shrinkage is low for these resins (~1–5 %) and their specific gravity is around 1.2–1.3 [71].
1.4.2 Dispersion methods

Polymer nanocomposites are defined as an interacting mixture of a polymer matrix and a nanometre size range solid phase. Extensive research has been carried out on fabricating epoxy nanocomposites efficiently. There are different approaches to ensure the nanotubes do not aggregate and are well dispersed in order to enhance the interfacial interactions with the epoxy matrix. The methods of fabrication of epoxy / CNTs nanocomposites such as direct solution mixing, functionalization the walls of the CNTs and use of surfactant molecules have been summarized below. The direct mixing procedures consist of dispersing untreated CNTs into an epoxy resin of relatively low viscosity by mechanical mixing, magnetic agitation or sonication, followed by, adding some hardener to complete the entrapment of the CNTs in the solid epoxy polymer [72, 73]. In another method direct mixing, untreated CNTs are added first to the hardener because its viscosity is lower than the epoxy resin, followed by curing with an epoxy resin [74-76].

One can also use a volatile solvent to lower the viscosity of an epoxy resin and thus favour the dispersion of the pristine CNTs into the matrix of the composite. After evaporation of the volatile solvent, the hardener is added as a curing agent [77]. In order to improve the bonding between the walls of the CNTs and epoxy matrix, it has been suggested that the walls of the CNTs can be modified by functionalization [78], wrapping the SWCNTs with polymer [79], grafting maleic anhydride onto the MWCNTs [80] or using surfactant molecules [81] to provide an efficient load transfer mechanism between the CNTs and the epoxy matrix.

1.4.3 Mechanical properties

Good adhesion and bonding between carbon nanotubes and matrix is crucial for high performance carbon nanotube-reinforced composites. It is found in general that there are six factors that have a great influence on the mechanical properties of carbon nanotubes reinforced epoxy composites [82-89].

- Types of carbon nanotubes and their functionalization.
- Surface area combined with the aspect ratio of the nano fillers
- Stiffness and strength of the epoxy resin matrix.
- The curing cycle of the reinforced epoxy composites
- If solvent was used, the presence of residual solvent in the reinforced epoxy composites
- The procedures used for the reinforced epoxy composite fabrication
Mechanical properties are an important measure of product quality, and tensile testing and dynamic mechanical analyses (DMA) can be used to assess the performance of carbon nanotubes-reinforced composites. A mechanical testing machine is used to create the stress-strain curve which can be used to calculate yield strength, Young’s Modulus, tensile strength and total elongation. DMA is used to measure the mechanical properties (modulus or stiffness and damping) as a function of temperature and/or frequency to identify the phase changes or structural changes of the materials where the stress can be applied in different orientations [90].

![Figure 1.4](image_url)

Figure 1.4 (A) Stress–strain curve of cured pure epoxy and nanocomposites with different weight fraction of unthreaded MWCNTs [91] and (B) with different surface modification MWCNTs [92]

The DMA provides an oscillatory force to the sample, causing a sinusoidal stress to be applied in the sample, which generates a sinusoidal strain. By measuring both the amplitude of the deformation at the peak of the sine wave and the lag between the stress and strain sine waves, quantities such as modulus including storage modulus $E'(G)$ and loss modulus $E''(G)$, and the damping factor, $\tan \delta = (E''/E)$ or $(G''/G)$ can be calculated [93]. The main mechanical properties of carbon nanotubes reinforced epoxy composites such as the tensile strength, yield
strength, impact strength; Young’s modulus, shear stress, fracture toughness, and hardness have been previously studied [67, 94, 95].

Schrand et al [67] suggested that the mechanical strength and stiffness increased significantly by incorporating even a small amount of CNTs in epoxy based composites because the extremely high modulus and strength predicted for carbon nanotubes can be translated into polymer based composites. Figure 1.4(A) shows the stress–strain response under tensile loadings of cured pure epoxy and nanocomposites containing MWCNTs. The stresses increased significantly with strain until reaching a maximum. This is conventionally known as the yield point which is rather difficult to define. It should correspond to the point at which permanent plastic deformation takes place [95].

**Figure 1.5 (A) Young’s modulus of and (B) ultimate tensile strength of epoxy-based composites containing non-functionalized nanoparticles [96]**

Kim and co-workers [92] have compared the different mechanical properties of pure epoxy with surface modified MWCNTS/epoxy composites as shown in Figure 1.4(B). They found that improved tensile strength is achieved in the case of the surface modified CNT/epoxy composites and the yield strain of surface modified and untreated CNT/epoxy composites are
higher than the neat epoxy resin. Gojny et al [96, 97] investigated epoxy nanocomposites consisting of different types of CNTs; SWCNTs, DWCNTs, MWCNTs or carbon black (CB) made by a standard three-roll calendaring technique. The authors found a linear increase of strength and Young’s modulus for CNTs/epoxy composites with a different maximum peak value of 2812 MPa at 0.3 wt%, 2885 MPa (+11%) at 0.3 wt%, and 2780 MPa at 0.1 wt% of SWCNTs, DWCNTs and SWCNTs respectively that decreased for higher MWCNTs loadings due to an increasing amount of agglomerates present in the cured composites as shown in Figure 1.5.

1.4.4 Fracture surface studies

In recent years, fracture surface studies have been used to give information about the failure behaviour and the interfacial bonding properties of nanocomposites. Researchers [94, 98] observed the fracture surface of the MWCNTS/epoxy composites after conducting tensile tests by using scanning electron microscopy (SEM). As shown in Figure 1.6(A), the untreated MWCNTs are dispersed poorly and are pulled out because they have weak interfacial bonding with the polymer matrix.

Figure 1.6 SEM images of the fracture surface of (A) 1 wt% of untreated MWCNTs/epoxy, (B) magnification (60,000X) of agglomerate shown in (A); (C) 3 wt% of untreated MWCNTs/epoxy, and (D) magnification (15,000X) of pull-out on fracture surface of 3 wt% untreated MWCNTs/epoxy [94, 98]

1.5 Raman spectroscopy

Vibrational spectroscopy involves two different, yet complementary spectroscopic techniques: Raman spectroscopy and infrared (IR). Raman spectral analysis has come of age as a method of analytical diagnostics dealing with measurement of radiation scattered from solid, liquid, or gaseous samples. The low intensity of Raman scattered radiation generally requires the use of lasers as a source of excitation. An attempt will now be made using the classical treatment of light scattering to describe the existence of the effect. The quantum-mechanical view of light
scattering is also covered in order to correct for the limitations of classical mechanisms in predicting Raman scattering intensities.

### 1.5.1 The classical approach

Through the classical approach of light scattering, the Raman effect is related to the interaction between an electric field of a monochromatic light (polarized electromagnetic radiation) and a molecule which is induced by the high energy incident beam. The amplitude of the electric field $E_x$ which has a frequency $v_o$ at any time ($t$) as [99]:

$$E_x(t) = E_x^0 \cos (2\pi v_o t) \quad (1.1)$$

The normal vibration vector ($q_{vib}$) for a diatomic molecule can be expressed as a function of time as:

$$q_{vib}(t) = q_{vib}^0 \cos (2\pi v_{vib} t) \quad (1.2)$$

where $q_{vib}(t)$ = the maximum vibrations of a diatomic molecule about the equilibrium position

When the electromagnetic wave (the monochromatic light) interacts with the electric charges in the molecule, it induces a dipole moment $\mu (t)$ where the nuclei are attracted by a negative pole and the electrons are moving to the positive pole. The dipole moment is proportional to the amplitude of the electric field $E_x$ and can be described by Equation 1.3 where $\alpha$ is known as the polarizability tensor of the molecule

$$\mu (t) = \alpha E_x(t) \quad (1.3)$$

The polarizability describes the chemical structure and composition of the molecule. The induced dipole will oscillate which radiates light (the scattered light) with different frequency components of the dipole oscillation. The polarizability may be approximated by a Taylor series expansion to obtain all frequency components of the dipole oscillation of the scattered light where $\alpha_o$ is the polarizability of the molecular mode at equilibrium position [100]

$$\alpha = \alpha_o + \frac{d\alpha}{dq_{vib}} q_{vib}(t) \quad (1.4)$$

Based on the vibrational displacement of Equation (1.3), the induced dipole moment $\mu (t)$ may be given as

$$\mu (t) = \alpha_o E_x^0 \cos (2\pi v_o t) + \left(\frac{d\alpha}{dq_{vib}} q_{vib}^0 \frac{E_x^0}{2}\right) \cos (2\pi (v_o - v_{vib}) t) + \cos (2\pi (v_o + v_{vib}) t) \quad (1.5)$$

The above Equation reveals that induced dipole moments are created at three distinct frequencies, namely $v_o, (v_o - v_{vib}),$ and $(v_o + v_{vib}),$ which results in scattered radiation at these same three frequencies. The first scattered frequency corresponds to the incident frequency, hence is elastic scattering (Rayleigh), while the latter two frequencies are shifted to lower or higher frequencies and are therefore inelastic processes [101]. The scattered light in
these latter two cases is referred to as Raman scattering, with the down-shifted frequency (longer wavelength) referred to as Stokes scattering, and the up-shifted frequency (shorter wavelength) referred to as anti-Stokes scattering [99].

1.5.2 The quantum mechanical approach

When a light wave (high energy photons) interacts over a molecule and distorts the cloud of electrons round the nuclei, the energy is released in the form of scattered radiation. The properties of the scattered radiation are different from the incident beam. The quantization of molecular vibrational energy levels is taken into account to be able to calculate the polarizability $\alpha$, and thus Raman intensities, in terms of the electronic properties of a molecule [102]. For the vibrational energy $E_{vib}$ of a diatomic molecule, it is a good approximation to write:

$$E_{vib} = (n + 1/2)\hbar\nu_{vib} \quad n = 0,1,2, \ldots \ldots$$

(1.6)

where the vibrational quantum number $n$ has only integral values, so the vibrational energy levels in the ground state in Figure 1.7 are equally spaced by the amount $\hbar\nu_{vib}$.

First, there is the possibility the excited molecule descends back to its original ground energy state where no change in frequency of the photon occurs. The scattering process will be the elastic scattering known as Rayleigh scattering. Secondly, a Stokes process has occurred where the second photon has a frequency $(\nu_0 - \nu_{vib})$ corresponding to the third term in Equation (1.5) of the discussion of the classic approach for the Raman effect. Thirdly, an anti-Stokes process results from the transition terminating at a vibrational energy level lower than the starting level which has a frequency $(\nu_0 + \nu_{vib})$ giving the same result as the second term in Equation (1.5). The abscissa of Raman spectrum is the wavenumber shift, which is defined as the difference in wavenumbers (cm$^{-1}$) between the observed radiation and that of the source. In practice this means that the weak anti-Stokes scattering is usually ignored in conventional Raman spectroscopy and only the Stokes spectrum is recorded.

![Figure 1.7 Mechanisms of various light-scattering processes, Rayleigh and non-resonance Raman (Stokes scattering, anti-Stokes scattering) where $\nu$ is the scattering photon frequency [99].](image)
1.5.3 Raman spectroscopy instrumentation

Generally speaking, a Raman microscope consists of five main parts: an excitation light source, an optical microscope, a spectrometer, a detector, and a data acquisition unit [103]. As shown in Figure 1.8, there are four paths in the grating spectrum capture, the laser light path only, the laser and Raman light path, the Raman light path only and capturing the data.

In the laser light path only (solid blue lines), the laser enters the spectrometer via a delivery optics tube containing an alignment mirror and the laser attenuation filter wheel and the required filter can be placed into the laser beam before it enters the system unit enclosure. A mirror aligns the laser light through a fixed objective lens and converges the beam into a 10 μm pinhole to ensure that the profile of intensity across the beam is as uniform as possible. The laser is collimated into parallel beams by a second movable objective lens. The laser beam is reflected by two mirrors onto the holographic notch filter [103].

In the laser and Raman light path (solid red lines), the angle of the holographic notch filter is sited up to reflect the laser beam out of the spectrometer into the optical path of the microscope.

Figure 1.8 The schematic illustration of a Raman optical system main assemblies [103]

A mirror is located in the microscope to reflect the laser beam down through the microscope objective lens to illuminate the sample on the mechanical stage. Then, below the mirror is a beamsplitter, which allows the sample to be illuminated with the white light. On the return path, the Rayleigh light is almost totally removed from the 180° backscattered light (Raman and Rayleigh) passing back through the microscope by the set of holographic filters. Notch filters will enable the collection of both Stokes (emission of phonons) and anti-Stokes (adsorption of phonons) Raman lines, while edge filters will allow collection of the Stokes Raman lines only [103].

In the Raman light path only (solid green lines), the Raman light comes out from the set of holographic filters, passes through a lens and is focused on to the slit assembly. Raman light is then recollimated through a lens and reflected off the input side of the prism mirror onto a diffraction grating. The grating disperses the incident light, and some of this light is reflected off the output face of the mirror into the focusing lens and onto the detector [103].
Finally in capturing the data, when light falls on the charge-coupled device (CCD) camera array, each pixel will have a certain charge generated in it, depending on the intensity of the light that fell upon it. If the light falling onto the CCD is dispersed, so that each pixel has a different wavelength irradiating it, the amount of charge from all illuminated columns in each row of pixels on the CCD array may be added together and plotted as a histogram of intensity versus row number, then calibrated to give spectrum, so each row can be assigned an equivalent wavenumber [103].

1.6 Raman studies of nanocarbons

1.6.1 Introduction

Raman Spectroscopy is a non-destructive and readily available tool used to characterize the lattice dynamics and vibrational spectroscopy of the carbon materials (graphite and related $sp^2$ carbon materials). In their review of applications of Raman spectroscopy in carbon nanotubes-based polymer composites, Yun et al [104] identified four characteristics of analysis of carbon nanotubes by Raman spectroscopy, including characterizing the crystallinity (the degree of graphitization), evaluating the diameter distribution of carbon nanotubes, determining the structure of nanotubes and determining the orientation of nanotubes within nanotube bundles.

Figures 1.9 (A), (B) and (C) show a typical Raman spectra using 633 nm (1.96 eV) laser excitation from 100 to 3000 cm$^{-1}$ taken from SWCNTs, DWCNTs respectively, but for MWCNTs in the range from 1000 to 3000 cm$^{-1}$.

The Raman spectra of SWCNTs, DWCNTs, and MWCNTs typically shows four Raman active modes: the radial breathing mode at low frequency below 400 cm$^{-1}$, the D band at 1250–1450 cm$^{-1}$, the G band at 1500–1605 cm$^{-1}$ and the G′ band at 2500–2700 cm$^{-1}$. Radial breathing modes are not present in MWCNTs. Each mode corresponds to the different vibration modes associated with the structure of CNTs [105-109].

1.6.2 Radial breathing modes (RBM)

The low energy modes (RBM) are the main features of a Raman spectrum of SWCNTs and DWCNTs and only occur in carbon nanotubes. RBMs are typically observed at Raman shifts less than 300 cm$^{-1}$ for SWCNTs [110]. For DWCNTs the low frequency ranges 400-200 cm$^{-1}$ and 200-100 cm$^{-1}$ have been observed for inner and outer tubes, respectively [111-113]. Their observation in the Raman spectrum provides direct evidence that a sample contains SWCNTs or/and DWCNTs. The Raman spectra of MWCNTs show no low frequency modes.

As shown in Figure 1.10, RBMs are first-order Raman processes and give an elastically scattered laser line resulting from radial vibrations of the carbon atoms (radial breathing mode of the tube) [110, 113]. In their analysis of Raman spectroscopy of carbon nanotubes, Dresselhaus et al [113] identified two characteristics of the RBM frequency. It is inversely proportional to the tube diameter (estimate the diameter distribution), and the $(n, m)$ chirality value of specific SWCNTs (semiconducting or metallic) can be assigned from actual Raman measurements using the Kataura plot.
Figure 1.9 Raman spectra of CNTs in the range 1000–3000 cm$^{-1}$ using 633 nm (1.96 eV) laser excitation; (A) HiPco SWCNTs [105], (B) DWCNTs (CVD) [106, 107] and MWCNTs [109].

Figure 1.10 The schematic representation of the radial breathing mode (RBM) mode for a zigzag SWNT (14, 0). All ball colours represent the C atoms according to the carbon-depth distribution in a carbon nanotube. Blue arrows represent the radial vibrations of the C atoms.

The RBM frequencies of SWCNTs-HiPco and of DWCNTs grown by CVD and by C$_{60}$ filled SWNT are compared in Figure 1.11 [10, 114]. Several studies [10, 106, 114] investigating the RBM modes have been carried out on DWCNTs grown by CVD or on C$_{60}$ filled SWCNTs at different $E_{\text{激光}}$ excitations. It was found that the RBM frequency for the outer tubes varied along with RBM frequency for the inner tubes and the interlayer distance of the DWCNTs varied from...
0.34 to 0.42 nm which could be calculated from radial breathing modes (RBM). The Kataura plot and the RBM frequency can be used to identify the type of the tube (semiconducting or metallic) [115, 116].

In general, the radial breathing modes of SWCNTs are not found in the vibrational modes of MWCNTs because the intensity of the modes vanishes when the inner diameter exceeds 2 nm [113, 114]. However, they have been observed in thin MWCNTs with inner tube diameters less than or equal to 2 nm [117] which could be related to the RBMs of the innermost tubes or could be due to the presence of iron catalyst (Fe₂O₃) encapsulated within the MWCNTs [118].

The relationship between the features of the RBM (ν) and SWCNTs structure and properties has been investigated widely. The Raman shift of the RBM (ν) is associated with the specific vibration of tube diameter by which the diameter of nanotubes can be easily estimated. The tube diameter (d) of SWCNTs bundles was reported to have the relationship with (ν): [110, 119]

$$\nu(cm^{-1}) = \frac{223.75}{d} + 14 \quad (1.7)$$

However, the tube diameter (d) of isolated individual SWCNTs was reported to have the relationships: [110, 120, 121]

$$\nu(cm^{-1}) = \frac{248}{d} \quad (1.8)$$

Or

$$\nu(cm^{-1}) = \frac{(214.4\pm2)}{d} + (18.7 \pm 2) \quad (1.9)$$

![Diagram showing RBM of SWCNTs and DWCNTs bundles](image)

Figure 1.11 The RBM of (A) the SWCNTs – HiPco bundle at excitation wavelength of 1.96 eV (633 nm) and (B) the DWCNTs bundle made from CVD and the DWCNTs bundle made from peapods at excitation wavelength of 2.31 eV (520 nm), S and M symbolizes to semiconducting and metallic respectively [10, 114]

The difference in Raman shift of the RBMs (ν) may be due to tube-tube interactions within a tube bundle, individual tubes wrapped in a surfactant, or isolated on a substrate surface. The shape and intensity of the RBM features changes with the variation of laser energy. Also the
intensity of RBM vibrational frequencies is proportional to the number of nanotubes [122]. The diameter of a nanotube can be calculated from its \((n, m)\) indices as follows [14, 123]:

\[
d(nm) = \frac{0.246}{\pi} \sqrt{n^2 + nm + m^2}
\] (1.10)

The chiral angle determined by the value of \(n\) and \(m\) indices as follows [123]

\[
\theta = \tan^{-1}\left(\sqrt{3} \left(\frac{n}{2m+n}\right)\right)
\] (1.11)

The determination of the \((n, m)\) indices relies on the measurements of the diameter and electronic transition energies \(E_{ii}\). In practice, such a tunable Raman system has been applied to the determination of the \((n, m)\) indices for a single nanotube. A Kataura plot [115] relates the \((n, m)\) indices and band gap energies as shown in Figure 1.12. The horizontal lines denote the laser photon energies. It is easy to know that the crossing of these lines with the inter-band energy bands defines the resonant Raman scattering windows for the relative carbon nanotubes.

![Figure 1.12 RBM wavenumber and chirality dependence of the interband energy \(E_{ii}\) between the \(i^{th}\) van Hove singularities for SWCNTs based on the extended tight binding model. The horizontal lines mark the \(E_{laser}\) regions where Raman spectra were acquired in 5 nm intervals. In the contour Raman maps the red (blue) colour corresponds to regions of maximum (minimum) Raman intensity in arbitrary units [115, 116]](image)

1.6.3 D-band

The D band is due to a second-order process which implies there is a defect-induced double resonance peak that arises from a resonant coupling of inelastic scattering by a phonon with elastic scattering associated with the defects in the graphitic material (carbon impurities and/or the defect of CNTs themselves) [124]. The D band frequency of the CNTs appears between 1250 and 1450 cm\(^{-1}\) and is therefore induced by defects in the nanotubes [104]. The D-band has been observed in both metallic and semiconducting SWNT Raman spectra between 1250 and 1450 cm\(^{-1}\) [110]. Wei et al [106] performed a series of Raman spectroscopy experiments to
find the D-band locations of DWCNTs. They found that the locations of D-band of the DWCNTs were 1301, 1311 and 1332 cm$^{-1}$ for $E_{\text{laser}}$ (785 nm) 1.58, (633 nm) 1.96 and (514 nm) 2.41 eV, respectively.

There was a downshift of D-band associated with the excited laser energy and the D-band was found to be a broad peak. Its peak frequency shifted to higher wavenumber values with increasing laser excitation energy by about 53 cm$^{-1}$/ eV (highly dispersive) and was affected by the nanotube diameter [124].

The dispersive behaviour of the D band comes from the coupled resonance between the excited electrons and the scattered phonons [125]. However, its intensity and line-width (Full width at half maximum of a peak, FWHM) are also found to be a function of the degree of the disorder of the graphitic material. Generally, the band intensity ratio in the first-order region $(I_D/I_G)$ is widely used to evaluate the degree of graphitization of the CNTs and the degree of functionalized nanotubes modified through covalent bonds [104]. It has been observed that $I_D/I_G$ intensities decrease with increasing crystallinity of the CNTs.

1.6.4 G-band (tangential modes)

The G band is a first-order Raman and multi-feature mode that is composed of several peaks with features around 1580 cm$^{-1}$. As shown in Figure 1.13, the G band splits into two main features, the higher energy component (G$^+$) and the lower energy component (G$^-$) observed due to in-plane vibrations along the tube axis and along the circumferential direction, respectively. However, the latter one for metallic nanotubes does not have a symmetric lineshape and can be fitted to a so-called Breit–Wigner–Fano (BWF) lineshape. for semiconducting nanotubes a narrow Lorentzian peak can be applied. In their analysis of Raman spectroscopy of carbon nanotubes, Dresselhaus et al [113] stated that the G-band frequency can be used for diameter characterization [126], and to distinguish between metallic and semiconducting SWCNTs through strong differences in their Raman lineshapes and to probe the charge transfer arising from doping a SWNT.

Jorio et al [127] stated that the position of the lower energy component, the G$^-$ ($v_{G^-}$) shows a clear diameter dependence whereas the higher energy component G$^+$ is almost independent of diameter. The wavenumber of the G$^-$ ($v_{G^-}$) mode decreases with decreasing tube radius.

$$(v_{G^-}) = (v_{G^+}) - \frac{C}{d^2}$$

with $C = C_S = 47.7$ cm$^{-1}$ nm$^2$ for semiconducting SWCNTs

with $C = C_M = 79.5$ cm$^{-1}$ nm$^2$ for metallic SWCNTs

Bandow et al [128] studied G-band of DWCNTs of by Raman scattering using different excitation wavelengths and their spectra compared to those of SWCNTs and C$_{60}$-SWNT peapods. They found that the frequency of the tangential displacement vibrational modes identified with these interior tubes was found to be downshifted by ~7 cm$^{-1}$ relative to that of the larger tubes. Typical Raman spectra of SWCNTs and DWCNTs in the range 1700-1200 cm$^{-1}$ are shown in Figure 1.14 [129].
It is apparent that the Raman spectrum of the DWCNTs has to be very similar and comparable to that of SWCNTs because of their small diameters. However, the G-band of the DWCNTs is broader than that of SWCNTs. It has been revealed that the G-band mode splitting decreases with increasing outer-tube diameter [129].

For large diameter MWCNTs, the tangential G-band of MWCNTs shows a peak appearing close to the graphite frequency of 1582 cm$^{-1}$. The G-band is derived from the in-plane vibration of the C=C bond and has a shoulder around 1604 cm$^{-1}$ which is a typical of defective graphite-like materials (D’-band).

### 1.6.5 G’-Band (2D-band)

In general, the G’ Raman features of all sp$^2$ carbon materials are believed to possess similar properties and is a second-order two-phonon process, as well as a D-band overtone (2D). For a two-phonon Stokes process, the elastic scattering process denoted in D-band is changed to an inelastic phonon emission process [130].

![Image](image.png)

**Figure 1.13** Schematic representations of the G-band mode for a zigzag SWCNTs (14,0). All colours represent the C atoms according to the carbon-depth distribution in a carbon nanotube. The carbon atom vibrations along the nanotube axis and vibrations of carbon atoms along the circumferential direction of the SWNT represented by black and blue arrows respectively.

The frequency of the second-order feature G’, however, was reported to range between 2500 and 2900 cm$^{-1}$, due to dispersion effects. Also it is the second-order overtone of the D band [131]. The frequency of the G’ linear dependence on the excitation laser energy ($E_{\text{Laser}}$ in eV) can be fitted to the Equation 1.13 [113]

$$v_{G'}(\text{cm}^{-1}) = 2420 + 106E_{\text{Laser}}$$  \hspace{1cm} (1.13)

However most SWCNTs have a single Lorentzian peak for G’-band, but there are some special isolated SWCNTs [132] and solubilised SWCNTs [133] that exhibit two peaks due to different processes.
Figure 1.14 Raman scattering spectra for the tangential mode region and D-band using a 633 nm excitation wavelength for (A) DWCNTs and (B) SWCNTs [129]

It was hypothesized [134] that the annealing of the bundled SWCNTs would lead to the disappearance of the lower frequency side of the G'-band, which is related to the presence of defects in the carbon nanotube structure and it. Additionally the G'-band can be used for differentiating between SWCNTs, DWCNTs and MWCNTs. The Raman G'-band is a sensitive and suitable tool to characterize doping (to monitor structural modifications of the nanotube sidewalls) and strains in SWCNTs [135], DWCNTs and MWCNTs.

Figure 1.15 Comparison of Raman scattering spectra for the G'-mode region for SWNT, C60 (peapods) and DWCNTs made from peapods using a 488 nm (2.540 eV) excitation wavelength [136]

In their work, as shown in Figure 1.15, Pfeiffer et al [136] demonstrated that the Voigtian fitted line of G’ band spectrum for DWCNTs made from peapods can be decomposed into two
peaks depending on the excitation energy and on the nanotubes that are in resonance with the excitation laser. They found that the line positions of the inner and the outer tubes are at 2640 and 2697 cm\(^{-1}\), respectively. The presence of these different peaks was recently attributed to the interaction between the inner and outer tubes, in analogy to double-layer graphene [136].

It has been demonstrated that the IG'/IG ratio increases for increasing crystallinity which is sensitive to doping and disorder [137, 138]. It has been emphasised that the diameter dependence of the most important phonons observed in the Raman spectra \(v_{G'}\) of isolated single-wall carbon nanotubes can be given by [138]

\[
v_{G'}(\text{cm}^{-1}) = v_{G'}^{0}(\text{cm}^{-1}) + C/d \tag{1.14}
\]

where \(v_{G'}\) the frequency of the G'-band, \(C\) is a constant, < 0 and \(d\) is the diameter of the nanotubes.

### 1.7 Stress transfer Raman studies in nanocarbon/epoxy composites

The stress transfer between the matrix and filler (reinforcing phase) controls the mechanical behaviour of composites. In this respect several studies have been carried out using Raman spectroscopy for evaluating and probing graphitic materials/matrix interactions in composites and investigating the strain or stress transferred to the graphitic materials from the matrix. Similarly carbon fibres and their composites have been probed by Raman spectroscopy in order to study the efficiency of the interfacial stress transfer [139, 140], the stiffness and the toughness [141] and residual stresses [142].

The deformation of carbon fibres in air, in a thermoplastic matrix, and in thermosetting matrix has been followed by Raman microscopy [141-143]. The authors have demonstrated the relationship between the structure and mechanical properties of both polyacrylonitrile (PAN) and pitch-based carbon fibres and they also found that the shift rate for the Raman band was proportional to the fibre modulus. Thereafter they determined the universal band shift calibration of \(-.5 \text{ cm}^{-1}/\text{GPa}\) from the slope of the line fitting of dependence of Raman band shift rate upon tensile modulus for P55, P75, P100 and P120 carbon fibres. This universal band shift has allowed the effective modulus of the nanotubes to be determined.

The features of the G'-band (intensity, FWHM and frequency) in the composites depend on many factors such as the kind of CNTs and their quality, the excitation laser energy \(E_{\text{laser}}\) and the on the dispersion of CNTs in a composite matrix. It is being highly sensitive to stress during deformation of the composites. During the application of tension in two different (0.1 wt %) SWCNTs/epoxy composites Cooper et al [144] monitored the G'(2D)-band of SWCNTs using an excitation frequency of 633 nm. They found that the G'-Raman peak position moved to a significantly lower (about \(-13 \text{ cm}^{-1}/\% \text{ strain}\)) wavenumber with tensile strain due to stress transfer to the nanotubes from the surrounding epoxy matrix.

Detailed examination of G'-Raman peak position of SWCNTs using an excitation frequency of 633 nm by Kao et al [145] showed that the band shift of the G'-Raman peak position for a cold-cured system (room temperature for 7 days) was found to be about \(-6 \text{ cm}^{-1}/\% \text{ strain}\) and for a hot-cured system (100 °C for 2h) about \(-6.8 \text{ cm}^{-1}/\% \text{ strain}\). They also found that for both
systems the G'-Raman peak shift plateaus when either the compressive or tensile strain reached a critical value. As shown in Figure 1.16, Cui et al [146] showed the shift of the peak position, from the SWCNTs embedded in a similar epoxy resin composite to a significantly lower level at about -12.7 cm\(^{-1}\) /% strain under tensile strain.

![Figure 1.16 Shift of the Raman G' bands shifts with tension and compression strain for SWCNTs/epoxy composites [146]](image)

Under a 1 % tensile strain in MWCNTs/epoxy composites, Cooper et al [144] observed that the G' band peak was shifted downwards by smaller amount compared to SWCNTs/epoxy composites. The low shift is attributed to either lower stiffness or to poor dispersion of the tubes in the epoxy matrix. Cui et al [146] monitored the position of the two components of the G' band monitored as a function of strain of DWCNTs made from peapods/epoxy composite in both tension and compression in the region +0.5 % to -0.5 % strain. They found that there was little shift of the lower frequency G'\(_1\) band component over the entire strain range but an approximately linear shift at the higher-frequency G'\(_2\) band component from the outer walls.

They also found a plateau of the band shift was reached at higher tensile and lower compression strain levels. They suggested that in DWCNTs/epoxy composites stress transfer takes place from the matrix to the outer wall of the nanotubes, but there is little stress transfer between the outer and inner walls. Also they use the stress-induced shift of the inner and outer wall to predict of the efficiency of internal stress transfer \(k_{i\text{in}}\) in the DWCNTS/epoxy composites.

Furthermore, In their review of Raman spectroscopy of strained SWCNTs [147], they identify the uniaxial strain as one of the major causes of intensity variation of the RBMs-band. The resonance condition (therefore the intensity) is affected by the uniaxial strain which shifts the electron transition energy \((E_{ii})\) closer or away from the laser excitation energy \((E_{\text{laser}})\). The variations the intensity of the RBM-bands of SWCNTs in SWCNTs/epoxy composites induced by axial deformation has been investigated [147, 148].
1.8 Conclusions

This chapter has explained the central importance of Raman studies to follow stress transfer in CNT (SWCNTs, DWCNTs and MWCNTs)/epoxy composites. Also this chapter has investigated nanotubes synthesis and characterization the mechanical properties and thermal stability of CNTs. Raman theoretical approaches (classical and quantum mechanical) have also been presented. The disperse approaches used to CNTs in epoxy composites, the mechanical properties of the epoxy composites and the fracture surfaces of the composites have been reviewed. Moreover this chapter has given an account of, and the reasons for the widespread use, of Raman spectroscopy in characterizing the morphology and the interaction of the CNT with the epoxy matrix in composites.

The most obvious finding to emerge from this chapter is that there are essentially three key components required for nanotube synthesis: a source of carbon, a source of heat and the presence of metallic catalyst particles. The key parameters for a successful synthesis method of CNT are the starting materials and the carbon deposition reaction (temperature, pressure, flow rate of the gases, etc). In addition, the diffusion of the carbon through the metal surface is the rate-determining step in the formation of CNTs. Decreasing the catalyst particle sizes and stabilizing at high temperature leads to MWCNTs being obtained preferentially to nanofibers and SWCNTs and/or DWCNTs preferentially to MWCNTs. It has been observed that the outermost diameters of SWCNTs, DWCNTs and MWCNTs are 0.6-1.3 nm, 1.5-6 nm, and 10-100 nm respectively.

One of the more significant findings to emerge from this chapter is that the most reliable mechanical property values are Young's modulus of ~1.0 TPa and ultimate tensile strength of 120 GPa because these are the values of monolayer graphene, which is the mother of all $sp^2$ carbons. According to TGA, the thermal stabilities of the CNTs are enhanced when increasing the number of walls (diameter). The Raman active mode features of CNTs are RBM, the D-band (the disorder-induced band), The G-band (graphitic tangential modes) and the G'-band (2D-band). However, RBMs were observed only in CNTs with inner tube diameters less than or equal to 2 nm.

This literature review shows that the methods of fabrication of CNTs/epoxy nanocomposites have a direct effect on the prospective mechanical properties. The agglomeration and the dispersation of CNTs are the major reasons that lead to differences in both modulus and strength of the CNTs/epoxy nanocomposite systems. How Raman scattering arises and the selection rules that govern the capture of Raman spectra have also been discussed.

Conventional mechanical testing (tensile test and DMA) is normally used as a tool to clarify the reinforcing ability of CNTs in an epoxy matrix, Raman spectroscopy has been employed to follow the stress induced changes in the Raman spectrum of CNTs (frequency, intensity and FWHM) and assess the stress transfer between the CNTs and the epoxy matrix, as well as, the inter-tube interactions.

The objectives and aims for the research which have been designed to answer certain gaps in the knowledge, has three major aspects; synthesis and characterization of MWCNTs, and the
synthesis, characterization and mechanical testing of epoxy-based composite reinforced with single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multiwall carbon nanotubes (MWCNTs) with different nanotube concentrations. The efficiency of stress transfer in such systems was followed using Raman spectroscopy which allows a signal to be obtained from the reinforcement without interference from the polymer matrix.
2 Chapter Two: Research methodology

2.1 General

In the present work, different types of nanocarbons were used; SWCNTs (HiPco) purchased from Carbon Nanotechnologies, Inc., of Houston, DWCNTs supplied by Toray Industries, Inc, and MWCNTs which were grown by injection catalytic chemical vapour deposition (CVD). The CNTs were then dispersed homogeneously in an epoxy matrix to produce composites. The structure of nanocarbons was determined by Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The stress induced changes in Raman spectra of nanocarbons in nanocarbons/ epoxy composites were investigated. Furthermore the evaluations of the influence of different weight concentration of MWCNTs on the mechanical and thermo-mechanical properties were also studied. It is important to note that all the experimental errors presented are the standard deviations.

2.2 Materials

Table 2.1 illustrates some of the main characteristics of the materials used in the synthesis of MWCNTs, and preparation of epoxy nanocomposites. Besides characteristics of the other CNTs

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Source</th>
<th>Dynamic viscosity mPa·s</th>
<th>Density $\rho$ g/cm$^3$ 25°C</th>
<th>Melting point °C</th>
<th>Boiling point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs (HiPco)</td>
<td>Black powder</td>
<td>Carbon Nanotechnologies, Inc., of Houston</td>
<td>Not applicable</td>
<td>1.45 [149]</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>DWCNTs (Lot T1101N)</td>
<td>Black powder</td>
<td>Toray Industries, Inc.</td>
<td>Not applicable</td>
<td>1.55 Calculated</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>MWCNTs (Nanocyl NC7000)</td>
<td>Black Powder</td>
<td>Nanocyl sa, Belgium</td>
<td>Not applicable</td>
<td>0.06 (Bulk)</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>MWCNTs (Aldrich 724769)</td>
<td>Black Powder</td>
<td>Sigma-Aldrich, Co.</td>
<td>Not applicable</td>
<td>0.20 (Bulk)</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Toluene</td>
<td>Colourless liquid</td>
<td>Fisher Scientific</td>
<td>0.6</td>
<td>0.87</td>
<td>-95</td>
<td>110-111</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>Colourless liquid</td>
<td>Sigma-Aldrich, UK</td>
<td>1.200</td>
<td>0.789</td>
<td>-114.3</td>
<td>78.4</td>
</tr>
<tr>
<td>Ferrocene</td>
<td>Light orange powder</td>
<td>Sigma-Aldrich, UK</td>
<td>1.490</td>
<td>172-174</td>
<td>249</td>
<td></td>
</tr>
<tr>
<td>Resin (Araldite-LY 5052)</td>
<td>Clear liquid</td>
<td>Huntsman Advanced Materials (Europe)</td>
<td>1000 -1500</td>
<td>1.16 - 1.18</td>
<td>Not applicable</td>
<td>&gt;200</td>
</tr>
<tr>
<td>Hardener (Aradur-5052 CH)</td>
<td>Clear liquid</td>
<td></td>
<td>40 - 60</td>
<td>0.93 - 0.95</td>
<td>Not applicable</td>
<td>135</td>
</tr>
</tbody>
</table>
2.3 Preparation of multiwall carbon nanotubes (MWCNTs) and their epoxy composites

2.3.1 Preparation of multiwall nanotubes (MWCNTs)

The synthesis of MWCNTs were synthesized according to the procedure given by Singh et al [150]. As shown Figure 2.1, a two stage furnace was used in the synthesis of MWCNTs, by the pyrolysis of toluene mixtures with ferrocene as the catalyst precursor in an Argon gas atmosphere. The temperatures of the first stage and the second stage of the furnace were controlled by a digital temperature controller CAL3200 and a eurotherm type 3126CC programmer, respectively. The preheating temperature was set to 200°C to vaporize the hydrocarbon and sublimate the catalyst. The reaction conditions were maintained at temperature of 760°C and 100 ml/min flow rate of argon gas. The flow rates of argon carrier gas (Pureshield Argon, The BOC Group plc, UK) were controlled by gas flow meters (Influx Measurements Ltd, UK- flow range 40 - 660 cm³/min).

The growth of MWCNTs was carried out on the interior surface of a bespoke silica quartz tubular reactor (Cambridge Glassblowing Ltd, UK, ≥ 95 % SiO₂, ID = 23 mm, OD = 25 mm and L-reactor = 700 mm) placed inside a horizontal electric furnace (Lenton thermal designs, UK-Model LFT 12/38/500). A glass syringe (SGE Analytical Science Pty Ltd, UK- Volume 10ml, ID 14.5mm), and programmable AL1000 syringe pump (World Precision Instruments, USA) were used to inject the mixtures of toluene and ferrocene. All experiments were conducted at atmospheric pressure.

The carrier gas (argon) was purged through to the two stage furnace using a flow rate of 300 ml/min for 5 min. The reaction time varied between 0.5-4 h for feedstock screening studies. A solution of ferrocene (5 wt% in toluene) was injected from a SGE syringe in to the first stage furnace (the preheater) at 0.04 ml/min by the programmable syringe pump. After completion of the hydrocarbon deposition process, the reactor was cooled down to ambient temperature in an argon gas medium for 12 h. The grown MWCNTs were collected from the interior surface of a tubular quartz reactor using a razor blade (10 cm length) which was mounted on one of the two sides of a wooden handle (~90 cm length). The tubular quartz reactors were weighed before and after each reaction to determine the yield collected from their walls. Following this, the samples were recovered and stored in glass jars in regular air-flow fume cupboards.

2.3.2 Preparation of nanocarbon / epoxy composites

2.3.2.1 Description of the process

The matrix system used in this study was low viscosity epoxy resin which supplied by Huntsman Co. It consists of Araldite LY5052 as an epoxy phenol novolak resin and Aradur 5052 CH as a liquid polyamine hardener with a weight mixing ratio of 100:38 respectively. The MWCNTs were used as made and the SWCNTs, DWCNTs and graphene as received.

An extensive mixing procedure was used to ensure good dispersion of the CNTs: CNTs were suspended in ethanol (17g) using an ultrasonic bath (VWR International Ltd, USC100TH , 30 W,
45 kHz) for 1.5 h. Then the resin (LY5052) (100 parts by weight, 100 g) of were added to the mixture, which was sonicated for a further 4 h.

For homogenization, the mixture was stirred at room temperature using a mechanical overhead stirrer (VWR International Ltd, SS10, 100 rpm) for two days, followed by sonication in the bath for 8 h. In order to remove ethanol residues, the mixture was mechanically stirred (100 rpm, 85°C) then at 50°C for 7 h and 12 h respectively. For de-gassing, the mixture was left in a thermostat vacuum oven (Townson and Mercer Ltd) at 70 °C for 30 min.

![Diagram](image.png)

Figure 2.1 View of the laboratory production of multiwalled carbon nanotubes by the ferrocene catalyzed pyrolysis of toluene

The hardener (HY5052) (38 parts by weight, 38 g) were added, after the mixture was cooled to room temperature, and mechanically stirred for 10 min. The mixture was put into a vacuum oven to de-gas for a further 15 min. For Raman testing and DMA, samples were prepared by carefully casting the mixture into a stainless steel square mould (160 x 160 x 5 mm) as shown in Figure 2.2. The tensile testing samples were cast into a polytetrafluoroethylene (Teflon, PTFE) mould, as shown in Figure 2.3.

After the prepared nanocomposites were cured at 100 °C for 2 h, they were removed immediately from the oven and left to cool at room temperature. For Raman investigations and thermo-mechanical measurements the nanocomposite samples were cut into rectangular specimens using a band-saw cutting machine (10-14 teeth pitch, 50 m/min). The nanocomposite samples were prepared with varying concentrations of MWCNTs i.e. 0.1, 0.2,
0.5 and 1.0 wt%, and for comparative purposes, the concentrations of SWCNTs and DWCNTs were 0.1 wt%.

2.4 Characterization of nanocarbon and nanocarbon / epoxy composites

2.4.1 Raman spectroscopy

2.4.1.1 Raman Scattering of Nanocarbons and their epoxy nanocomposites

The Raman spectra of the nanocarbon powders, neat epoxy resin and nanocarbon/epoxy nanocomposites were observed at room temperature using a Renishaw Raman imaging microscope system 1000 grating lightpath with Olympus BHM microscope. A notch (Rayleigh line rejection) filter with a limit of 100 cm\(^{-1}\) was used. Excitation frequencies of 830 nm (1.49 eV), 780 nm (1.59 eV), 632.8 nm (1.96 eV), and 514 nm (2.41 eV) polarized laser excitation lines and a back-scattering geometry were used to collect the Raman signals without the use of a polarization analyser.
A fixed laser power was employed with maximum value of 1.20 mW and focused on to a spot size of about 1 µm in diameter with MD plan 50x objective lens (numerical aperture 0.75). For graphene and its nanocomposite, an incident maximum laser power of 0.11 mW was applied. Spectra were acquired using Wire 1.3 software in the range 2500-2800 cm\(^{-1}\) and over 100-3000 cm\(^{-1}\) (Stokes shift) with the continuous extended grating mode. The spectra collection was repeated a number of times to reduce the signal noise and were acquired in the absence of room lights to avoid any interference in the spectrum as shown in Table 2.2 which provides typical collection parameters for the samples.

**Table 2.2** The average acquisition times and the accumulations of the Raman spectra were used for the epoxy nanocomposites and the nanocarbon powders using 632.8 nm (1.96 eV) laser excitation lines.

<table>
<thead>
<tr>
<th>Epoxy Nanocomposites</th>
<th>Acquisition Times, s</th>
<th>Accumulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs</td>
<td>10</td>
<td>One</td>
</tr>
<tr>
<td>DWCNTs</td>
<td>20</td>
<td>One</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>70</td>
<td>Five</td>
</tr>
<tr>
<td>Neat Resin</td>
<td>10</td>
<td>One</td>
</tr>
<tr>
<td>Nanocarbon powders</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SWCNTs</td>
<td>10</td>
<td>One</td>
</tr>
<tr>
<td>DWCNTs</td>
<td>10</td>
<td>One</td>
</tr>
<tr>
<td>MWCNTs</td>
<td>10</td>
<td>One</td>
</tr>
</tbody>
</table>

All the Raman band spectra were analyzed by Lorentizan routines. The spectrometer's wavenumber shift was calibrated using the Raman mode of Si at 520.2 cm\(^{-1}\). For the same batch of material, the Raman spectra were presented as the average of spectra from three different specimens. To increase the reliability five measurements of Raman spectra were taken in different positions on 1 µm\(^2\) of loosely compacted forms of the nanocarbon powders.

### 2.4.1.2 A Raman spectroscopic investigation of deformation behaviour

Rectangular specimens with dimensions of 61 mm length, 14 mm width, and 3 mm thickness were loaded axially using a four-point bending rig, which was located on the Raman microscope stage as shown in Figures 2.4 and 2.5. The second order (G’-band) of nanocarbons in nanocarbon / epoxy nanocomposites was observed as a function of applied strain. The incident laser beam always kept aligned parallel to the strain axis so that spectra were principally obtained from nanotubes within the composites being subjected to axial strain.
Figure 2.4 The typical prepared composite specimens for Raman spectroscopy investigation of specimens for 0.1, 0.2, 0.5 and 1.0 wt% MWCNTs/epoxy composites respectively.

Figure 2.5 Specimen setting in the four point bending rig showing tensile loading on the top surface.

The composites were loaded axially in tension using a four-point bending rig which was located on the Raman microscope stage. The composite beams were deformed step-by-step in ~0.1 % strain intervals, determined from Vishay Micro-measurement EA-06-240LZ-120/E strain gauges, with a gauge factor of 2.09 that were attached to the surface by ethyl cyanoacrylate adhesive. Two 100 mm long white wires (10/0.1 mm copper, Maplin Electronics, UK) were connected to the terminals of the strain gauge via lead-free silver solder applied by a soldering iron (15 W Maplin Electronics, UK) as shown in Figure 2.6.

An intelligent digital multimeter (Thurlby 1905a) was used to measure the change in resistance which corresponds to the applied strain. The conditions for tensile deformation of CNT/epoxy nanocomposites were loading of the nanocomposites up to 1.5 % strain with several Raman spectra obtained at each strain level.
2.4.2 Bulk density determination

The bulk or the apparent density of the powders is defined as the ratio of the measured mass to the total volume which includes their particles volume and the internal void volume [151]. A modified version of the international standard ISO 60 method [152] was used to determine the bulk density of the as-produced MWCNTs powders, Nanocyl NC7000 and Aldrich 724769. A glass funnel of volume 10 cm$^3$ was filled with the MWCNTs powders and the powder compacted using a glass rod to reduce the volume of voids that may also be measured.

2.4.3 Thermogravimetric analysis

It was possible to identify the thermal stability and the degree of purity of the nanocarbons by using thermogravimetric analysis (TGA) and following the actual weight loss (or gain) due to decomposition, oxidation or dehydration. Using a Netzsch-Gerätebau GmbH - STA 449 C Jupiter thermo-microbalance, it was possible to simultaneously undertake TG and DSC.

A sample of about 3 mg of each nanocarbon was subjected to a continuous rate of 5 °C/min up to the maximum temperature of 900 °C with an air flow rate in the furnace of 100 ml/min. The residual weight value for each run at room temperature was recorded. To assess the repeatability of the results, each sample was analyzed three times.

2.4.4 Scanning electron microscopy (SEM)

2.4.4.1 Basics of scanning electron microscopy

Scanning electron microscopy (SEM) is one of the more practical ways for the examination and analysis of sample microstructure, morphology and chemical composition characterization. It produces images of a sample by scanning it with a focused beam of electrons in environmental vacuum. The signals produced from the electron beam and specimen interactions are detected simultaneously with an electron detector [153] Elastic interactions and inelastic interactions are the main interaction categories. The latter include Auger electrons, cathodoluminescence, characteristic X-rays and secondary electrons (SE). Backscattered electrons (BSE) are known...
as elastic interactions. Energy dispersive X-ray spectroscopy (EDS) in SEM is used for chemical analysis from characteristic X-rays produced by the incident electron beam to determine non-carbonous impurities such as catalysts and surface treatments species. The number and energy of the X-rays emitted from the sample can be measured by energy-dispersive spectrometer.

2.4.4.2 Nanocarbon morphologies

The form and structure of the SWCNTs, DWCNTs, MWCNTs and graphene was analysed by SEM. A Philips XL 30 microscope, equipped with a field emission gun (FEG), was used with an acceleration voltage between 5 and 20 kV, a working distance of 10 mm, and secondary electron (SE) imaging mode. The mean diameter of 77 tubes for the MWCNTs produced was measured from 5 SEM images at magnifications of >20,000x, while the average lengths of different CNT arrays were identified at magnifications up to 250x.

A dry method for sample preparation was achieved by addition of a small amount of nanocarbons with a stainless steel microspatula upon the surface of aluminium 12.5 mm pin stubs (Agar, UK-G301). The stubs were mounted with double-sided carbon tape (Agar, UK-G3347N) to make a good adhesive base for the nanocarbons. Conductive fast drying silver paint (Agar, UK-G3691) was applied to bridge the stub to the surface of the powder samples and allowed to dry before imaging. Point and rectangle EDX analysis scans were carried out from 0.01 keV to 20 keV over the three areas examined at magnification 2500x using an accelerating voltage 20 kV and the validation was carried out with the Bruker Esprit 1.8 software.

2.4.4.3 Fracture surface of carbon nanotubes / epoxy composites

The surface topography characterization of the tensile test fracture specimens were examined in detail using a Philips XL 30 SEM with FEG and acceleration voltage between 10 and 20 kV, a 10 mm working distance and secondary electron (SE) imaging mode. The sample preparation was achieved in the same manner like the carbon nanotubes powders expect that thin gold layers were deposited on the fractured specimens using an Edwards Sputter Coater S150B. Conductive fast drying silver paint was applied bridging the stub to the surface of the specimens and left to dry before imaging.

2.4.5 Transmission electron microscopy (TEM)

2.4.5.1 Basics of transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is an efficient tool for the microscopic characterization of materials over size ranges from the atomic scale up to the micrometer level and beyond [154]. TEM uses a high-voltage beam transmitted through the sample, typically at 100-200 kV accelerating voltage [155]. In a TEM, an electron beam passes through a condenser lens to concentrate the beam on the sample. Some of the electrons pass all the way through; others hit
molecules in the sample and scatter. The modified beam then passes through an objective lens, a projector lens and onto a fluorescent screen where the final image is observed [154, 155]

2.4.5.2 TEM observation of nanocarbons

A Philips CM200 TEM with a tungsten (W) filament was used to identify the growth morphology and crystallinity of the tubular structures. The microscope was operated at 200 kV and magnifications of 100k-300k were used to image the structures of the SWCNTs, DWCNTs, MWCNTs and graphene.

TEM specimens were prepared according to the procedure in Ayache et al [156]. CNTs were placed inside 7 ml vial by long serrated tips tweezer angled to 45° (Agar Scientific). The vial was then filled by 5 ml of ethanol solvent (Fisher Scientific, UK). The resulting suspensions were agitated using an ultrasonic bath at room temperature for fifteen minutes to separate the agglomerated CNTs. Once the solution homogeneity was complete, a few droplets were dropped onto a holey carbon film which was attached to the shiny surface of 300 meshes of copper grids (S147-3, Agar Scientific Ltd) using a micropipette (P20, Gilson Scientific Ltd). The copper grids were ready once the ethanol had completely evaporated.

2.4.6 DMA of carbon nanotube/epoxy composites

The dynamic modulus, the loss modulus and mechanical damping or internal friction of the polymeric materials are commonly determined with a dynamic thermo-mechanical analyzer (DMA). The modulus indicates stiffness of the material which may be a shear, tensile or flexural modulus, depending upon the clamp type installed on the instrument.

Specimens with dimensions of ~ 60 mm length, ~ 13 mm width, and ~ 3 mm thickness were tested by Dynamic Mechanical Analysis Q8000 in conjunction with the TA instruments universal analysis 2000 version 4.4A control software as shown in Figure 2.7. The testing was performed by a three-point bending clamp type, “DMA multi-frequency-strain mode and “temp ramp/freq sweep” test. Under constant test parameters of 1 Hz frequency, heating rate 3 °C /min, soak time 5 min and 0.007% maximum strain, the specimens were scanned over the -100 to 200 °C temperature range.

To keep the movable clamp in contact with the specimens, a 0.1 N force (preload force) was applied. The three-point bending clamp was calibrated according to the procedures in the instrument control software.

2.4.7 Tensile testing of carbon nanotube/epoxy composites

In order to understand how the incorporation of carbon nanotubes into an epoxy polymer affects the tensile properties, a series of tensile tests were performed at 25 °C, using an Instron 5569 machine (model twin column table top No., 5569, USA), with the static tension/compression load cell of capacity ±50 kN, as shown in Figure 2.8.
After the extensometer calibration was performed, the axial extensometer (MTS 634.11 with a 25 mm gauge) was used to record changes in the gauge length values. The specimens were loaded to uniaxial tension using a cross-head speed of 1.5 mm/min until failure. This relatively low speed was chosen because the materials were brittle with a low strain to failure. The calibration and balancing of extensometer and the test control was carried out using Bluehill 2 materials testing software (Instron). Dumb bell shaped specimens [157, 158] were used for each measurement and flash was removed by grade 60 and 240 silicon carbide grinding papers. The surfaces were also polished using grade 400 and 800 silicon carbide grinding papers. In addition BS EN ISO 527-1:2010 [159] was used for performing the tensile tests.
3 Chapter Three: Synthesis and characterization of multiwall carbon nanotubes (MWCNTs)

3.1 Introduction

In order to study interfacial stress transfer in MWCNTs nanocomposites, it is necessary to use crystalline MWCNTs with a high aspect ratio and a strong Raman G’-band so that one can examine peak shifts under load. These types of nanotubes are currently not available commercially and had to be produced in the laboratory.

A variety of methods have been reported to produce MWCNTs to obtain highly crystalline, defect-free high purity MWCNTs, such as the arc-evaporation technique, laser-ablation methods and chemical vapour deposition (CVD). The latter approach has a number of attractive features, as that it can be undertaken at low temperature (600–900 °C) and at ambient pressure in a simple and economic way using different states of hydrocarbons (solid, liquid or gas) on various substrates.

Generally, the CVD method allows the growth of nanotubes in a variety of forms, such as powder, films, in aligned or entangled state. The yield, structural control and purity are better in CVD than the arc and laser methods but the CVD-grown MWCNTs possess poorer crystallinity. Injection chemical vapour deposition was used to grow MWCNTs, with a strong G’ band and high aspect ratio, to be used in the composites in this thesis.

3.2 Effect of injection duration on MWCNTs yield and catalyst yield

The growth of aligned MWCNTs arrays by CVD has been optimised to make MWCNTs for composites applications which have been studied by several groups [36, 44, 160, 161]. In general, the MWCNTs diameter, length, alignment and yield produced by the injection CVD method are affected by the following synthesis parameters:

- The hydrocarbon precursor (chemical nature, flow rate)
- The growth temperature
- The catalyst (particle size, concentration)
- The catalyst support
- The reaction time
- The carrier gas (mixture concentration, flow rate)
- The growth pressure

The first experiments examined the impact of reaction time on both the length and diameter of the MWCNTs along the quartz tube under constant conditions.
MWCNTs were grown at 760 °C, using a 100 ml/min Argon flow rate at atmospheric pressure. A toluene solution with 5.0 wt % ferrocene concentration was injected at a feed rate of 0.04 ml/h. The injection time was varied from 30 to 240 minutes.

The percent yield and the catalyst yield were calculated using the following Equations:

\[
\text{MWCNTs Yield, } \% = \frac{m_{\text{MWCNTs (product)}}}{m_{\text{C (feedstock)}}} \times 100
\]

(3.1)

\[
\text{Catalyst Yield} = \frac{m_{\text{MWCNTs (product)}}}{m_{\text{Fe (feedstock)}}}
\]

(3.2)

where \(m_{\text{C (feedstock)}}\) is the mass of carbon atoms in the feedstock, \(m_{\text{Fe (feedstock)}}\) is the mass of iron atoms in the feedstock and \(m_{\text{MWCNTs (product)}}\) is the mass of MWCNTs produced.

These formulae assume that all the iron (Fe) becomes a catalyst. The percent yield and the catalyst yield were found to be constant for all runs as shown in Table 3.1. Therefore the most favourable condition was the one which give the largest quantity of MWCNTs per run i.e. 240 min.

**Table 3.1 The yield and the catalyst yield for the different injection times**

<table>
<thead>
<tr>
<th>Injection duration of 5.0 wt % ferrocene / toluene solution, min</th>
<th>30</th>
<th>60</th>
<th>120</th>
<th>180</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNTs yield, wt %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.0 ± 10</td>
<td>14 ± 4.0</td>
<td>9.0 ± 5.0</td>
<td>7.0 ± 4.0</td>
<td>16.0 ± 7.0</td>
<td></td>
</tr>
<tr>
<td>Catalyst Yield, (g MWCNTs / g Fe)</td>
<td>7.0 ± 5.0</td>
<td>8 ± 2.0</td>
<td>5.0 ± 3.0</td>
<td>4.0 ± 2.0</td>
<td>9.0 ± 4.0</td>
</tr>
<tr>
<td>Mass of product (g)</td>
<td>0.13 ± 0.10</td>
<td>0.30 ± 0.1</td>
<td>0.39 ± 0.2</td>
<td>0.47 ± 0.30</td>
<td>1.42 ± 0.64</td>
</tr>
</tbody>
</table>

3.3 The change in MWCNTS morphology along the quartz tube

The furnace was divided into 5 sections based on the temperature profile as shown in Figure 3.1 and Table 3.2. These regions were used to categorise the nanotubes and understand how their morphology depended on the location, the feedstock concentration and variation of reaction temperature along the tube. As shown in Figure 3.1, the hot region was region 3 and 10 cm in length. The temperature varied by ± 2°C within this hot zone and convection driven circulation was seen at the ends of the quartz tubes.

3.3.1 Effect of the injection duration along the reactor tube location

3.3.1.1 The length of MWCNTs arrays (\(L_{\text{MWCNTs}}\))

The MWCNTs are found to form arrays as shown in Figure 3.2. However, in the third and the fourth regions some irregular agglomerates were produced for a reaction time of 30 min, whereas the MWCNTs produced for 240 min injection time were relatively cleaner. As shown in Figures 3.4(B) and (C) and Table 3.3, the array lengths of MWCNTs produced from 240 minutes injection were much longer than for 30 minutes injection.
Also the array lengths along the reactor quartz tube exhibit peaks for 30 and 240 min injection times in the second and fourth regions (hot regions), respectively. However, the cold regions (the first and fifth regions) have shorter MWCNTS array lengths for the injection times investigated. It is important to note that no recognisable MWCNTS arrays were observed in the first region for 240 minutes injection. This may be due to catalyst particles retaining a higher activity over a longer time compared to 30 min injection. It seems possible that these results are due to the thermal decomposition rate of toluene not being identical along the quartz tubular reactor. The increasing array length suggests that a strong link may exist with the temperature, which must supply enough energy to dissociate toluene to have long MWCNTs arrays [44, 162].

![Figure 3.1 The temperature profile along the quartz tube](image)

**Table 3.2 The temperature characteristics of the quartz tube regions.**

<table>
<thead>
<tr>
<th>Region</th>
<th>Tube location, cm</th>
<th>Temperature range, °C</th>
<th>Average temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>10 - 20</td>
<td>469 - 706</td>
<td>623 ± 77</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>20 - 30</td>
<td>706 - 755</td>
<td>735 ± 16</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>30 - 40</td>
<td>755 - 759</td>
<td>760 ± 02</td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
<td>40 - 50</td>
<td>759 - 709</td>
<td>739 ± 17</td>
</tr>
<tr>
<td>5&lt;sup&gt;th&lt;/sup&gt;</td>
<td>50 - 60</td>
<td>709 - 393</td>
<td>582 ± 102</td>
</tr>
</tbody>
</table>

### 3.3.1.2 The outer diameter of MWCNTs

The results in Figures 3.4(A) and (C) and Table 3.3, show that the MWCNTs diameters have similar broad distributions and similar maxima of the variation curves within error bars along the reactor quartz tube for both 30 and 240 minutes injection times. In both reactions, the average diameter increased along the furnace from region 1 to region 4 then the average diameters decreased in region 5. It was observed that the largest diameter MWCNTs were grown in the hottest region for both the 30 and 240 minutes’ injection times, however in the colder regions smaller diameters were grown.

It has been proposed that the form of MWCNTs is closely related to the diameters of the iron catalyst particles [42, 44, 162, 163]. Seemingly, the larger catalyst particles deposit on the
quartz reactor walls due to a long residence time, a relatively low argon flow rate in the reactor, and the available hydrogen not efficiently shaping nanoparticles into the desired narrow size distribution.

<table>
<thead>
<tr>
<th>Region</th>
<th>30 min injection time</th>
<th>240 min injection time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region 1</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>Region 2</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>Region 3</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Region 4</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
<tr>
<td>Region 5</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 3.2 SEM images of arrays of MWCNTs in all regions at scale bar 1mm produced using injection times of 30 min and 240 min. The red arrows indicate MWCNTs arrays.
Chapter Three: Synthesis and characterization of Multiwall carbon nanotubes (MWCNTs)

<table>
<thead>
<tr>
<th>Region</th>
<th>30 min injection time</th>
<th>240 min injection time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region 1</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>Region 2</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>Region 3</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Region 4</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
<tr>
<td>Region 5</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 3.3 SEM images of diameters of MWCNTs in all regions at scale bar 1µm produced using injection times of 30 min and 240 min
Chapter Three: Synthesis and characterization of Multiwall carbon nanotubes (MWCNTs)

Figure 3.4 (A) The temperature profile along the quartz tube; (B) and (C) the array lengths (Figure 3.2) and the diameters (Figure 3.3) of the MWCNTs for injection times of 30 and 240 minutes respectively.
Table 3.3 The typical values of the outer diameters and the array lengths for the MWCNTs produced from injection times of 30 and 240 minutes

<table>
<thead>
<tr>
<th>Region</th>
<th>(d_{\text{out}}, \text{nm} )</th>
<th>(L_{\text{MWCNTs}}, \mu\text{m} )</th>
<th>(d_{\text{out}}, \text{nm} )</th>
<th>(L_{\text{MWCNTs}}, \mu\text{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Region 1</td>
<td>62 ± 26</td>
<td>66 ± 13</td>
<td>55 ± 15</td>
<td>-</td>
</tr>
<tr>
<td>Region 2</td>
<td>70 ± 26</td>
<td>150 ± 25</td>
<td>64 ± 17</td>
<td>109 ± 48</td>
</tr>
<tr>
<td>Region 3</td>
<td>69 ± 24</td>
<td>141 ± 10</td>
<td>79 ± 10</td>
<td>223 ± 84</td>
</tr>
<tr>
<td>Region 4</td>
<td>80 ± 36</td>
<td>104 ± 14</td>
<td>94 ± 26</td>
<td>295 ± 48</td>
</tr>
<tr>
<td>Region 5</td>
<td>45 ± 15</td>
<td>56 ± 19</td>
<td>71 ± 16</td>
<td>85 ± 12</td>
</tr>
</tbody>
</table>

3.3.2 Raman spectroscopy of the MWCNTs produced

3.3.2.1 Selection of the most appropriate Raman laser

Raman lasers with different excitation energies were used to identify the most appropriate laser to obtain sharp and strong G\(^-\) bands. First of all, the Raman features of MWCNTs were investigated with a 633 nm laser. Figure 3.5 shows the Lorentzian fitting of the Raman spectra (He–Ne laser, 633 nm) of MWCNTs which were produced using an injection time of 240 minutes in the 3rd region (temperature range 755 – 759 °C). It can be observed that the first–order Raman spectrum shows two strong bands- the G-band and the D-band and the second–order has a single sharp G\(^-\) band and two weak bands, G\(^*\)- band and a D+G- band.

![Fitted Raman spectra of MWCNTs](image)

Figure 3.5 Fitted Raman spectra of MWCNTs; (A) 1000 to 1800 cm\(^{-1}\)(B) 2000 to 3000 cm\(^{-1}\). The original spectrum is solid black line; the fitting peaks are dashed green lines and the total fitting curve is presented as a dashed red line.

Figure 3.6 compares the Raman spectra of MWCNTs obtained using an Ar\(^+\) ion laser (514.5 nm), a He–Ne laser (633 nm), and near infrared (NIR) (785 nm and 830 nm) lasers. Table 3.4 summarizes the frequency and the FWMH (full width maximum height) of the Raman bands obtained from the different lasers. While the first-order Raman spectra shows two strong bands, the G-band and the D-band, a third weaker band (D\(^-\) band) is also observed. Further analysis showed that the second–order region has a single sharp G\(^-\)band and two weak bands, G\(^*\)-band and D+G-band around 2955/2900, 2464/2472 cm\(^{-1}\) (with 514 nm / 633 nm lasers).

However, the G\(^'\)-band is detected as a weak peak in the form of a wide modulated bump using near infrared (NIR) (785 nm and 830 nm) lasers respectively. The G\(^*\)- band and D+G- band are not strong enough to appear using these excitation wavelengths.
Figure 3.6 (A) Normalized Raman spectra of MWCNTs to the G'-band intensity and, (B) Lorentzian fits of normalized G' band line shape of the MWCNTs using an Ar+ ion laser, 514.5 nm; a He–Ne laser, 633 nm; a NIR, 785 nm laser and a 830 nm laser taken with a laser power of about 1.2 mW.

3.3.2.2 Dispersive effects of the D-band, G-band and G'-band

The best fit parameters for the dispersion of these bands with respect to the excitation energy are shown in Table 3.4. The G-band (~1581 cm⁻¹) does not depend on the laser energies because it does not have any dispersive behaviour. The slope of the laser excitation energy dependence, the G'- band frequency is found to be 98 cm⁻¹/eV, which is approximately two times greater than the G' band (50 cm⁻¹/eV) as shown in Figure 3.7. The dependence of the Raman shift of a mode on the energy of the exciting laser, the dispersion effect, is consistent with other researchers [164, 165] who state that the origin of the dispersive effects of the D-band and the second order G'-band are due to the resonant Raman process.
Table 3.4 Raman spectroscopy characteristic bands of MWCNTS using an Ar+ ion laser, 514.5 nm; a He–Ne laser, 633 nm; a NIR, 785 nm laser and 830 nm laser

<table>
<thead>
<tr>
<th>Property</th>
<th>Types of laser used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>514 nm (2.41 eV)</td>
</tr>
<tr>
<td>D</td>
<td>( \nu ) (cm(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>FWHM (cm(^{-1}))</td>
</tr>
<tr>
<td>D'</td>
<td>( \nu ) (cm(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>FWHM (cm(^{-1}))</td>
</tr>
<tr>
<td>G</td>
<td>( \nu ) (cm(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>FWHM (cm(^{-1}))</td>
</tr>
<tr>
<td>G'</td>
<td>( \nu ) (cm(^{-1}))</td>
</tr>
<tr>
<td></td>
<td>FWHM (cm(^{-1}))</td>
</tr>
</tbody>
</table>

Figure 3.7 Shift of (A) the G-band, (B) the D-band and (C) the G'-band for MWCNTs as a function of the energy of the exciting laser.

Table 3.5 The dispersive effect parameters of the Raman band features in MWCNTs

<table>
<thead>
<tr>
<th>Raman bands for the MWCNTs</th>
<th>( \left( \frac{\partial \omega_r}{\partial E_{\text{laser}}} \right) ) cm(^{-1})/eV</th>
<th>The intercepts at 0 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-band</td>
<td>-1</td>
<td>1581</td>
</tr>
<tr>
<td>D-band</td>
<td>50</td>
<td>1233</td>
</tr>
<tr>
<td>G'-band</td>
<td>98</td>
<td>2464</td>
</tr>
</tbody>
</table>
3.3.2.3 Band intensity ratios and linewidths

From Figure 3.8 we can see the normalized Raman spectra obtained using a He–Ne laser, 633 nm for MWCNTs, produced in the 5 regions using injection times of 30 minutes and 240 minutes. All of the spectra show the D, G and D’ bands in the first-order Raman spectra and the G*, G’ and D+G bands in the second-order Raman spectra.

![Raman spectra diagram]

Figure 3.8 Typical normalized offset Raman spectra lines of the MWCNTs using a laser excitation of 633 nm (1.96 eV) in the range 100-3000 cm⁻¹ for injection times of: (A) 30 minutes and (B) 240 minutes in the 5 regions.

The presence of MWCNTs was substantiated with SEM images where MWCNTs can be easily observed as shown in Figure 3.3. It has been suggested that the intensity of the G-band is used as a reference in determining the relative intensity ratio to quantify the extent of difference in crystallinity in carbon materials because it is dependent on the structure of the
material, incident laser beam intensity and sample shape. The relative Raman intensity is also insensitive to the instrument and atmospheric conditions [166]. The intensity of the band is measured as the height of the fitted peak. In order to assess the change in the degree of crystallinity of MWCNTs, the average values $I_D/I_G$, $I_G'/I_G$ ratios and the G' band linewidth (FWHM (G')) along the reaction tube were used as shown in Figure 3.9.

It is considered that the changes in Raman bands are dependent upon the degree of crystallinity, because the MWCNTs diameters have similar broad distributions along the reactor quartz tube for both 30 and 240 minutes injection times. In Figure 3.9 (A) the results show that the $I_D/I_G$ ratio decreases for both 30 minutes and 240 minutes injection times for regions 1-4, and increases in the fifth region. The lowest values of $I_D/I_G$ ratio are found to be around 0.44 and 0.65 for both 30 minutes and 240 minutes, respectively. Thus the growth temperatures required to obtain fewer defects in MWCNTs are around $760 \pm 2$ °C and $739 \pm 17$ °C for both 30 minutes and 240 minutes production respectively. It was reported that the $I_G'/I_G$ ratio is very sensitive to the defect density in MWCNTs [161, 167]. However, although the $I_G'/I_G$ ratios values are scattered for 240 minutes production, there is a clear increase for 30 minutes productions for regions 1-4 as shown in Figure 3.9 (B). The highest value of $I_G'/I_G$ ratio is found around 1.47 and 1.17 for both 30 minutes and 240 minutes respectively.

The FWHM of the G' band of the MWCNTs along the reactor quartz tube for both 30 and 240 minutes injection times is shown in Figure 3.9(C). An increase of the FWHM of the G' band with increasing temperature along the reactor quartz tube is observed for 240 minutes injection times coupled with a decrease of the FWHM of the G' band found for 30 minutes. For regions 1-4, the changes of FWHM of the G' band suggest that the crystallinity increases and decreases for 30 and 240 minutes injection times, respectively. In regions 3-5 the relatively moderate values of linewidth (66-73 cm$^{-1}$) indicate a similar degree of crystallinity for both 30 and 240 minutes injection times in these growth regions.
Chapter Three: Synthesis and characterization of Multiwall carbon nanotubes (MWCNTs)

Figure 3.9 (A) The ratio of the intensity of D- Raman peak and G- Raman peak ($I_D/I_G$) (B) ratio of the intensity of G- Raman peak and G'- Raman peak ($I_G'/I_G$) and (C) FWHM of the G'- bands for MWCNTs obtained using laser excitation of 633 nm (1.96 eV) in the range 100-3000 cm$^{-1}$ for injection times of 30 minutes and 240 minutes.
Chapter Three: Synthesis and characterization of Multiwall carbon nanotubes (MWCNTs)

3.4 Standard material for composite studies

Based on the findings within section 3.3, it was decided that the MWCNTs would be produced along the tube reactor using an injection time of 240 minutes and collected from regions 2, 3 and 4. The samples were mixed together and characterized in detail for use in the further investigations.

3.4.1 Scanning electron microscopy (SEM) analysis

From Figure 3.10, we can see that the MWCNTs are predominantly aligned in chunks of entangled tube bundles, which are curved and twisted with each other. There are also a few of non-tubular irregular agglomerates as shown in Figure 3.10(B). In addition, some bright points (Fe catalysts) can also be observed at the intersection of the MWCNTs. On average, the histogram in Figure 3.11 indicates that the MWCNTs have array lengths of 223 ± 85 µm and are 73 ± 23 nm in outer diameter. The actual length of MWCNTs is higher than the array length probably because of the curvature of the MWCNTs.

![Figure 3.10 Typical SEM images of the standard MWCNTs material at different magnifications with scale bars (A) 1 mm, (B) 50 µm (the non-tubular irregular agglomerates surrounded by solid red lines), (C) 10 µm, (D) 5 µm, (E) 2 µm, (F) 500 nm (the outer diameter of MWCNTs represented by solid green lines)](image-url)
Chapter Three: Synthesis and characterization of Multiwall carbon nanotubes (MWCNTs)

3.4.2 Energy Dispersive X-ray Analyses (EDX)

Energy dispersive X-ray analysis (EDX) was used to determine the atomic percentage of Fe particles in the as-made MWCNTs as shown in Figure 3.12. The results obtained are shown in Table 3.6 which reveals the presence of significant amounts of Fe (13 ± 5 wt %) in the as-produced MWCNTs.

![Energy Dispersive X-ray Analyses (EDX)](image)

Figure 3.12 EDX spectrum of pristine MWCNTs powder

Table 3.6 EDX analysis of pristine MWCNTs powder

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>87 ± 3</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>13 ± 5</td>
</tr>
</tbody>
</table>

3.4.3 Transmission electron microscopy (TEM) analysis

As seen in Figure 3.13, TEM images show the MWCNTs are entangled tubular structures with a hollow tube inside. Based on root-mechanism growing (yellow arrows), some encapsulated particles (orange arrows), and encapsulated particles attached to the nanotube walls due to the continuous injection of the ferrocene (green arrows) were observed. As can be seen in the histogram which presented in Figure 3.14, MWCNTs are 61 ± 24 nm and 9 ± 3 nm of average
outer and inner diameters respectively. The relative amount of MWCNTs was higher than that of irregular non-tubular objects.

Nanometer-sized Fe metal particles with 72 ± 37 nm lengths and 13 ± 5 nm diameters were found to be embedded within the MWCNTs and are similar to or even larger than the inner diameter of the nanotube. From the TEM image in Figure 3.13(F), we can see the constituent graphene shells of a multilayer nanotube with a 0.33 nm gap. The Fe appeared as dark spots as indicated by the red arrows as shown in Figure (D) and (E). The outer diameter values obtained by TEM were lower than those obtained by SEM by about 15 % because of the measurement errors caused by sampling or sample preparation.

Figure 3.13 TEM image of the standard MWCNTs material at different magnifications with scale bars (A) 2 µm, (B) 500 nm, (C) 200 nm, (D) 100 nm, (E) 50 nm, (F) 5 nm (inset with scale bar 1 nm)
Chapter Three: Synthesis and characterization of Multiwall carbon nanotubes (MWCNTs)

Figure 3.14 (A) The TEM image of as-grown MWCNTs with the inner and outer diameters measurements, (B) outer diameters distribution of the standard MWCNTs material and (C) inner diameters distribution of the standard MWCNTs material

3.4.4 Thermogravimetric analysis (TGA)

To assess the quality and the purity of the MWCNTs, thermogravimetric analysis (TGA) was used. Figure 3.15 presents the weight-loss TGA curves for as-produced MWCNTs. The blue solid, black solid, red dash, and green dash dot lines correspond to the TGA, differential thermal gravimetric curve (-DTGA), peak sum fitting, and Gaussian line fitting for -DTGA, respectively.

Also the -DTGA curve has significantly, two peak maxima, at 547 ± 3 °C and at 601 ± 2 °C which corresponded to the oxidation temperatures (T_{ox}). This finding corroborates the ideas of Scheibe et al [168] (heating rate of 10 °C min^{-1}) who suggested that the difference in oxidation temperature of fractions of MWCNTs over a range of 50 °C is related to MWCNTs containing different amounts of initial defects in their structure.

Furthermore, it is also important to note that the MWCNTs started to oxidize at an onset temperature of around 494 ± 3 °C and an endset point at 620 ± 5 °C. The onset temperature is defined by the intercept of two tangents in the TGA curve, where the first tangent is extrapolated from a linear portion of the curve prior to the transition, and the second tangent is extrapolated from the point of inflection of the decrease in the TGA curve. The endset temperature defined by the intercept of two tangents in the TGA curve, where the first tangent is extrapolated from the point of inflection of the decrease in the TGA curve, and the second tangent is extrapolated from the linear portion of the curve after the complete burn off in the TGA curve [169].
Chapter Three: Synthesis and characterization of Multiwall carbon nanotubes (MWCNTs)

After complete heating, the residual mass percentage of iron oxide Fe₂O₃ at room temperature was 13 ± 2 wt%. The mass percentage of iron remaining was calculated by assuming complete conversion of the catalyst Fe to Fe₂O₃ according to

\[ 4 \text{Fe} + 3 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O}_3 \quad 3.3 \]

The calculated iron content was 9 ± 1 wt% which is consistent with the EDX analysis of Fe (13 ± 5 wt%).

![Figure 3.15](image1.png)  
Figure 3.15 The thermogravimetric analysis of as-produced MWCNTs in air. The original TGA line and their corresponding derivatives DTGA are solid blue and black lines respectively. The Gaussian fitting peak is represented by the dashed green line.

3.4.5 Visual appearance

As shown in Figure 3.16, the visual colour of the MWCNTs is black like most sp² carbon allotropes, such as graphene, carbon black, graphite, amorphous carbon and fullerenes which are black (under normal conditions).

![Figure 3.16](image2.png)  
Figure 3.16 Photograph of MWCNTs grown for 4 hours at 760 °C, 100 ml/min Argon flow rate using a feed rate of 0.04 ml/h with 5.0 wt% ferrocene concentrations in toluene solution.
3.4.6 The true density

Thostenson et al [170] expressed the correlation between the true density of MWCNTs and the inner and outer diameters, assuming that the density of graphite is 2.25 g/cm$^3$ as:

$$\rho_{\text{MWCNTs}} = \frac{\rho_{\text{graphite}} (d_{\text{out}}^2 - d_{\text{in}}^2)}{d_{\text{out}}^2} \tag{3.4}$$

where $d_{\text{out}}$ and $d_{\text{in}}$ the diameter of the outermost tube and the innermost tube respectively (nm)

Using Equation 3.4 and the diameters data in Figure 3.14, a sigmoid shape of densities is obtained and presented in Figure 3.17. There is a clear trend of increasing true density with increasing outer diameter. While the calculated true density is between 1.95 and 2.24 g/cm$^3$, the mean density is $2.19 \pm 0.06$ g/cm$^3$. It should be noted that the MWCNTs contain 9 ± 1% of iron. This will have the effect of increasing the density of the MWCNTs but the amount of increase will depend upon the position of the Fe particle in the tubes (e.g., in the central hole or tube wall).

![Figure 3.17 The true density of the MWCNTs as a function of their outer and inner diameters](image)

3.4.7 The surface area

Based on the outside surface area of MWCNTs and the difference between the surface area of the outermost tube and the innermost tube, the surface area of MWCNTs can be expressed in m$^2$/g as[171]:

$$S_{\text{MWCNTs}} = \frac{4000 \cdot d_{\text{out}}}{\rho_{\text{graphene}} (d_{\text{out}}^2 - d_{\text{in}}^2)} \tag{3.5}$$

where $\rho_{\text{graphene}}$ is the density of graphene 2.2 g/cm$^3$, $d_{\text{out}}$ and $d_{\text{in}}$ the diameters of the outermost tube and the innermost tube respectively (nm). Using Equation 3.5 and the diameter data in Figure 3.14, there is a clear trend of decreasing surface area of MWCNTs with increasing outer
diameter as shown in Figure 3.18. It is apparent that the surface area of the MWCNTs as calculated is between 12 to 70 m²/g with a mean value of 34 ± 11 m²/g. Previous studies have reported the measured surface areas of pristine MWCNTs range from 10 to 500 m²/g [151].

![Figure 3.18 The variation in the surface area with the outer diameters of MWCNTs](image)

3.5 Comparison with commercial MWCNTs

3.5.1 The bulk density

The bulk density was measured using the method described in Chapter 2, Section 2.4.2. From the data in Figure 3.19, it is apparent that the bulk density, including the pore volume, of the pristine MWCNTs (0.11 g/cm³) is higher the Nanocyl NC7000 (0.07 g/cm³) and lower than Aldrich 724769 (0.19 g/cm³) MWCNTs by nearly 60%, respectively. The technical data sheets provided similar values of 0.06 and 0.20 g/cm³ for Nanocyl NC7000 and Aldrich 724769 respectively.

![Figure 3.19 The bulk density of the as-produced, Nanocyl NC7000, and Aldrich 724769 MWCNTs powders](image)
3.5.2 Raman spectroscopy characterization

3.5.2.1 Raman spectra dependence on MWCNTs quality

The background-subtracted Raman spectra, normalized to the maximum intensity of the G'-band of the MWCNTs produced using injection times of 30 and 240 minutes, are compared to commercial carbon nanotubes in Figure 3.20. It is apparent that the intensity of the G'-band and G-band for MWCNTs produced using injection times of both 30 and 240 minutes are much stronger than for the commercial MWCNTs Nanocyl NC7000 and 724769 Aldrich MWCNTs. Additionally, the intensity of D-band is much lower than that of commercial MWCNTs Nanocyl NC7000 and 724769 Aldrich materials confirming the growth of highly -graphitized MWCNTs in this study.

![Raman spectra comparison](image.png)

**Figure 3.20** The typical normalized offset Raman spectra lines of the MWCNTs using 633 nm(1.96 eV) laser excitation in the range 100-3000 cm\(^{-1}\) from an injection time of 30 and 240 minutes compared with the commercial MWCNTs Nanocyl NC7000 and 724769 Aldrich materials (* technical data sheet values)

Strong and sharp G'-band peaks have been found with a frequency 2657 cm\(^{-1}\) for the MWCNTs prepared in this study while the commercial MWCNTs Nanocyl NC7000 and 724769 Aldrich MWCNTs have broader, weaker and lower frequency G'-band peaks. In Table 3.7 there is a clear trend of downshifting of the G-band frequency by \(~10\) cm\(^{-1}\) with increasing tube diameter, while the D-band and G'-band frequencies upshift with increasing tube diameter by \(~5\) cm\(^{-1}\) and \(~20\) cm\(^{-1}\) respectively. The \(I_G/I_D\) ratio can be sufficient to estimate change in crystallinity. As shown in Figure 3.21 and Table 3.7, the ratio decreases with increasing tube diameter, while the D- and G'-band frequencies increase with increasing tube diameter.

The present findings seem to be consistent with other research which found that A change of the Raman intensity could be correlated with structural defects revealing that the tube is not uniform [172].
Table 3.7 Raman spectroscopy characteristic bands of MWCNTs produced using an injection time of 30 and 240 minutes in the 3rd region compared with the commercial MWCNTs Nanocyl NC7000 and 724769 Aldrich

<table>
<thead>
<tr>
<th>Property</th>
<th>Types of MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>240 min</td>
</tr>
<tr>
<td>Diameter (nm)</td>
<td>78 ± 10</td>
</tr>
<tr>
<td>D (cm(^{-1}))</td>
<td>1332 ± 2</td>
</tr>
<tr>
<td>FWHM (cm(^{-1}))</td>
<td>166 ± 22</td>
</tr>
<tr>
<td>D' (cm(^{-1}))</td>
<td>1614 ± 3</td>
</tr>
<tr>
<td>FWHM (cm(^{-1}))</td>
<td>28 ± 7</td>
</tr>
<tr>
<td>G (cm(^{-1}))</td>
<td>1579 ± 3</td>
</tr>
<tr>
<td>FWHM (cm(^{-1}))</td>
<td>63 ± 3</td>
</tr>
<tr>
<td>G' (cm(^{-1}))</td>
<td>2657 ± 4</td>
</tr>
<tr>
<td>FWHM (cm(^{-1}))</td>
<td>66 ± 6</td>
</tr>
<tr>
<td>I(_G^`)/I(_G)</td>
<td>1.23 ± 0.14</td>
</tr>
</tbody>
</table>

Figure 3.21 The Raman peak intensity ratio of G' band over G band measured using a 633 nm excitation laser for the MWCNTs produced along the tube reactor for injection time of 30 and 240 minutes compared with the commercial MWCNTs Nanocyl NC7000 and 724769 Aldrich materials.
3.6 Conclusions

The work reported in this present chapter was designed to produce multiwall carbon nanotubes (MWCNTS) using chemical vapour deposition (CVD) and catalytic pyrolysis of a 5.0 wt% ferrocene / toluene solution for different injection times. This research was undertaken to determine the effect of the injection duration along the reactor tube location on the length of MWCNTs arrays and the diameter of MWCNTs, as well as the intensity values of the G' Raman peak. A standard material (MWCNTs) was then chosen with a high aspect ratio and a strong and sharp G' Raman peaks which should be useful particularly for interface studies in composites.

Furthermore, this study has investigated the structure, morphology and physical properties of the MWCNTs using Raman spectroscopy, TEM, SEM, and TGA. Theoretical approaches were used to calculate the true density and the surface area. In addition, comparison on the bulk density and the Raman spectrum information with other commercial MWCNTs was undertaken.

The most obvious finding to be drawn from the present chapter is that the standard material (MWCNTs) chosen was made using an injection time of 240 min, which gave the best percentage yield (ca.16 wt%). The morphology was observed by SEM, showing chunks (arrays) of entangled tube bundles 223 ± 85 μm in array lengths and 73 ± 23 nm in outer diameters and approximately 87 wt% pure based on SEM/EDX analysis. The present study predicts both the mean true density value to be around 2.00 g/cm³ and a mean surface area value of 34 ± 11 m²/g. It is apparent that the bulk density of the pristine MWCNTs (0.11 g/cm³) is higher and lower than Nanocyl NC7000 (0.07 g/cm³) and 724769 Aldrich materials, respectively.

The second major finding was that most of the MWCNTs have different curvatures of entangled tubular structures with a hollow tube inside. Shown by TEM to be 61 ± 24 nm and 9 ± 3 nm averages outer and inner diameters, respectively, and accompanied by numerous iron particles around 72 ± 37 nm in length and 13 ± 5 nm a diameter. TGA and DTG curves of MWCNTs reveal thermal stability in air up to 601 ± 2 °C.

Because the relative Raman ratio \( \frac{I_G}{I_{2D}} \) ratio of the prepared MWCNTs is higher than the commercial materials by about 10 times, it was shown that well defined Raman spectra were obtained from the prepared MWCNTs excited with a 633 nm (He-Ne) laser. It was considered that the prepared MWCNTs were better than those for the commercial materials and so should be useful for interface studies in composites.
4 Chapter Four: Single-walled carbon nanotubes (SWCNTs) and their epoxy composites

4.1 Introduction

In the present chapter, the structure of SWCNTs, formed by high-pressure CO conversion (HiPco), was determined by Raman spectroscopy using different lasers, SEM, TEM and TGA. Furthermore, the shift of position and width of the G'-Raman band for SWCNTs in an epoxy matrix was used for monitoring the interface and load transfer between nanotubes and the epoxy matrix in composites both for cyclic deformation up to 1 % maximum loading strain and for cyclic deformation up to 0.5, 1, and 1.5 % maximum loading strains. Additionally the strain-induced intensity changes in RBM-bands were studied for the composites under tension.

4.2 Raman spectra data analysis of SWCNTs (HiPco)

Figure 4.1 illustrates the main characteristics of the Raman spectra of SWNT (HiPco) in the range 100–3000 cm⁻¹. The strong Raman bands at 1590 ± 3 cm⁻¹ (FWHM, 19 ± 2 cm⁻¹), 1552 ± 3 cm⁻¹ (FWHM, 14 ± 3 cm⁻¹) and 1529 ± 4 cm⁻¹ (FWHM, 46 ± 5 cm⁻¹) (G band) are attributed to a combination of the tangential C-C stretching modes. The band at 1307 ± 3 cm⁻¹ (FWHM, 43 ± 4 cm⁻¹) (D band) arises from the disorder-induced mode and the band at 2602 ± 6 cm⁻¹ (FWHM, 63 ± 6 cm⁻¹) (G'-band) is an overtone of the D band. The RBMs-band have small Raman shifts that were observed typically between 150 and 400 cm⁻¹ [173]. These results are consistent with those of studies discussed in Chapter 1, Section 1.2.

![Raman spectra graph](image)

Figure 4.1 The Raman spectra for the SWCNTs (HiPco) in the range between 100 and 3000 cm⁻¹ excited with 633 nm (He-Ne) laser
Many of the Raman modes are related to graphite and are seen at similar frequencies in nanotubes [174]. Figure 4.2 compares the typical Raman spectra taken from the SWCNTs HiPco powder in the frequency region (100–3000 cm$^{-1}$) with (from the top to the bottom) 830 nm (1.49 eV), 780 nm (1.59 eV), He–Ne 632.8 nm (1.96 eV), and 514 nm (2.41 eV) laser excitation lines. The most important four Raman features in the SWCNTs are shown: the RBM bands, the D-band, the tangential G-band, and the G'-band. Significant differences in their relative intensities of the Raman features in all spectra for each laser wavelength can be observed.

It should be noted that the spectra obtained for 830 nm (1.49 eV) and 780 nm (1.59 eV) laser excitation lines are quite similar. The same applies for the spectra obtained with He–Ne 632.8 nm (1.96 eV), and 514 nm (2.41 eV) laser excitation lines. While the G-band is relatively unaffected by laser excitation line, the RBM-bands become stronger and the G'-band becomes weaker as laser wavelength is increased. Figure 4.3 shows the Raman G'-band of the SWCNTs (HiPco) obtained with four different laser lines. The most striking result is that the frequencies and the (FWHM) linewidth are very sensitive to the laser excitation energy as previously reported by Dresselhaus et al [173].

Figure 4.2 Raman spectra for the SWCNTs (HiPco) in the range between 100 and 3000 cm$^{-1}$ excited at four different laser frequencies.
Chapter Four: Single-walled carbon nanotubes (SWCNTs) and their epoxy composites

Figure 4.3 Raman spectra for the SWCNTs (HiPco) in the range between 2100 and 2800 cm\(^{-1}\) excited at four different laser frequencies, frequency (cm\(^{-1}\)), FWHM (cm\(^{-1}\)).

As stated before, the position of the RBM \(v(\text{cm}^{-1})\) in SWNT bundles (HiPco) was reported to correlate linearly with the tube diameter \(d\) according to the relationship \([175, 176]\):

\[
d(\text{nm}) = \frac{223.75}{v(\text{cm}^{-1})-14} \tag{4.1}
\]

Figure 4.4 compares the RBMs-band of SWNT (HiPco), using different laser energies. The relative intensities and the position of the RBM bands depends on the laser excitation energy. The 514 nm (2.41 eV) Raman spectrum is fitted with 9 Lorentzian lines centred at 309, 266, 258 (strongest peak), 242, 224, 211, 201, 180, and 146 cm\(^{-1}\). The He–Ne 632.8 nm (1.96 eV) Raman spectrum is fitted with 7 Lorentzian lines centred at 386, 337, 296, 283, 257 (strongest peak), 219 and 194 cm\(^{-1}\). The 785 nm (1.59 eV) Raman spectrum is fitted with 7 Lorentzian lines centred at 295, 265 (strongest peak), 231, 223, 212 and 202 cm\(^{-1}\). The 830 nm (1.49 eV) Raman spectrum is fitted with 7 Lorentzian lines centred at 275, 235 (strongest peak), 226, 215, 205, 197 and 185 cm\(^{-1}\).

Using Equation 4.1 and the frequencies of the RBMs-band of the SWCNTs (HiPco) with different laser energies, it is apparent that the calculated tube diameters are in the range 0.60 - 1.69 nm as shown in Figure 4.4. The histogram in Figure 4.5 indicates that the mean tube diameters is 1.02 ± 0.22 nm. The present findings seem to be consistent with Nikolaev et al [11] who found the diameter distribution of the SWCNTs produced at 1200 °C and 10 atm CO pressures, to be in the range 0.60 - 1.4 nm.
Figure 4.4 Typical examples of RBMs-band ‘radial breathing modes’ of the SWCNTs (HiPco) in the range 100 - 500 cm\(^{-1}\) excited with (A) 514 nm (Ar\(^+\)), (C) 633 nm (He-Ne), (E) 785 nm and (G) 830 nm lasers and the corresponding Estimated diameter distribution of the SWCNTs (HiPco) obtained by Raman spectroscopy; (B), (D), (F), and (H), respectively.
4.3 Raman spectra data analysis of the LY5052/HY5052 epoxy resin system

The LY5052/5052CH epoxy phenol novolak resin system was used as the thermosetting matrix for composite preparation. The resin component, Araldite LY5052 consists of 60-100 % epoxy phenol novolak resin and 30-60 % butanedioldiglycidyl ether [177]. The hardener Aradur 5052CH components comprises three amine cross-linking agents; two aliphatic primary amines (30-60 % 2,2-dimethyl-4,4-methylenebis(cyclohexylamine) and 30-60% isophorone diamine) and an aromatic tertiary amine (3-7 % 2,4,6-tris(dimethylaminomethyl) phenol) [178]. 50 parts by weight of epoxy resin (Araldite LY5052) were mixed thoroughly with 19 parts by weight of hardener Aradur 5052CH [179].

The Raman spectrum of a hot cured LY5052/5052CH epoxy phenol novolak resin system (100°C for 2h) is shown in Figure 4.6. The relationship between the Raman bands of the epoxide vibrations and the epoxy resin curing process has been investigated previously [180, 181]. It is reported that the epoxide Raman bands 1230 - 1280 cm\(^{-1}\) and their Raman intensity depend on the concentration of epoxy groups in the resin mixture [180] which the Raman intensity decreases as the consumption of epoxy groups increses (cured epoxy resin). The typical weak peak at 1246 cm\(^{-1}\) can be used to follow the consumption of epoxide groups from the resin as shown in Figure 4.6 [180, 181]. The band assignments obtained from the analysis for the Raman spectra of the hot-cured LY5052 / HY5052 epoxy resin system in the range 100-3000 cm\(^{-1}\) are presented in Table 4.1 [182-184]
Figure 4.6 Raman spectrum of the hot cured epoxy resin system 5052 in the region 1000-3000 cm$^{-1}$ and inset 1200-1350 cm$^{-1}$ excited by a 632 nm (1.96 eV) laser. The original spectrum is solid violet line; the fitting peaks are dashed green line and the total fitting curve represented by a solid red line.

Table 4.1 The band assignments for the Raman spectra of the LY5052/HY5052 epoxy resin system [182-184]

<table>
<thead>
<tr>
<th>Band position, cm$^{-1}$</th>
<th>Assignment</th>
<th>Band position, cm$^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2930, 2904, 2869, 2846</td>
<td>CH$_2$ epoxy sym. stretch and CH$_2$ alkyl asymmetric stretch</td>
<td>790</td>
<td>Adjacent H for $p$-sub benzene</td>
</tr>
<tr>
<td>1612, 1603</td>
<td>Aromatic/hetero ring and benzene ring quadrant (C=C) stretching</td>
<td>1051</td>
<td>Aromatic rings, $p$-sub. benzene ring</td>
</tr>
<tr>
<td>1587</td>
<td>Weak NH$_2$ scissoring</td>
<td>851, 823</td>
<td>Sym. ring vibration of epoxy ring</td>
</tr>
<tr>
<td>1481, 1460, 1441</td>
<td>Aromatic ring breathing</td>
<td>790</td>
<td>Adjacent H wag for $p$-sub benzene</td>
</tr>
<tr>
<td>1298</td>
<td>CH$_2$ deformation</td>
<td>772, 719, 706</td>
<td>$\nu$C–C aliphatic chains</td>
</tr>
<tr>
<td>1246</td>
<td>Very strong C-O stretching and Ring breathing of the epoxy ring</td>
<td>1179</td>
<td>$p$-sub. benzene ring</td>
</tr>
<tr>
<td>1179</td>
<td>$p$-sub. benzene ring</td>
<td>640</td>
<td>$p$-sub. benzene</td>
</tr>
<tr>
<td>1051</td>
<td>Aromatic rings, $p$-sub. benzene ring</td>
<td>491, 346</td>
<td>$\delta$ C–C aliphatic chains</td>
</tr>
<tr>
<td>851, 823</td>
<td>Sym. ring vibration of epoxy ring</td>
<td>181, 164</td>
<td>Lattice vibrations</td>
</tr>
</tbody>
</table>
4.4 Scanning electron microscopy analysis (SEM)

4.4.1 The microstructure

Figure 4.7 shows SEM images of SWNT (HiPco) taken at several magnifications. The low magnification images reveal that the SWCNTs are agglomerates and have a fairly uniform appearance. At the highest magnification, it is observed that there is a high density of clusters of web-like ropes, randomly entangled with an abundance of cross-linked bundles of carbon filaments in which the individual nanotubes are not revealed.

4.4.2 Energy dispersive x-ray analysis (EDX)

EDX spectra analysis indicated that the SWNT (HiPco) contain Fe as well as C, O, Cl and Si elements as shown in Figure 4.8. The Si is presumably from the glassware used in the nanotube purification. The presence of chlorine is indicative of residual chlorine remaining after the HCl reflux of the sample during purification. It seems that this purification process is not efficient. A possible explanation for the strong oxygen peak is might be due to bonded oxygen located at defect sites along the tube or at the tube ends. Another possible explanation for this is that O$_2$ is adsorbed on the surface which comes from the wet air oxidation used to remove the amorphous carbon or it seems possible comes from the oxygen which is bound to the Fe in the ferric oxide (Fe$_2$O$_3$) [185, 186].

![SEM images](image)

Figure 4.7 SEM images of the SWNT bundles (HiPco) at different magnifications with scale bars (A) 10 µm, (B) 5 µm, (C) 2 µm, (D) 500 nm.
Chapter Four: Single-walled carbon nanotubes (SWCNTs) and their epoxy composites

Figure 4.8 Energy dispersive X-ray (EDX) spectrum for SWNT bundles (HiPco)

Table 4.2 The elements weight % content of SWNT bundles (HiPco) as derived from EDAX spectra

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>83 ± 5</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>6 ± 4</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>11 ± 2</td>
</tr>
<tr>
<td>Chlorine (Cl)</td>
<td>0.36 ± 0.1</td>
</tr>
<tr>
<td>Silicon (Si)</td>
<td>0.1 ± 0.04</td>
</tr>
</tbody>
</table>

4.5 Transmission electron microscopy analysis (TEM)

Figure 4.9 shows TEM images of the SWNT bundles (HiPco) taken at several magnifications. In general, the SWNT bundles (HiPco) are mostly in a bundled form which have an average rope diameter of about 41 ± 23 nm and are accompanied by numerous iron particles around 3 ~ 4 nm in diameter (black dots marked by red arrows).

4.6 Thermogravimetric analysis (TGA)

Figure 4.10 shows the results of TGA analysis of the SWNT bundles (HiPco) in air. One main peak was clearly observed, at 444 ± 3°C, which corresponded to the oxidation temperature ($T_{ox}$). The thermal stability is also reported as the mean value of temperature ($T_{ox}$) at which the most intense peak occurs in the derivative thermogravimetric curve (DTGA) where the major carbon component oxidizes [169]. Furthermore, it is also important to note that the SWCNTs started to oxidize at an onset temperature of around 391± 4 °C and are almost completely by burned off at 484 ± 3°C. After complete heating, the residual mass percentage of iron oxide (Fe$_2$O$_3$) at room temperature is 14 ± 1 wt%. The mass percentage of remaining iron was calculated by assuming complete conversion of the catalyst Fe to Fe$_2$O$_3$ according to

$$4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$$  \hspace{1cm} (4.2)
The calculated iron content was 9.8 ±1 wt% which was consistent with the EDX analysis value of Fe 6 ± 4 wt %).
Figure 4.10 Thermogravimetric analysis of the SWCNTs (HiPco) in air. The original TGA line and the corresponding derivatives DTGA are solid blue and black lines respectively. The Gaussian fitting peak is dashed red line.

4.7 Deformation of the SWNT/epoxy composites

4.7.1 Raman spectra of SWCNTs in epoxy composites

Figure 4.11(A) shows the spectra of neat hot cured epoxy resin, of the SWCNTs (HiPco) bundles and the SWNT/epoxy composites in the range 1000-3000 cm\(^{-1}\) excited using a 633 nm (He-Ne) laser. It is clear that the high relative intensities of main peaks of the SWCNTs HiPco compared to the cured epoxy in the nanocomposites even at 0.1 wt% loading, are due to the resonance Raman scattering of SWCNTs. Figure 4.11(B) compares the G'-band of the SWCNTs (HiPco) bundles and of the SWCNTs (HiPco) bundles in SWCNTs/epoxy composites in the range 2500-2800 cm\(^{-1}\). The G'-band is retained as a bell shape and its frequency is upshifted by about 12 cm\(^{-1}\) in the composites compared with that of the SWCNTs powders; the FWHM is narrowed by about 15 cm\(^{-1}\). A possible explanation may be due to the susceptibility of SWCNTs to pre-compression because of the residual stresses and curing contraction or polymerization shrinkage generated in the hot-cured system [187, 188].
Chapter Four: Single-walled carbon nanotubes (SWCNTs) and their epoxy composites

4.7.2 Analysis of deformation using Raman spectroscopy

4.7.2.1 Tensile loading up to 1.5 % strain

The hot-cured SWCNTs / epoxy composite system was subjected to tensile loading up to 1.5 % strain. Figure 4.13 compares the \( G' \)-band in the undeformed state and at 1.5 % strain for the SWCNTs in the hot-cured SWNT / epoxy composites system. There is a clear trend of down shifting in the wavenumber with increasing the strain. The shifts of the position and the FWHM of the \( G' \) band versus composite strain are shown in Figure 4.14(A) and (B), respectively. It is apparent that the \( G' \) band position shifts with strain over the whole range. The average initial rate of band shift was found to be \(-14.10 \pm 3.28 \text{ cm}^{-1} / \% \text{ strain}\).
The deformation behaviour shows three typical regions: linear elastic deformation behaviour up to and around 0.7 % with a down shift of 12 cm⁻¹, then non-linear behaviour from 0.7 to 1.1 % strain where gradual interface damage between nanotubes and polymer matrix occurs and finally a plateau region where there is interfacial breakdown [187]. It is well known, during deformation of the hot-cured SWCNTs / epoxy composites, the G’ band position shifts with strain to a lower wavenumber and higher wavenumber in tension and compression, respectively [187].

What is interesting is the FWHM of the G’-band narrowing in the strain range 0 - 0.3 % strain; thereafter the width is broadening. Hence, a possible explanation for this might be that the pre-compression of the nanotubes due to residual stresses in the strain range 0 - 0.3 % strain from the matrix shrinkage is due to thermal contraction on cooling from the processing temperature and/or and curing contraction or polymerization shrinkage. Kao et al [189] found band broadening during both tensile and compression deformation.

![G’-Raman spectra of hot-cured SWNT (HiPco) / epoxy nanocomposites](image)

Figure 4.12 A typical G’-Raman spectra of hot-cured SWNT (HiPco) / epoxy nanocomposites in the range 2500-2800 cm⁻¹, excited using a 633 nm (He-Ne) laser, in the undeformed state and at 1.5 % tensile strain.
Figure 4.13 The typical examples of; (A) the shift of G'-band positions of the SWCNTs HiPco versus tensile strain of hot-cured SWCNTs HiPco / epoxy nanocomposites. The overall fitting is represented by a solid green line, the 0 - 0.7 % strain region liner fitting is a dashed red line, the 0.7 – 1.1 % strain region polynomial fitting is a dashed blue line and the 1.1 – 1.5 % strain region liner fitting is a dashed purple line (B). The G'-band FWHM of the SWCNTs HiPco versus tensile strain tensile strain of hot-cured SWNT (HiPco) / epoxy nanocomposites. The overall polynomial fitting is presented by a solid red line.

4.7.2.2 Loading and unloading to the same maximum strain

The responses of the G'-band positions and their widths (FWHM) to the three cycles of loading and unloading to the same maximum strain level (1% strain) are shown in Figure 4.14 (A) and (B) respectively. It is observed that the hysteresis areas for cycles 1, 2 and 3 were very similar indicating that the nanotubes were in less tension on the unloading part of the cycle which, consistent with the observation of Kao et al [189].
Chapter Four: Single-walled carbon nanotubes (SWCNTs) and their epoxy composites

The reason for this, however is not clear, but it may be because that the greatest amount of interfacial failure has occurred in loading cycle 2 and no more damage takes place. If we now turn to the zero-strain G’- band position, it is shifted to a lower wavenumber by about 0.6, 0.8 cm\(^{-1}\) in loadings 2 and 3 respectively. Turning now to the FWHM, the peak decreased in width as the composite was strained up to about 0.3 % strain upon loading, followed by broadening when unloading. The peak narrowed up to about 0.3 % strain, followed by broadening.

During the loading steps 2 and 3, the broadening and narrowing are repeated in the same manner. However, there are no significant differences between the three cycles up to 0.3% strain; the loop area for loading cycle 3 is larger than for loading cycles 1 and 2. Further analysis showed that the width of the pre-strain G’- band was found to be narrower by about 0.5, 0.6 cm\(^{-1}\) for loadings 2 and 3 respectively.

![Diagram A](image1.png)
![Diagram B](image2.png)

Figure 4.14 Variation of the G’-band of the hot-cured SWNT / epoxy nanocomposites for three cycles of loading and unloading up to 1.0 % maximum strain (A) band positions and (B) band FWHM
4.7.2.3 Estimation of the interfacial energy dissipated during the cyclic deformation

Kao et al [189] correlated the observed hysteresis areas in G'-band positions to the energy dissipated in cold-cured (room temperature for 7 days) epoxy nanocomposites using the SWCNTs (HiPco), to the level damage at the nanotube-matrix interface using the SWCNTs (HiPco) and the same epoxy resin as in this study. Figure 4.15 shows the derived stress – strain curve of the hot-cured SWCNTs/epoxy composites subjected to a cycle of the loading and unloading. The nanotube band shift in G'-band wavenumber can be converted to a meaningful stress using the universal band shift rate of - 5 cm⁻¹GPa from carbon fibres [109].

Furthermore, the estimated loading and unloading energies can be calculated from integration of second order polynomial curve-fitted equations. Subsequently the estimated energy of dissipation in the deformation cycle was obtained by subtracting the unloading energy from the loading energy. The energy dissipated at the interface and the extent of damage of the interface were determined using the equations of Kao et al [189] where the density of epoxy resin and SWCNTs are 1.1 and 1.45 g/cm³ [149] respectively; 0.1 wt% SWCNTs dispersed in the composites; nanotube bundle diameters (D_{ropes(SWCNTs)}) of 1 nm and 30 nm and an energy needed to break SWCNTs/epoxy interface completely of about 25 J/m² [190].

![Figure 4.15](image-url)

Figure 4.15 The derived stress-strain curve for the loading and unloading cycle to demonstrate the determination of the energy dissipated in the hot-cured SWCNTs/epoxy composites

Table 4.3 shows the calculated energy dissipated in the composites and at the interface, as well as the predicted extent of interface damage in the hot-cured SWCNTs/epoxy composites during the cyclic deformation up to 1 % maximum loading strain. It found that there was no significant difference in the energy dissipation over the 3 loading cycles. It was around 4–5 J/m² and the extent of interface damage were found to be constant over the subsequent cycles.
Another important finding arises from the comparison between the hot-cured composite system and the cold-cured one of Kao et al [189]. It was observed that the energy dissipated in the hot-cured system and at the interface, as well as the extent of interface damage upon the deformation cycle 1 was about 10 times lower than in the corresponding cold-cured system. This finding may be explained by the applied strain level may not be high enough to cause any further damage due to the presence of residual thermal stress in the hot-cured system. It can be concluded that the hot-cured system had good bonding between nanotubes and the matrix accompanied by better efficiency of interfacial stress transfer than in the cold-cured system [187, 189].

Table 4.3 The energy dissipation in the composites and at the interface and the predicted extent of the interface damage in the hot-cured SWCNTs/epoxy composites during the cyclic deformation up to 1% maximum loading strain

<table>
<thead>
<tr>
<th>Diameter of D SWCNTs, nm</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolated Isolated Bundled</td>
<td>Isolated Isolated Bundled</td>
<td>Isolated Isolated Bundled</td>
<td></td>
</tr>
<tr>
<td>1 1* 30</td>
<td>1 1* 30</td>
<td>1 1* 30</td>
<td></td>
</tr>
<tr>
<td>Energy dissipated in the composites, MJ/m³</td>
<td>0.4 5* 0.4</td>
<td>0.4 3* 0.4</td>
<td>0.5 2* 0.5</td>
</tr>
<tr>
<td>Energy dissipated at the interface, J/m²</td>
<td>0.12 1.15* 3.7</td>
<td>0.12 0.7* 3.5</td>
<td>0.1 0.5* 4</td>
</tr>
<tr>
<td>Extent of interface damage, %</td>
<td>0.5 4.5* 15</td>
<td>0.5 2.7* 14</td>
<td>0.5 2* 16</td>
</tr>
</tbody>
</table>

* Kao et al [189] work-cold cured resin

4.7.2.4 Cyclic deformation with increasing maximum strains

Figure 4.16 shows the influence of a succession of loadings up to 0.5, 1.0 and 1.5 % strain, on the G'-band positions and its FWHM. It can be seen in the initial cycle that the loading curve overlaps the unloading one, in which the G'-band shifts approximately linearly with strain. The strain–shift relationship of the G'-band becomes non-linear for the loading cycle as the maximum loading strain is increased. It is clear that the strain–shift profile of the G' band moves to a higher wavenumber compared to the previous cycle. The loop area was found to increase in size as the level of the maximum loading strain increased. These findings corroborate the ideas of Kao et al [189], who suggested that the stress is fully transferred from the matrix to the nanotubes in the initial cycle (cycle 1) and the composite are being subjected to permanent interfacial damage of the nanotube–matrix interface in the higher strain cycles 2 and 3. In addition, they suggested that the interface is subjected to irreversible damage in the composites in cycles 2 and 3. For the FWHM curve, however there are no
significant differences between the three cycles up to 0.3% strain, but the loop areas for the loading cycles increased as the level of loading strain increased. It is interesting to note that the strain-induced changes of both the wavenumber positions and widths of the G'-bands are reversible.

Figure 4.16 The features of G'-band of the hot-cured SWCNTs / epoxy nanocomposites for cyclic deformation up to 0.5, 1.0 and 1.5 % maximum loading strains (A) band positions and (B) band FWHM

4.7.2.5 Effect on the intensity of the RBM Raman bands

Overall, no significant differences are found between the shifts of the RBM positions within the limits of experimental error (±1 cm⁻¹) as can be seen from Figure 4.17. Figure 4.18(A) compares the intercorrelations among the low-frequency Raman spectra of SWNT bundle powders and the SWNT bundle in the undeformed and 1.5 % strain loaded SWNT/ epoxy composites. The intensities vary with strain for all RBM peaks. The low-frequency Raman spectra were fitted with six Lorentzian components centred at 333, 299, 283, 255, 219 and 197 cm⁻¹ as shown in Figure 4.19(B).
Figure 4.19 compares the information provided by the theoretical Kataura plot [191] with the RBM features in undeformed SWNT/epoxy composites. The tubes that are in resonance with the 633 nm laser ($E_{\text{laser}} = 1.96$ eV) are semiconducting nanotubes with ($E_{22}^{\delta}$) and ($E_{11}^{\gamma}$) transitions.

Figure 4.18 (A) Typical RBM-band Raman spectra comparing SWCNTs bundles powder with the SWCNTs in undeformed and 1.5% loaded strain SWNT/epoxy composites. (B) RBM-band Raman spectra of SWCNTs in undeformed SWNT/epoxy composites

Figure 4.20 compares the RBM intensity variations to the intensity at zero strain of the six Lorentzian components in the range up to 1.5% strain. In tension, the 299 cm$^{-1}$, 255 cm$^{-1}$ (maximum intensity), 283 cm$^{-1}$ and 197 cm$^{-1}$ peak intensities increased, whereas for the 333 cm$^{-1}$ peak, its intensity decreased. The 219 cm$^{-1}$ peak intensity seems to have a constant value. These findings further support the effect of deformation upon resonance of carbon nanotube which will be discussed in Chapter 7.
Overall for the semiconducting nanotubes the RBMs are changed in intensity under deformation strain, however the metallic nanotubes RBMs at 218 cm$^{-1}$ are not changed. The present findings seem to be consistent with Lucas et al. [148] who suggest the van Hove singularity (VHS) in the nanotube electronic DOS shifts higher or lower in energy when the nanotube is under uniaxial strain. The band gaps of the nanotubes are thus moved closer (or further away) from the laser excitation energy which affects the resonance condition and therefore affects the Raman intensity. It seems possible that these tubes are not totally in resonance and/or the resonance windows of ($E_{11}^N$) is broadened by uncertain factors [147]. The assignments of the $n$ and $m$ values will be discussed in Chapter 7.

![Figure 4.19](image-url) The Kataura plot [191] used to determine the metallic or semiconducting nature of the SWCNTs in resonance with the 633 nm laser excitation energy. The green line indicates the excitation energy of the 633 nm laser and the area between the two solid green lines represents the resonance window. The violet open circle is used to mark a Raman frequency where the RBM intensity should be strong.
4.8 Conclusions

This chapter has investigated the structure, morphology, and physical properties of SWCNTs using Raman spectroscopy, TEM, SEM, and TGA. The second aim was to study the stress transfer in epoxy composites reinforced with SWCNTs to clarify the reinforcing ability of the SWCNTs in an epoxy matrix. This work was undertaken to assess the stress transfer efficiency at the SWCNTs / epoxy interface with tensile deformation and with cyclic loading using the variation of stress sensitive G'-band positions and widths (FWHM).

The most obvious finding to be drawn from the present chapter is that the SWCNTs (HiPco) were of high-quality with low amounts of side-wall defects and other carbon impurities. The morphology was observed by SEM, showing a high density of clusters of web-like ropes and an approximate 83 ± 5 wt % purity based on SEM/EDX analysis. However, most of the SWCNTs consist of bundles of well-aligned carbon filaments shown by TEM size 41 ± 23 nm and accompanied by numerous iron particles around 3 ~ 4 nm in diameter.

The diameters of the SWCNTs, which were deduced from the Raman shift of the RBM mode, were mostly in the range 0.60 - 1.69 nm and with an average diameter of 1.02 ± 0.22 nm. The TGA and DTG curves of SWCNTs revealed thermal stability in air up to 444 ± 3 °C. It has been shown that well defined Raman spectra can be obtained from SWCNTs excited using a 633 nm (He-Ne) laser and the typical weak peak of 1246 cm\(^{-1}\) in the Raman spectra of neat epoxy and composites.
Another finding to be drawn from the present chapter is that during deformation good stress transfer from resin to SWCNTs occurred up to around 0.7% strain, and then the level of the interfacial damage was increased. These results support the idea that more interface damage occurs with bundles.

There are RBM intensity variations of the six Lorentzian components of the SWCNTs in the hot-cured SWCNTs / epoxy composites up to 1.5% strain. These findings further support the idea that deformation affects the resonance conditions of carbon nanotubes.
Chapter Five: Double-walled carbon nanotubes (DWCNTS) and their epoxy composites

5.1 Introduction

In the present chapter, the structure of DWCNTs, formed by CVD was analysed by Raman spectroscopy using different lasers, SEM, TEM and TGA. Furthermore, the change of position and width of the Raman G'-band for DWCNTs in an epoxy matrix was used for monitoring the interface and load transfer between nanotubes and the epoxy matrix in composites and also for cyclic deformation. Additionally, the strain-induced intensity changes in the RBM-bands were studied in tension for the composites.

5.2 Raman spectra data analysis of DWCNTs

Figure 5.1 illustrates the main characteristics of the Raman spectra of DWCNTs in the range 100 – 3000 cm\(^{-1}\). The strongest Raman bands are at 1588 ± 0.2 cm\(^{-1}\) (FWHM, 23 ± 0.3 cm\(^{-1}\)), with a shoulder at 1551 ± 0.3 cm\(^{-1}\) (FWHM, 28 ± 2 cm\(^{-1}\)) (G band). The very weak band at 1327 ± 1 cm\(^{-1}\) (FWHM, 29 ± 1 cm\(^{-1}\)) (D band) arises from the disorder-induced mode, the band at 2636 ± 0.5 cm\(^{-1}\) (FWHM, 73 ± 3 cm\(^{-1}\)) (G' band) is an overtone of the D band and the RBM-bands (radial breathing modes) have small Raman shifts that were observed typically between 100 and 400 cm\(^{-1}\) [173]. The present findings seem to be consistent with other research which was discussed in Chapter 1, Section 1.2.

![Raman spectrum](image.png)

Figure 5.1 The Raman spectrum for DWCNTs in the range between 100 and 3000 cm\(^{-1}\) excited using a 633 nm (He-Ne) laser
Chapter Five: Double-walled carbon nanotubes (DWNT) and their epoxy composites

The G' band line shape of the DWCNTs can be explained in terms of contributions from different components which are in resonance with a 633 nm (He-Ne) laser near 2650 cm\(^{-1}\). The lower frequency G'\(_1\) at 2609 (FWHM, 63) cm\(^{-1}\) is related to the nanotube inner walls while the higher frequency G'\(_2\) at 2645 (FWHM, 50) cm\(^{-1}\) is related to the nanotube outer wall and is more intense than the lower frequency G'\(_1\) component as shown in Figure 5.2. This result is in corroborating the findings of a great deal of the previous work in Chapter 1 Section 1.6.5.

![Figure 5.2 Lorentzian fits of the Raman spectrum of DWCNTs for the G'-bands near 2650 cm\(^{-1}\) excited at 633 nm (He-Ne) laser. The original spectrum line is shown as solid black line, the overall fitting peak is solid red line and the fitted two peaks are dashed green lines, (frequency (cm\(^{-1}\)) (FWHM, cm\(^{-1}\)).](image)

Figure 5.3 compares typical Raman spectra taken from the DWCNTs in the frequency region (100–3000 cm\(^{-1}\)) with - from the top to the bottom - 830 nm (1.49 eV), 780 nm (1.59 eV), He–Ne 632.8 nm (1.96 eV), and 514 nm (2.41 eV) laser excitation lines. The most important four Raman features in the nanotubes are shown: the RBM bands, the very weak D-band, the tangential G-band, and the G'-band. However, for the Raman features in all spectra except the G-band, significant differences in their relative intensities for each laser wavelength are observed.

It should be noted that the spectra obtained for 830 nm (1.49 eV), 780 nm (1.59 eV) laser excitation lines are quite similar in band intensity; the same applies for the spectra obtained with He–Ne 632.8 nm (1.96 eV), and 514 nm (2.41 eV) laser excitation lines. While the G-band is the most intense peak with the 830 nm (1.49 eV) laser excitation line, the RBM-bands and the G'-band are very strong and very weak respectively. With the He–Ne 632.8 nm (1.96 eV) laser excitation line, the RBM-band is weak while the G'-band is strong. The very weak intensity of the D band for all laser wavelengths indicates that these DWCNTs are of high quality.
Figure 5.3 Raman spectra for DWCNTs excited using four different laser frequencies in the range between 100 and 3000 cm\(^{-1}\).

Figure 5.4 shows the Raman G'-band of the DWCNTs obtained with four different laser lines. The G' band contains two Lorentzian peaks that we have identified as G'\(_1\) and G'\(_2\). Table 5.1 illustrates the main characteristics of the two peaks (G'\(_1\) and G'\(_2\)). It is observed that the two peaks tend to become closer together and the overall FWHM decreases with decreasing energy of the laser and becomes one peak with the NIR 830 nm laser (1.49 eV). This finding corroborates the ideas of Villalpando-Paez [192], who suggested that the double resonance process is occurring independently in each layer of the DWCNTS and with higher \(E_{\text{laser}}\) values make it easier to detect the two peaks (G'\(_1\) and G'\(_2\)).
Table 5.1 The G'-band doublet parameters from DWCNTs bundles excited using four different laser wavelengths (fitted to the Lorentzian peaks)

<table>
<thead>
<tr>
<th>Types of laser used</th>
<th>514 nm (2.41 eV)</th>
<th>633 nm (1.96 eV)</th>
<th>785 nm (1.58 eV)</th>
<th>830 nm (1.49 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \omega ) (cm(^{-1}))</td>
<td>FWHM (cm(^{-1}))</td>
<td>( \omega ) (cm(^{-1}))</td>
<td>FWHM (cm(^{-1}))</td>
</tr>
<tr>
<td>G(^{-1}) (Outer Tube)</td>
<td>2684 ± 1</td>
<td>59 ± 1</td>
<td>2625 ± 2</td>
<td>50 ± 3</td>
</tr>
<tr>
<td>G(^{+}) (Inner Tube)</td>
<td>2645 ± 1</td>
<td>50 ± 3</td>
<td>2585 ± 3</td>
<td>30 ± 2</td>
</tr>
<tr>
<td>G(^{-1}) FWHM (cm(^{-1}))</td>
<td>2631 ± 1</td>
<td>50 ± 3</td>
<td>2584 ± 1</td>
<td>30 ± 2</td>
</tr>
<tr>
<td>G(^{+}) FWHM (cm(^{-1}))</td>
<td>57 ± 4</td>
<td>63 ± 2</td>
<td>56 ± 5</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5.5 compares the RBM-bands of DWCNTs using different laser energies. Using Equation 4.1 and the frequencies of the RBMs-band of DWCNTs in Figure 5.5, the histograms of inner and outer tube diameters were obtained and are presented in Figures 5.6(A) and (B) respectively. It is apparent that the average calculated inner and outer tube diameters are in range of 0.61 - 0.99 nm and 1.2 - 1.35 nm, respectively. The histograms in Figures 5.6 also indicate that the mean inner and outer tube diameters are 0.82 ± 0.13 nm and 1.47 ± 0.16 nm respectively. The interlayer distance of the DWCNTs is therefore about 0.325 nm according to the Raman calculation, which is close to the interlayer distance in graphite (0.333-0.335 nm) and also corresponds to the value determined by Villalpando-Paez et al and Hod et al [193, 194].

Figure 5.5 RBMs-band ‘radial breathing modes’ of DWCNTs in the range 100 - 500 cm\(^{-1}\) excited using 830 nm, 785 nm, 633 nm (He-Ne), and 514 nm (Ar\(^{+}\)) lasers.
Chapter Five: Double-walled carbon nanotubes (DWNT) and their epoxy composites

5.3 The true density

Using Equation 3.4 and the diameter data in Figure 5.6, the mean density is calculated as 1.55 ± 0.15 g/cm$^3$.

5.4 The surface area

Using Equation 3.5 and the diameter data in Figure 5.6, it is apparent that the mean calculated value of the surface area of DWCNTs is 1796 ± 0.13 m$^2$/g. This value, however, is obviously higher than the measured surface area of DWCNTS bucky papers (568.7 m$^2$/g) and of SWCNTs (641.7 m$^2$/g) by a factor of about three [195, 196]. A possible explanation is because the experimentally measured values [195, 196] were for ropes or bundles of CNTs rather than isolated DWCNTs.

5.5 Scanning electron microscopy analysis (SEM)

5.5.1 The microstructure

Figure 5.7 shows SEM images of DWCNTs taken at several magnifications. The low magnification images reveal that DWCNTs are agglomerated and have a fairly uniform appearance as shown in Figures 5.7(A) and (B). In the highest magnification picture, a high density cluster of web-like ropes randomly entangled with an abundance of entwined bundles of carbon filaments in which the individual nanotubes are not revealed was observed in Figures 5.7(C) and (D).

5.5.2 Energy dispersive X-ray analyses (EDX)

Energy dispersive X-ray (EDX) spectra analysis indicated that the DWCNTs bundles contain 99.67 ± 0.06 wt% of carbon. It is noted that the DWCNTs bundles are free from oxygen and iron elements contrary to the behaviour of SWCNTs (HiPco).

Figure 5.6 Estimated diameter distribution of isolated DWCNTs obtained using Raman spectroscopy and Equation 4.1, (A) outer diameters and (B) inner diameters.

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Using Equation 3.4 and the diameter data in Figure 5.6, the mean density is calculated as 1.55 ± 0.15 g/cm$^3$.

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Chapter Five: Double-walled carbon nanotubes (DWNT) and their epoxy composites

Figure 5.7 SEM images of the DWCNTs bundles at different magnifications with scale bars (A) 10 µm, (B) 5 µm, (C) 2 µm and (D) 500 nm.

Figure 5.8 The energy dispersive X-ray (EDX) spectrum for the DWCNTS bundles.

5.6 Transmission electron microscopy analysis (TEM)

Figure 5.9 shows TEM images of DWCNTs bundles taken at several magnifications. On average, the DWCNTs are mostly of bundled forms which have average rope diameters of about 20 ±14 nm without any obvious iron particles.
Figure 5.9 TEM images of DWCNTS bundles at different magnifications with scale bars
(A) 1 µm, (B) 200 nm, (C) 100 nm, (D) 20 nm, (E) 10 nm, (F) 2 nm.

5.7 Thermogravimetric analysis (TGA)

Figure 5.10 shows the results of TGA analysis of the DWCNTs bundles in air. It shows significantly two peaks, at 132 ± 1 °C and at 683 ± 6 °C in the derivative thermogravimetric curve (DTGA). The first peak in the range 108 - 159 °C corresponds to residual water being removed or evaporated and the other peak corresponds to the oxidation temperatures ($T_{ox}$). In the original TGA line, it is also important to note that the DWCNTs started to oxidize at an onset temperature of around 626 ± 5 °C and are almost completely burned off at 738 ± 9 °C. After complete combustion, the residual mass percentage at room temperature is 3 ± 3 wt% which is within the detection limit of the instrument.
Figure 5.10 The thermogravimetric analysis of the DWCNTs bundles in air. The original TGA line and the corresponding derivative DTGA are shown by solid blue and black lines respectively. The Gaussian fitting peak presented as a dashed red line.

5.8 Deformation of DWCNTs/epoxy composites

5.8.1 Raman spectra of DWCNTs in epoxy composites

Figure 5.11(A) shows the spectra of the neat hot-cured epoxy resin, DWCNTs and the DWCNTs/epoxy composites in the range 1000-3000 cm⁻¹ excited using a 633 nm (He-Ne) laser. It is clear that the high relatively intensities of the main peaks of the DWCNTs compared to the cured epoxy in the nanocomposites, even at 0.1 wt% loading are due to the resonance Raman scattering of the DWCNTs. As can be seen from Figure 5.11(B), the G'-band line shape for the DWCNTs in the DWCNTs/epoxy composites was fitted to two contributions, the higher frequency G'₁ at about 2644 cm⁻¹ (FWHM, 59 cm⁻¹) corresponding to the outer wall nanotube and the other lower frequency G'₂ at 2609 cm⁻¹ (FWHM, 46 cm⁻¹) corresponding to the inner wall nanotube.

Figure 5.11(B) compares the G'-band of the DWCNTs and of the DWCNTs in DWCNTs/epoxy composites which made up one peak in the range 2500 - 2800 cm⁻¹. It was observed that the G'–band shape of the DWCNTs in DWCNTs/epoxy composites was wider than for the DWCNTs powder. However, it is frequency downshifted by about 8 cm⁻¹ in the composites and its width had no significant change when compared with that of the DWCNTs bundles.

The G'-band spectrum from Figure 5.12 can be fitted to two peaks compared with Figure 5.2 which shows, that although there are no significant difference in frequencies for the inner and outer tubes of the DWCNTs bundles and the DWCNTs bundles in DWCNTs/epoxy composites. Surprisingly, the relative intensities between the higher frequency G'₁-band and the lower one G'₂-band was changed from 2:1 to 1:1 for the DWCNTs powder and for the DWCNTs
in the undeformed DWCNTs/epoxy composite. It should noted that the higher frequency $G'_1$ band and the lower one $G'_2$-band have become broader by 9 cm$^{-1}$ and narrower by 7 cm$^{-1}$ respectively. A possible explanation may be the susceptibility of the DWCNTs to pre-compression due to the generation of residual stresses in hot cured systems [187].

![Raman spectra of epoxy, DWCNTs and hot-cured DWCNTs/epoxy nanocomposites in the range 100-3000 cm$^{-1}$ excited using 633 nm (He-Ne) laser.](image)

Figure 5.11 (A) Raman spectra of epoxy, DWCNTs and hot-cured DWCNTs/epoxy nanocomposites in the range 100-3000 cm$^{-1}$ excited using 633 nm (He-Ne) laser. (B) $G'$-Raman spectra of epoxy, DWCNTs bundles and hot-cured DWCNTs/epoxy nanocomposites in the range 2500-2800 cm$^{-1}$ excited using a 633 nm (He-Ne) laser. (Frequency (cm$^{-1}$) / (FWHM, cm$^{-1}$)).

However, the findings of the current study do not support previous research [197] where the thermal annealing of bucky paper DWCNTs up to 2000 °C had no significant effect on the overall line shape of the $G'$ peak taken with $E_{\text{laser}} = 1.92$ eV. It seems possible that these results are due to residual stresses caused by matrix shrinkage as consequence of thermal contraction on cooling from the processing temperature.
Figure 5.12 Lorentzian fits of the Raman spectrum of the DWCNTS G'-bands near 2650 cm\(^{-1}\) excited using a 633 nm (He-Ne) laser. The original spectrum line represented by solid black lines, the overall fitting peak as a solid red line and the fitted two peaks are dashed green lines, (frequency (cm\(^{-1}\)) / FWHM, cm\(^{-1}\)).

5.8.2 Analysis of deformation using Raman spectroscopy

5.8.2.1 Tensile loading up to 1.5 % strain

The hot-cured DWCNTS/epoxy composite systems were subjected to tensile loading up to 1.5 % strain. Figure 5.13 compares the undeformed state from 1.5 % strain state of the G'-band for the DWCNTs in the hot-cured DWCNTS / epoxy composites system. There is a clear trend of down shifting in the wavenumber and narrowing with increasing strain.

The shifts of the position of the overall G' band, the higher frequency G'\(_1\)-band (outer tubes) and the lower one G'\(_2\)-band (inner tubes) versus composites strain are shown in Figures 5.14(A), (C) and (E) respectively, as well as their corresponding width changes (FWHM) (B), (D) and (F). It is apparent that the G' band positions are downshifted and become narrower with strain over the range, except the lower G'\(_2\)-band (inner tubes) which behaves like the FWHM of SWCNTs (HiPco) in the hot-cured SWNT / epoxy composite system, where they become narrower in the strain range 0 - 0.3 % strain, followed by broadening.

During loading, both the positions of the higher frequency G'\(_1\)-band (outer tubes) and the lower one G'\(_2\)-band (inner tubes) components decreased almost linearly up to 0.3 % strain and then continued in nonlinear behaviour up to 1 % strain for the higher frequency G'\(_1\)-band (outer tubes), while the lower one G'\(_2\)-band (inner tubes) reached a plateau at \(\geq 0.4\) % strain. The average initial rate of band shift of the overall G' band, the higher frequency G'\(_1\)-band (outer tubes) and the lower one G'\(_2\)-band (inner tubes) were found to be: - 21.50 ± 1.20, - 24.85 ± 0.54, and - 18.72 ± 1.09 cm\(^{-1}\) /% strain respectively.
Chapter Five: Double-walled carbon nanotubes (DWNT) and their epoxy composites

Figure 5.13 Typical G'-Raman spectra of hot-cured DWCNTs / epoxy nanocomposites in the range 2500-2800 cm$^{-1}$ excited using a 633 nm (He-Ne) laser in the undeformed state and at 1.5 % axial strain.

As discussed in Chapter 1, Section 1.7, the slopes of the fitting lines of the higher frequency G'_1-band (outer tubes) and the lower one G'_2-band (inner tubes) are an indication of the efficiency of internal stress transfer $k_i$ between the layers. This ratio was found to be about 0.75 [75]

It has been hypothesized that the level of reinforcement of nanotubes in composites can be estimated from the rate of shift of the G'-Raman bands with strain when the composite is deformed [109, 187]. Using 0.01 wt% DWCNTs (peapod) /epoxy composites, Cui et al [75] found minimal shift (-1.1 cm$^{-1}$/% strain) of the lower one G'_2-band (inner tubes) and an approximately linear shift (- 9.2 cm$^{-1}$/% strain) of the higher frequency G'_1-band (outer tubes) in tension. They predicted stress transfer takes place from the matrix to the outer wall of the nanotubes, but there is little stress transfer between the outer and inner walls due to slippage of the inner wall of the DWCNTs (peapod).

Surprisingly, it was found that the average initial rate of band shift of the higher frequency G'_1-band (outer tubes) about 3 times higher than DWCNTs (peapod) bundles in the hot-cured DWCNTs / epoxy composites system on strain. Furthermore the lower G'_2-band (inner tubes) of DWCNTs (CVD) bundles in this present study are higher by about 17 times than DWCNTs bundles (peapod) in the earlier study [75], respectively. This means that there is much better wall-to-wall stress transfer in the DWCNTs (CVD)

It seems possible that these results are due to the DWCNTs (CVD)/matrix interface being stronger than the interface in DWCNTs (peapod)/matrix interface and also poor inter-wall bonding of the DWCNTs (peapod) walls. Another possible explanation for this is that the DWCNTS (CVD) has significantly fewer defects, as indicated from the very weak Raman D band in Figure 5.1.

What is interesting in the linewidths (full width at half maximum) of the lower G'_2-band (inner tubes) is the narrowing in the strain range 0 - 0.3 % strain, thereafter the width is broadening,
while the linewidths (full width at half maximum) of the higher frequency G'₁-band (outer tubes) is narrowing until they reach a plateau at about 1% strain. This indicates a slight compression as a result of shrinkage of the resin during the curing process is in the strain range 0 - 0.3 % strain.

Figure 5.14 Shift of the G'-band position during tensile deformation for the hot-cured DWCNTs/epoxy nanocomposites excited using a 633 nm (He-Ne) laser, (A) fitted to one Lorentizan peak (C) for the higher frequency G'₁-band (outer tubes) (E) for the lower one G'₂-band (inner tubes) and (B) (D) and (F) the corresponding changes of the widths of G'-band (FWHM) respectively.

5.8.2.2 Loading and unloading to the same maximum strain

The response of the position of the overall G' band for three cycles of loading and unloading applied to the same maximum level strain (1 % strain), and their corresponding width changes (FWHM) are shown in Figure 5.15(A) and (B), respectively. It is observed that the hysteresis occurs by loading and then unloading in the same manner back to zero strain. It is surprising
that the deformation behaviour is similar to SWNT/epoxy composites seen by Raman spectroscopy in Chapter 4.

![Diagram](image_url)

**Figure 5.15 (A)** Variation of G'\textsuperscript{-}band of the overall G'\textsuperscript{-}band for the hot-cured DWCNTs / epoxy nanocomposites for three cycles of loading and unloading up to 1.0 % maximum strain fitted as a one Lorentizan fitted peak and (B) the corresponding changes of the width of G'\textsuperscript{-}band (FWHM) for three cycles of loading and unloading up to 1.0 % maximum strain

In the same manner, strain-induced narrowing (FWHM linewidths) is observed upon loading as the composites were strained stepwise from 0 % to 0.6 % strain, followed by broadening and upon unloading the peak G'\textsuperscript{-}band widths. The present findings seem to be consistent with SWNT /epoxy composites, however, the strain tipping point found for the SWCNTs and the DWCNTs are different, at 0.3 and 0.6 % respectively.

5.8.2.3 **Cyclic deformation up to increasing maximum strains**

Figure 5.16(A) and (B) presents the influence of a succession of loading up to 0.5, 1.0 and 1.5 % strain, up on the overall G'\textsuperscript{-}band positions and their FWHM, respectively. It can be seen in the initial cycle that loading curve overlaps the unloading one in which the G'\textsuperscript{-}band shifts approximately linearly with strain. The strain–shift relationship of the G'\textsuperscript{-}band becomes non-linear, as the maximum loading strain is increased. It is clear that the strain–shift profile of the G'
band moves to a lower wavenumber compared to the previous cycle. The loop area is found to increase in size as the level of the maximum loading strain is increased.

**Figure 5.16 (A) Vari**ation of G'-band of the overall G'-band for the hot-cured DWCNTs / epoxy nanocomposites for cyclic deformation for 0.5, 1.0 and 1.5 % maximum loading strain fitted as a one Lorentizan fitted peak and (B) the corresponding changes of the width of G'-band (FWHM)

These findings corroborate the ideas of Kao et al [189] who suggested that the stress is fully transferred from the epoxy matrix to the SWCNTs in the initial cycle as the composite become subjected to the permanent interfacial damage of the nanotube–matrix interface in cycles 2 and 3. Kao et al [189] suggested that the interface is subjected to irreversible damage in the composites during cycles 2 and 3.

For the FWHM curve, the overall G'-band widths revert back to a closer higher value than the original pre-strain and the loop areas for the loading cycles increase with the number of loadings. It is remarkable that the strain-induced changes of the wavenumber positions and widths of the G’-bands are reversible at low strains. The present findings seem to be consistent with SWNT /epoxy composites; however the strain tipping point found for SWNT and DWCNTs are again different and found to be at 0.3 and 1.0 % respectively.

**5.8.2.4 Effect on the intensity of the RBM Raman bands**

As shown in Figure 5.17, overall, no significant differences are found between the shifts of the RBM positions within the limits of experimental error (±1 cm\(^{-1}\)) but the intensities vary with strain for all RBM peaks. The low-frequency Raman spectra were fitted with ten Lorentzian components centred at 338, 308, 289, 284, 253, 218, 176, 167, 154 and 125 cm\(^{-1}\).

Figure 5.18(A) compares the low-frequency Raman spectra of DWCNTs powders and DWCNTs in the undeformed and 1.5 % strain loaded DWCNTs/ epoxy composites. Because the low frequency Raman shifts are inversely proportional to the nanotube diameter, the RBM features in the range of 200–350 cm\(^{-1}\) arise from the inner tubes while peaks below 200 cm\(^{-1}\) are typically associated with the outer-tubes.

The RBM band of the outer tubes in DWCNTS powder centred at 165 cm\(^{-1}\) was divided to two Lorentzian components centred at 167 and 154 cm\(^{-1}\) in the undeformed DWCNTS/ epoxy composites, whereas the intensity increased for the RBMs arising from the inner tubes. The
reason for this is not clear, but it may be possible that the interaction with the polymer matrix and the residual stress on the nanotubes affects their resonance conditions.

Figure 5.17 The RBM positions for the DWCNTs/ epoxy composites as a function of strain for the 338 (solid squares), 307 (solid circles), 289 (up solid triangles), 284 (down solid triangles), 253 (solid diamond), 218 (lift solid triangles), 176 (right solid triangles), 167 (solid hexagon), 154 (star) and 125 (solid pentagon) cm\(^{-1}\) peaks.

The most intense prominent RBM features in resonance with the \(E_{\text{laser}} = 1.96\) eV are at 253 and 154 cm\(^{-1}\) which corresponds to inner tubes with a diameter \(\approx 0.93\) nm and to outer tubes with a diameter \(\approx 1.59\) nm in the undeformed DWCNTs/ epoxy composites.

Figure 5.19 compares the information provided by the theoretical Kataura plot [191] with the RBM features in undeformed DWCNTs/ epoxy composites. We can see that the inner tubes that are in resonance with the 633 nm laser \((E_{\text{laser}} = 1.96\) eV) are semiconducting nanotubes with \((E_{25}^{S})\) and \((E_{25}^{P})\) transitions, however there are also unassigned nanotubes at 218 and 338 cm\(^{-1}\) that will be discussed in Chapter 7. Most of the outer tubes are semiconducting nanotubes with \((E_{34}^{S})\) and \((E_{34}^{P})\) transitions, however the RBMs at 167 and 176 cm\(^{-1}\) are unassigned and are probably from metallic nanotubes with \((E_{11}^{M})\) transitions.

Figures 5.20 and 21 compare the RBM intensity variations to the intensity at zero strain for the ten Lorentzian components in the range up to 1.5 % strain. In tension, the 307, 289, 283, 154, and 253 cm\(^{-1}\) peak intensities increased which represent inner tubes, whereas for the 218,167 and 125 cm\(^{-1}\) peaks which represent the outer tubes the intensities decreased. The 338 and 176 cm\(^{-1}\) peak intensities show almost constant. These findings further support the idea of the effect of deformation upon resonance of carbon nanotubes as discussed in Chapter 1, Section 1.7. Overall the semiconducting inner and outer walls in resonance with \(E_{\text{laser}} = 1.96\) eV, change in intensity during deformation strain.
Figure 5.18 (A) Typical RBM-band Raman spectra of DWCNTs powder compared with the DWCNTs in undeformed and 1.5% strain loaded DWCNTs/epoxy composites. (B) RBM-band Raman spectra of DWCNTs in an undeformed DWCNTs/epoxy composites.

The present findings seem to be consistent with those of Lucas et al. [148] who suggest the van Hove singularity (VHS) in the nanotube electronic DOS shifts higher or lower in energy when the nanotube is under uniaxial strain. The band gaps of the nanotubes are thus moved closer or further away from the laser excitation energy, which affects the resonance condition and therefore affects the Raman intensity. However the 338 cm\(^{-1}\) semiconducting peak, the metallic inner and outer walls with \((E_{22}^m)\) transitions in resonance with the \(E_{\text{las}}=1.96\) eV are not changed in intensity during deformation. It seems possible that these tubes are not totally in resonance and/or the resonance windows of \((E_{11}^n)\) and \((E_{22}^n)\) are broadened by uncertain factors [147].
Figure 5.19 The Kataura plot [191] used to determine the metallic or semiconducting nature of DWCNTs in resonance with excitation energy of the 633 nm laser for (A) the inner tubes and (B) the outer tubes. The green line indicates the excitation energy of the 633 nm laser and the area between the two solid green lines represents the resonance window. The open circle is used to mark a Raman frequency where the RBM intensity is strong.
Figure 5.20 Shift of the intensities of the RBM-band of strain upon the DWCNTs/epoxy composites for the 338 (solid squares), 307 (solid circles), 307 (solid circles), 289 (up solid triangles), 284 (down solid triangles), 253 (solid diamond) and 218 (lift solid triangles) cm$^{-1}$ peaks for the inner tubes.
Chapter Five: Double-walled carbon nanotubes (DWNT) and their epoxy composites

Figure 5.21 Shift of the intensities of the RBM-band of strain upon the DWCNTs/epoxy composites for the 176 (right solid triangles), 167 (solid hexagon), the 154 (star) and 125 (solid pentagon) cm\(^{-1}\) peaks for the outer tubes.

5.9 Conclusions

This chapter has investigated the structure, morphology, and physical properties of DWCNTS powders using Raman spectroscopy, TEM, SEM, and TGA. The second aim as to study the stress transfer in epoxy composites reinforced with DWCNTs using Raman spectroscopy to clarify the reinforcing ability of the DWCNTs in an epoxy matrix.

The most obvious finding to be drawn from the present chapter is that the DWCNTs (CVD) were of high-quality with low amounts of side-wall defects and other carbon impurities. The morphology was observed by SEM, showing a high density cluster of web-like ropes and approximately 98 wt % pure based on SEM/EDX analysis. However, most of the DWCNTs consist of bundles of well-aligned carbon filaments, shown by TEM to be mostly 20 ± 14 nm diameter bundles free from any iron particles. The diameters of the DWCNTs, deduced from the Raman shift of the RBM mode, mostly range from 1.2 - 1.35 nm in outer diameter and 0.60 - 0.99 nm in inner diameter, having a mean value of 1.47 ± 0.16 and 0.82 ± 0.13 nm from a Gaussian distribution analysis respectively. Moreover, the interlayer spacing of DWCNTs has a mean value of 0.325 nm. TGA and DTG curves of DWCNTs reveal a high thermal stability in air up to 683 ± 6 °C.

The present study predicts both the mean true density value of 1.55 ± 0.15 g/cm\(^3\) and a mean surface area value of 1796 ± 0.2 m\(^2\)/g. It has been shown that well-defined Raman
spectra can be obtained from DWCNTs excited at 633 nm (He-Ne) laser where the G’ band line shape of the DWCNTs bundles is split into two peaks. The lower frequency G’₁ is related to the inner wall nanotubes while the higher frequency G’₂ is related to the outer wall and is more intense than the lower frequency G’₁ peak.

Another finding to be drawn from the present chapter is that the level of the interfacial adhesion between DWCNTs and the epoxy matrix was decreased with the repeated loading cycles to the same maximum strain. It was also shown that the overall G’-peak narrowed as the composites were loaded, followed by broadening upon unloading and there are no significant hysteresis loops of the G’- band widths (FWHM) with cyclic deformation with increasing maximum strain.

There are RBM intensity variations of the DWCNTs in the hot-cured DWCNTs / epoxy composites during deformation. These findings further support the idea of the effect of deformation upon resonance of carbon nanotubes and the inner nanotubes wall is stressed during deformation due to good inter-wall bonding.
6 Chapter Six: Multiwall carbon nanotubes (MWCNTs) and their epoxy composites

6.1 Introduction

The preparation and characterization of the MWCNTs was described in Chapter 3. In the present chapter, the structure of the MWCNTS composites was determined by Raman spectroscopy and SEM. Furthermore, the Raman shift of position and width of G'-band for the MWCNTs in an epoxy matrix used for monitoring the interface and load transfer between nanotubes and the epoxy matrix in composites either for tensile deformation or for cyclic tensile deformation. The aim of this chapter is to evaluate and validate the mechanical and viscoelastic properties of hot-cured MWCNTS /epoxy composites at different weight contents of MWCNTs. DMA was used to determine storage modulus, loss modulus and tan delta of the composites over a range of temperature from -100 °C to 200 °C. Tensile tests were carried out at 25 °C to record tensile strength, elongation and modulus values. The nanotube dispersions were investigated by SEM.

6.2 Deformation of the MWCNTS /epoxy composites

6.2.1 Raman spectra of the MWCNTs and the MWCNTS /epoxy composites

Figure 6.1(A) shows the spectra of the neat hot-cured epoxy resin, as-produced MWCNTs powder and the MWCNTS/epoxy composite excited using 633 nm (He-Ne) laser in the range 1000-3000 cm⁻¹. It is clear that the high intensities of main peaks of the as-produced MWCNTs compared with the cured epoxy in the nanocomposites are strongly related to the resonance Raman scattering of the MWCNTs.

Figure 6.1(B) compares the G'-band of the as-produced MWCNTs and as-produced MWCNTs in MWCNTs / epoxy composites in the range 2500-2800 cm⁻¹. The G’-band retains its bell shape but its frequency is upshifted by about 8 cm⁻¹ for the composites compared with that of the as-produced MWCNTs and the FWHM is narrowed by about 7 cm⁻¹. A possible explanation may be due to the susceptibility of MWCNTs to pre-compression due to the generation of internal residual stresses caused during the curing shrinkage as well as the thermal shrinkage in hot-cured systems [187].

6.2.2 Analysis of deformation using Raman spectroscopy

6.2.2.1 Tensile Loading up to 1.5 % tensile strain

The hot-cured MWCNTS / epoxy composites were subjected to tensile loading up to 1.5% strain. Figure 6.2 compares the G’-band in the undeformed state and at 1.5 % strain state for
the MWCNTs in the hot-cured MWCNTs (0.1 wt%) / epoxy composite. There is a small downshift in the wavenumber and narrowing with increasing tensile strain.

Figure 6.1 (A) Raman spectra of the epoxy, as-produced MWCNTs and hot-cured MWCNTs / epoxy nanocomposites in the range 100-3000 cm⁻¹ excited using a 633 nm (He-Ne) laser (B) G' band of the MWCNTs powders and hot-cured MWCNTs / epoxy nanocomposites in the range 2500-2800 cm⁻¹ excited using a 633 nm (He-Ne) laser. (Frequency (cm⁻¹) / (FWHM, cm⁻¹)).

The shifts of the position of the G' band with strain for the different concentrations of MWCNTs/epoxy composites system are shown in Figure 6.3 (A) 0.1 % (C) 0.2 % (E) 0.5 % and (G) 1.0 % and the corresponding change in the G'-band FWHM shown in (B), (D), (F), and (H) respectively. It is apparent that the G' band positions are downshifted and the linewidths are broadened with strain except for the 0.1 wt% MWCNTs/epoxy composites which become narrowed over the strain range.
Chapter Six: Multiwall carbon nanotubes (MWCNTs) and their epoxy composites

Figure 6.2 A typical G’-Raman spectra of hot-cured (0.1 wt %) MWCNTs / epoxy nanocomposites in the range 2500-2800 cm⁻¹ excited using a 633 nm (He-Ne) laser in the undeformed state and at 1.5 % axial strain

It is observed that the average initial slope are -3.43 ± 1.34, -2.08 ± 0.73, -2.55 ± 0.80 and -1.34 ± 0.56 cm⁻¹/ % strain for 0.1, 0.2, 0.5 and 1.0 wt% concentration of MWCNTs in the composite respectively. It can be seen that the peak-shift rate for the G’- band from 0.2, 0.5 and 1.0 wt% concentration of MWCNTs in the composite are decreased by 40, 25, 60 % compared to that of 0.1 wt% concentration of MWCNTs in the composite. These differences may be attributed to a poorer dispersion for the higher concentration of MWCNTs, as will be seen later.

6.2.2.2 Loading and unloading to the same maximum strain for 0.1 wt% MWCNTs/epoxy composites

The responses of the G’-band positions and their widths (FWHM) are shown in Figure 6.4(A) and (B) respectively for the three cycles of loading and unloading, applied to the same maximum strain maximum level (1 % strain). It is observed that the hysteresis areas for cycles 1, 2 and 3 are similar indicating that the nanotubes are in less tension on the unloading part of the cycle. If we now turn to the zero-strain G’- band position, it become shifted to the higher wavenumber. This seems to be consistent with the observations of Kao et al for SWCNTs [189].

Turning now to the FWHM, the peak narrowed slightly in the composites upon loading, followed by slight broadening upon unloading. During the loading cycles 2 and 3, the broadening and narrowing are repeated in the same manner. However, there are no significant differences between the three cycles and the loop areas are not obvious for the loading cycles.

A hysteresis loop of G’- band positions was observed to develop due to the change of the stress transfer efficiency between the loading and the unloading steps. There are no significant hysteresis loops of G’- band widths (FWHM) where the peak narrowed for the composites upon loading, followed by broadening upon unloading.
Chapter Six: Multiwall carbon nanotubes (MWCNTs) and their epoxy composites

Figure 6.3 Typical examples of the shift of G’-band positions versus tensile strain up to 1.5 % strain for the hot-cured MWCNTs / epoxy nanocomposites excited using a 633 nm (He-Ne) laser for different wt% MWCNTs; (A) 0.1 % (C) 0.2 % (E) 0.5 % and (G) 1.0 % and the corresponding change of G’-band width (FWHM); (B), (D), (F), and (H), respectively.
Figure 6.4 (A) Variation of the position of the G'-band for three cycles of loading and unloading up to 1.0% maximum strain fitted as a one Lorentizan peak and (B) the corresponding the change of G'-band FWHM for the 0.1 wt% MWCNTs/epoxy composite in tension.

6.2.2.3 Cyclic deformation with increasing maximum strain

The shifts of the position of the G' band versus strain for the 0.1 wt% MWCNTs/epoxy composites up to 0.5, 1.0 and 1.5% strain are shown in Figure 6.5(A) and (B) the corresponding the change of G'-band FWHM. It can be seen in the initial cycle that the loading curve overlaps the unloading one in which the G'-band shifts approximately linearly with strain. The strain–shift relationship of the G'-band becomes non-linear for the loading cycle, as the maximum loading strain is increased. It is clear that the strain–shift profile of the G' band moves to lower wavenumber. The loop area is found to increase in size with the level of the maximum loading strain.

These findings corroborate the ideas of Kao et al [189] for SWCNTs, who suggested that the stress is fully transferred from the matrix to the nanotubes in the initial cycle and the composite is then subjected to gradual damage of the nanotube–matrix interface in the other cycles 2 and...
3. In addition, they suggested that in cycles 2 and 3 the interface is subjected to irreversible damage in the composites.

For the FWHM curve, the overall G'-band widths revert back to a slightly higher value than the original pre-strain and the loop areas for the loading cycles increase with the number of loading strains. It is remarkable that the strain-induced changes of the wavenumber positions and widths of G'-bands are reversible. However, the G'-band narrows upon loading and hysteresis is not observed clearly in the mechanical response of the overall G'-band widths.

6.3 Dynamic mechanical properties

Figure 6.6 shows the variation with temperature of the storage modulus ($E'$), the loss modulus ($E''$) and the damping properties, tan $\delta$ of the neat epoxy. The epoxy resin's storage modulus (energy stored elastically during deformation) decreases as the temperature increases where the mobility of the polymer chains increases. A significant drop in the storage modulus occurs as the bulk epoxy resin changes from a rigid, glassy state to a more rubbery state at the $T_g$.

The $\alpha$-transition and $\beta$-transition are observed in the high temperature region and below 0°C, respectively and also on the loss modulus ($E''$) (Energy converted to heat during deformation) and tan $\delta$ curves. The $\beta$-transition is associated the movement of the side groups, the $\alpha$-transition is attributed to the movements of the main chain in the epoxy resin [198-200]. Generally, the values of the transition temperature $T_g$ may be taken in several ways; from the onset of the drop in the storage modulus ($E'$) curve (98 ± 2°C) or from the maximum peaks of the loss modulus ($E''$) curve (108 ± 2°C) and of the maximum peak of the tan $\delta$ curve (125 ± 0.9°C). The tan $\delta$ curve peak is a popular measurement technique for the $T_g$ as it is usually easier to isolate and indicates the point where the ratio of viscous response to elastic response is the highest [198, 199].
Figure 6.6 Typical DMA data for the hot-cured epoxy resin where the black, red and blue arrows referring to the $T_g$ values from the onset of the drop in the storage modulus ($E'$), from the maximum peaks of the loss modulus ($E''$) curve and of tan delta ($\delta$) curve in the high temperature region

6.3.1 The storage modulus ($E'$)

The storage modulus as a function of temperature for the epoxy and the composites reinforced with different concentrations of MWCNTs are shown in Figures 6.7(A). At low temperatures, all the samples have high values of the storage (elastic) modulus which continue to decline between -70 and -50 °C and between 10 °C and 50 °C. It is interesting to note that in the storage modulus ($E'$) increased for 0.1 and 0.2 wt% MWCNTS content followed by a decrease for 0.5 and 1.0 wt% MWCNTS content.

In Figures 6.7(B), it is noted that the modulus at 25 °C (the glassy region) is higher than the neat epoxy and is improved by about 30 % for 0.1, 0.2, 0.5 and 1.0 wt% MWCNTs respectively as seen in Table 6.2. Therefore, there are no significant differences in storage modulus of the composites. In Figure 6.8(C) one should notice there is a strong increase of the onset temperature of the drop in the storage modulus ($E'$) drop curve for 0.1 and 0.2 wt% MWCNTs followed by a continuous decrease for 0.5 and 1.0 wt% MWCNTs in the rubbery region at elevated temperatures.
Chapter Six: Multiwall carbon nanotubes (MWCNTs) and their epoxy composites

Figure 6.7 (A) Storage modulus ($E'$) of hot-cured MWCNTs/epoxy composites at different weight contents of MWCNTs over a range of temperatures from (-100 °C to 200 °C). (B) The storage modulus as a function of weight fraction of MWCNTs at 25 °C. (C) The onset of the drop in the storage modulus ($E'$) curve as a function of weight fraction of MWCNTs in the rubbery region.

Table 6.1 The average storage modulus ($E'$) of neat epoxy and hot-cured neat epoxy and MWCNTs/epoxy composites at 25 °C for different weight contents of MWCNTs

<table>
<thead>
<tr>
<th>Sample</th>
<th>The storage modulus ($E'$), (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>1970 ± 25</td>
</tr>
<tr>
<td>0.1 wt% MWCNTs</td>
<td>2600 ± 100</td>
</tr>
<tr>
<td>0.2 wt% MWCNTs</td>
<td>2563 ± 105</td>
</tr>
<tr>
<td>0.5 wt% MWCNTs</td>
<td>2560 ± 22</td>
</tr>
<tr>
<td>1.0 wt% MWCNTs</td>
<td>2533 ± 73</td>
</tr>
</tbody>
</table>

6.3.2 The loss modulus ($E''$)

Figure 6.8 compares the behaviour of the loss moduli (peak heights and their shifts) of the epoxy and nanocomposites for different loadings in the -100 - 200°C temperature range. It is
appears that there are two main distinct structural transitions, the $\beta$-transition and $\alpha$-transition but only the $\alpha$-transition will be considered further.

Figure 6.8 The loss modulus ($E''$) of the hot-cured MWCNTS/epoxy composites at different weight contents of MWCNTs over a range of temperatures. (A) Full range from (-100 °C to 200 °C), (B) the $\alpha$-transition from 75 °C to 150 °C, and the corresponding maxima loss modulus peaks shifting in $\alpha$-regions in (C)

The $\alpha$-transition showed a continuous increase in peak height for higher MWCNTS-contents as shown in Figure 6.8(B). The peak temperatures are also increased up to 0.2 wt %, followed by no significant differences between 0.2, 0.5 and 1 wt % in comparison to the pure epoxy peak as shown in Figure 6.9 (C). It is that the displacement the peaks of loss modulus $E''$ to higher temperatures may be due to a reduction in the chain flexibility of the epoxy matrix or a delay in maximum chain slippage of the epoxy polymer in the composite systems [199, 201, 202].

6.3.3 The loss factor (tan $\delta$)

Figure 6.9(A) presents complete sets of tan $\delta$ curves in the 75-200 °C temperature ranges for the pure epoxy and nanocomposites with different MWCNTs concentration. The tan $\delta$ curve of the pure epoxy shows strong peak at the highest temperature in the $\alpha$-region. In fact, tan $\delta$ is a meaningful property and also represents the ratio of the viscous versus elastic contributions of the material in a given condition. One should notice that there is slight increase in the temperatures of the maximum tan delta peaks in the $\alpha$-region ($T_\delta$) in comparison to the pure
epoxy peak, but there is no significant changes for the 0.5 wt% and 1.0 wt% composites, as well as almost identical peak heights as shown in Figure 6.9(B).

![Figure 6.9: Tan δ of the hot-cured MWCNTs/epoxy composites with different weight contents of MWCNTs over a range of temperatures. (A) The α-relaxation from (75 °C to 200 °C), and (B) the corresponding maxima the loss factor (tan δ) peaks shifting in α-regions.](image)

6.4 Mechanical properties

6.4.1 Stress-strain curves

Figure 6.10 shows the typical stress-strain curves up to failure of the hot-cured neat epoxy and MWCNTs/epoxy composites for different weight content of MWCNTs. The average mechanical properties from the tensile tests are presented in Table 6.2 and Figure 6.10 compares the intercorrelations between modulus, strength, and MWCNTS weight fraction of the epoxy composite samples. The stress–strain curves show a clear trend of a non-linear relationship up to the maximum stress and the addition of MWCNTs obviously affected the mechanical properties of the composites. Furthermore, the Young’s modulus is calculated from the slope of a least squares regression line fit to the part of the stress strain curve in the strain interval 0.0005 ≤ ε ≤ 0.0025 of the stress-strain curves [159].
Chapter Six: Multiwall carbon nanotubes (MWCNTs) and their epoxy composites

Figure 6.10 Stress-strain curves of the hot-cured neat epoxy and MWCNTs/epoxy composites with different weight contents of MWCNTs

Table 6.2 The Young’s modulus ($E$), tensile strength ({$\sigma_{\text{max}}$}) and the fracture strain (%) of the hot-cured neat epoxy and MWCNTs/epoxy composites with different weight contents of MWCNTs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s modulus, MPa</th>
<th>Tensile Strength, MPa</th>
<th>Ultimate tensile strain, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>2658 ± 153</td>
<td>46 ± 13</td>
<td>3.2 ± 0.9</td>
</tr>
<tr>
<td>0.1 wt% MWCNTs</td>
<td>2878 ± 186</td>
<td>62 ± 12</td>
<td>3.7 ± 0.37</td>
</tr>
<tr>
<td>0.2 wt% MWCNTs</td>
<td>2777 ± 105</td>
<td>54 ± 9</td>
<td>3.0 ± 0.9</td>
</tr>
<tr>
<td>0.5 wt% MWCNTs</td>
<td>2742 ± 123</td>
<td>58 ± 5</td>
<td>3.4 ± 0.7</td>
</tr>
<tr>
<td>1.0 wt% MWCNTs</td>
<td>2746 ± 066</td>
<td>52 ± 10</td>
<td>2.7 ± 0.8</td>
</tr>
</tbody>
</table>

The general tendency of the data in Table 6.3 and Figure 6.11(A) is that the Young’s moduli of the MWCNTs/epoxy composites are improved by the addition of MWCNTs in comparison with the neat epoxy. However, the system with 0.1 wt% content has the best modulus enhancement. There is also increasing of the tensile strength for the all composites compared with the neat epoxy resin. Furthermore, it is apparent that the elongation at break (ultimate tensile strain) is increased for the content of 0.1 wt% MWCNTs followed by a decrease with higher loading.
Figure 6.11 (A) The Young’s modulus (B) tensile strength and (C) fracture strain of the hot-cured neat epoxy and MWCNTS/epoxy composites for different weight contents of MWCNTs.
6.4.2 Tensile fracture surface analysis by SEM

Figures 6.12, 6.13, 6.14, 6.15 and 6.16 show the morphology of the tensile fracture surface of the neat hot cured epoxy and 0.1wt%, 0.2wt%, 0.5wt%, and 1.0wt% MWCNTs/epoxy composites respectively.

Figure 6.12 shows the morphology of the tensile fracture surface of the neat epoxy. It is apparent from this figure that the neat epoxy is free of air voids. The cracks steps are parallel to the crack-propagation direction and the plane between them is flat and featureless, as shown in the higher magnification in Figure 6.12(C) and (D) which indicate a typical morphology feature of brittle fracture behaviour, thus accounting for the low fracture toughness of the neat epoxy [203-205].

![Figure 6.12 SEM fracture surface of the hot-cured neat epoxy at different magnifications with scale bars (A) 1 mm, (B) 100 µm, (C) 5 µm and (D) 1 µm.](image)

The fracture surfaces of 0.1wt% MWCNTs/epoxy composites taken from the tensile test are shown in Figure 6.13. It is apparent from this figure that the composite surface is obviously rough and free of air voids. Figure 6.13(B) demonstrates an important finding that each plane contains at least one MWCNT observed as bright spots dispersed in the epoxy resin matrix, as well as some entangled MWCNTs pulled out of the epoxy–nanotube matrix [203-205]
Chapter Six: Multiwall carbon nanotubes (MWCNTs) and their epoxy composites

Figure 6.13 SEM fracture surface of the hot-cured 0.1 wt% MWCNTs/epoxy composite at different magnifications with scale bars (A) 100 µm and (B) 1 µm. Pulled out MWCNTs are marked with solid red arrows.

Figure 6.14 shows the morphology of the tensile fracture surface of 0.2 wt% MWCNTs/epoxy composite. It is apparent from this figure that the composite surface is obviously rougher than the 0.1 wt% MWCNTs/epoxy composite and also free of air voids. Another important finding was that the MWCNTs were well dispersed (crack plane contains at least one MWCNT) in the epoxy resin matrix but some entangled MWCNTs can still be observed in the epoxy matrix and some MWCNTs were seen completely pulled out of the fracture surface. It seems possible that the weak interface between the MWCNTs and polymer makes it easy for MWCNTs to pull out holes of the polymer matrix completely as shown the green arrows in Figure 6.14(B).

Figure 6.15 shows the morphology of the tensile fracture surface of 0.5 wt% MWCNTs/epoxy composites. It is apparent from this figure that the composite surface is much rougher and their crack becomes more random as well as being free of air voids. Another important finding was that MWCNTs were well dispersed in epoxy resin matrix (crack plane contains at least one MWCNT) but an agglomeration of several MWCNTs was also observed in the fracture surface. Some MWCNTs were seen pulled out of the fracture surface. The number of pulled out MWCNTs in the agglomeration areas is more than those in the well dispersed areas.
Figure 6.15 SEM fracture surface of the hot-cured 0.5 wt% MWCNTs/epoxy composite at different magnifications with scale bars (A) 1 mm (agglomerated area represented by yellow round dots and the well dispersed area by red round dots), (B) 100 µm, (C) 1 µm (higher magnifications of agglomerated area) with dashed yellow arrows and (D) 1 µm (higher magnifications of dispersed area) with dashed red arrows. Pulled out MWCNTs indicated by solid red arrows.

Figure 6.16 shows the morphology of the tensile fracture surface of 1.0 wt% MWCNTs/epoxy composite. Another finding was that more agglomeration areas of several MWCNTs were observed on the fracture surface when the CNT content increased to 1.0 wt%. Another important finding was that the number of pulled out MWCNTs in the agglomeration areas is more than those in the dispersed areas. Some MWCNTs were seen pulled out of the fracture surface. It seems possible that the weak interface between MWCNTs and polymer makes it easier for MWCNTs to pull out of the polymer matrix completely as shown the green arrows in Figure 6.16(C). Furthermore the cracks radiate out from the agglomerates (defects) which initiate failure that leads to a reduction in strength.
Figure 6.16 SEM fracture surface of the hot-cured 1.0 wt% MWCNTs/ epoxy composite at different magnifications with scale bars (A) 1 mm (agglomerated areas represented by yellow round dots and the well dispersed area by red round dots), (B) 100 µm, (C) 1 µm (higher magnifications of agglomerated area) with dashed yellow arrows and (D) 1 µm (higher magnifications of dispersed area) with dashed red arrows. Pulled out MWCNTs indicated by solid red arrows.

6.5 Discussion

6.5.1 Young’s moduli of the MWCNTs comparison

The Young’s modulus of the nanotube-reinforced composites can be predicted, based on the G’-band shift rate, using the simple rule of mixture for discontinuous fibre-reinforced composites [206]:

\[ E_c = K_e \phi_{CNT} E_{eff(CNT)} + (1 - \phi_{CNT}) E_m \]  

where \( E_{eff(CNT)} \) is the effective modulus of MWCNTs, \( E_m \) is the epoxy matrix modulus, \( \phi_{CNT} \) is the volume fraction of nanotubes and \( K_e \) is a factor that takes into account the effect of the misorientation and the finite length of the nanotubes which is less than unity and is found to be 1/9 for 3D random composite systems [109, 207]. The volume fraction of nanotubes depends on the weight fraction of MWCNTs in each composite and the \( E_m \) is taken from the experimental values from the tensile test as 2.70 ± 0.15 GPa. It has been demonstrated that the effective Young’s modulus of both single- and multiwall carbon nanotubes in epoxy-matrix composites...
can be determined using the stress-induced shift of the same G'-band in carbon nanotubes [109], therefore the universal calibration leads to:

\[ E_{\text{eff}}(\text{CNT}) = \frac{1.3 \times S(0)}{-0.05} \]  

where \( S(0) \) is the band shift rate (cm\(^{-1}\)/%) and \( E_{\text{eff}}(\text{CNT}) \) is in GPa.

Table 6.3 illustrates the predicted effective elastic modulus of MWCNTs and their epoxy composites. There was a significant positive correlation between the G'-band shift rate of the MWCNTs and their effective modulus. Although the mass fraction of MWCNTs has increased up to ten times compared to the 0.1 wt% MWCNTs/epoxy composites, it was observed that the G'-band shift rate decreased. It was expected that with an increase of the volume fraction of MWCNTs, the G'-band shift rate should be constant or at least to not decrease. This inconsistency may be due to the weak bonding between MWCNTs and matrix and weak interlayers in MWCNTs, curviness and high wt% areas of agglomeration of CNTs as was seen in the SEM images.

### Table 6.3 Calculation the effective elastic modulus of MWCNTs based on the G'-band shift rate using Raman spectroscopy

<table>
<thead>
<tr>
<th>Sample</th>
<th>G'-band shift rate, ( S(0) ) (cm(^{-1})/%)</th>
<th>MWCNTs effective modulus, ( E_{\text{eff}} ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 wt% MWCNTs</td>
<td>-3.43 ± 1.34</td>
<td>92 ± 9</td>
</tr>
<tr>
<td>0.2 wt% MWCNTs</td>
<td>-2.08 ± 0.73</td>
<td>46 ± 5</td>
</tr>
<tr>
<td>0.5 wt% MWCNTs</td>
<td>-2.55 ± 0.80</td>
<td>79 ± 8</td>
</tr>
<tr>
<td>1.0 wt% MWCNTs</td>
<td>-1.34 ± 0.56</td>
<td>37 ± 4</td>
</tr>
</tbody>
</table>

Equation (6.1) and the epoxy matrix modulus, \( E_m \) which was taken from the experimental values as 2.70 ± 0.15 GPa for the tensile tests and 1.97 ± 0.02 GPa for DMA analysis, were used to calculate the effective modulus of MWCNTs powders based on the experimental tensile testing and DMA analysis.

### Table 6.4 Calculated effective Young’s modulus of MWCNTs powders based on the experimental tensile testing, Dynamic mechanical analysis (DMA) and Raman spectroscopy results for the nanotube reinforced composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>The effective Young’s modulus of MWCNTs, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMA</td>
</tr>
<tr>
<td>0.1 wt% MWCNTs</td>
<td>190 ± 10</td>
</tr>
<tr>
<td>0.2 wt% MWCNTs</td>
<td>99 ± 10</td>
</tr>
<tr>
<td>0.5 wt% MWCNTs</td>
<td>50 ± 2</td>
</tr>
<tr>
<td>1.0 wt% MWCNTs</td>
<td>33 ± 7</td>
</tr>
</tbody>
</table>

Table 6.4 and Figure 6.17 provide the results obtained from the calculation of the effective modulus of MWCNTs based on the experimental tensile testing, DMA and Raman spectroscopy. It is interesting to note that in all cases that the effective modulus of MWCNTs decreases as the mass fraction of the MWCNTs is increased. There are similarities between the
results obtained by tensile tests and those presented by Raman spectroscopy in 0.1, 0.2 and 1.0 wt% MWCNTs. However the low wt% values determined by DMA are somewhat higher than the values of tensile test and the Raman spectroscopy.

![Graph showing effective elastic modulus vs weight fraction of MWNTs](image)

**Figure 6.17** The effective Young’s modulus of MWCNTs determined from DMA, tensile test and Raman spectroscopy.

### 6.5.2 Effect of wt% MWCNTs on the mechanical properties

It was observed that the Young’s modulus of the neat epoxy (2658 ± 153 MPa) is higher than its storage modulus (1970 ± 25 MPa). However, the Young’s modulus is similar conceptually to the storage modulus but measured in a different way. This finding corroborates the ideas of Menard [208] who suggested that the reasons such tests are very different is that the material is constantly stretched in the stress–strain test and is oscillated in the DMA test.

The general tendency is that the Young’s moduli of the MWCNTs/epoxy composites are improved for the content at different weight contents of MWCNTs. However, the system with 0.1 wt% content has the best modulus enhancement. It might be related to the interface interaction between carbon nanotubes and matrix being poor and/or the MWCNTs being not homogeneously distributed in the epoxy matrix [209].

Overall, increasing the addition content of MWCNTs more than 0.1 wt% did not lead to a further improvement in strength and the elongation at break (ultimate tensile strain). It is well known that the dispersion of MWCNTs and the interfacial adhesion between the CNTs and matrix have been identified as major contributing factors for the levels of reinforcement of the MWCNTs/epoxy composites. A possible explanation for the improvement in 0.1 wt% MWCNTs content might be due to the existence of the better dispersion of MWCNTs in the matrix resin. The decrease of strength with high MWCNTs content could be attributed to the dispersion of CNTs not being uniform, and the significant agglomeration of MWCNTs that fails to transfer their potential mechanical properties to the matrix effectively [210, 211].

This finding corroborates the ideas of Zhou et al [210], who suggested that at a high strain level, the stress concentration caused by the agglomerated MWCNTs initiated a crack, which
made the composites fail prematurely, however at a low strain levels, the agglomerated particles increased the stiffness of the material.

6.6 Conclusions

This chapter has investigated the central importance of stress transfer Raman studies in epoxy composites reinforced with MWCNTs to elucidating the reinforcing ability of the MWCNTs in an epoxy matrix. This chapter was undertaken to assess the stress transfer efficiency at the MWCNTS / epoxy interface with tensile deformation and with cyclic loading using the variation of stress sensitive G'- band positions and widths (FWHM), also to determine the effect of different weight fraction of untreated MWCNTs on the stiffness and on the thermomechanical properties of the MWCNTS / epoxy composites using tensile testing and dynamic mechanical analysis (DMA).

The most obvious finding to be drawn from the present chapter is that the reinforcement of the epoxy with different loadings of MWCNTs would be useful, but our results showed that the best reinforcement at low loadings of MWCNTs. The 0.1 wt% of MWCNTS/epoxy composites has displayed their maximum reinforcement efficiency because the MWCNTs have maximum Young's modulus, Raman band shift rate and tensile strength. Moreover, at higher content, nanotubes tend to agglomerate which lead to poorer mechanical properties.

The second major findings from the theoretical calculations and experiments based on the experimental tensile testing, DMA and Raman spectroscopy show that the effective Young's modulus of MWCNTs are in generally good agreement. However, more agglomeration areas of several MWCNTs were observed when the MWCNTs content increased to 1.0 wt%. The dispersion of MWCNTs and the interfacial adhesion between the CNTs and matrix have been identified as major contributing factors for the levels of reinforcement of the MWCNTS/epoxy composites.
Chapter Seven: Effect of deformation upon the Raman Spectra of carbon nanotube / epoxy composites

7.1 Relations between the G'-band frequency and tensile strain

7.1.1 Introduction

The effect of the stress transfer within SWCNTs, DWCNTs and MWCNTs upon their ability to reinforce epoxy composites can be followed from the rate of shift of the G'-band per unit strain for tensile deformation of 0.1wt% CNTs/epoxy nanocomposites.

Comparisons between the shift of G'-band frequency of the SWCNTs, DWCNTs and MWCNTs in epoxy composites for 1.5% maximum loading strain, all fitted as a one Lorentizan peak, excited at 633 nm (He-Ne) laser are presented in Figure 7.1(A). The general tendency for the hot-cured system is that the G'-band is downshifted and the their initial rate was found to be \(-14.1 \pm 3.3 \text{ cm}^{-1}/\%\) strain for the SWCNTs in epoxy composites. This value is higher than that of a hot-cured system [187] by a factor of two. This difference can be explained in part by the better dispersion of SWCNTs in the composites which results in better adhesion to the epoxy matrix, as well as better efficient reinforcement. Another possible explanation for this is due to the hot-cured system exhibit more residual stresses than the cold-cured one.

---

**Figure 7.1 (A)** The shift of the G'-band position and (B) the change of widths of the G'-band (FWHM) for hot cured SWCNTs, DWCNTs and MWCNTs / epoxy composites up to 1.5 % maximum loading strain fitted to one Lorentizan peak (excited using a 633 nm (He-Ne) laser)
The general tendency the hot-cured system is that, the overall G'-band is downshifted and the their initial rates were found to be -21.5 ± 1.2 and -3.4 ± 1.3 cm⁻¹/strain for the DWCNTs and MWCNTs in epoxy composites, respectively in Figure 7.1(A). One unanticipated finding was that the initial shift rates of the DWCNTs are higher than SWCNTs and MWCNTs in epoxy composites. These later results differ from Cui et al [75] who found that the initial shift rates of the higher frequency G'-band (outer tubes) of the, DWCNTs (peapods) is lower than SWCNTs in cold-cured epoxy composites. This result may be explained by the greater perfection of DWCNTs (CVD) in which the Raman D-band (defects) is weak.

Figure 7.1(B) shows the G’ band linewidths (full width at half maximum) plotted as a function of strain for SWNT, DWCNTs and MWCNTS/epoxy composites. It is interesting to note that the G’ band linewidths of DWCNTs are higher than for the SWCNTs and MWCNTs in the undeformed CNT/epoxy composites. It is clear from this figure that the DWCNTS and MWCNTS nanotubes respond in a similar behaviour while the SWCNTs have different behaviour with strain. The G’ band linewidths of SWCNTs increase (broadening) while those of DWCNTs and MWCNTs decrease (narrowing) with strain. There are similarities between the broadening behaviour of the G’ band linewidths in this study and the G band linewidths described by Kumar et al [212]. The authors assumed that the strain-induced broadening observed in semiconducting SWCNTs is attributed to inhomogeneity, which is expected if the strain is not uniformly distributed along the length of the nanotubes. Another possible explanation for narrowing the G’ band linewidths of DWCNTs and MWCNTs with strain this is that the contributions from the outer tubes shift downwards relative to those that from the inner walls in DWCNTs and MWCNTs, hence the peaks overlap more, reducing the overall apparent peak width.

Equation (6.1) and the G’-band shift rate for CNT/epoxy composites were used to calculate the effective modulus of SWCNTs, DWCNTs and MWCNTs which are listed in Table 7.1. It can be observed that DWCNTs are stiffer than SWCNTs and MWCNTs by a factor of two and of six respectively, probably due to that the inner and outer walls are both stressed during tensile deformation and their smaller size as opposed to regular MWCNTs. Another possible explanation for this is that the greater perfection of DWCNTs (CVD) in which the Raman D-band (defects) is weak.

Table 7.1 Calculation the effective Young’s modulus of 0.1 wt% CNTs / epoxy composites based on the G’-band shift rate using Raman spectroscopy

<table>
<thead>
<tr>
<th>Sample</th>
<th>G’-band shift rate, S (0) (cm⁻¹/%)</th>
<th>CNTs effective Young’s modulus, $E_{eff}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs/Epoxy</td>
<td>-14.1 ± 3.3</td>
<td>367 ± 3</td>
</tr>
<tr>
<td>DWCNTs/Epoxy</td>
<td>-21.5 ± 1.2</td>
<td>559 ± 1</td>
</tr>
<tr>
<td>MWCNTs/Epoxy</td>
<td>-3.4 ± 1.3</td>
<td>92 ± 9</td>
</tr>
</tbody>
</table>

7.1.2 SWNT/epoxy composites

A lot of work has been done to investigate the Raman spectroscopy of uniaxial strained SWCNTs through bending SWCNTs/polymer composites to probe the interface damage between the polymers and nanotubes [189], to measure the interfacial shear strength of the
nanotubes-matrix interface [213] and to measure strain fields around fibres in a glass fibre–reinforced polymer composite [214, 215] using Raman peak shift in D-, G-, G'- Raman band frequencies. However, the G'- Raman band shift rate per unit strain of individual isolated SWCNTs is as large as - 40 cm⁻¹/% strain [216]. In the nanocomposites is significantly lower and ranges from -1.3 to -15 cm⁻¹/% strain. This wide range is attributed to the SWCNTs bundle size, poorer dispersion of the tubes, as well as differences in the interfacial adhesion to the matrix [109, 187, 217].

7.1.3 DWCNTs/epoxy composites

In Figure 7.2(A), the shift of the G₁'-band (outer walls) compared to the G₂'-band position (inner walls) is presented with increasing uniaxial strain for DWCNTs / epoxy nanocomposites. It is interesting to note that the average initial rates of the higher frequency G₁'-band (outer tubes) and the lower one G₂'-band (inner tubes) in DWCNTs / epoxy composites are found to be, – 24.9 ± 0.5, and – 18.7 ± 1.1 cm⁻¹/% strain respectively. Cui et al have speculated that the stress transfer parameter kᵢ is given by the ratio of the slopes of the lines for the inner and outer layers (dω₂/dω₁) which indicates the stress transfer affecting between layers in all DWCNTs (CVD) / epoxy composites. Therefore, the stress transfers parameter kᵢ was 0.75 ± 0.20 for theses DWCNTs (CVD) whereas for the DWCNTs (peapod) it was found to be 0.05 ± 0.04. It may be that the walls of DWCNTs (CVD) fit more tightly than in the DWCNTs (peapod).

It has been demonstrated that the high efficiency of internal stress transfer of CNT results in an increasing of the rate of G' band shift in composites upon increasing tensile strain [187, 189]. The observed increase in shift rates of the G' band of the DWCNTs could be attributed to cross links between the inner and outermost walls of the DWCNTs which offers the possibility of improving interlayer load transfer. Another possible explanation for this is that there is good adhesion and bonding between the DWCNTs and epoxy matrix which increase the polymer stress transfer into the outermost walls of the nanotubes.

In Figure 7.2(B), the change of the G₁'-band widths (FWHM) (outer walls) compared to G₂'-band widths (FWHM) (inner walls) are presented under incrementally applied strain for DWCNTs (CVD)/ epoxy nanocomposites. It can be seen that the behaviour of the G₂' band linewidths (FWHM) (inner walls) in DWCNTs increase (broadening) is similar to the widths of SWCNTs behaviour. Also those of the G₂' band linewidths (FWHM) (outer walls) in DWCNTs decrease (narrowing). However the widths difference between the undeformed and at 1.5% strains for SWCNTs and the G₂' band linewidths (FWHM) (inner walls) in DWCNTs are 5 and 15 cm⁻¹, respectively. This observation could be attributed to the good inner-wall stress transfer.
Chapter Seven: Effect of deformation upon the Raman Spectra of carbon nanotube / epoxy composites

Figure 7.2 (A) The shift of the G\textsuperscript{1}'-band (outer walls) and G\textsuperscript{2}'-band position (inner walls) for the hot-cured DWCNTs / epoxy nanocomposites excited using 633 nm (He-Ne) laser and (B) the corresponding changes of the of the G\textsuperscript{1}'-band and G\textsuperscript{2}'-band widths (FWHM)

7.1.4 MWCNTS/epoxy composites

Through the stress transfer model for MWCNTs [218] the Raman spectra of the stress-induced shift rate of the G\textsuperscript{1}'-band in carbon nanotubes in epoxy composites have been computer simulated to estimate the load transfer efficiency of any nanotubes in the (5n,5n) family where n is an integer. The G\textsuperscript{1}'-band was chosen because it has a higher strain sensitivity compared with the Raman first order band, particularly at low levels of strain. All calculations were performed on computational software programs Mathematica 8 and OriginPro 8.5.

Most studies in the field of Raman spectroscopy have only focussed on the Stokes Raman process where G\textsuperscript{1}'-peak is described by Lorentzian function, given by [219]:

$$I(\omega) = \frac{I_0}{\pi \Gamma} \frac{1}{(\omega - \omega_{G1})^2 + \Gamma^2}$$  \hspace{1cm} (7.1)

where $I(\omega)$ is the resulting intensity of a forced damped harmonic oscillator model of phonon excitation, $I_0$ is the maximum intensity of the G\textsuperscript{1}'-peak, (arbitrary units), $\Gamma$ is the half width at half maximum intensity, HWHM (cm\textsuperscript{-1}), while FWHM (cm\textsuperscript{-1}) is the full width at half maximum intensity = 2$\Gamma$ (cm\textsuperscript{-1}) , $\omega$ is the oscillating frequency of an external field, (cm\textsuperscript{-1}), and $\omega_{G1}$ is the centre of G\textsuperscript{1}'-peak which is the natural vibration frequency of carbon nanotubes in the composites, (cm\textsuperscript{-1}).

It has been demonstrated that the frequency of the G\textsuperscript{1}'-peak depends on the tube diameter of the isolated SWCNTs [220] through:
where $\omega_{G'}$ is the frequency $G'$-peak in graphene (cm$^{-1}$) that is laser energy dependent and $D$ is the diameter (nm) of the individual tubes in MWCNTs and SWCNTs. The stress sensitive Raman bands (G and G' band) have been identified as major contributing factors for the decline of the stress transfer behaviour of CNT/polymer composites and to control its interfacial adhesion.

The laser dependence of the frequency $G'$-peak in graphene has been adapted to carbon nanotubes by subtraction of the stress transfer efficiency parameter for the CNTs (outer wall)/polymer interface and for the inner walls interface within the CNTs, as well as the applied strain and the stress-induced shift rate of the $G'$-band in carbon nanotubes which is defined as:

$$\omega_{G'} = \omega_{G'_0} - (k_i * S(0) * \varepsilon) \quad (7.3)$$

where $k_i$ is the stress transfer efficiency parameter, $S(0)$ is the stress-induced shift rate of the $G'$-band, (cm$^{-1}$) and $\varepsilon$ is the applied strain, (%). After substitution Equation (7.5) in Equation (7.4), the frequency of the $G'$-peak is written as:

$$\omega_{G'} = (\omega_{G'_0} - (k_i * S(0) * \varepsilon) - (\frac{35.4}{D}) \quad (7.4)$$

The relationship between the transmittance of light $T$, % and the number of graphene layers has been widely investigated and monolayer graphene is found to transmit about 97.7% of visible white light [221]. The most extreme case ($T=100\%$) is when the light is fully transmitted through the outmost wall of the SWCNTs/polymer composites. Hence the intensity of the frequency of the $G'$-peak is affected by the absorption the light. Based on the frequency of the $G'$-peak of Equation (7.4), the intensity, $I(\omega)$ of Equation (7.1) may be given between the limits $2500 \text{ cm}^{-1} \leq \omega \leq 2800 \text{ cm}^{-1}$ as

$$I(\omega) = \frac{1}{\pi} \left[ \frac{1}{(\frac{T}{1*7} + \omega - \omega_{G'_0}} + (k_i * S(0) * \varepsilon + \frac{35.4}{D})^2 + R^2 \right] \quad (7.5)$$

Finally the line shapes of the $G'$-peak for SWCNTs/epoxy composites were calculated for each strain in the range 0.0 - 1.5%, in which the laser light is being transmitted through the SWCNTs, (5, 5) layer is given by:

$$I(\omega) = \frac{1}{\pi} \left[ \frac{1}{25 * (0.954)^6} \left( \frac{1}{\omega - 2667 + (1+4 * \varepsilon + \frac{35.4}{D(5,5)})^2 + (25)^2} \right) \right] \quad (7.6)$$

In Figure 7.3 the experimental shift of the Raman $G'$ bands positions and widths (FWHM) as a function of strain from 0 to 1.5 % for the hot-cured 0.1wt % SWCNTs /epoxy nanocomposites and their corresponding model simulation calculated by Equation (7.6) with symmetrical Lorentzian are shown. As seen in Figure 7.3(A) there is a very good agreement with the measured and the line simulation shapes of the $G'$-peak for SWCNTs in SWCNTs /epoxy composites upon tensile loading as a function of strain from 0 to 1.5 %. It is known, that whenever there is good adhesion between nanotubes and a polymeric matrix there is a linear
relationship obtained, but when there is a gradual loss of adhesion the line begins to deviate from linearity. The G’-band shift is linear up to about 0.7% strain followed by a deviation from linearity where debonding occurs, giving a change in stress transfer efficiency between the nanotubes and polymeric matrix.

Figure 7.3 (A) Experimental shift of the Raman G’ bands positions and their corresponding model simulation and (B) Experimental shift of the Raman G’ bands widths (FWHM) and their corresponding model simulation as a function of strain from 0 to 1.5 % for a hot cured 0.1 wt % SWNT /epoxy nanocomposite.

The SWCNTs (n=1) were described by a (5, 5) layer and the family of ten coaxial commensurate tubes for MWCNTs is shown in Figure 7.4 which it can be presented by (5n, 5n), (5n-1, 5n-1), (5n-2, 5n-2),……., (5n-9, 5n-9) for the outermost wall, the ninth wall, the eighth wall,……., and the innermost wall, respectively. The separation between individual walls in MWCNTs is constant (~0.35 nm) for this family in tubes. The outermost wall (5n, 5n) is in contact directly with the polymer epoxy matrix. The relationship between the transmittance of light Τ, % and the number of graphene layers has been widely investigated where monolayer graphene is found to transmit about 97.7% of visible white light [221] as shown in Figure 7.5.

Recently, in graphene optical studies have shown that the transmittance of the light is decreasing as the number of graphene layers increasing. There was an argument, however, about the dependence of the wavelength of the light and its transmission through the graphene layers [222, 223].this has to be taken into account in our calculations.
Figure 7.4 The depicted geometry for MWCNTs where $n=10$. The outermost wall (50, 50) is in contact directly with the polymer epoxy matrix.

Figure 7.5 A schematic diagram representing the scattered light from the layers of MWCNTs.
For the line shapes of the G'-peak for MWCNTs/epoxy composites, the transmission values follow the geometric sequence with common ratio 0.954 (=0.977+0.977), were calculated for each strain in the range 0.0-1.5% is given by: for \( n = 10 \) layers

\[
I(\omega) = \frac{1}{\pi} \left[ \frac{\frac{1}{25} (0.954)^n}{\left( \omega - 2678.53 + ((0.7)^{-n} + 14 + \frac{35.4}{D(5n,5n)}) \right)^2} \right]^{n-1} \text{Outermost tube} + \frac{1}{\pi} \left[ \frac{\frac{1}{25} (0.954)^{n-1}}{\left( \omega - 2678.53 + ((0.7)^{-n+1} + 14 + \frac{35.4}{D(5(n-1),5(n-1))}) \right)^2} \right]^{n-2} \text{Innermost tube} + \ldots + \frac{1}{\pi} \left[ \frac{\frac{1}{25} (0.954)^1}{\left( \omega - 2678.53 + ((0.7)^{-1} + 14 + \frac{35.4}{D(5,5)}) \right)^2} \right] + (25)^2 \text{Innermost tube}.
\]

The individual components of the G'-band from the family of the nanotubes and the resultant overall G' band are presented in Figure 7.6 using the Equation (7.7). In order to know the appropriate value of the stress transfer efficiency parameters, \( k_i \), to the experimental shift of the Raman G' bands, the value of the stress transfer efficiency parameters, \( k_i \), were changed between zero and one in steps of 0.1.

![Figure 7.6 The simulated Raman spectrum for G' bands for MWCNTs in MWCNTs/epoxy nanocomposites at 0 % strain](image)

The different values of the stress transfer efficiency parameters, \( k_i \), as a function of strain from 0 to 1.5 % for hot cured 0.1wt % MWCNTs/epoxy nanocomposites, along with the
experimental shift of the Raman G' bands positions and their corresponding model simulation as a function of strain from 0 to 1.5 % for hot cured 0.1wt % MWCNTs /epoxy nanocomposites are presented in Figure 7.8.

![Graph](image_url)

**Figure 7.7** The Experimental shift of the Raman G' bands positions (solid navy hexagons) and their corresponding model simulation (solid green downtringles) as a function of strain from 0 to 1.5 % for hot cured 0.1wt % MWCNTS /epoxy nanocomposites and the different values of the stress transfer efficiency parameter, $k_i$, as a function of strain from 0 to 1.5 % for hot-cured 0.1wt % MWCNTS /epoxy nanocomposites.

The calculations of the resulting line shapes of the G'-peak induced stresses, for 10 layers, yielding a best fit with a shear transfer efficiency parameter, $(k_i = 0.7)$. Some authors [75, 218] have speculated that the limiting cases for the shear transfer efficiency parameter corresponding to perfect and no shear transfer (full slip) are $k_i = 1.0$ and $k_i = 0$, respectively as shown in Figure 7.7. The reason for this could be attributed to the imperfect interface bonding between layers, therefore the shear stress decreases steadily as the number of layers increases. In addition, the load is taken mainly by the outside layer and the inner layers offer decreasing reinforcement.

Comparisons between the experimental and simulated of the G'-bands downshifts are presented in Figure 7.8(A). It is observed that the G' band shifts approximately linearly and suggest that good bonding between the MWCNTs and epoxy matrix. However on increasing the tensile strain the shift becomes non-linear. For MWCNTs/epoxy composites, the most striking result to emerge from Figure 7.8(B) is that the narrowing of G'-band up to 1.5% strain
found in both the experimental and simulated data. This is probably due to the outer walls being more highly strained than the inner walls, leading to larger band shifts for the outer walls components of the G' band spectrum (Figure 7.6).

Figure 7.8 (A) Experimental shift of the Raman $G'$ bands positions and their corresponding model simulation and (B) Experimental shift of the Raman $G'$ bands widths (FWHM) and their corresponding model simulation as a function of strain from 0 to 1.5% for the hot cured 0.1wt % MWCNTs/epoxy nanocomposite, where $(k_i \approx 0.7)$ for the simulated data.

7.2 Relations between the RBM-band intensities and tensile strain

7.2.1 Introduction

The effect of the stress transfer within SWCNTs, and DWCNTs upon their ability to reinforce epoxy composites can be followed by the changes of the RBM-band intensity per unit strain. The experimental RBM-band intensity for 0.1wt% SWNT/epoxy and DWCNTs/epoxy nanocomposites in tension was validated using the Lorentzian lineshape function to assess the impact of the interface between the nanotubes and matrix on the stress transfer between the epoxy matrix and nanotubes. Radial breathing modes of SWCNTs and DWCNTs are not found in multiwall carbon nanotubes (MWCNTs), because the radial breathing mode requires all carbon atoms to translate in-phase in the radial direction [224]
7.2.2 SWNT/epoxy composites

The RBM intensity variations of SWCNTs under tensile deformation of SWCNTs/epoxy composites can be used for the assignment of SWNT structure. The structure assignments are based on the tight-binding model (TB1) [217]. The nanotubes RBMs are expected to be at wavenumbers more than 230 cm\(^{-1}\) for semiconducting nanotubes and at 219 and 197 cm\(^{-1}\) for metallic ones.

The intensity of RBMs 299, 283, 255 and 197 cm\(^{-1}\) increases in tension as shown in Figure 4.21, which means that the corresponding nanotubes moves closer to resonance conditions in tension. The (9, 2), (8, 4), (9, 4) and (13, 4) nanotube assignments are preferred for the 299, 283, 255 and 197 cm\(^{-1}\) RBMs, respectively because their predicted [217] intensity changes in tension are in the same direction as the measured ones (Table 7.2).

Table 7.2 List of Raman radial breathing modes for SWCNTs, predicted indices which define the nanotube structure \((n, m)\) and their diameters observed in SWCNTs/epoxy composites excited using a 633 nm (He-Ne) laser and their intensity behaviour during deformation

<table>
<thead>
<tr>
<th>RBM in SWCNTs/epoxy composites (cm(^{-1}))</th>
<th>(d) (nm)</th>
<th>Intensity variations in tension</th>
<th>Possible chirality [217, 225, 226]</th>
</tr>
</thead>
<tbody>
<tr>
<td>333 (Semiconducting)</td>
<td>0.70</td>
<td>Down</td>
<td>(6,4)</td>
</tr>
<tr>
<td>299 (Semiconducting)</td>
<td>0.79</td>
<td>Up</td>
<td>(8.3) (10.0) (9.2) (7.5)</td>
</tr>
<tr>
<td>283 (Semiconducting)</td>
<td>0.83</td>
<td>Up</td>
<td>(7.5) (8.4) (11.0)</td>
</tr>
<tr>
<td>255 (Semiconducting)</td>
<td>0.92</td>
<td>Up</td>
<td>(11.1) (9.4) (10.3)</td>
</tr>
<tr>
<td>219 (Metallic)</td>
<td>1.09</td>
<td>Constant</td>
<td>(13.1) (12.3) (8.8)</td>
</tr>
<tr>
<td>197 (Metallic)</td>
<td>1.23</td>
<td>Up</td>
<td>(13.4) (15.0) (14.2) (9.9)</td>
</tr>
</tbody>
</table>

7.2.3 DWCNTS/epoxy composites

The RBM intensity variations of DWCNTs under tensile deformation of DWCNTs/epoxy composites were used for the assignment of DWCNTS structure. The structure assignments were based on the tight-binding model (TB1) [217]. Most of the RBM nanotubes for the inner walls are expected to be semiconducting nanotubes except 218 cm\(^{-1}\) which is a metallic one. Most of the RBMs for nanotube outer walls are expected to be metallic nanotubes except 125 cm\(^{-1}\) which is a semiconducting one. The 307, 289, 284, 253 and 125 cm\(^{-1}\) RBM intensities increase in tension as shown in Figures 5.21 and 5.22, which means that the corresponding nanotubes move closer to resonance conditions in tension.

The (6, 5) (9, 2), (8, 4), (9, 4) and (24, 1) nanotubes are preferred for the 307, 289, 284, 253 and 125 cm\(^{-1}\) RBMs, respectively because their predicted [217] intensity changes in tension are in the same direction as the measured ones (Table 7.2). The 167 and 154 cm\(^{-1}\) RBM intensities
decreases in tension, because the predicted (17, 2) and (13, 9) intensities respectively move further away from the resonance conditions in tension. The 338, 218 and 176 cm\(^{-1}\) RBM intensities are seen to be constant in Figures 5.21 and 5.22. It is difficult to explain this result, but it might be related to the armchair (8,8) being a candidate for the 218 cm\(^{-1}\) RBM, because of its constant value within axial strain, and the (6,4) and (17,2) nanotubes being candidates for the 338 cm\(^{-1}\) and 176 cm\(^{-1}\) RBMs respectively.

Table 7.3 List of Raman radial breathing modes for DWCNTs, predicted indices which define the nanotube structure \((n, m)\), and their diameters observed in DWCNTs/epoxy composites excited using a 633 nm (He-Ne) laser and their intensity behaviour during deformation

<table>
<thead>
<tr>
<th>Walls</th>
<th>RBM in DWCNTs/epoxy composites (cm(^{-1})); (tube type)</th>
<th>d (nm)</th>
<th>Intensity variations in tensions</th>
<th>Chirality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner</td>
<td>338 (Semiconducting)</td>
<td>0.70</td>
<td>constant</td>
<td>(6,4)</td>
</tr>
<tr>
<td></td>
<td>307 (Semiconducting)</td>
<td>0.76</td>
<td>up</td>
<td>(6,5)</td>
</tr>
<tr>
<td></td>
<td>289 (Semiconducting)</td>
<td>0.81</td>
<td>up</td>
<td>(9,2)</td>
</tr>
<tr>
<td></td>
<td>284 (Semiconducting)</td>
<td>0.86</td>
<td>up</td>
<td>(7,5)</td>
</tr>
<tr>
<td></td>
<td>253 (Semiconducting)</td>
<td>0.97</td>
<td>up</td>
<td>(11,1)</td>
</tr>
<tr>
<td></td>
<td>218 (Metallic)</td>
<td>1.18</td>
<td>constant</td>
<td>(13,1)</td>
</tr>
<tr>
<td>Outer</td>
<td>176 (Metallic)</td>
<td>1.37</td>
<td>constant</td>
<td>(17,2)</td>
</tr>
<tr>
<td></td>
<td>167 (Metallic)</td>
<td>1.50</td>
<td>down</td>
<td>(16,4)</td>
</tr>
<tr>
<td></td>
<td>154 (Metallic)</td>
<td>1.69</td>
<td>down</td>
<td>(13,9)</td>
</tr>
<tr>
<td></td>
<td>125 (Semiconducting)</td>
<td>2.02</td>
<td>up</td>
<td>(24,1)</td>
</tr>
</tbody>
</table>

The possible configuration for the DWCNTs are: (metallic outer, semiconducting inner), (semiconducting outer, metallic inner), (semiconducting outer, semiconducting inner) and (metallic outer, metallic inner) [192]. For the RBMs data in Table 7.3 the possible pairs of nanotubes with the correct interlayer distance (~0.35 nm) are listed in Table 7.4. It can be seen that they are all metallic outer and semiconducting inner DWCNTs with this laser excitation (1.96 eV)

Table 7.4 Raman peak positions and the calculated diameters for the DWCNTs

<table>
<thead>
<tr>
<th>Outer diameter, cm(^{-1})(nm)</th>
<th>Inner diameter cm(^{-1})(nm)</th>
<th>Interlayer distances, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>154 (1.60) (Metallic)</td>
<td>253 (0.93) (Semiconducting)</td>
<td>0.335</td>
</tr>
<tr>
<td>176 (1.38) (Metallic)</td>
<td>338 (0.68) (Semiconducting)</td>
<td>0.347</td>
</tr>
<tr>
<td>167 (1.48) (Metallic)</td>
<td>288 (0.82) (Semiconducting)</td>
<td>0.333</td>
</tr>
</tbody>
</table>

7.3 Conclusions

This chapter has explained the central importance of stress transfer Raman studies in the 0.1 wt% CNT (SWNT, DWCNTS and MWCNTS)/epoxy composites undertaken by following the experimental shift of the G\(^{'\)} band position in tension deformation and its width, as well as by the intensity variation of RBMs (SWCNTs and DWCNTs). The experimental shift of G\(^{'\)} band position in tension deformation and its width was validated using the Lorentzian lineshape function to assess the impact of the interface between the nanotubes and matrix on the stress transfer between the epoxy matrix and nanotubes.
Chapter Seven: Effect of deformation upon the Raman Spectra of carbon nanotube / epoxy composites

The most obvious finding to be drawn from the present study is that the DWCNTs are stiffer than SWCNTs and MWCNTs by a factor of two and of six respectively.

One of the more significant findings to emerge from this study is that the stress transfer efficiency factor $k_i$ between the inner walls of the DWCNTs and MWCNTs are 0.75 and 0.7 respectively. This value which may be similar for all CVD MWCNTs and DWCNTs. DWCNTs are different from DWCNTs (peapods) for which $k_i$ is about 0.05. What is surprising is that these findings are consistent with those of Gong et al [230] who found $k_i$ is about 0.6 for stress transfer between the layers in multilayer graphene.

The second major finding was that there are RBM intensity variations of SWCNTs and DWCNTs in the hot-cured epoxy composites to the intensity at zero strain in the range up to 1.5% strain, respectively. These findings further support the idea of the effect of deformation upon resonance of carbon nanotube and that he inner nanotube walls are stressed during deformation.
8 Chapter Eight: Conclusions and suggestions for further work

8.1 Conclusions

This thesis has investigated the central importance of stress transfer Raman studies in epoxy composites reinforced with the CNTs (SWCNTs, DWCNTs and MWCNTs) to elucidate the reinforcing ability of the CNTs in an epoxy matrix. This project was undertaken to synthesise and characterize MWCNTs and determine the effect of different weight fractions of untreated MWCNTs on the stress transfer efficiency at the MWCNTs / epoxy interface and on the stiffness on the thermomechanical properties of the MWCNTs / epoxy composites. It was undertaken to assess the stress transfer efficiency at the CNT / epoxy interface and at the inter-walls of the CNTs with tensile deformation and with cyclic loading.

8.1.1 Carbon nanotubes

8.1.1.1 MWCNTs manufacture

Optimized conditions were applied to produce MWCNTs with a high yield, high aspect ratio and well-defined G’ Raman peak MWCNTs. The longest injection times gave MWCNTs with the highest yield, highest aspect ratio and strongest G’ Raman peak.

8.1.1.2 Morphology

The morphology was observed by SEM for SWCNTs and DWCNTs, showing a high density of clusters of web-like ropes and approximately 83 ± 5 wt % and 98 wt % carbon purity, respectively, based on SEM/EDX analysis. For the MWCNTs, chunks (arrays) of entangled tube bundles were obtained approximately 87 wt% carbon pure based on SEM/EDX analysis.

8.1.1.3 Size, surface area and true density

TEM of SWCNTs and DWCNTs showed bundles mostly 41 ± 23 nm and 20 ± 14 nm in bundles diameter, respectively, however for the MWCNTs the average outer diameters were 61 ± 24 nm. The diameters of the SWCNTs, which were deduced from the Raman shift of the RBMs had a mean value 1.02 ± 0.22 nm and for DWCNTs a mean value 1.47 ± 0.16 nm in outer diameter and 0.82 ± 0.13 nm in inner diameter was obtained.

The theoretical studies showed that the mean true density value of the MWCNTs was higher than for the DWCNTs however the mean surface area value of the DWCNTs was higher than that of the MWCNTs.
8.1.1.4 Thermal stability

TGA and DTG curves of CNTs revealed that the DWCNTs were the most thermally stable CNTs in air. They are stable up to 683±6 °C which is higher than the other SWCNTs and MWCNTs materials.

8.1.2 Carbon nanotube / epoxy composites

The most obvious finding to be drawn from the present chapter is that the reinforcement of the epoxy resin with different loadings of MWCNTs would be useful, but our results showed good reinforcement at low loadings of MWCNTs can be attributed to the good MWCNTs/epoxy dispersion. The 0.1 wt% of MWCNTs/epoxy composites displayed their maximum reinforcement efficiency experimentally because the nanocomposites have the maximum Young’s modulus, Raman band shift rate and tensile strength. Moreover, at higher content, the nanotubes tend to agglomerate and the nanocomposites have poorer mechanical properties.

One of the more significant findings to emerge from this study is that the stress transfer efficiency factor $k_i$ between the inner walls of the DWCNTs and MWCNTs are 0.75 and 0.7 respectively. This value which may be similar or all CVD MWCNTs and DWCNTs is different from DWCNTs (peapods) for which the stress transfer efficiency factor $k_i$ is about 0.05.

The second major finding was that there were RBM intensity variations for the SWCNTs and DWCNTs in the hot-cured epoxy composites from zero strain up to 1.5% strain, respectively. These findings further support the idea of the effect of deformation upon resonance of carbon nanotubes and that the inner nanotube walls are stressed during deformation and/or there is also good inter-wall bonding as seen in the shift of the lower frequency $G’_1$ component which is related to the inner wall nanotubes for the DWCNTs.

8.2 Suggestions for further work

8.2.1 Mechanical properties of SWCNTs and DWCNTs epoxy composites

This thesis has investigated the mechanical properties and dynamic-mechanical thermal analysis of MWCNTs/epoxy composites over a range of composition. These results suggest investigating the mechanical properties and dynamic-mechanical thermal analysis of SWNT and DWCNTs epoxy composites with different compositions should also be undertaken.

8.2.2 Improving the processing methods

Based on the present study of the micromechanical properties of MWCNTs/epoxy composites by Raman, tensile tests and dynamic-mechanical thermal analysis (DMTA), a further study could be useful to improve the composite processing methods to obtain dispersed high loadings of MWCNTs (for compositions > 0.2wt% of MWCNTs).
8.2.3 Surface modification for all nanotubes

A study similar to this one should be carried out on different surface modified single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multiwall carbon nanotubes (MWCNTs) to understand how the modified surface of nanotubes affects the dispersion of the CNTs and the stress transfer efficiency in composites.

8.2.4 Using other polymer matrices

One particular epoxy resin was used for the composites because of its transparency and low fluorescence. Other polymer matrices might be also used such as different epoxy resins, polyester resin [231, 232] and poly(methyl methacrylate) (PMMA) [233], poly (vinyl alcohol) (PVA) [234-236], gelatine [237], polystyrene (PS) and styrene isoprene (SI) [238].

8.2.5 Using different Raman laser wavelengths

In order to study different tube configurations (S inner, M outer), (S inner, S outer) and (M inner, M outer) in DWCNTs other laser wavelengths are needed to bring them in resonance during tensile deformation in composites. This would enable the broadening and the narrowing of the G'-band of SWCNTs, DWCNTs and MWCNTs to be studied during deformation.

8.2.6 Other nano-reinforcements

Generally, nano-reinforcements could be used for improving the tensile properties and lowing impeding crack propagation in the composites. A number of novel nanocarbons have been discovered and reported as recent nano-reinforcements such as graphene and graphene oxides (GO) [239]. An example of the potential use of graphene is given below.

8.2.7 Preliminary data analysis of graphene composites

8.2.7.1 Introduction

Due to its exceptional electron transport, mechanical properties, and high surface area, graphene has emerged as a subject of enormous scientific interest. The aim of this section is to investigate the structure of graphene by Raman spectroscopy using different lasers, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Graphene prepared in the School of Materials / Manchester University according to the patent applications numbers RJW/MP6813661, and RJW/MP6806897. Further, in order to follow the interfacial and load transfer between graphene and the epoxy matrix in composites during tensile deformation, the Raman shift of position and width of G'-band, graphene in an epoxy matrix was used. Furthermore the performance of a 1wt% graphene composite was compared with MWCNTs/epoxy composites made in the same way.
8.2.7.2 Raman spectra data analysis of as-produced graphene powders

Figure 8.1 illustrates the main characteristics of the Raman spectra of as-produced graphene powders in the range 1000–3000 cm\(^{-1}\). The strong Raman bands at 1579 ± 3 cm\(^{-1}\) (FWHM, 24 ± 2 cm\(^{-1}\)), (G band) are attributed to a combination of the in-plane C-C stretching modes. The band at 1330 ± 2 cm\(^{-1}\) (FWHM, 41 ± 1 cm\(^{-1}\)) (D band) arises from the disorder-induced mode, the band at 1614 ± 4 cm\(^{-1}\) (FWHM, 20 ± 4 cm\(^{-1}\)) (D’- band) arises from the disorder-induced mode and the band at 2661 ± 6 cm\(^{-1}\) (FWHM, 70 ± 3 cm\(^{-1}\)) (G’- band) is an overtone of the D band, \(I_G\)/\(I_D\) = 0.86 ± 0.13.

![Figure 8.1](image-url)

Figure 8.1 (A) Raman spectrum of epoxy, as-produced graphene powders and (B) comparison between Raman spectra of MWCNTs and as-produced graphene powders excited at 633 nm (He-Ne) laser in the range 1000-3000 cm\(^{-1}\).

In particular, it is noted from chapter 3 that the MWCNTs and graphene powders show a close similarity (in position and FWHM) of all Raman bands G, D, D’ and G’- bands. It is
observed, however, that the full width at half maximum (FWHM) of the G band and D-band of the MWCNTs is somewhat higher than the corresponding in graphene powder. Considerably more work will need to be done to evaluate the structures and properties of graphene using different laser wavelengths.

8.2.7.3 Scanning electron microscopy (SEM) analysis

Figure 8.2 shows typical scanning electron microscopy (SEM) images of the graphene powder. Different morphologies were observed which the powder surface consists of a large number of nanosheets.

![Figure 8.2 SEM images of the graphene powder at different magnifications with scale bars (A) 50µm, and (B) 2µm](image)

8.2.7.4 Transmission electron microscopy (TEM) analysis

Figure 8.3 shows flakes of few-layer graphene films on a holey carbon TEM grid which exhibits typical foldings [240], wrinkles and corrugation within the layers and at the edges as shown in Figure 8.3(A). Few layers materials is visualized in Figure 8.3 (B) (Marked by red arrow)

![Figure 8.3 TEM images of as-produced graphene powders at different magnifications with scale bars 0.5 µm and 0.1 µm](image)

These findings provide the following insights for future research on imaging graphene using Scanning Electron Microscope (SEM) and the transmission electron microscope (TEM)
8.2.7.5 Raman spectra of graphene powder in epoxy composites

Figure 8.4(A) shows the spectra of neat hot cured epoxy resin, graphene powders and the graphene/epoxy composite excited at 633 nm (He-Ne) laser in the range 1000-3000 cm\(^{-1}\). Strong intensities of the main peaks of the graphene powders in the cured epoxy nanocomposites are an indication of the strong resonance Raman scattering of the graphene.

Figure 8.4 (A) Raman spectra of the epoxy, graphene powder and hot-cured graphene (1wt%) / epoxy nanocomposites excited using a 633 nm (He-Ne) laser in the range 100-3000 cm\(^{-1}\). (B) G’-Raman spectra of epoxy, graphene powder and hot-cured graphene (1 wt%)/ epoxy nanocomposites excited using a 633 nm (He-Ne) laser in the range 2500-2800 cm\(^{-1}\).

Figure 8.4(B) compares the G’-band of the as-produced graphene powder and graphene in graphene powder (1 wt %) / epoxy composites in the range 2500-2800 cm\(^{-1}\). The G’-band retains its bell shape but its frequency upshifted by about 10 cm\(^{-1}\) on the composites compared with that of the as-produced graphene powder. The FWHM is also broadened by about 10 cm\(^{-1}\). A possible explanation may be due to the susceptibility of graphene to pre-compression due to the generation of residuals stresses in hot-cured system [187].
8.2.7.6 Performance of the graphene / epoxy composites

The hot-cured graphene powder / epoxy composite system was subjected to tensile loading up to 0.4% strain. The shifts of the position of the G’ band versus different graphene (1wt %) /epoxy composites system strain are shown in Figure 8.5. It is apparent that the G’ band positions are downshifted and the linewidths become narrowed.

![Graphene (1 wt%) / Epoxy nanocomposites](image)

Figure 8.5 The shifting of the G’-band positions with tensile deformation up to 0.4 % strain of hot-cured graphene (1 wt%) / epoxy nanocomposites excited using a 633 nm (He-Ne) laser and (B) the corresponding change of the G’-band widths (FWHM)

8.2.7.7 Performance comparison between the graphene and MWCNTS / epoxy composites

Band shift data were obtained previously for the MWCNTs in epoxy composites (Figure 7.8) and the data for 1wt% MWCNTs loading are shown in Figure 8.6 a long with data for graphene. It is apparent that the G’ band positions of 1 wt% graphene /epoxy composites are downshifted in the same manner with strain as 1 wt% MWCNTs /epoxy composites. The average initial slope of the G’ band positions of graphene composites are, however higher than for MWCNTs composites by a factor of four.
Figure 8.6 Experimental frequencies of the Raman G' bands as a function of strain from 0 to 0.4 % for hot cured 1.0 wt % graphene and for hot cured 1.0 wt % MWCNTs/epoxy nanocomposites.

8.2.7.8 Young’s moduli comparison of the MWCNTs and graphene

Using equation (6.2) It has been demonstrated that the effective Young's modulus of both multiwall carbon nanotubes and graphene in epoxy-matrix composites can determine using the stress-induced shift of the same G'-band in carbon nanotubes [109] as described in Chapter 6. What is surprising is that the effective Young's modulus of graphene is higher than for the MWCNTs by a factor four as seen in Table 8.1

Table 8.1 Calculation the effective elastic modulus of graphene and MWCNTs based on the G'-band shift rate using Raman spectroscopy

<table>
<thead>
<tr>
<th>Sample</th>
<th>G'-band shift rate, S (0) (cm⁻¹/%)</th>
<th>Effective modulus, $E_{eff}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 wt% MWCNTs*</td>
<td>-1.34 ± 0.56</td>
<td>35 ± 4</td>
</tr>
<tr>
<td>1.0 wt% graphene</td>
<td>-5.18 ± 2.49</td>
<td>135 ± 2</td>
</tr>
</tbody>
</table>

*average of 3 measurements (Chapter 6)

This indicates better reinforcement from graphene. It would be interesting to assess the effects of other different concentration (0.1, 0.2, 0.5 and 10 wt %) of graphene in the stress transfer inside graphene/epoxy composites compared with the MWCNTs/epoxy composites and to evaluate the mechanical properties of the graphene composites.


9 References


References


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